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Opacity and entanglement of polymer chains

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Abstract

We argue that the mean crossing number of a random polymer configuration is simply a measure of opacity, without being closely related to entanglement as claimed by several authors. We present an easy way of estimating its asymptotic behaviour numerically. These estimates agree for random walks (theta polymers), for self-avoiding walks, and for compact globules with analytic estimates giving $\log N$, $a - b/N^{2\nu-1}$, and $N^{1/3}$, respectively, for the average number of crossings per monomer in the limit $N \to \infty$. While the result for compact globules agrees with a rigorous previous estimate, the result for self-avoiding random walks disagrees with previous numerical estimates.

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Topological properties of linear polymer chains are, strictly speaking, only defined for closed rings where the theory of knots can be applied with several non-trivial results [1–3]. But even for open chains, quantities like linking, twist, and writhe can be used. Important applications are in supercoiling of DNA, DNA electrophoresis [4], and the supposed absence of knots in protein backbones [2]. Another class of problems where entanglement should play a crucial (but so far not yet fully understood) role is that of the rheology of semidilute solutions.

One important quantity for studying entanglement is the *writhe* which is defined as the number if signed crossings in a projection of a 3D non-self-intersecting oriented curve, averaged over all projections. If two parts of the curve seem to cross when seen from a particular angle, this crossing contributes +1 or −1 to the writhe, depending on whether the direction of the front part is obtained by a right or left turn from the direction of the part behind it. Its interest stems from the fact that for closed loops it is related to linking which is a topological invariant [3].

The *number of crossings* C was introduced in [1, 5] as a simplified version of the writhe. In this, all crossings contribute with the same sign. Of particular interest is its average value $\langle C \rangle$, averaged over all angles of projection, called the *mean crossing number*. In the papers cited it was shown that, for a self-avoiding random walk (SAW) of N straight bonds,

$$\langle C \rangle \sim N^{\alpha} \qquad \text{for} \quad N \to \infty \tag{1}$$

with $1 \leqslant \alpha \leqslant 2$. Numerical simulations gave $\alpha = 1.122 \pm 0.005$, but it was argued that this might actually be a lower estimate, the true value being higher [1].

In later simulations, Arteca [6] found a value of 1.20 ± 0.04 for SAWs and 1.34–1.4 for protein backbones [7]. Indeed an increase of the value of $\langle C \rangle$ had also been seen in [1] for SAWs with self-attraction, and it was conjectured in [7, 8] that $\langle C \rangle$ is a useful observable for detecting the coil–globule transition. Due to its supposed importance, $\langle C \rangle$ was called the 'entanglement complexity' in [9], and was shown there (by non-rigorous arguments) to be <1.4 for random configurations.

It is the purpose of this paper to show that $\langle C \rangle$ can be easily estimated by using well known formulae for generic intersections of random fractals [10]. Take two fractal sets X and Y with dimensions D_X and D_Y, embedded in a space of dimension d. Then, their intersection has dimension $D_{X\cap Y} = D_X + D_Y - d$ for nearly every relative position and orientation, provided that this intersection is non-empty. In the present case, X is the curve to be studied, Y is a line of view (therefore $D_Y = 1$) which passes through X, and $d = 3$. This gives

$$D_{X\cap Y} = D_X - 2. \tag{2}$$

If this is positive, the average number of intersections between the line of view and X increases as $m \sim N^{D_{X\cap Y}/D_X}$ for $N \to \infty$. Actually, for this to be true we either have to assume that X is a true fractal without a lower length cut-off (which is not true for random walks (RWs) with finite step size a), or we have to fatten Y. Thus we consider instead of a single line of view a cylinder whose thickness is of the order of the step size a (the precise value is irrelevant), and the above number of intersections has to be interpreted as the number of crossings between projected bonds within a distance $\mathrm{O}(a)$. This scales in the same way as the number of crossings per bond. Thus we obtain immediately

$$\langle C \rangle / N \sim N^{\tilde{\alpha}} \tag{3}$$

with

$$\tilde{\alpha} = \alpha - 1 = D_{X\cap Y}/D_X = 1 - 2/D_X. \tag{4}$$

This is the case for compact (collapsed) polymers where $D_X = 3$ and therefore

$$\tilde{\alpha} = 1/3 \qquad \text{(compact globules)} \tag{5}$$

in perfect agreement with the exact results of [11, 12] and with the numerical values for protein backbones.

This argument has to be modified when $D_X \leqslant 2$. For $D_X < 2$ (i.e., for SAWs where $D_{\mathrm{SAW}} = 1/\nu$ with $\nu = 0.5877$ [13]), the above argument gives, *mutatis mutandis*, not the leading term but the first subleading correction. The leading term is $\langle C \rangle / N \sim$ constant since $\langle C \rangle / N$ cannot vanish for $N \to \infty$ [1, 5]. The average number of intersections per bond scales now as $m \sim \text{constant} - N^{D_{X\cap Y}/D_X}$. This gives

$$\langle C \rangle / N \sim a_0 - a_1 / N^{-\tilde{\alpha}} \qquad \text{(SAW)} \tag{6}$$

with $\tilde{\alpha}$ given by equation (4).

For $D_X = 2$, finally, we expect logarithmic dependence. This is the case for ordinary RWs and for Θ-polymers (actually, since we want no true self-intersections, we should consider here only the latter. But we shall speak of RWs for simplicity. Later, in equation (9), we will also allow true RWs). The number of times a projection of an N-step RW comes back to a previously visited site, within a finite distance a, increases $\sim \ln N$ [14], and therefore

$$\langle C \rangle / N \sim \ln N \qquad \text{(RW)}. \tag{7}$$

In order to verify equations (6), (7) numerically, we performed Monte Carlo simulations. (We did not carry out simulations for the collapsed case since there the theoretical result is too

obvious.) In these simulations we in fact calculated not $\langle C \rangle$ itself, but a closely related quantity which should show the same asymptotic behaviour and is much easier to calculate numerically.

We consider walks on a simple cubic lattice, and consider only projections along one of the three axes. We consider the sites i on the projection plane which are visited m_i times with $m_i > 1$, and count the number of pairs of visits to the same site. Dividing this by $N + 1$, we obtain

$$B = \frac{1}{2(N+1)} \sum_i (m_i - 1)m_i \tag{8}$$

where i runs over all sites the plane. We call this the 'opacity'. It can obviously also be defined for ordinary (i.e. non-self-avoiding) walks. If there are no double visits in the projection, the opacity is zero, while it diverges with N for a compact object whose thickness along the line of view diverges with N.

The main differences for B with respect to $\langle C \rangle$ are that we do not require transversality of the crossings and do not do any angular averaging. Indeed, we project along atypical directions where bonds would not intersect transversely but overlap, so C cannot be properly defined. As a consequence, the numerical calculation of B is trivial in comparison with the calculation of $\langle C \rangle$, for any given configuration. Nevertheless, we conjecture that both show the same asymptotic behaviour. Indeed, if this were not the case (i.e., if C depended strongly on the angle of view), $\langle C \rangle$ would be an average over a strongly fluctuating quantity and would presumably not be of much practical use. But there exists strong evidence that projections and intersections of random fractal objects show generic features independent of the angle of projection and of the intersection. Finally, our theoretical discussion used generic projections, and applies therefore, strictly speaking, only to $\langle C \rangle$. If we find agreement for B, this suggests that the arguments are correct for $\langle C \rangle$ *a fortiori*.

For RWs, we can indeed estimate B more precisely, and give the prefactor in the analogue of equation (7). A projection of an N-step lattice RW along one of the coordinate axes is a RW of $2N/3$ steps in the plane, for large N. The number of distinct sites visited by the latter is $\approx (2\pi N/3)/\ln N$ [14]. Thus $m \approx (3/2\pi) \ln N$, and

$$B \sim \frac{3}{2\pi} \ln N \qquad \text{(RW)}. \tag{9}$$

Results from 10^4 RWs of 4×10^5 steps each are shown in figure 1, together with the prediction of equation (9). Adding an offset which we had not tried to calculate analytically and which turned out to be precisely -0.4 within the estimated error bars, we find perfect agreement.

For simulating SAWs we used the PERM algorithm [15] with Markovian anticipation bias [16]. This sample contained 5×10^6 SAWs (of which approximately 150 000 were strictly independent) of length 4000. Results are shown in figure 2. There we show also the curve $1.39 - 1.415/N^{0.1754}$ which obviously gives a perfect fit for large N, verifying equation (6). We should point out that our numerical values are in surprisingly close agreement with those shown in figure 3 of [1], given the fact that we do not measure exactly the same quantity. In particular, if we made a least-squares fit to our data with $400 < N < 1500$, we would also get $\alpha \approx 1.1$, in rough agreement with [1]. But clearly such a fit would have a disastrous chi-squared. This clearly suggests that corrections to normal scaling have been mistaken in [1, 6] for an anomalous power law.

Up to now we have considered only walks on the simple cubic lattice. Off-lattice polymers can be treated in the same way, by replacing the condition of exact coincidence by an approximate one. Two monomers i and k contribute then to $B(\hat{n})$, where $\hat{n}$ is the direction of projection, if $|(\vec{x}_i - \vec{x}_k)\hat{n}| < \epsilon$ for some suitably chosen accuracy ϵ. Notice that the scaling behaviour of $B(\hat{n})$ should not depend on ϵ. We should add finally that B can also be

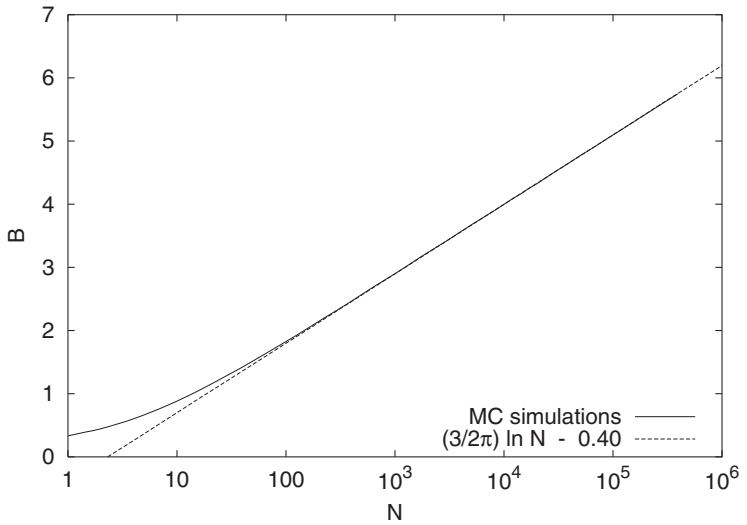

Figure 1. A log–linear plot of B versus N for ordinary RWs (full curve). The dashed curve shows the analytic prediction of equation (9), with an additive constant not predicted by theory. The value of this constant obtained by fitting the data is -0.398 ± 0.03.

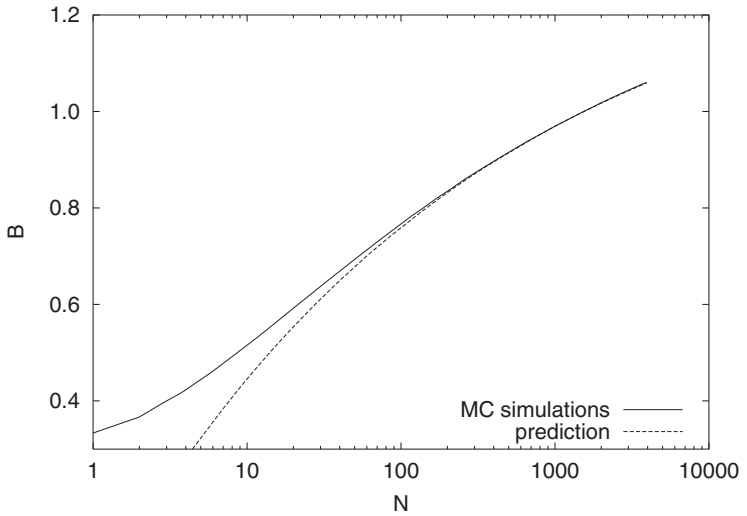

Figure 2. A log–linear plot of B versus N for SAWs (full curve). The dashed curve shows the analytic prediction of equation (6), where we have fitted numerically the constants $a_0 = 1.39$ and $a_1 = 1.415$.

evaluated for any set of sites, not necessarily lined up to form a topologically linear chain. We can use it therefore to measure opacities of branched polymers, vesicles, clusters, or droplets.

Although we have not proven rigorously that B scales in the same way as $\langle C\rangle/N$, we believe that there is little room to doubt it. If we accept this, neither $\langle C\rangle$ nor B are proper measures of entanglement. For B this is obvious since it completely disregards linkage between monomers. And $\langle C\rangle$ does not change when an overcrossing is changed to an undercrossing and vice versa, which should have an influence on any properly defined entanglement measure.

Instead, both $\langle C \rangle$ and B are measures of opacity. Of course they can be used to monitor the theta transition from an open coil to a collapsed globule, since the transparency of a coil decreases during the collapse. But it is not clear what advantage they offer compared, e.g., to the gyration radius. The large corrections to the asymptotic behaviour seen in figure 2 (which have even misled some previous authors to postulate anomalous scaling laws) should be a warning that the interpretation of numerical values might be difficult sometimes. In any case, since the calculation of B is much simpler than that of $\langle C \rangle$, while it gives basically the same information, it should be preferred in any application.

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