The polymer theta-point as a knot delocalisation transition

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We study numerically the tightness of prime flat knots in a model of self-attracting polymers with excluded volume. We find that these knots are localised in the high temperature swollen regime, but become delocalised in the low temperature globular phase. Precisely at the collapse transition, the knots are weakly localised. Some of our results can be interpreted in terms of the theory of polymer networks, which allows to conjecture exact exponents for the knot length probability distributions.

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The presence of knots in single ring macromolecules, or of chain entanglement in polymer melts, has fundamental consequences at the physical, chemical and biological level. For example, the dynamics of a ring polymer in a gel depends crucially on its topology. The replication and the transcription of circular DNA are controlled by enzymes affecting the topology, the topoisomerases. Knots have even been identified in some proteins in their native state. It is easy to imagine the importance that the degree of knot localisation can strongly influence the function of topoisomerases.

These examples all concern heteropolymers in non-equilibrium situations. Here we investigate the interplay between topology and temperature in a simpler context, by studying the equilibrium properties of (prime) knots in homopolymers when these are cooled below their theta temperature. Under such conditions we find that knots definitely loose their usual property of being localized within restricted portions of the chains.

It is very difficult to include topological constraints within a statistical mechanical description of a polymer, since they imply a global control of its conformations. So far, most work has concentrated on the probability of occurrence of knots and much less has been done on the physically relevant problem of precisely quantifying the knot size. Besides attempts to measure knot size directly, most studies have given only indirect, and often incomplete information on knot localisation. For a ring polymer in the infinite temperature, good solvent regime, it was found numerically that the presence of a prime knot leads to a simple multiplication of the partition sum with a factor proportional to the length $L$ of the macromolecule. Moreover, for the relation between the radius of gyration and $L$ (Eq. (1)), evidence was given that neither the amplitude $A$ nor the critical exponent $\nu$ depends on the topology. These results suggest that knots are somehow localised within the chain. On the other hand, in a recent study of the force-extension relation for knotted polymers in good solvent, corrections to scaling are interpreted in terms of a length scale indirectly measuring the knot size. From this, it is concluded that knots are only weakly localised, in a sense that will be defined below.

Even if it is computationally quite hard to directly quantify the length of a knot in three-dimensional space, the same is not true for flat knots which result from the projection of a closed curve onto a plane. Such projections are well known from knot theory where they are at the basis of the determination of topological invariants. Experimentally flat knots can be realized by adsorbing polymers like DNA, or even macroscopic chains on a plane. In the former case thermal fluctuations can allow the system to reach equilibrium in two dimensions.

A flat knot can be drawn as a number of crossings connected with arcs. At each crossing some monomers have to detach from the plane. If the adsorption interaction is sufficiently strong, any non-minimal number of crossings becomes very unfavourable energetically. For example, for the trefoil knot, this minimal number is three and there are six arcs. In Ref. [1] it was shown that for a ring of length $L$ with excluded volume and at infinite temperature, there is typically one of the arcs whose length is of order $L$, whereas the total length of all the other arcs, $l$, is much smaller: $l \ll L$. More precisely, $\langle l \rangle$, the average value of $l$, was found not to diverge with $L$. In this case one says that the knot is localised. If in contrast, $\langle l \rangle \sim L^\beta$, one speaks of weak localisation ($0 < \beta < 1$) or delocalisation ($\beta = 1$) of the knot.

In the present Letter, we investigate the size of flat knots when the temperature $T$ is lowered, or equivalently, when the quality of the solvent gets worse. Under these circumstances the polymer will undergo a collapse transition from a coil to a globule shape below a theta point temperature $T_\theta$. Our main result is that in the collapsed phase knots are delocalised. At the theta-point,
we find them to be weakly localised with $t = 3/7$.

A model for flat knots can be defined [16] on the square lattice whose set of edges is extended with the diagonals of the squares. The bonds of the polymer can visit each edge and each vertex of this extended lattice at most once. A diagonal can only be occupied if at the same time the other, perpendicular diagonal within the same elementary square is also occupied. Each pair of occupied diagonals represents a crossing (not to be considered as a lattice vertex) in the projection of the knot. Thus, one has to further specify which of the two diagonal bonds goes under the other one. The model is simulated within the grand canonical ensemble, where a fugacity $K$ is assigned to each bond of the ring polymer, while the number of crossings is constrained to the minimum consistent with the topology. As usual, to include the possibility of theta collapse, we associate an attractive energy with each pair of lattice vertices that is visited by non-consecutive bonds. Fig. 1 shows a configuration with the topology of a trefoil.

![Typical configuration of a polymer with a trefoil knot in the low T collapsed phase.](image)

In our Monte Carlo approach, a Markov process in the configuration space of the polymer is constructed by a combination of local and non-local moves. These are chosen as in Ref. [16] and are such as to ensure invariance of the polymer topology. Averages at fixed $T$ are then calculated using a multiple Markov chain (MMC) implementation in the fugacity $K$ [17]. This guarantees an exhaustive sampling of configurations also at rather low temperatures [18]. First, we obtain precise estimates of $K_c(T)$, the critical fugacity above which the grand canonical average $\langle L \rangle = \infty$. Since for the case of a flat trefoil, there are only three pairs of diagonals occupied, we can expect that $T_\theta$ is very close to the value of an interacting self-avoiding ring model without crossings. To verify this, we investigated the average squared radius of gyration $\langle R_g^2 \rangle_L$ [16] as a function of $L$ for this case. Fig. 2 reports our results for different $T$'s. One expects that asymptotically

$$\langle R_g^2 \rangle_L \sim A L^{2\nu}$$  \hspace{1cm} (1)

Our data clearly show the expected three regimes. At high $T$'s, we are in a self-avoiding walk regime with $\nu \approx 3/4$. At low $T$'s we determine an exponent $\nu = 0.49 \pm 0.02$, consistent with the value appropriate for a collapsed polymer, $\nu = 1/2$. Finally, close to $1/T = 0.67$ we find a $\nu$ in agreement with that at the theta-point, i.e. $\nu = 4/7$ [20]. Hence, we estimate $1/T_\theta = 0.67 \pm 0.02$, fully consistent with determinations for unknotted rings [21]. We also conclude that the exponent $\nu$ at the theta-point and in the collapsed phase is not modified by changing the topology from that of a flat unknot to that of a flat trefoil.

![Log-Log plot of $\langle R_g^2 \rangle_L$ as a function of $L$ for a ring with trefoil knot. From top to bottom : 1/T = 0.50, 0.67(≈ 1/T_θ), 0.8. The dot-dashed, the dashed, and the dotted lines have slopes 3/2, 8/7, and 1.0, respectively.](image)

In order to characterise the tightness of the trefoil knot, we consider all its six arcs and determine the statistics of their lengths $l_1 \leq l_2 \leq \ldots \leq l_6$. Clearly the largest arc must always have a length proportional to $L$. In Fig. 3, we plot the average length of the second largest arc, i.e. $\langle l_5 \rangle_L$, as a function of $L$. For high $T$'s, we see that $\langle l_5 \rangle_L$ saturates at large enough $L$. Moreover, all the other arc lengths remain much smaller, typically only a few bonds. We conclude that in the swollen regime the knot is localised. The quantity $\langle l \rangle_L / L = (\sum_{i=1}^{5} l_i) / L$ approaches zero when $L \to \infty$. At $T_\theta$, we find instead that $\langle l_5 \rangle_L$ grows as $L^t$, with $t = 0.44 \pm 0.02$. All other lengths remain again very small. Thus, the typical shape of the polymer appears to be that of a figure eight, as found also at $T = \infty$ [4]. We also conclude that the knot is weakly localised.

Finally, and most interestingly, we find that in the collapsed phase, and for $L$-values that are sufficiently large, $\langle l_5 \rangle_L \sim L$, implying a delocalisation of the knot. In this case, there is ample evidence that also the average length of smaller arcs, like $\langle l_4 \rangle_L$, starts to grow proportional to
for still longer polymer lengths. We suspect that in sufficiently long polymers all average arc lengths will become extensive in $L$. Thus, a description in terms of a figure eight breaks down in the collapsed phase.

It is possible to associate a polymer network $G$ with $N$ segments $[22]$ to each flat knot configuration with the same number of non-microscopic arc lengths $[14]$. Interest in polymer networks was revived recently by a successful full development concerning DNA denaturation $[23]$. The same type of approach was subsequently applied in $[14]$ where it was found that flat knots with excluded volume at $T = \infty$ are always localised. Our data for $T > T_\theta$ support this conclusion, and moreover convincingly show that localisation is present throughout the whole high temperature phase (Fig.3).

On the basis of a network description, this time with interacting polymer segments, it is possible to gain further insight into some of our results. Let $G$ be such a network with $n_k$ vertices of degree $k$ connected by $N$ arcs of total length $L$. The partition sum $Z_G(l_1, \ldots, l_N)$ of the network scales as $[22, 24]$

$$Z_G(l_1, \ldots, l_N) = K_c^{L} l_1^{\nu_d L} F_G \left( l_1^{-1}, \ldots, l_N^{-1} \right)$$

(2)

where $F_G$ is a scaling function and $\gamma_G = 1 - \nu d \mathcal{L} + \sum_k n_k \sigma_k$. Here $d$ is the dimension of space and $\mathcal{L}$ is the number of independent loops in the network. The lengths of the network segments $l_k$ corresponding to macroscopic knot arcs, are $l_1 \leq \ldots \leq l_N$. Finally, the exponents $\sigma_k$ are anomalous dimensions associated to the $k$-leg vertices of the field theory describing the polymer in the continuum limit $[22]$. In two dimensions, Coulomb gas methods allow an exact determination of the $\sigma_k$'s. In particular, at $T = \infty$, where polymers are described by the $n \to 0$ limit of a critical $O(n)$-model, one has $\sigma_k = (2 - k)(9k + 2)/64 [22]$. On the other hand, the theta-point is described by the critical low temperature phase of the $O(n = 1)$-model, for which $\sigma_0 = (2 - k)(2k + 1)/42 [21]$. Finally, following $[23]$, we assume that the properties of the low $T$ regime can be related to those of dense polymers, which are described by the low $T$ phase of the $O(n = 0)$-model. For this case special care has to be taken, and one ends up with a scaling form for $Z_G$ which is slightly different from Eq.(3) $[24]$. Yet, despite these differences, the network picture can still be applied to flat knots with $\sigma_k = (4 - k^2)/32 [20]$.

When in a network one or more arcs become very short, and hence the crossings on which they are incident approach each other very closely, the network should be replaced by another, contracted one with fewer segments and crossings, and a different $\gamma_G$. In this way, it can be understood that even though any projection of a trefoil contains six arcs, at a more coarse grained level, the typical contribution appearing in a numerical simulation can come from a network with fewer crossings. This is what happens, for example, at the theta-point, where we found that the flat trefoil looks like a figure eight ($l_4 \sim O(1)$). At $T_\theta$, where $\nu = 4/7$, $[10]$ predicts that the partition function of a figure eight network scales as

$$Z_8 = K_\gamma^{c-L} (l - l)^{6-\nu} F_8 \left( \frac{l}{L} \right)$$

(3)

with $\gamma_8 = -12/7$. For $l/L \to 0$, this partition sum should in its turn reduce to that of a self-avoiding ring at the theta-point, which is known to scale as $Z \sim K^{c-L} L^{-\nu_d}$. This simple analysis $[23]$ then teaches us that $F_8(x) \sim x^{c}$ for $x \to 0$, with $c = -(\gamma_8 - 1 + \nu_d) = 11/7 \approx 1.57$. Hence, for $l \ll L$ we predict that

$$Z_8 \sim K^{c-L} (l - l)^{-\nu_d} l^{-c}$$

(4)

In Fig. 4 (left) we present our data for $p(l_5)$, the probability distribution of $l_5$, at $T = T_\theta$. From (4) it follows that $p(l_5) \sim l_5^{-\nu_d}$. A fit to this form leads to $c = 1.63 \pm 0.08$, consistent with the above prediction. Finally, we get from $[10]$ that $l_5 \sim L^{3/7}$, in good agreement with the numerical estimate $l_5 \sim L^{4.4 \pm 0.42}$. We expect that $t = 3/7$ is an exact result which characterises the weak localisation of the knot at the theta-point.

At $T < T_\theta$, an analysis using the results of $[26]$ can still be made for a ring with the shape of a figure eight, and leads to the prediction $c = 11/8$. In Fig. 4 (right), we also show our data for $p(l_5)$ at $1/T = 0.8 > 1/T_\theta$. There is indeed an initial power law decay with an exponent $1.34 \pm 1.2$. But in this case, $p(l_5)$ flattens for larger $l_5$-values and it is this broadening which eventually leads to the delocalisation of the knot. The presymptotic slope indicates that for relatively small $l_5$, the weakly localised figure eight network configurations are still dominating the partition sum. When $l_5 \sim L$ one can get no help from network scaling arguments in determining $p(l_5)$. Indeed, such arguments are only valid for $l_5 \ll L$ which is not the relevant range when $l_5 \sim L$.  

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We verify that also for other prime knots, such as the $5_1$ and $7_1$, the typical network configuration at $T = T_\theta$ is still the number eight and delocalization occurs for $T < T_\theta$.

In conclusion, we find that a flat prime knot in an adsorbed polymer remains localised as long as $T > T_\theta$, becomes weakly localised at $T_\theta$, and eventually delocalises at $T < T_\theta$. While delocalisation is supported by strong numerical evidence, other results are fully consistent with our predictions based on a polymer network approach. One may speculate that the delocalisation found here could be a more general phenomenon for the topology of interacting polymers.

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