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Flory-type theory of a knotted ring polymer

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A mean field theory of the effect of knots on the statistical mechanics of ring polymers is presented. We introduce a topological invariant which is related to the primitive path in the ''polymer in the lattice of obstacles'' model and use it to estimate the entropic contribution to the free energy of a nonphantom ring polymer. The theory predicts that the volume of the maximally knotted ring polymer is independent of solvent quality and that the presence of knots suppresses both the swelling of the ring in a good solvent and its collapse in a poor solvent. The probability distribution of the degree of knotting is estimated and it is shown that the most probable degree of knotting upon random closure of the chain grows dramatically with chain compression. The theory also predicts some unexpected phenomena such as ''knot segregation'' in a swollen polymer ring, when the bulk of the ring expels all the entanglements and swells freely, with all the knots concentrated in a relatively small and compact part of the polymer. [S1063-651X(96)10012-X]

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Modern polymer physics is based on the analogy between a polymer chain and a random walk. While this analogy has been extremely fruitful in predicting the long-wavelength static and dynamic properties of polymer chains (radius of gyration, relaxation time, etc.), it misses one of the most important attributes of polymer chains, namely, their ability to form permanent entanglements, i.e., knots. Although there is a very successful phenomenological theory (the reptation model [1]) of the effect of temporary entanglements on the dynamics of polymers which give rise to the viscoelasticity of polymer liquids, there is no comparable theory of permanent entanglements which play an important role in biological systems (e.g., DNA rings in bacteria). Our understanding of the latter is limited by the fact that, despite the progress in the mathematical theory of classification of knots and topological invariants [2], there are only few rigorous results on the entropic properties of knots [3,4], and further attempts in this direction encounter severe mathematical difficulties [5]. Computer simulations [6–8], however insightful, have some basic limitations.

What appears to be missing in the area of polymer topology is a simple ''physical'' model which could give some testable physical predictions. The main purpose of the present work is to trade mathematical sophistication for the simplicity and effectiveness of such a physical approach and to formulate a model that goes along the lines of the simple Flory mean field theory of linear polymers and takes into account topological constraints, albeit in a very primitive and incomplete manner.

It is also worth mentioning what we do *not* attempt to accomplish here: as we pursue a scaling-type approach, we cannot capture the subtle differences between simple knots, such as, for instance, trivial knot, trefoil, figure eight, etc.; we only hope to be able to describe general tendencies for very complex knots. As far as biological applications involving DNA molecules are concerned, our model does not apply to current experiments on rather small DNA rings [9,10] such as plasmids, but may be relevant to very large circular DNA (e.g., that of bacteria). We also stress that we are speaking of topological constraints on the dsDNA as an entire thread, and do not have in mind linking of the two strands in the duplex, that is related to biologically important issue of superhelicity [11].

We address two questions: (1) What is the equilibrium size of a polymer ring, depending on both solvent characteristics (or monomer interactions) and knot topology? A similar question for linear polymers, where topology is not an issue, is discussed in every textbook on polymer physics, and it is known that the Flory theory yields a very good approximation for both swelling in good solvent and collapse in poor solvent. Clearly, almost the same behavior, except for some subtle chain end-related effects, is expected for a *phantom* ring polymer (which can cross itself). Our goal is to consider a *nonphantom ring*, with quenched knot topology.

(2) What is the probability distribution of various knots obtained upon random closure of a linear polymer, or by random motion of a *phantom* ring with annealed topology?

As we wish to build up a simple theory, we do not attempt to characterize knots by sophisticated polynomial invariants. Instead, we introduce the following construction. Consider a polymer chain in some spatial conformation and denote by L the contour length of the chain. Let us first construct a tube that contains the polymer chain and is sufficiently narrow such that the topology of the tube as a whole is the same as that of the polymer. We now inflate the tube such that its length L is preserved, while its cross section is roughly the same everywhere along the tube (we assume that different tube portions cannot penetrate each other). This inflation will eventually end when the inflated tube fills the main part of the volume within its loops. Let us denote by D the diameter of the tube in this maximally inflated state. We state that the aspect ratio of the maximally inflated tube

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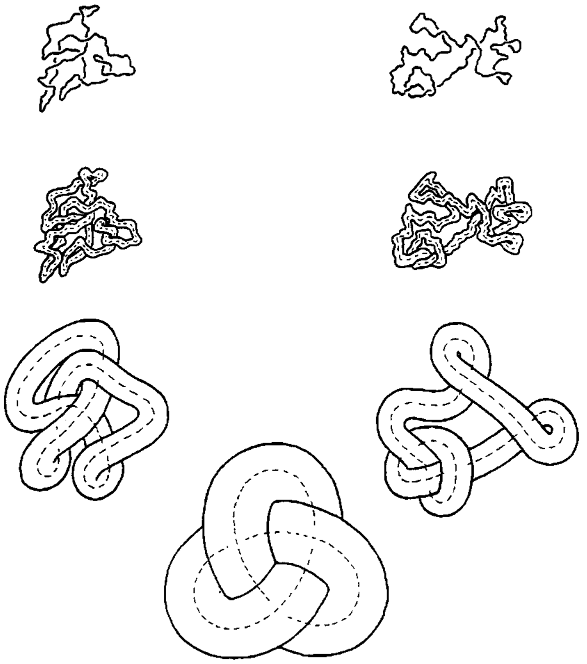

FIG. 1. Illustration of the tube inflation procedure. Two different yet topologically equivalent loop conformations are shown. The thin tube centered around the polymer closely resembles the conformation of the polymer itself. When the tube is inflated, with the contour length of its axis preserved, all the small scale ''jigglings'' of the polymer conformation get gradually eliminated, and finally we arrive at the maximally inflated shape that is independent of the initial conformation, but only on the knot topology.

$$p \equiv L/D \tag{1}$$

is a topological invariant. It is a weak invariant since there may be many topologically different knots that have the same value of p [12]. Nevertheless, p is a topological invariant, in the sense that if we take two closed curves in three-dimensional space that are geometrically different but identical with regard to their topology, then tube inflation, as described above and as illustrated in Fig. 1, will work independently of initial geometries and will result in identical (''maximally inflated'') geometrical shapes of the corresponding tubes and, therefore, will yield identical p values. This happens because the redistribution of the ''stored'' length among the loops is unrestricted in this single linear chain problem and thus, inflation does not encounter spin-glass-type frustrations and leads to some well defined optimum [13]. A closely related definition of a topological invariant was introduced in Ref. [14], in the context of vortex tubes in fluid mechanics.

If the ring is not knotted in the conventional sense, or if it forms the trivial knot, its inflation leads to a simple torus shape with $D \sim L$ and thus $p \simeq 1$. On the other hand, the more complex knot we have, the less is its ''inflation capability.'' Physically, since real polymers have a finite thickness, there is a maximal knot complexity that can be achieved which corresponds to a knot that is so dense that any inflation over an already existing diameter would be impossible. If we imagine a polymer chain made of monomers whose length is equal to their thickness, we conclude that the maximal value of $p = L/D \simeq N$ is of the order the number of monomers per polymer chain. Thus, our topological invariant can take values in the interval

$$1 \leqslant p \leqslant N \tag{2}$$

and it provides a rough measure of knot complexity: more complex knots correspond generally to higher p values. To illustrate the later conjecture, it is worth mentioning that the topological invariant p has the property of additivity: for the composite knot, whose components have topological invariants p_1 and p_2, the topological invariant is given by

$$p \simeq p_1 + p_2 . \tag{3}$$

We note that the topological invariant p is closely related to the primitive path of the chain in a lattice of obstacles [1]. In order to clarify this point we introduce a self-consistent representation of a complex knot in terms of an ''effective'' lattice of obstacles. The polymer trajectory on this lattice is represented by a primitive path which is measured in units of the lattice constant (this makes the topological invariant independent of lattice deformation). Maximal inflation is equivalent to lattice enlargement up to the point in which the polymer chain becomes completely stretched along the primitive path and, therefore, p can be interpreted as the chain length measured in units of the expanded lattice constant. The above analogy allows one to estimate the number of topologically different knots with a given p value. Since a lattice of obstacles can be mapped onto the Cayley tree [15], this quantity should grow exponentially with p:

$$\mathcal{K}(p) \sim e^{\lambda p}, \tag{4}$$

where λ is some numerical constant, generally of order unity.

We proceed to estimate the polymer chain size dependence on solvent quality and topology, the latter represented by the topological invariant p. Following the classical Flory approach, the equilibrium polymer size is given by the balance of rubberlike elasticity and interactions between monomers dispersed in the polymer volume. This is described by the minimization of the free energy,

$$F = F_{elast} + F_{interact} . \tag{5}$$

The interaction term for the ring is identical to that of the linear chain,

$$\frac{F_{interact}}{T} \simeq \frac{BN^2}{R^3} + \frac{CN^3}{R^6} \simeq \frac{B}{a^3}\frac{N^{1/2}}{\alpha^3} + \frac{C}{a^6}\frac{1}{\alpha^6}, \tag{6}$$

where R is the actual size of the polymer, $\alpha = R/a\sqrt{N}$ is the linear swelling (or collapse if less than unity) factor, B and C are the second and the third virial coefficients, respectively, and a is the monomer size.

The problem is to obtain a plausible estimate for the entropic part which would account for the frozen topology of the polymer ring. To this end we suggest the following approximation based on the construction of the maximally inflated tube which occupies a volume of order LD^2. Let us deform it affinely so that it occupies the volume of the chain R^3, but preserves the geometrical shape that it has in the maximally inflated state, and call this deformed tube ‘‘R-size tube.’’ Let L_R and D_R be the length and the diameter of the R-size tube, respectively. Since the R-size tube is obtained by an affine transformation of the maximally inflated tube, we have $L_R/D_R = p$, and since it occupies the whole volume of the polymer, $L_R D_R^2 = R^3$. We obtain

$$L_R \simeq R p^{2/3}, \quad D_R \simeq R p^{-1/3}. \tag{7}$$

The main assumption of this work is that in order to estimate the entropic (i.e., elastic) free energy, we consider our polymer as a phantom chain, but confined within the R-size tube. The entropy of a phantom polymer confined in a tube is independent of the way this tube is embedded in 3D space; one can estimate the entropy of a phantom polymer in a simple torus-shaped tube, or even that of a linear polymer in a straight tube, with polymer ends attached to the tube ends. This gives

$$\frac{F_{elast}}{T} \simeq \frac{L_R^2}{Na^2} + \frac{Na^2}{D_R^2} = \alpha^2 p^{4/3} + \alpha^{-2} p^{2/3}, \tag{8}$$

where the first and the second terms describe chain elongation along the tube and squeezing within the tube diameter, respectively (see, for example, [16]). We balance the free energy contributions (6) and (8) and obtain the following equation for α:

$$\alpha^5 p^{4/3} - \alpha p^{2/3} - \frac{B}{a^3}\sqrt{N} - \frac{C}{a^6}\frac{1}{\alpha^3} = 0. \tag{9}$$

This equation is the central result of our work. It is similar to the equation [see [16], Eq. (13.5)] for linear or phantom polymer, except for the inclusion of p-dependent factors. Recall that the terms in Eq. (9) describe chain elongation along the tube, chain compression across the tube, and two- and three-body interactions, respectively. Guided by considerations of simplicity, in the following we will describe our results in terms of polymer chain size $R = \alpha a \sqrt{N}$ and take $B \simeq a^3 \tau$ and $C \simeq a^6$, where τ denotes the dimensionless deviation from the θ temperature. Inspection of Eq. (9) reveals the following regimes.

(i) *Good solvent regime* is realized when $\tau > \sqrt{p/N}$; in this regime entropic elasticity associated with chain elongation along the tube [first term in Eq. (9)] competes with two-body-repulsion (third term), yielding

$$R \sim a N^{3/5} \tau^{1/5} p^{-4/15}. \tag{10}$$

The N and temperature dependence of polymer size ($R \sim N^{3/5}$) is identical to the linear or phantom polymer case, but there is an important prefactor that gets smaller for complex knots with large p values. Note that the chain size in this regime can be smaller than the size of a Gaussian phantom chain, $a\sqrt{N}$; this happens in the range $p^{1/2}N^{-1/2} < \tau < p^{4/3}N^{-1/2}$, or, in other words, for sufficiently complex knots with $p > (\tau\sqrt{N})^{3/4}$. Only a relatively simple knot in a truly good solvent $[p < (\tau\sqrt{N})^{3/4}]$ is swollen compared to the Gaussian phantom size. At smaller τ or higher p (more complex knot) the polymer crosses over to the quasi-Gaussian regime.

(ii) *Quasi-Gaussian regime* is realized when $-\sqrt{p/N} < \tau < \sqrt{p/N}$; in this regime elasticity associated with chain elongation along the tube competes with three-body repulsion and chain elasticity across the tube, the latter two being of the same order of magnitude. This gives

$$R \sim a N^{1/2} p^{-1/6}, \tag{11}$$

i.e., the N dependence of the chain size remains of the Gaussian type, but the coefficient gets smaller for more complex knots.

At even smaller (more negative) τ or for smaller p (simpler knots) the polymer crosses over to the poor solvent regime.

(iii) *Poor solvent regime* is realized when $\tau < -\sqrt{p/N}$; in this regime the two-body attractive term in Eq. (9) competes with three-body repulsion, yielding

$$R \simeq a|\tau|^{-1/3} N^{1/3}\left[1 + |\tau|^{-4/3}\left(\frac{p}{N}\right)^{2/3}\right]. \tag{12}$$

The main term here is an obvious result, because in the presence of strong intermonomer attraction the polymer must collapse into a dense sphere (globule) with N-independent density. We included the correction due to the next most important term, which is chain compression in the tube. This indicates that a heavily knotted globule is less compact compared to its phantom counterpart.

(iv) *Maximally tightened knot regime* is realized when $p \sim N$ and, interestingly, it does not depend on solvent quality and interactions. In this regime,

$$R \simeq a N^{1/3}, \tag{13}$$

and, thus, a tightly knotted ring is always compact.

The free energy F_{elast} (8) can be related to the probability distribution of the knots that form in the process of formation a ring by random contacts between the ends of a linear polymer (assuming that the ends remain glued upon contact). An identical distribution is obtained from the collection of the instantaneous configurations of a phantom (freely passing through itself) ring whose overall size R is maintained by either monomer interactions (solvent) or an external field (e.g., a box). Indeed, F_{elast} is determined by the volume in configuration space which is available to the nonphantom polymer with a given quenched knot topology, and this volume is obviously proportional to the probability to get this same knot topology in a phantom system that goes freely from one topology to the other. Thus, the probability to obtain a knot with given p value can be written as

$$\mathcal{P}(p) \sim \mathcal{K}(p)\exp[-F_{elast}/T] \sim \exp[\lambda p - \alpha^2 p^{4/3} - \alpha^{-2} p^{2/3}], \tag{14}$$

where we have used estimate (4) for the number $\mathcal{K}(p)$ of different knots with a given p.

Inspection of Eq. (14) indicates that for swollen polymers ($\alpha > 1$, $R > a\sqrt{N}$) trivial or simple knots with $p \sim 1$ are the most probable, while for collapsed polymers ($\alpha < 1$) the probability distribution (if $\lambda > 4\sqrt{2}/3 \approx 1.9$) is peaked at

$$p_{optimal}(R) \sim \alpha^{-6} \sim N(Na^3/R^3)^2. \tag{15}$$

Thus, the most likely degree of knotting grows with chain compression and reaches its maximal value $p \sim N$ for a maximally compact globule with $R \sim aN^{1/3}$.

The intuitive expectation that topological constraints suppress both swelling in a good solvent and collapse in a poor solvent, is in perfect agreement with our conclusions. Indeed, our results confirm that when chain topology is frozen before changing the quality of a solvent, a knotted polymer appears underswollen in a good solvent and overswollen in a poor solvent (compared to an unknotted one).

Our results for the scaling exponents, (10,11), agree with computational data of Ref. [17], where ring sizes, $R(K)$, were studied for several different ring topologies K, including unknot, trefoil, figure eight, and double trefoil. It was found that critical indices $\nu(K)$ in $R(K) \sim N^{\nu(K)}$ are the same (within statistical errors) for all tested knots K, namely, close to 0.6 or to 0.5 for rings with or without excluded volume, respectively.

The simplest theory presented above does not distinguish between a trivial knot ($p=1$) and a phantom ring. In reality, entropy loss is caused by exclusion of knotted conformations even for a trivial knot ring. We expect that a trivial nonphantom knot, when collapsed, has the shape of a crumpled globule [18], whose fractal properties differ from those of a phantom globule. To improve the theory, we consider confinement in the R-size tube of a nonphantom unknotted polymer instead of a phantom one; exclusion of knotting for a chain confined within an R-size tube gives rise to an additional term in the elastic free energy (8) that scales as α^{-6}. Indeed, expression (8) has to be modified in the case when the chain is compressed both across and along the tube; in the latter case, the scaling form of free energy can be obtained from the fact that the resulting osmotic pressure must depend on N and tube volume $L_R D_R^2 \sim R^3$ only through the polymer density, N/R^3. This leads only to the redefinition of the C/a^6 coefficient in Eq. (9) and does not affect the scaling forms of all our main results (10)–(13), (15). More subtle corrections may be needed if one is to incorporate delicate properties of the collapsed state [19], with the fractal dimension of the polymer backbone itermediate between 3, dictated by the scale-invariant segregation of crumples in the crumpled globule model [18], and 2, which corresponds to the a self-entangled globule which obeys the Gaussian statistics of a melt.

Despite its simplicity, our theory gives rise to the following unexpected result. Let us return once again to the good solvent regime and examine the possibility of an uneven distribution of knots along a chain with a given value of p. Suppose that the chain adopts a conformation in which a part of length of about p monomers forms a dense region where all of the knots are located, and another part of $N-p$ monomers which swells freely in the good solvent. As long as $p \ll N$, our theory gives for this ''phase segregated'' state a free energy of about p for the ''collapsed'' knotted part plus about $(N-p)^{1/5} \approx N^{1/5}$ for the freely swollen loop part, yielding about $N^{1/5}$ on total (assuming $p \ll N^{1/5}$). On the other hand, a state with a uniform distribution of knots gives, after substitution of Eq. (10) into Eqs. (6) and (8), a much higher free energy, of order $N^{1/5} p^{4/5}$ $(p \gg 1)$. Thus, while for $N^{1/5} \ll p \ll N$, thermodynamics favors a uniform distribution of knots along the chain contour, our theory predicts that segregation of knots will take place for less knotted chains, with $p \ll N^{1/5}$. This prediction can be tested by computer simulations and experiments.

A preliminary version of this work has been published in Ref. [20].

Note added in proof. When this paper was under consideration in the journal, we learned of the work [21] where the same topological invariant p has been implemented in computer experiments. The values of p were computed for several knots, and certain justification was obtained for the idea that fluctuations of the polymer are dominated by conformations centered around the axis of the R-size tube.

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[12] There are some inherent uncertainties in the definition of p, related to the definition of the ''diameter'' of a sharply curved tube, as well as assumptions made about flexibility of the central tube axis during the inflation. For example, if one attempts to approximate this axis with a broken line of some n straight segments, the value of p will be (slightly) dependent on n. This is why p is indeed a rather weak topological invariant.
[13] The shape of maximally inflated tube is at least qualitatively similar to the (maximally extended) conformation of a strongly charged polyelectrolyte ring of the same topology. This gives

rise to an analogy of our topological invariant p with the so-called ‘‘energy of a knot’’; see, for instance, S. Fukuhara, in *Fete of Topology*, edited by M. Matsumoto *et al.* (Academic Press, New York, 1988), p. 443.

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