Worm-like Polymer Loops and Fourier Knots

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Every smooth closed curve can be represented by a suitable Fourier sum. We show that the
ensemble of curves generated by randomly chosen Fourier coefficients with amplitudes inversely
proportional to spatial frequency (with a smooth exponential cutoff), can be accurately mapped on
the physical ensemble of worm-like polymer loops. We find that measures of correlation on the scale
of the entire loop yield a larger persistence length than that calculated from the tangent-tangent
correlation function at small length scales. The conjecture that physical loops exhibit additional
rigidity on scales comparable to the entire loop due to the contribution of twist rigidity, can be tested
experimentally by determining the persistence length from the local curvature and comparing it with
that obtained by measuring the radius of gyration of dsDNA plasmids. The topological properties of
the ensemble randomly generated worm-like loops are shown to be similar to that of other polymer
models.

Classical polymer theories, from Debye to Flory to De Gennes [1] and beyond, make extensive use of the analogy
between conformation of a chain molecule and a Brownian random walk (BRW). In mathematically idealized
form, such a random walk is thought of as a Wiener trajectory \( \vec{r}(\tau) \) generated by the measure \( P \{ \vec{r}(\tau) \} \propto \exp \left[ -\text{const} \int (\partial \vec{r}/\partial \tau)^2 \, d\tau \right] \), where \( \tau \) is a parameter running along the trajectory. The BRW model brings powerful
mathematical techniques, such as the diffusion equation, to bear on polymers but, however fruitful, this
method has its limitations. For example, it is fundamentally unable to reproduce the fact of finite extensi-
ability of polymer chains stretched by a strong force [2]. Another field in which the Wiener trajectory model fails miserably is the study of polymers with knots. Indeed, simulations of discrete polymer models, or random poly-
gons with \( N \) steps, show [3, 4, 5], that the probability of a trivial knot configuration decays exponentially with
\( N \rightarrow \infty \), so it is not surprising that these models do not exhibit finite extensibility. A better continuum model
of polymers which can handle the constraints imposed both by finite extensibility and by the presence of knots,
and can describe the elastic response of such objects, is that of a worm-like chain. However, while the statistical
physics of linear worm-like polymers is well understood, little is known about the conformations and the topology
of worm-like loops (WLL). Our goal in this article is to work out a method allowing computational generation of
an ensemble of smoothly curved conformations of such polymers and to carry out the statistical analysis of their
geometric and topological properties.

The conformations of worm-like polymers are generated by the measure \( P \{ \vec{r}(s) \} \propto \exp \left[ -\text{const} \int (\partial^2 \vec{r}/\partial s^2)^2 \, ds \right] \), subject to the con-
straint of non-extensibility, \( |\partial \vec{r}/\partial s| = 1 \). That simply means that conformations are Boltzmann weighted
by the bending energy proportional to the squared curvature. In more general elastic models [6], the three
generalized curvatures describing the object could be treated as independent Gaussian variables. However,
this is true only for linear (with open ends) filaments and attempts to generalize these methods to the case of
closed loop failed because the loop closure conditions introduce a non-local coupling between the curvatures
that makes the problem practically intractable (except for the case of small fluctuations of a planar ring in
which this coupling can be explicitly taken into account [7]). One natural way to generate the conformations of
a closed loop is to expand each component \( r^i(\tau) \) in a Fourier series:

\[
r^i(\tau) = \sum_{n=1} A_n^i \cos \left( \frac{2\pi n \tau}{T} \right) + B_n^i \sin \left( \frac{2\pi n \tau}{T} \right) \quad . \tag{1}
\]

Here, \( \tau \) is a parameter along the curve \( \vec{r}(\tau) \) \( 0 \leq \tau \leq T \) and the summation goes up to some cutoff frequency \( n_{\text{max}} \) (if the series converges sufficiently rapidly, the cut-
off can be replaced by infinity). Any configuration of a sufficiently smooth closed loop can be fully described
by the set of Fourier coefficients \( \{ A_n^i, B_n^i \} \), giving rise to the concept of Fourier knots introduced in [8]. Notice
that a Fourier knot is a much more general concept than the more traditional Lissajou knot, for which only one
frequency is present for each coordinate direction.

Using the above prescription one can generate an en-
semble of loops of different shapes by taking the Fourier
coefficients from some random distribution. However,
even though all the loops have the same period \( T \), their
contour lengths $L_T = \int_0^T d\tau' |d\mathbf{r}/d\tau'|$ are different for each realization of the Fourier coefficients. Even more importantly, since, in general, $|\partial \mathbf{r}/\partial \tau| \neq 1$, loops generated by (1) do not obey the inextensibility condition and can not be used to model worm-like polymers. In order to generate an ensemble of different conformations of an inextensible loop of some well-defined contour length, one has to transform to a representation in which trajectories are parametrized by the arclength $s$

$$ s(\tau) = \int_0^\tau d\tau' |d\mathbf{r}/d\tau'|, \quad \text{with} \quad |\partial \mathbf{r}/\partial s| = 1 \tag{2} $$

and then bring all the generated conformations to the same contour length by a suitable affine transformation of all lengths and coordinates (this transformation does not affect the topology since the latter is independent of the parametrization). Thus, we can replace $L_T = s(T)$ by any standard length $L$, provided that we rescale all lengths using the affine transformation: $\mathbf{r} \rightarrow \mathbf{r}L/L_T$. Therefore, in three steps (generation of random coefficients and Fourier summation (1), reparametrization (2), and affine transformation $s \rightarrow sL/L_T$), of which the latter two couple all Fourier harmonics together in a complex way, we obtain a statistical ensemble of smoothly bent conformations of an inextensible loop of length $L$. Let us now check if this ensemble is representative of physical conformations of a worm-like loop which possesses some characteristic bending and (possibly) twist rigidities.

The first step is to recognize that on length scales much larger than some microscopic cutoff, the conformations of a worm-like polymer are well represented by those of a BRW. For the latter, the amplitudes of the Fourier coefficients and Fourier summation (1), reparametrization (2), and affine transformation $s \rightarrow sL/L_T$, of which the latter two couple all Fourier harmonics together in a complex way, we obtain a statistical ensemble of smoothly bent conformations of an inextensible loop of length $L$. Let us now check if this ensemble is representative of physical conformations of a worm-like loop which possesses some characteristic bending and (possibly) twist rigidities.

The first step is to recognize that on length scales much larger than some microscopic cutoff, the conformations of a worm-like polymer are well represented by those of a BRW. For the latter, the amplitudes of the Fourier coefficients can be readily shown to be of the form $\{A_n, B_n\}_{BRW} = \lambda/n$ for $n \leq n_{\text{max}}$ and zero otherwise, where $\lambda$ is a random number (say, uniformly distributed between $-1$ and $1$; the choice of another symmetric interval is equivalent to rescaling the contour length, see below). As will be demonstrated in the following, short scale behavior characteristic of WLL can be obtained by replacing the abrupt cutoff $n_{\text{max}}$ by Fourier coefficients that decrease smoothly with a characteristic decay frequency $n_0$.

$$ \{A_n^i, B_n^i\}_{WLL} = \lambda e^{-n/n_0}/n, \tag{3} $$

(notice that the WLL and the BRW expressions for the coefficients coincide for $n \ll n_0$).

The next step is to notice that the conformations of linear worm-like polymer are governed by the persistence length, which marks the cross-over between straight line conformations at small length scales and random walk type behavior at large length scales. We expect that on small scales, the conformations of linear worm-like polymers and WLL are quite similar and that for the latter this cross-over is represented in Fourier space in terms of $n_0$. Of course, the analogy is meaningful only as long as $n_0 \gg 1$, when there is a sufficiently broad range of length scales between the persistence length and the contour length of the knot. The characteristic property of the worm-like chain model is exponential decay (as $\exp(-s/l_1)$) of the tangent-tangent correlation function, which defines the persistence length $l_1$; similarly, for WLL on length scales sufficiently small compared to the entire loop, one expects that $\langle t(s) \cdot t(0) \rangle \simeq \exp(-s/l_1)$, where $\langle \rangle$ denotes averaging both over the contour of a given loop and over the ensemble of loops. This expectation is confirmed in Figure (1b), where the logarithm of the correlation function is plotted against the dimensionless arclength $s/l_1$. The choice $l_1 = 0.43/n_0$ allows us to superimpose data for different values of $n_0$ in the range $30 \leq n_0 \leq 270$ (the small shift of the exponent is the result of the finite discretization of the contour length $s$).

At first sight, analogy with worm-like chain models of linear polymers suggests that on length scales much larger than $l_1$ the conformations of the loops are those of BRW with step size (Kuhn length) given by twice the persistence length, $2l_1$. However, this analogy is open to question because the large scale behavior of a loop is strongly affected by the loop closure constraint and it is not clear, a priori, whether the same persistence length controls both the small and the large scale behavior. We therefore decided to apply our method to generate a representative ensemble of configurations of WLL and use it to compute the tangent-tangent correlation function and the mean squared distance between two well-separated points $s$ and $s' (|s - s'| \gg l_1)$ along the contour.

A simple estimate shows that on length scales much larger than the persistence length, the tangent-tangent correlation function of a WLL approaches a constant negative value $\langle t(s) \cdot t(0) \rangle \simeq -2l_2/L$ where $l_2$ is, in general, different from $l_1$ (the negative value of the correlation follows from the fact that the tangent has to turn back on itself in order to come back to its initial direction upon traversing the contour of the loop). In Fig. (1b) this correlation function is plotted in the interval $0.1 < s < 0.5$ (here and in the following we take $L = 1$) for different values of $n_0$. Upon averaging the correlation functions over the oscillations, all the results for different values of $n_0$ can be collapsed to a single horizontal line by dividing them by $l_2 = 0.575/n_0$. We therefore establish that unlike the case of linear worm-like chains in which only a single persistence length exists, WLL have at least two distinct persistence lengths, with $l_1/l_2 \simeq 3/4$.

We now proceed to compute the mean squared distance between two points on the loop separated by a contour distance $s$, $\langle \langle R^2(s) \rangle \rangle = (1/L) \left\langle \int_0^L |\mathbf{r}(s') - \mathbf{r}(s)|^2 ds' \right\rangle$. Since we expect WLL to behave like BRW on scales much larger than some persistence length $l_3$, the probability distribution of $R^2(s)$ can be easily written down assuming that both $s \gg$
The conclusion that local and global statistical properties of worm-like loops are characterized by two different persistence lengths, \( l_1 \) and \( l_2 \) (\( l_2 = l_3 \)), respectively, is a new result of this work. Although analytical theory of worm-like loops does not exist at present, we can offer some tentative considerations about the origin of the two persistence lengths, based on the study of small fluctuations of elastic rings [6]. For rings of zero linking number that possess both bending and twist persistence lengths, it was shown that while on small scales writhe fluctuations depend only on the bending persistence length (on such scales the ring is essentially straight and bending and twist decouple), both bending and twist persistence lengths contribute to the writhe on larger scales, for which the global geometry of the closed ring becomes important. Extrapolating this result to the case of a strongly fluctuating loop considered in this work, suggests that while \( l_1 \) represents the pure bending contribution to the persistence length, \( l_2 \) contains both the bending and the twist contributions and is therefore larger than \( l_1 \) [13].

We now turn to the topological properties of WLL and examine the dependence of the trivial knot probability \( P_0 \) on the cutoff frequency \( n_0 \). Since \( n_0 \) determines the Kuhn length defined as either \( 2l_1 \) or the \( 2l_2 \), we can bring our knotting probability data to a form comparable to that for discrete polymer models, where trivial knot probability depends on the number of segments \( N \). In our case, we generate Fourier knots as completely smooth curves, but we can define the number of effective segments as the ratio of the contour length to the Kuhn length. For long random–walk-like polymers, this definition coincides with the standard one accepted in polymer physics for the Kuhn segments [11] but there remains an ambiguity associated with the choice of \( N_1 = L/2l_1 \) or \( N_2 = L/2l_2 \).
In order to resolve this ambiguity we will measure the probability to obtain a trivial knot as a function of the cutoff frequency $n_0$.

To address the topology of the loops computationally, we employ the knot analysis routine due to R. Lua \cite{Lua} which identifies knots by computing the Alexander polynomial invariant $\Delta(t)$ at one value of argument, $t = -1$, and Vassiliev invariants of degrees two, $v_2$, and three, $v_3$. This set of invariants is widely considered as powerful enough for reliable identification of the trivial knot for all lengths achievable in practical computations. The details of this topological routine are described in \cite{Lua}.

The data on the trivial knot probability are shown in Figure 3. As this figure indicates, the trivial knot probability fits well to the exponential

$$P_0(n_0) \sim \exp[-n_0/242]. \quad (4)$$

Notice that since this relation involves only the cutoff on the Fourier series, formula \eqref{P0} can be re-interpreted in purely mathematical form, not involving any references to polymers, or, for that matter, to any physics. While there is no fundamental understanding of the origin of this large cutoff ($n_0^* = 242$) at present, our formulation hints at the existence of a hitherto unexplored connection between Fourier analysis and topology of space curves and will hopefully stimulate new work on this fundamental problem.

In summary, we have shown that the choice of random Fourier coefficients with amplitudes that decay with frequency as $n^{-1} \exp(-n/n_0)$, generates a statistical ensemble of Fourier knots whose local properties coincide with those of worm-like polymers with persistence length that scales as $1/n_0$. We found that even though WLL behave on large scales as BRW as expected, the effective step size of this BRW is larger than that calculated from the local persistence length of the loop. This new prediction can be directly tested by experiments on double stranded DNA loops that can monitor both local (persistence length) and global (e.g., radius of gyration) properties of the polymers (see, e.g., \cite{Lyubchenko, Scipioni, Bussiek}). We also demonstrated that similar to discrete models of polymers or random polygons, our Fourier knots exhibit exponential decay of the unknotting probability with the number of effectively straight segments, or, equivalently, with the maximal spatial frequency included in Fourier expansion. The characteristic cross-over determined by this exponential decay represents a large number, which, although in the same ballpark as for other known models, remains an unexplained puzzle.

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