Curvature Distribution of Worm-like Chains in Two and Three Dimensions

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Bending of worm-like polymers carries an energy penalty which results in the appearance of a persistence length $l_p$ such that the polymer is straight on length scales smaller than $l_p$ and bends only on length scales larger than this length. Intuitively, this leads us to expect that the most probable value of the local curvature of a worm-like polymer undergoing thermal fluctuations in a solvent, is zero. We use simple geometric arguments and Monte Carlo simulations to show that while this expectation is indeed true for polymers on surfaces (in two dimensions), in three dimensions the probability of observing zero curvature anywhere along the worm-like chain, vanishes.

1 Introduction

Semi-flexible polymers are usually modeled as space curves (either continuous or discrete) that possess bending rigidity. Following the linear theory of elasticity of slender rods, the bending energy of such worm-like polymers is taken to be a quadratic functional of the local curvature [1]. The curvature is a local geometrical property of a continuous curve - the reciprocal of the radius of the tangential circle at any point along the curve. In discrete models the curvature is the angle (per unit length) between adjacent segments, in the limit when the length of these segments goes to zero (see below). The calculation of the statistical properties of such polymers involves generating a representative statistical ensemble of different conformations of space curves and weighting them by appropriate Boltzmann factors. Since these statistical weights are Gaussian functions of the local curvature, one expects that the most probable value of the curvature is zero, i.e., that the probability distribution of curvature is peaked at the origin. This expectation agrees with our intuition about semi-flexible polymers: since they deviate from straight lines only on length scales exceeding their persistence length, the local curvature of a typical configuration is expected to vanish almost everywhere. As we will show in the following using both analytical arguments and Monte Carlo simulations, the above conclusions hold only in two dimensions; surprisingly, the most probable value of the curvature in three dimensions is not zero!

2 Curves, curvature and measure

Consider a space curve defined by a vector $\vec{r}(s)$ (with respect to some space-fixed coordinate system), where the parameter $s$ is the arclength. The shape and the orientation of the curve are completely determined (up to uniform translation) by the direction of the tangent to the curve at every point along its contour, $\hat{t}(s) = d\vec{r}/ds$:

$$\vec{r}(s) = \int_0^s ds' \hat{t}(s')$$  \hfill (1)

Since the tangent is a unit vector, $|\hat{t}(s)| = 1$, it can be represented as a point on a sphere of unit
radius; the coordinates of this point are given by
the two spherical angles $\theta$ and $\phi$. Finally, one
can introduce a local property of the curve, the
curvature, defined as:

$$\kappa(s) = \frac{d^2\vec{r}}{ds^2} = \frac{d\vec{t}}{ds}$$ (2)

Let us introduce a discrete version of the con-
tinuous curve of length $L$, by dividing it into $N$
segments of length $\Delta s$ ($N\Delta s = L$), such that
the orientation of the $n$’th segment connecting
points $s$ and $s + \Delta s$ is defined by the direction
of the tangent at point $s$. One can define the
orientation of the $n$’th tangent vector (i.e., the
$n$’th segment) in terms of the $(n - 1)$’th one

$$\hat{t}_n = \cos(\Delta \theta)\hat{t}_{n-1} + \cos(\Delta \varphi)\sin(\Delta \theta)\hat{n}_{n-1} + \sin(\Delta \varphi)\sin(\Delta \theta)\hat{b}_{n-1}$$ (3)

As shown in Fig. 1, $\Delta \theta \in [0,\pi]$ is the angle
between the $n$’th and the $(n - 1)$’th segments
and $\Delta \varphi \in [-\pi,\pi]$ is the polar angle between
the two planes defined by $\hat{t}_{n-2} \times \hat{t}_{n-1}$ and $\hat{t}_{n-1} \times \hat{t}_n$. 
In the continuum limit $\Delta \varphi$ becomes the angle
of rotation of the normal $\hat{n}$ and the binormal
$\hat{b}$, with respect to the tangent $\hat{t}$ to the curve.
In differential geometry this triad $\hat{t}$, $\hat{n}$ and $\hat{b}$ is
referred to as the Frenet frame and its rotation
as one moves along the curve is governed by the
Frenet-Serret equations. As we will show in the
following, in the limit of a continuous curve the
angle $\Delta \theta$ is proportional to the curvature (one
can also show that the torsion is proportional
to the angle $\Delta \varphi$ [2]).

The calculation of statistical averages involves
integration over all possible configurations of the
polymer with respect to the measure $D\{\vec{r}(s)\}$ or, alternatively, over $D\{\vec{t}(s)\}$. Dis-
cretization allows us to replace this measure by
the product of contributions of its segments,

$$D\{\vec{t}(s)\} \rightarrow \Pi_n(d\vec{t}_n),$$
where the measure of a single segment is given by

$$d\vec{t} = \sin(\Delta \theta) d(\Delta \theta) d(\Delta \varphi)$$ (4)

The local curvature of a discrete curve can be
defined by replacing the differentials by differ-
ences in Eq. [2]

$$\Delta s\kappa_n = \sqrt{(\hat{t}_{n+1} - \hat{t}_n)^2} = \sqrt{2(1 - \cos(\Delta \theta))}$$ (5)

where we used the equalities $(\hat{t}_{n+1})^2 = (\hat{t}_n)^2 = 1$ and $\hat{t}_{n+1} \cdot \hat{t}_n = \cos(\Delta \theta)$. This definition of
the curvature is consistent with the one used in
the Frenet-Serret theory only if $\kappa\Delta s << 1$, in
which case $\kappa\Delta s \approx |\Delta \theta|$. Using Eqs. 4 and 5 it is straightforward to show that:

$$d\vec{t}(s) = d(\Delta \varphi)(s)\Delta s^2\kappa(s) d\kappa(s)$$ (6)

The above discussion applies to curves in 3 di-
dimensions. In 2 dimensions the measure is rep-
resented by a single angle $\theta$ so that in the dis-
crete representation of a curve, the angle be-
 tween successive segments, $\Delta \theta$, varies in the
interval $[-\pi, \pi]$. Unlike the 3d case in which the
curvature is a positive definite quantity (see Eq.
[2]), the curvature of a planar curve can be either
positive or negative (the torsion is zero every-
where). The direction of the tangent vector can
be represented as a point on a unit circle and,
therefore, the measure is given by

$$d\vec{t}(s) = d(\Delta \theta)(s) \approx \Delta s d\kappa(s), \quad \text{in } 2d \quad (7)$$

We conclude that in summing over the con-
figurations of 3d curves, one can replace the
measure in the laboratory frame, $D\{\vec{r}(s)\}$, by
that in terms of the intrinsic coordinates of the
deformed line, which is proportional to $\kappa(s) D\{\kappa(s)\}$. This differs from the corresponding
measure for 2d curve which is proportional to
$\propto D\{\kappa(s)\}$.

3 Curvature distribution of
worm-like polymers

In the worm-like chain model (WLC) a polymer
is modeled as semi-flexible rod whose elastic
energy is governed only by the curvature [3]:

$$E_{WLC} = \frac{1}{2}b \int ds\kappa^2(s) - \frac{1}{2}b \sum_n \Delta s\kappa_n^2$$ (8)

where $b$ is the bending rigidity. This energy is
invariant under polar rotations and conse-
quently the torsion angle $\Delta \varphi$ is uniformly
distributed in the range $[-\pi, \pi]$. In 3 dimensions, the probability $p(\kappa) d\kappa$ of observing a value of
the curvature in the interval between $\kappa(s)$ and
$\kappa(s) + d\kappa$ at a point $s$ along the contour of the
curve, is proportional to the product of corresponding Boltzmann factor by the measure $\kappa d\kappa$ (see Eq. 6),

$$p(\kappa)d\kappa = l_p\Delta s\exp\left[-\frac{1}{2}l_p\Delta s\kappa^2\right]\kappa d\kappa$$  \hspace{1cm} (9)

where $l_p = b/k_B T$ is the persistence length (for $L >> l_p$ the polymer length does not affect the statistics of the curvature). Inspection of Eq. 9 shows that if one rescales the curvature as $\kappa \rightarrow \tilde{\kappa} = \kappa\sqrt{l_p}\Delta s$, the probability distribution functions of polymers with different bending rigidities can be represented by a single master curve $\tilde{\kappa}\exp[-(1/2)\tilde{\kappa}^2]$. This scaling may lead to the conclusion that changing the persistence length is equivalent to changing the discretization. Indeed, calculation of properties such as the mean curvature of a curve depends on the discretization length $\Delta s$ and diverges in the continuum limit, $\langle \kappa \rangle = \lim_{\Delta s \rightarrow 0}(l_p\Delta s)^{-1/2} = \infty$. This, however, is not true in general and calculation of physical observables such as the tangent-tangent correlation function, yields well-behaved results:

$$\langle \hat{t}(0) \cdot \hat{t}(s) \rangle = \langle \hat{t}_0 \cdot \hat{t}_n \rangle = \langle \cos(\Delta \theta) \rangle^n$$  \hspace{1cm} (10)

From Eqs. 9 and 5 one can easily conclude that: $\langle \cos(\Delta \theta) \rangle = 1 - \Delta s/l_p \sim \exp[-\Delta s/l_p]$. Inserting the above expression into Eq. 10 one gets the WLC relation:

$$\langle \hat{t}(0) \cdot \hat{t}(s) \rangle = \exp[-s/l_p]$$  \hspace{1cm} (11)

This correlation function and all properties that can be derived from it, such as the mean square end to end distance, depend only on the persistence length and are independent of the discretization.

4 Simulations and analytical results

In order to study the curvature distribution function of a worm-like polymer numerically, we performed Monte-Carlo simulations of a discrete polymer made of $N$ equal segments, in 3d. To generate the conformations of a polymer we used the following moves (see ref. [4]): a point between two neighboring segments is picked at random and a randomly oriented axis that passes through this point is defined. Then, the entire part of the polymer that lies on one side of the chosen point, is rotated about the axis by an angle $\psi$ which is uniformly distributed in the range $[-\pi, \pi]$ (see figure 2). Since in the WLC model the total energy (in dimensionless units, $k_B T = 1$) of a discrete polymer is:

$$E_{WLC} = b \sum_n [1 - \cos(\Delta \theta_n)]$$  \hspace{1cm} (12)

the change of energy in a move is given by

$$\Delta E_{WLC} = b [\cos(\Delta \theta_n)_{old} - \cos(\Delta \theta_n)_{new}]$$  \hspace{1cm} (13)

A move is accepted or rejected according to Metropolis rule and statistics is collected following equilibration determined by convergence of the total energy (after at least $10^6$ moves). In order to double check our method, we calculated the tangent-tangent correlation function and the mean square end to end distance as well and confirmed that they agree with well-known analytical results for worm-like chains (not shown). Inspection of Fig. 3 shows that there is perfect agreement between our simulation results and the analytical expression, Eq. 9. The two main features of the distribution are the existence of a peak at a finite value of the curvature and the fact that the probability to observe zero curvature vanishes identically. At first sight, the prediction that any local measurement on a worm-like chain will yield a non-vanishing curvature, contradicts our intuition about stiff polymers. Note, however, that experiments (e.g., by AFM) that monitor the configurations of semi-flexible polymers such as dsDNA, do not directly measure the curvature but rather the local bending angle. Even though $\langle \kappa \rangle = 1/\sqrt{l_p}\Delta s$ does not vanish, the average local angle (measured on length scales smaller than the persistence length) $\langle \delta \theta \rangle = \sqrt{\Delta s/l_p}$ is always small.

The above discussion applies to worm-like polymers that do not have intrinsic curvature (their curvature is generated by thermal fluctuations only). Although the WLC model has been applied [5] to interpret mechanical experiments
on individual double stranded DNA (dsDNA) molecules [6], it has been suggested [7] that ds-DNA has sequence-dependent intrinsic curvature. In this case, the experimentally observed local curvature of dsDNA contains both the contribution of intrinsic curvature and that of thermal fluctuations [8]. The generalization to the case of spontaneous curvature is straightforward: even though the expression for the bending energy Eq. 8 is replaced by
\[ E_{WLC} = \frac{1}{2} b \int ds \delta \kappa^2(s) \rightarrow \frac{1}{2} b \sum_n \Delta s (\kappa_n - \kappa_0,n)^2 \] (14)
the measure is not affected and depends only on the dimensionality of the problem. Using the discrete form of curvature Eq. 5 the distribution function of curvature for a given intrinsic curvature \( \tilde{\kappa}_0 \) is:
\[ p(\tilde{\kappa}|\tilde{\kappa}_0) d\tilde{\kappa} = A(\tilde{\kappa}_0)\tilde{\kappa} e^{-\frac{1}{2}l(\tilde{\kappa}-\tilde{\kappa}_0)^2} d\tilde{\kappa} \] (15)
where
\[ A(\tilde{\kappa}_0) = \left[ \int d\tilde{\kappa} \tilde{\kappa} \exp(-\frac{1}{2}l(\tilde{\kappa}-\tilde{\kappa}_0)^2) \right]^{-1/2} \] (16)
is a normalization factor and \( l \) is the persistence length. An experiment measuring the curvature distribution of an ensemble of conformations of a polymer with a specific primary sequence \( \{\kappa_0(s)\} \), would measure the distribution Eq. 15 from which the intrinsic curvature can be calculated as a fit parameter. If one monitors the curvature distribution of an ensemble of random copolymers whose sequences are characterized by a distribution of intrinsic curvature \( p(\tilde{\kappa}_0) \), the corresponding curvature distribution function will be:
\[ p(\tilde{\kappa}) = \int d\tilde{\kappa}_0 p(\tilde{\kappa}|\tilde{\kappa}_0)p(\tilde{\kappa}_0) \] (17)
In order to check this result we performed Monte Carlo simulations with different distributions of \( \tilde{\kappa}_0 \). As can be observed in Fig. 4 the simulations are in perfect agreement with the analytical results for the curvature distribution calculated using Eq. 17.

5 Discussion

Finally, we would like to comment on the applicability of our results to present and future experiments. To the best of our knowledge, all experiments that probed the local curvature of DNA (by electron microscopy [9] and by SFM [10, 8]) were done on dsDNA molecules deposited on a surface. It has been argued that in this case one has to distinguish between strong adsorption in which case dsDNA attains a purely 2d conformation, and weak adsorption in which the 3d character of the adsorbed macromolecule is maintained, at least in part (see ref. [11]). While in the former case the measure of Eq. 7 applies and the most probable curvature vanishes [12], in the latter case one should use the 3d measure of Eq. 6 for which the most probable curvature is finite and the probability to observe zero curvature vanishes. New experiments that could probe the 3d conformations of DNA and other worm-like polymers are clearly necessary to test our predictions.

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Fig. 1 3 successive segments are shown by black arrows. $\Delta \theta$ is the angle between the $(n-1)'$th segment (the radius of the unit sphere) and the $n'$th segment. $\Delta \varphi$ is the polar angle defined by the projection of $\hat{t}_n$ (dashed arrow) on the plane defined by the normal $\hat{n}_{n-1}$ and the binormal $\hat{b}_{n-1}$ (red arrows).

Fig. 2 Sketch of a Monte Carlo move. The right hand part of the curve rotates with random angle $\psi$ with respect to a random axis (dashed red line) passing through a random point $m$.

Fig. 3 Distribution function of scaled curvature $\tilde{\kappa}$ for a polymer of $N = 10^4$ segments of length $\Delta s = 1$ each. The empty symbols are the simulation results for $l_p = 25$ (black squares), $l_p = 50$ (red circles) and $l_p = 100$ (green triangles). The rigid line is the analytical scaled distribution function $\tilde{\kappa} \exp\left[-(1/2)(\tilde{\kappa})^2\right]$ where $\tilde{\kappa} = \kappa \sqrt{l_p \Delta s}$. There are no fit parameters.

Fig. 4 In all figures the blue squares and green diamonds are the histograms of curvature and of intrinsic curvature, respectively. The red line is the analytical distribution function computed using Eq. 17.
Figure 1: Caption of Fig. 1.

Figure 2: Caption of Fig. 2.

Figure 3: Caption of Fig. 3.
Figure 4: Caption of Fig. 4.