Distribution Function of the End-to-End Distance of Semiflexible Polymers

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Abstract

The distribution function of the end-to-end distance of a semiflexible polymer, \( G(R; L) \) (where \( R \) denotes the end-to-end distance and \( L \) the contour length), is calculated using a meanfield-like approach. The theory yields an extremely simple expression for \( G(R; L) \) which is in excellent agreement with Monte Carlo simulations. The second and fourth moments of \( G(R; L) \) agree with exact results for a semiflexible polymer in both the random coil and the rod limit.
Many properties of isolated, flexible polymer molecules are now understood [1]. For example, theoretical methods can be used to calculate the distribution function of flexible polymer molecules to very high accuracy. Unfortunately, many polymer molecules have too much internal stiffness to be successfully modeled as flexible chains [2]. This is especially true for several important biopolymers such as actin, DNA, and microtubules [3]. A measure of the stiffness of a polymer is the persistence length, $l_p$. To understand the persistence length, consider two points on the polymer separated by a length $l$ along the contour of the polymer backbone and construct the tangent vectors to this contour. The persistence length is the length along the contour over which these tangent vectors become uncorrelated. Thus, for $l < l_p$ the tangent vectors would have significant correlation and for $l > l_p$ the tangent vectors would have little correlation. Typical values of $l_p$ for biopolymers range from several nm to a few mm. If the contour length $L$ of a polymer is of the same order of magnitude as $l_p$ (or smaller) then the flexible chain model is inadequate for describing the polymer. For such a polymer it is imperative to include bending rigidity to describe the conformations of the chain. An appropriate model, called the semiflexible or wormlike model, was introduced in 1949 by Kratky and Porod [4]. The semiflexible model has been shown to provide a good starting point in the description of polymers with significant internal stiffness.

In contrast to the situation of isolated, flexible polymers, there are many properties of semiflexible polymers that are not understood. Inspired by recent experiments [5,6] that have probed the properties of semiflexible biological molecules, there has been a renewed interest in understanding their shapes. A central quantity for understanding the shape of a polymer is the distribution of end-to-end distances. Such a distribution function can, in principle, be measured by scattering experiments. Furthermore, it can be used to calculate the structure factor, which is needed as input in describing the dynamics of polymers. Therefore, finding a simple expression for this distribution function which is also accurate over a wide range of stiffness is important for further theoretical progress in understanding the properties of stiff chains. This paper provides just such a simple expression for the distribution of end-to-end distance of an ideal, semiflexible polymer chain.

There have been several studies of the distribution of the end-to-end distance of semiflexible chains [7–9]. Most of these studies have started by considering the chains near the rod limit and have computed corrections in powers of $t^{-1}$, where $t$ represents the ratio of the contour length to the persistence length. These calculations are very complicated and, more importantly, they do not provide reliable results in the interesting case where $t$ is of the order one. Recently [10], Wilhelm and Frey [WF] have reported careful analytic and numerical (Monte Carlo) calculations for the radial distribution function of the end-to-end distance for a range of values of $t$. Their analytic expressions consist of infinite series of parabolic cylinder functions (for two dimensions) and Hermite polynomials (for three dimensions). These expressions compare extremely well with their simulation results. Our approach differs from these previous studies. In this paper we use the method of our recent meanfield theory of semiflexible polymers [11] to obtain a simple expression for the distribution function of the end-to-end distance. This expression is surprisingly accurate when compared to the analytic theory and simulations results for the range of $t$ studied in [10].

The Hamiltonian for the semiflexible chain is taken to be [12]

$$\mathcal{H} = \frac{l_p}{2} \int_0^L ds \left[ \frac{\partial u(s)}{\partial s} \right]^2$$

(1)
where \( l_p (= \kappa/k_B T \) with \( \kappa \) being the bending rigidity) is the persistence length, \( u(s) (= \partial r(s)/\partial s) \) is the unit tangent vector to the curve \( r(s) \) which describes the chain contour, \( s \) is the position measured along the chain contour, and \( L \) is the contour length of the entire chain. The distribution function of the end-to-end vector \( R \) is

\[
G(R; L) = \langle \delta \left( R - \int_0^L u(s) ds \right) \rangle
\]

(2)

where the average is evaluated with respect to a thermal weight function, \( \Psi[u(s)] \),

\[
\langle \ldots \rangle = \frac{\int \mathcal{D}[u(s)] \ldots \Psi[u(s)]}{\int \mathcal{D}[u(s)] \Psi[u(s)]}
\]

(3)

The thermal weight function for the semiflexible chain is

\[
\Psi[u(s)] = \delta(u(s)^2 - 1) \exp(-\mathcal{H}[u(s)])
\]

(4)

In an earlier paper \[11\] we showed that when the weight \( \Psi[u(s)] \) is replaced by

\[
\Psi_{MF}[u(s)] = \exp \left\{ -\frac{1}{2} \int_0^L \left( \frac{du}{ds} \right)^2 ds - \lambda \int_0^L [u(s)^2 - 1] ds - \epsilon[u(0)^2 - 1] - \epsilon[u(L)^2 - 1] \right\}
\]

(5)

and the parameters \( \lambda \) and \( \epsilon \) are chosen variationally through a stationary phase approximation, then the hard constraint \( u(s)^2 = 1 \) is replaced by the thermally averaged constraint \( \langle u(s)^2 \rangle = 1 \). This result had been conjectured by Lagowski et al. \[13\]. We also established that imposing the constraint \( \langle u(s)^2 \rangle = 1 \) for every point on the chain requires two parameters; specifically, the parameter \( \epsilon \) is required to suppress the fluctuations at the ends of the chain \[11,13\]. Furthermore, if one uses only the variational parameter \( \lambda \), as suggested elsewhere \[14\], then one obtains a Gaussian expression for \( G(R; L) \) which is wrong. In more recent work \[13\] we showed that the same strategy, \textit{i.e.}, replacing the exact thermal weight by Eq. (4) and evaluating \( \lambda \) and \( \epsilon \) variationally, produces excellent quantitative results for the elastic response of a semiflexible chain under tension. Notice that the optimal values of \( \lambda \) and \( \epsilon \) depend on the property of interest.

Following these earlier works \[11,13\] we shall calculate \( G(R; L) \) by replacing the true thermal weight in Eq. (4) by \( \Psi_{MF}[u(s)] \) in Eq. (4) and use a stationary phase approximation to set \( \lambda \) and \( \epsilon \). The equation for \( G(R; L) \) with the weight given by \( \Psi_{MF}[u(s)] \) is

\[
G(R; L) = \Omega \int_{-\infty}^{+\infty} \frac{d^3k}{(2\pi)^3} \int d\lambda \int d\epsilon \int \mathcal{D}[u(s)] \Psi_{MF}[u(s)] \langle -\mathbf{k} \cdot [R - \int_0^L u(s) ds] \rangle
\]

(6)

where \( \Omega \) represents a normalization constant. The functional integral over \( u(s) \) in Eq. (6) is done by replacing \( u \) by \( v = u - k/2\lambda \). The resulting path integral corresponds to a harmonic oscillator that makes a transition from \( u(0) - k/2\lambda \) to \( u(L) - k/2\lambda \) in imaginary “time” \( L \). Using the standard result for the harmonic oscillator propagator \[16\] the distribution function \( G(R; L) \) becomes

\[
G(R; L) = \int d\lambda \int d\epsilon \exp(-F(\lambda, \epsilon))
\]

(7)
where

\[
F(\lambda, \epsilon) = \frac{3}{2} \left[ \log \left( \frac{\lambda L - 2\epsilon}{4\lambda^2} \right) + \log \left( \frac{\sinh(\omega L)}{\omega l_p} \right) + \log(\alpha\beta) \right]
- \lambda L - 2\epsilon + \left( \frac{\gamma}{\beta} \right) \left( \frac{\lambda^2 R^2}{\lambda L - 2\epsilon} \right) + \text{const.} \tag{8}
\]

with

\[
\alpha = \frac{\epsilon}{2} + \frac{l_p\omega}{4} \coth \left( \frac{\omega L}{2} \right) \tag{9}
\]
\[
\beta = \frac{\epsilon}{2} + \frac{l_p\omega}{4} \tanh \left( \frac{\omega L}{2} \right) + \frac{1}{\lambda L - 2\epsilon} \tag{10}
\]
\[
\gamma = \frac{\epsilon}{2} + \frac{l_p\omega}{4} \tanh \left( \frac{\omega L}{2} \right) \tag{11}
\]

and

\[
\omega = \left( \frac{2\lambda}{l_p} \right)^{1/2} \tag{12}
\]

For the case of large \(L\) the function \(F(\lambda, \epsilon)\) may be written in the somewhat more manageable form

\[
F(\lambda, \epsilon) = Lf(\lambda) + \frac{3}{2} \log(2\epsilon + l_p\omega) - 2\epsilon - \frac{9}{2} \log(l_p\omega) + O \left( \frac{1}{L} \right) + \text{const.} \tag{13}
\]

where \(f(\lambda) = (3/2)\omega - \lambda(1 - r^2)\) and \(r = R/L\). Thus, as \(L\) becomes larger the function \(F(\lambda, \epsilon)\) becomes more sharply peaked and the stationary phase approximation becomes more accurate. For leading order in \(L\) the stationarity condition for \(\lambda\) is \(f'(\lambda) = 0\), which gives

\[
\left( \frac{\lambda l_p}{2} \right)^{1/2} = \frac{3}{4} \left( \frac{1}{1 - r^2} \right) \tag{14}
\]

and we find that \(\epsilon\) does not show any significant, leading order variation with \(r\). Substituting the stationary values of \(\lambda\) and \(\epsilon\) into Eq. \(13\) for \(F(\lambda, \epsilon)\) yields the desired simple, approximate expression for \(G(R; L)\),

\[
G(R; L) = \frac{N}{(1 - r^2)^{9/2}} \exp \left( -\frac{9L}{8l_p(1 - r^2)} \right) \tag{15}
\]

where \(N\) is a normalization constant and we have again taken the leading orders in \(L\) in the exponential and in the prefactor. In our earlier work \[11\] we showed that the stationary phase approximation reduces the persistence length from \(l_p\), which obtains in an exact treatment of the thermal weight in Eq. \(4\), to \(l_{MF} = (2/3)l_p\). Identifying the effective persistence length \(l_{MF}\) with the measured persistence length of the polymer produces a simple approximate expression for the radial probability density of a semiflexible chain in three dimensions,

\[
P(r; t) = \frac{4\pi N r^2}{(1 - r^2)^{9/2}} \exp \left( -\frac{3t}{4} \frac{1}{(1 - r^2)} \right) \tag{16}
\]
where \( t = L/l_{MF} \). The normalization constant is determined by the requirement that

\[
\int_0^1 P(r; t)dr = 1. \tag{17}
\]

The integral can be evaluated by the substitution \( r = x/\sqrt{1 + x^2} \) to yield

\[
N = \frac{4\alpha^{3/2}e^\alpha}{\pi^{3/2}(4 + 12\alpha^{-1} + 15\alpha^{-2})} \tag{18}
\]

where \( \alpha = 3t/4 \).

The distribution function, \( P(r; t) \), vanishes as \( r^2 \) as \( r \to 0 \) and also vanishes at \( r = 1 \). The peak of the distribution function occurs at \( r_{\text{max}} = [(\eta + \sqrt{\eta^2 + 14})/7]^{1/2} \), where \( \eta = (5/2) - \alpha \). As expected, when \( t \to 0 \), then \( r_{\text{max}} \to 1 \) and \( P(r, t) \to \delta(r - 1) \). In Fig. (1) we plot \( P(r; t) \) for the five values of \( t \) for which WF [10] have presented simulation data. For comparison, the results of the analytic expressions obtained by WF [10] are also presented. For very stiff chains (\( t = 0.5 \) in Fig. (1)) the WF theory gives a more accurate estimate of the peak [17]. Nevertheless, over the range of \( t \) examined by WF [10] our simple expression in Eq. (16) reproduces the data quite accurately.

In order to further assess the validity of our theory we have also calculated the second and fourth moments using the radial distribution function in (16). The moments are given by

\[
\mu_n \equiv \langle r^n \rangle = \int_0^1 r^n P(r; t)dr. \tag{19}
\]

The same substitution that was used to evaluate the integral in Eq. (17) can be used to find the moments, yielding

\[
\mu_2 = \frac{\left(\frac{3}{2}\right) - \frac{4\alpha + 10}{4\alpha^2 + 12\alpha + 15}}{15} \tag{20}
\]

\[
\mu_4 = \frac{15}{4\alpha^2 + 12\alpha + 15} \tag{21}
\]

for the second and fourth moments. In the limit of \( \alpha \to \infty \) (random coil limit) \( \mu_2 \to 3/2\alpha \) and \( \mu_4 \to 15/4\alpha^2 \), both of which coincide with results using exact moments [12]. Similarly both \( \mu_2 \) and \( \mu_4 \) tend to unity in the limit of \( \alpha \to 1 \) (hard rod limit), which is once again the exact result.

The theory outlined here provides surprisingly accurate results for \( P(r; t) \). The correct limiting behavior is obtained for \( P(r; t) \) and for the first two moments. Furthermore, our theory can be systematically applied to other problems involving semiflexible chains. Thus it appears that the meanfield-like approach used here may be useful for treating a wide variety of problems in which the rigorous enforcement of the constraint \( u(s)^2 = 1 \) is difficult to enforce.

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[16] Feynman, R. P. and Hibbs, A. R., “Quantum Mechanics and Path Integrals”, (McGraw-Hill, New York, 1965).
[17] In the extreme limit $t \to 0$ we expect $P(r; t) \sim \beta(t)\delta(1-r)$ where $\beta(t)$ is the area under the $\delta$-function. It is clear that Eq. (16) goes to the correct limit as $t \to 0$. For very small $t$, $\beta(t)$ would be approximately the area under a rather sharply peaked function at $r = 1$ (see the $t = 0.5$ case in Fig. (1)). Although our theory overestimates the peak by about ten percent it is clear that the area under $P(r; t)$ and the width are very close to the simulation results.
Fig. 1: Comparison of $P(r,t)$ obtained with Monte Carlo simulations (represented by symbols) for $t = 10, 5, 2, 1, \text{and } 0.5$ and with analytic theories (represented by curves) for the same values of $t$. The curves and symbols are arranged so that the largest value of $t$ is the left most and the smallest value of $t$ is the right most. The dark lines corresponds to Eq. (16) and the light lines are based on the approximate theory of Wilhelm and Frey [10].