Shapes of Knotted Cyclic Polymers

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Momentary configurations of long polymers at thermal equilibrium usually deviate from spherical symmetry and can be better described, on average, by a prolate ellipsoid. The asphericity and nature of asphericity (or prolateness) that describe these momentary ellipsoidal shapes of a polymer are determined by specific expressions involving the three principal moments of inertia calculated for configurations of the polymer. Earlier theoretical studies and numerical simulations have established that as the length of the polymer increases, the average shape for the statistical ensemble of random configurations asymptotically approaches a characteristic universal shape that depends on the solvent quality. It has been established, however, that these universal shapes differ for linear, circular, and branched chains. We investigate here the effect of knotting on the shape of cyclic polymers modeled as random isosegmental polygons. We observe that random polygons forming different knot types reach asymptotic shapes that are distinct from the ensemble average shape. For the same chain length, more complex knots are, on average, more spherical than less complex knots. This paper is a shorter, revised version of the article Ref. [12]. For more details, see Ref. [12].

1 Introduction

It is an accepted convention in studies of shape and size of polymer chains to characterize actual configurations adopted by the polymers by calculating their inertial properties. The radius of gyration, i.e. the root mean square distance from the center of mass, is a standard measure of polymer size. In simulation studies, the mass of the polymer is assumed to be equally distributed among the vertex points of the simulated chains. Studies of overall polymer size reveal that the radius of gyration of circular polymers for a fixed knot type scales like that of self-avoiding walks [1, 2, 5, 13, 14] with an estimated scaling exponent $\nu = 0.5874 \pm 0.0002$ [11] while phantom polymers behave like neutral ideal chains with the scaling exponent $\nu = 0.5$.

Studies of shapes of polymer chains use the three principal moments of inertia calculated for a given configuration of the chain to build an ellipsoid with the same ratio of its principal moments of inertia as those of the given polymer configuration. Kuhn [9] was first to propose that the overall shape of random coils formed by polymer chains at thermodynamic equilibrium should, for entropic reasons, have the shape of a prolate ellipsoid. His proposal has been confirmed in numerical simulation studies (see e.g. Refs. [6, 15, 16]) and also in experimental measurements [7, 10]. In the present study, we address how the shape and overall size of polymer chains are influenced by the presence of knots in these polymers.

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Similarly to earlier studies of polymer shapes, we characterize the shape based on inertial properties and construct the ellipsoid of inertia. The ellipsoid of inertia is defined using the moment of inertia tensor,

$$T_{ij} = \frac{1}{2N^2} \sum_{n=1}^{N} \sum_{m=1}^{N} (X_n^i - X_m^i) \cdot (X_n^j - X_m^j) \; (i = 1, 2, 3; \; j = 1, 2, 3), \tag{1}$$

where X_n^i denotes the i^{th} coordinate of the n^{th} vertex and N is the number of vertices in the polygon on which one has equally distributed the mass of the polymer. As T_{ij} is a real symmetric tensor, it has three real eigenvalues λ_1, λ_2, λ_3 giving the three principal moments of inertia and determining the corresponding eigenvectors providing the principal axes of inertia. The square roots of λ_1, λ_2, λ_3 define the semi-axis lengths of the associated *ellipsoid of inertia*. However, the ellipsoid of inertia does not have the same moments of inertia as the polygon it represents. To have this property, the semi-axis lengths a, b, and c should have values corresponding to $\sqrt{3\lambda_1}$, $\sqrt{3\lambda_2}$, and $\sqrt{3\lambda_3}$, respectively. The ellipsoid with these semi-axis lengths is what we call the *characteristic inertial ellipsoid* [12] of the given polymer. The characteristic inertial ellipsoid has the attractive property that it is its own characteristic inertial ellipsoid.

The semi-axis lengths a, b, and c of the characteristic inertial ellipsoid are used to define two measures of polymer shape: asphericity (denoted A) and prolateness (denoted P). The asphericity is a number between 0 (implying a spherical shape, when $a = b = c$) and 1 (implying a rod-like shape, when $b = c = 0$) and is defined by

$$A(a, b, c) = \frac{(a-b)^2 + (a-c)^2 + (b-c)^2}{2(a+b+c)^2}. \tag{2}$$

The prolateness has values between -1 (perfectly oblate ellipsoid, when $a = b > c$) and 1 (perfectly prolate ellipsoid, when $a > b = c$) and is defined by

$$P(a, b, c) = \frac{(2a-b-c)(2b-a-c)(2c-a-b)}{2(a^2+b^2+c^2-ab-ac-bc)^{3/2}}. \tag{3}$$

Note that both A and P are invariant of scale and symmetric in a, b, and c.

As discussed in Ref. [12], traditionally the principal moments of inertia λ_1, λ_2, and λ_3 have been used as the arguments to A and P instead of the semi-axis lengths a, b, and c. However, this leads to a bias for large dimensions in A. By using the semi-axis lengths, we eliminate this bias. Specifically, the squared radius of gyration and A and P (using the semi-axis lengths) provide a three-dimensional orthogonal system that separates the measurement of size from shape [12].

2 Results

We have analyzed equilateral random polygons from 6 to 48 edges with a step size of 2 and from 50 edges to 500 edges by a step size of 10 edges. For each number of edges, we generated 400,000 random knots using the hedgehog method [8]. To identify the knot type of each of the polygons, we calculated the HOMFLY polynomial [4] using the program of Ewing and Millett [3]. The generated random polygons were divided into the individual knot types and their shapes were analyzed in terms of asphericity and prolateness.

Fig. 1 shows how the average asphericity and prolateness depend on the knot type and the length of the polygon. It is interesting to analyze some of these profiles in order to understand better their meaning.

The asphericity profile for unknots shows that for small number of segments (say 6 and 8 segments), the unknotted polygons deviate strongly from spherical symmetry. However, the

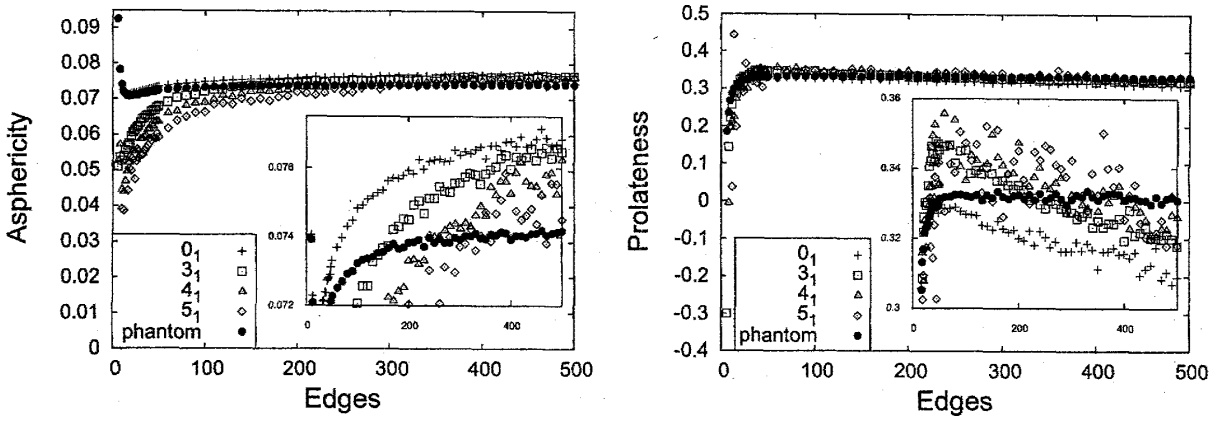

Figure 1: Scaling profiles for the average asphericity (left) and average prolateness (right) of knotted polygons and phantom polygons. The insets provide zoomed-in views, permitting better differentiation between polygons forming the different knot types.

asphericity values in this range do not tell us whether the polygons are aspherical due to adopting discoidal planar configurations or due to forming elongated shapes. Inspection of the right panel of Fig. 1 reveals, however, that unknotted polygons with 6 or 8 segments have, on average, positive prolateness. Therefore, we can conclude that the dominant deviation from spherical symmetry for unknotted polygons with small number of segments is towards forming elongated configurations. This contrasts with the negative prolateness of polygons with 6 segments that form trefoil knots and have on average an oblate shape (negative prolateness). However, polygons forming trefoil knots with increasing number of segments quickly become prolate on average and their asphericity increases.

A more general comparison of the asphericity of polygons forming different knot types reveals that for a given number of segments, the polygons forming more complex knots are on average more spherical, i.e. have lower asphericity, than polygons forming less complex knots. We expect however that for very long polymers, the asphericity values of various simple knots will approach the same universal value.

A general comparison of prolateness of polygons forming various knot types reveals that for a given number of segments, the prolateness of less complex knots is lower than that of more complex knots. It is interesting to note that for the individual knot types analyzed here, the prolateness reaches its maximal value for relatively short polygons ($n < 70$) and then shows a decrease. It may seem contradictory that the decrease in prolateness with the increasing chain length is associated with increasing asphericity. However, there is no real contradiction as the flattening of a rugby ball shape from its sides decreases its prolateness and increases its asphericity. The joint correlation of asphericity and prolateness for increasing numbers of edges is shown in Fig. 2. Here one can observe the limiting tendency of these quantities.

After exploring the asphericity and prolateness profiles for polygons forming individual knot types, let us analyze the corresponding profiles for the ensemble average of all polygons grouped together. Such a statistical set represents phantom polygons that can freely undergo intersegmental passages such as those exemplified by circular DNA molecules in the presence of type II DNA topoisomerase. Of course, the profile of all polygons is the weighted average of profiles for individual knot types where the relative probability of a given knot type is taken into account. Therefore, for very small number of segments, where unknots dominate, the profile for phantom polygons closely follows that of the unknots. As polygon sizes increase and nontrivial knots

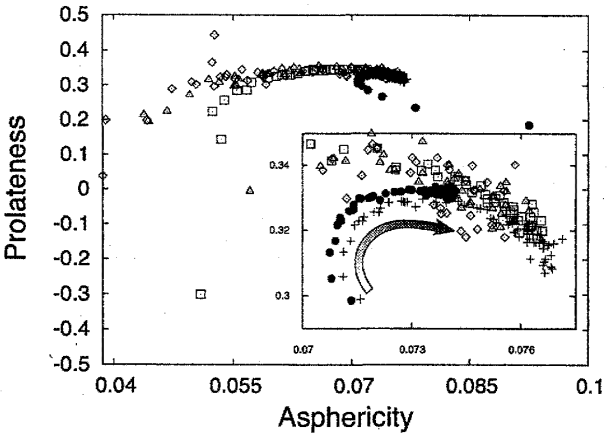

Figure 2: Average asphericity and prolateness for phantom polygons, 0_1, 3_1, and 4_1 knotted polymers with increasing length. The arrow shows the direction with increasing numbers of edges. The key for this graph is the same as in Fig. 1. The inset provides a zoomed-in view, permitting better differentiation between polygons forming the different knot types.

become frequent, the asphericity and prolateness of phantom polygons rapidly approach their respective characteristic constant values.

We have concentrated on scale independent measures of overall shape adopted by modeled polymers like asphericity and prolateness. However, size also matters and to completely describe inertia preserving ellipsoids that characterize the shapes of knotted polymers with a given length, one needs to consider the absolute sizes of these ellipsoids, where the natural size measure is the statistical segment length. Fig. 3 presents the characteristic inertial ellipsoids for the average shapes of the knots 0_1, 3_1, and 4_1 and also of phantom chains formed by 500 edge polygons. This form of presentation (nested ellipsoids) allows visual comparison of average shapes of polygons with different topology. We can see that the ellipsoid characterizing unknots forms the external shell and therefore is bigger than ellipsoids characterizing nontrivial knots. As the knots get more complicated, the ellipsoids representing them become smaller. However, they maintain very similar aspect ratios and it is hardly visible that 4_1 knots are on average more spherical than unknots (see Fig. 1). The most internal shell in Fig. 3 represents phantom polygons as these have the smallest overall dimensions from this set of knots. However, more complex knots, e.g. the 10_{165} knot, would be smaller than phantom polygons with 500 edges. The situation presented in Fig. 3 illustrates the particular case of 500 edge polygons.

What would be the corresponding image for very long chains? We conjecture that for such a situation, the nested ellipsoids would be very closely spaced, like onion skins. The external skin would be still that of the unknot, and the sequential skins would be ordered according to the complexity of the knots 3_1, 4_1, five crossing knots, six crossing knots, etc. Toward the center of the onion, one would have extremely complex knots, while the skin representing the average size of phantom knots would be placed between the external skin representing unknots and the internal skins representing the most complex knots possible for this size of the polygon. We also conjecture that the external skins (i.e. ellipsoids) representing simple prime knots would all be asymptotically close to the aspect ratio attained by the ellipsoid representing unknots, while very complex knots would be more spherical. At this point, we are uncertain whether the order of the skins for all knots will be the same for all chain sizes, i.e. whether there could be an example of two knot types where one would have its overall dimensions smaller than the other at 500 segments, for example, but not at 1000 segments. However, it is probably safe to

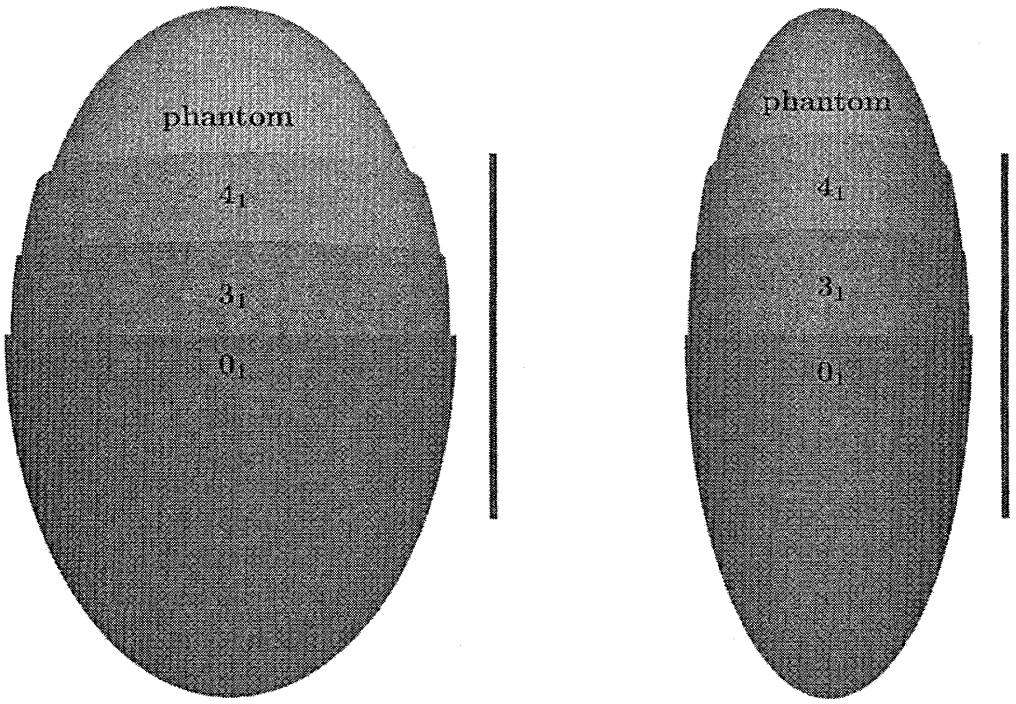

Figure 3: Average ellipsoids for 500 edge 0_1, 3_1, 4_1, and phantom polygons as seen along the two shortest axes of inertia. The bar to the right of the ellipsoids represents the size of 10 statistical segments.

conjecture that the order of skins (ellipsoids) representing knots belonging to the same family of knots (like simple torus knots 3_1, 5_1, 7_1, etc.), will always follow the order of the minimal crossing number, provided that the number of segments in the polygon is significantly bigger than the minimal number of segments needed to form most complex knots under consideration.

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