Polymer persistence length characterized as a critical length for instability caused by a fluctuating twist

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We establish the identity of the persistence length of an easily bendable polymer with the critical length for the onset of elastic instability toward bending induced by the root-mean-square twist. For a polymer of arbitrary bending stiffness the identity remains approximately valid; the ratio of persistence length to critical length is always within 20% of unity.

Bresler and Frenkel were the first to model a polymeric molecule in solution as a thin elastic rod subject to thermal bending fluctuations.[1,2] An equivalent model, the "wormlike chain," was later formulated and analyzed by Kratky and Porod.[3,4] The fundamental parameter of the behavior of a fluctuating rod is a characteristic length λ (unfortunately, most often designated as $1/2\lambda$ in the polymer literature) defined as

$$\lambda = B/k_B T , \tag{1}$$

where B is the Hooke's Law constant for bending and $k_B T$ is Boltzmann's constant times the temperature in kelvin. Actually, B is a bending stiffness averaged over the principal directions of the generally anisotropic cross section of the rod,[2] but we consider only the case of a circular cross section.

A familiar property of the persistence length[4] is embodied in the limiting formula

$$\langle R^2 \rangle \rightarrow 2\lambda L , \tag{2}$$

where $\langle R^2 \rangle$ is the mean-square end-to-end distance of the fluctuating rod, L is the length of the rod taken along its axis, and the limit is in an asymptotic sense as $L \rightarrow \infty$. The distribution of end-to-end distances obeys the central-limit theorem for long rods: $\langle R^2 \rangle$ becomes proportional to L, the length of a continuous three-dimensional random walk; and the persistence length λ is recognized as half the length of an elementary step of the walk (or, in polymer language, half the length of an equivalent segment).

From Eq. (1) we see as well that the persistence length is very long when fluctuations are suppressed (low T) or when the polymeric material is highly resistant to bending. In these conditions, the axis of the rod is approximately straight. We are led to expect a direct correlation between λ and the scale of length on which the fluctuating axis of the rod is approximately straight. In fact, we have the formula[2]

$$\langle \cos\theta \rangle = e^{-l/\lambda} , \tag{3}$$

where θ is the angle between vectors tangent to the axis of the rod, one at the point s_a along the axis, the other further along at s_b, with the arc length $s_b - s_a$ equal to l. From Eq. (3) we learn that the persistence length is the correlation length for the directional correlation function $\gamma(l)$,

$$\gamma(l) = \langle \cos\theta(l) \rangle . \tag{4}$$

When $l = \lambda$, $\cos\theta$ has fallen on the average to the fraction e^{-1} of its initial value unity (assumed, for all intents and purposes, for contour lengths much less than the persistence length). A related characterization of λ is that it equals the average projection of the end point of an infinitely long fluctuating rod on the direction of the rod at its starting point.[4]

We show here that the persistence length can be characterized in yet another way. When an elastic rod is subjected to a *twisting* moment, the state in which its axis is straight is always one of equilibrium. But, for a given twist, a rod of length greater than a critical value is in a state of *unstable* equilibrium if its axis is straight.[5,6] The equilibrium state of lowest elastic energy then has a bent axis. We will establish that the persistence length is approximately equal to the critical length for the onset of elastic instability of a class of thermal twisting fluctuations. Further, the persistence length is *exactly* equal to the critical length in the limit $B/C \rightarrow 0$, where C is the Hooke's Law constant for twisting.

We consider a thin rod with uniform circular cross section, bending constant B, and twisting constant C. In its undeformed state of zero elastic energy, its axis is straight. When bent and twisted, the elastic energy U associated with a segment between two cross sections at s_a and s_b is a functional,

$$U = \int_{s_a}^{s_b} \left[\tfrac{1}{2} B (\varphi_1'^2 + \varphi_2'^2) + \tfrac{1}{2} C \varphi_t'^2 \right] ds , \tag{5}$$

where $\varphi_1(s)$ and $\varphi_2(s)$ are angular rotations (bends) about two orthogonal directions in the cross section, $\varphi_t(s)$ is an angular rotation about the tangent to the axis (twist), and primes denote derivatives with respect to axial contour length s. The three Euler equations written, respectively, for the functions φ_1, φ_2, and φ_t, establish immediately that their derivatives are constant in equilibrium states. The equilibrium curvature $\kappa(s)$ of the axis is therefore constant, since

$$\kappa^2 = \varphi_1'^2 + \varphi_2'^2 . \tag{6}$$

The equilibrium twist $\omega(s)$ about the axis is also constant,

$\omega(s)$ being identified with φ_t'. The energy of an equilibrated deformation may then be written as

$$U=\tfrac{1}{2}Bl\kappa^2+\tfrac{1}{2}Cl\omega^2\ , \tag{7}$$

where $l=s_b-s_a$.

As a consequence of the identity[5]

$$\tau=\omega-(d/ds)\tan^{-1}(\varphi_1'/\varphi_2')\ , \tag{8}$$

the differential-geometric torsion $\tau(s)$ of the equilibrium axis is also constant. The equilibrium axis, with constant curvature and torsion, must be a circular helix. Moreover, since φ_1' and φ_2' are constants, the constant values of τ and ω are equal,

$$\tau=\omega\ . \tag{9}$$

We will need the result of an exercise in differential geometry,

$$\cos\theta_{ab}=(\tau^2+\kappa^2)^{-1}\{\tau^2+\kappa^2\cos[l(\tau^2+\kappa^2)^{1/2}]\}\ , \tag{10}$$

where κ and τ are the constant curvature and torsion, respectively, of a helical arc of length l. The angle θ_{ab} is that between the tangent to the arc at s_a and the tangent to the arc at s_b, with the difference s_b-s_a equal to l. When the curvature is zero, the helix is a straight line, and Eq. (10) gives the correct result, $\theta_{ab}=0$.

Consider now our thin rod with a definite constant twist ω but with a straight axis. The twist ω is induced by a transient moment **M** of thermal origin directed along the axis, hence perpendicular to the cross sections. Suppose that the cross section at s_b is then tilted through an angle θ_{ab}. The twisting component of the moment **M** drops by a factor $\cos\theta_{ab}$, so the value of twist drops by the same factor and becomes equal to $\omega\cos\theta_{ab}$. The energy associated with twist drops from $\tfrac{1}{2}Cl\omega^2$ to $\tfrac{1}{2}Cl\omega^2\cos^2\theta_{ab}$. The overall elastic energy, formerly equal to $\tfrac{1}{2}Cl\omega^2$, becomes

$$U=\tfrac{1}{2}Cl\omega^2\cos^2\theta_{ab}+\tfrac{1}{2}Bl\kappa^2\ , \tag{11}$$

as the axis assumes the shape of a helix with curvature. We are investigating the onset of instability of the straight axis and, hence, need consider only small curvatures κ.

With Eqs. (9) and (10), and small κ, Eq. (11) takes the form

$$U=\tfrac{1}{2}Cl\omega^2+\tfrac{1}{2}\kappa^2 l[B+2C(\cos\omega l-1)]\ . \tag{12}$$

The new energy is less than that of the twisted but straight rod, $\tfrac{1}{2}Cl\omega^2$, if the term in square brackets is negative. Then, the straight rod is unstable and bends to a helical arc. For sufficiently small values of l, the bracketed term in Eq. (12) is clearly positive, but when l exceeds the value l^*,

$$l^*=\omega^{-1}\cos^{-1}[1-(B/2C)]\ , \tag{13}$$

the straight axis is unstable.

Let ω have the root-mean-square of its fluctuating values, computed in routine fashion from the energy in Eq. (7),

$$\omega_{\rm rms}=(k_BT/Cl)^{1/2}\ . \tag{14}$$

TABLE I. The values of $l^*_{\rm rms}/\lambda$ as a function of σ.

σ	$l^*_{\rm rms}/\lambda$	σ	$l^*_{\rm rms}/\lambda$
−1.0	1.000	−0.2	1.075
−0.9	1.008	−0.1	1.086
−0.8	1.017	0.0	1.097
−0.7	1.026	0.1	1.108
−0.6	1.035	0.2	1.120
−0.5	1.045	0.3	1.132
−0.4	1.054	0.4	1.145
−0.3	1.065	0.5	1.158

Note that $\omega_{\rm rms}$ depends on the length of the segment considered. The longer the segment, the less is the twist (an intensive quantity) that can be produced in it by available thermal energy. We consider the critical length $l^*_{\rm rms}$ for instability induced by an rms twist. With $l=l^*_{\rm rms}$ in Eq. (14), substitution of Eq. (14) into Eq. (13) yields

$$l^*_{\rm rms}=(C/k_BT)\{\cos^{-1}[1-(B/2C)]\}^2\ . \tag{15}$$

We proceed to establish that this quantity equals the persistence length in a limiting case.

The relative values of B and C are constrained by the formula

$$B/C=1+\sigma\ , \tag{16}$$

where σ is called Poisson's ratio.[5,6] For all known materials (steel, wood, plastics, etc.) it has a positive value less than 0.5. However, contradictions with physical laws are encountered only if σ falls outside the interval $(-1,\tfrac{1}{2})$; negative values greater than -1 are allowed. In fact, when a single DNA polymer in solution is modeled as a thin circular rod, and values of B and C are deduced from current data, the values of σ calculated from Eq. (16) are as low as -0.7.[7] At any rate, we consider the limit $\sigma\to-1$, or $B/C\to 0$.

When $\epsilon=B/C$ is a small quantity, we have the following estimate:

$$\begin{aligned}\cos^{-1}(1-\tfrac{1}{2}\epsilon)&=\sin^{-1}[1-(1-\tfrac{1}{2}\epsilon)^2]^{1/2}\\&=\sin^{-1}[\epsilon^{1/2}+O(\epsilon^{3/2})]\\&=\epsilon^{1/2}+O(\epsilon^{3/2})\ .\end{aligned}$$

The square of this quantity equals $\epsilon+O(\epsilon^2)$. The immediate result of substitution into Eq. (15) is

$$\lim_{\sigma\to-1} l^*_{\rm rms}=B/k_BT\equiv\lambda\ , \tag{17}$$

as stated. In words, *if the rod bends much more easily than it twists, then its persistence length is the length past which the root-mean-square twist induces instability toward bending.*

We obtain a formula for the ratio $l^*_{\rm rms}/\lambda$ from Eqs. (1), (15), and (16),

$$l^*_{\rm rms}/\lambda=(1+\sigma)^{-1}\{\cos^{-1}[\tfrac{1}{2}(1-\sigma)]\}^2 . \tag{18}$$

This ratio depends only on the value of Poisson's ratio. As σ increases in its allowed range from its smallest value -1, $l^*_{\rm rms}/\lambda$ exhibits an unremarkably monotone behavior, and we merely tabulate it. From Table I we see that $l^*_{\rm rms}/\lambda$ never exceeds its limiting value of unity by more than 16%.

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