Auxiliary Field Theory of Polymers with Intrinsic Curvature

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ABSTRACT: We treat polymer chains with an intrinsic curvature, which we model by a continuum extension of a microscopic model with preferred bending angle. From this model, we obtain a modified form of the mean-field Hamiltonian used to describe semiflexible chains. We then employ an auxiliary field operator to enforce the mean curvature constraint along with a torsional constraint. Using this formalism, we provide analytic results for the tangent-tangent correlator $\langle \boldsymbol{u}(s)\cdot\boldsymbol{u}(s')\rangle$, mean square radius of gyration $\langle S^2\rangle$, and mean square separation $\langle R^2\rangle$. We also obtain approximate results for the force−extension behavior of these chains, and discuss possible extensions to curved polymers with excluded volume and other self-interactions.

1. Introduction

With time, the theory of single polymer chains has generally progressed toward more and more explicit descriptions of the microscopic details of polymer chains. Since the middle of the last century, the field has moved from the classic "Gaussian" flexible polymer models[1−5] through "wormlike" polymer models accounting for chain stiffness,[6−9] to models considering intrinsic curvature and torsion[10−12] or confinement on curved surfaces.[13] Indeed, models describing polymers with intrinsic curvature or other detailed internal structure have become particularly relevant in light of the increasing interest in biopolymers like RNA, DNA, and polypeptides. Here, microscopic "secondary" structure can have a dramatic influence on chain conformation[14−17] and mechanical properties,[18−20] and it cannot simply be abstracted away from physical models.

One would certainly like a simple model of polymer chains with internal structure like a preferred curvature or torsion. In fact, this has been accomplished through earlier work on the Bugl−Fujita chain[21] and its related variant, the Yamakawa chain.[10] Both these models treat chains with energies that are quadratic in the local difference from the preferred curvature and torsion, with Kratky−Porod-like local inextensibility constraints. By following an analogy with quantum-mechanical treatments of angular momentum, one can derive exact results for the radius of gyration $\langle S^2\rangle$, mean-square end-to-end distance $\langle R^2(L)\rangle$, and other experimental quantities for the Yamakawa chain. However, the resulting formalism of generalized Wigner functions and angular correlation coefficients is intimidating. One requires infinite sums to evaluate many experimental values, nor is there a transparent, easily evaluated scheme for approximating them. The theoretical rigor of these models is commendable, but one might wish for a simpler, approximate model. This has been provided in part by helpful analyses of fluctuating, elastic helical rods.[22,23] Nevertheless, one might prefer a treatment which begins with a primitive derivation of a field theory rather than imposing fluctuations on an existing static model, a difference akin to that between models of Brownian motion using a explicit velocity probability distribution and path integral approach, e.g., the Fokker−Planck equation, and those taking basic hydrodynamics with added white noise, e.g., the Langevin equation.[3]

Indeed, the theoretical situation for curved polymers rather resembles that which existed for wormlike polymers before the advent of the "mean-field" models which replaced the Kratky−Porod model's stringent constraints on local extensibility with more tractable global constraints. The mean-field approach has both simplified the theoretical notation and provided closed form results for experimentally relevant quantities, although they are generally not accurate beyond the second moment.

Following that spirit, we introduce a new auxiliary field model to treat polymers with an intrinsic curvature κ_0 and zero average torsion as elastic, curly chains under thermal fluctuations. The resulting path integral model applies to "ribbonlike" polymers, e.g., chains with backbones of directly linked benzene moieties and some supramolecular assemblages.[24,25] The model also holds for general, "phone cord"-like elastic bodies with no or low intrinsic torsion, and can be taken to the "macroscopic" limit of bodies outside the thermal regime as $kT \to 0$. Though one would like to model polymers with an arbitrary torsion, this simple model nevertheless captures the important features of an intrinsically curved chain, including oscillatory behavior. We derive the auxiliary field model as the continuum form of a microscopic model of rigid rods with a preferred bending angle, much as one can find the semiflexible model by extension of the freely jointed-chain picture of polymer chains. To treat this continuum form, we introduce an additional auxiliary field ψ to account for the preferred curvature. This field comes in addition to the mean field that we use to enforce the global length constraint. We neglect excluded-volume interactions and any *explicit* preferred torsion in our intrinsically curved chains in order to simplify the model. We weight the torsion *implicitly* instead, as we outline with a model with a change-of-curvature term and a constant ψ. However, we will see that this first model is too cumbersome, leading us to use a nonlocal, spatially varying auxiliary field $\psi(s - s')$ to enforce average curvature and an implicit torsional constraint. This constraint favors zero average torsion, and yields a model of an oscillatory chain that curls upon itself rather than wandering freely as the freely jointed (i.e., semiflexible) chain without a torsional constraint does.

Once we have obtained a saddle-point solution for $\psi(s - s')$, we use the resulting theory to calculate the tangent-tangent correlator $\langle \boldsymbol{u}(s)\cdot\boldsymbol{u}(s')\rangle$, which resembles the correlator of a wormlike chain, but with an oscillating prefactor $\cos(\tilde{\kappa}_0[s - s'])$, where $\tilde{\kappa}_0$. We then compute the mean square radius of gyration $\langle S^2\rangle$ and the mean square separation vector $\langle R^2(s - s')\rangle$ for these intrinsically curved chains, and find a close relation to the exact results produced from Yamakawa's theory for a chain with curvature $\tilde{\kappa}_0$ and zero average torsion. We

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subsequently discuss the long-time, equilibrium stretching behavior of our model chain under an externally imposed force, and find an extremely high restoring forces at large deformations. Finally, we mention the problem of excluded volume for intrinsically curved chains, and offer suggestions for how excluded volume and other contact interactions could modify our findings. Particularly interesting is the prospect that excluded-volume interactions could generate a helical ground state like that known to exist for α -helical peptides or nonbiological helical foldamers.[24,25]

2. Hamiltonian for the Curved Chain

2.1. Derivation of the Model. We treat intrinsically curved polymers via a modification of the theory of semiflexible (or wormlike) chains which has been developed over the past few decades.[7] This model now stands along with the flexible random walk model as one of the basic tools of polymer physics. Let us consider a polymer chain whose configuration is defined by the space curve $\boldsymbol{r}(s)$, where s parametrizes the contour length along the chain. We make this a semiflexible chain by requiring that it does not bend or stretch easily. A number of specific forms have been proposed for the Hamiltonian of such a chain, but all incorporate a bending energy of the form

$$E_{\text{bend}} = \int_0^L \mathrm{d}s\, \frac{\epsilon}{2}\kappa(s)^2 \tag{1}$$

where ϵ is a bending modulus and κ is the curvature $\kappa = |\mathrm{d}\boldsymbol{u}/\mathrm{d}s|/|\boldsymbol{u}(s)|$, $\boldsymbol{u}(s)$ being the chain's tangent vector, $\mathrm{d}\boldsymbol{r}/\mathrm{d}s$. If we take $|\boldsymbol{u}(s)| = 1$, we can eliminate the vector magnitude in the denominator to obtain a bending energy of the form $E_{\text{bend}} = \int_0^L \mathrm{d}s\ {}^1/_2\epsilon(\mathrm{d}\boldsymbol{u}/\mathrm{d}s)^2$. The strict constraint $|\boldsymbol{u}(s)| = 1\ \forall\ s$ can be satisfied through an analogy to the description of angular momentum in quantum mechanics (as is done in treatments of the Kratky−Porod model[10]). What this approach gains in rigor, however, is lost to the corresponding cost of inelegant, complicated final expressions for most quantities of experimental interest. Equivalent, closed form results can be recovered if one replaces the Kratky−Porod constraint $\delta(|\boldsymbol{u}(s)| - 1)$ with an average length constraint $\int_0^L \mathrm{d}s\ \boldsymbol{u}(s)^2 = L$, as Ha and Thirumalai do.[8,26] With this change, one arrives at a mean-field Hamiltonian for a configuration $[\boldsymbol{u}(s)]$ of the form

$$\beta\mathscr{H}[\boldsymbol{u}(s)] = \int_0^L \mathrm{d}s\, \left[\frac{l_{\text{p}}}{2}\left(\frac{\mathrm{d}\boldsymbol{u}}{\mathrm{d}s}\right)^2 + \phi(\boldsymbol{u}^2 - 1)\right] \tag{2}$$

where $\beta = (kT)^{-1}$, l_{p} is the persistence length [equal to ϵ/kT in eq 1] over which the chain "remembers" its direction $\boldsymbol{u}(s)$, and ϕ acts as a Lagrange multiplier that enforces the average length constraint. This *average* length constraint removes the mathematical complexities of treating the Kratky−Porod model, while reproducing that model's results for the mean square radius of gyration $\langle S^2\rangle$ and mean-square separation $\langle R^2(s - s')\rangle$ to within a simple numerical rescaling of the persistence length.[8,26] Physically, one would expect this approximation to be a good one for a free or weakly stretched/compressed chain. After all, segments reasonably far from the end points of such a chain should experience essentially identical forces, and hence they can be treated reasonably well by a common constraint. This argument is further supported by comparison with explicit numerical simulations of chains with local length constraints (i.e., chains eq 2 with a varying $\phi(s)$).[8,26] Admittedly, these comparisons underscore the fact that the mean-field model will necessarily produce different results for higher moments of the chain, as its treatment of segments near the chain ends will be inaccurate. However, we feel the transparency and utility of the mean-field model in treating nearly-free chains justifies such minor departures.

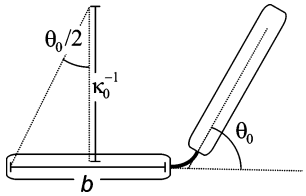

Figure 1. Drawing of a pair of links of length b, joined at an angle θ_0. Examining the diagram, we see that the "radius of curvature" κ_0^{-1} of this pair is given by $l/[2\tan(\theta_0/2)]$.

With this as our background, we move on to describe polymers with a preferred intrinsic curvature, which we parametrize by a new constant κ_0. One can derive a Hamiltonian for this intrinsically curved chain by considering a microscopic model of a chain made of N rigid links of length b with a preferred angle between links θ_0, as seen in Figure 1. We assign each link a unit vector $\hat{\boldsymbol{u}}$ to describe its direction. These link directions relate to the preferred angle θ_0 as $\langle\hat{\boldsymbol{u}}\cdot\hat{\boldsymbol{u}}'\rangle = \cos(\theta_0)$, where $\hat{\boldsymbol{u}}$ and $\hat{\boldsymbol{u}}'$ are the directions of any two adjacent links. Taking $\theta_0 = 0$ for the moment, it is clear that the energy function for a pair of links is simply $E = -\Omega(\hat{\boldsymbol{u}}\cdot\hat{\boldsymbol{u}}')$, where Ω is a bending modulus for the links such that $E \approx {}^1/_2\Omega(\Delta)^2$ for small angles Δ between them. For the case $\theta_0 \neq 0$, we will require an energy function that has a minimum at θ_0, and retains the same bending modulus about this minimum. A suitable energy function for the single pair of links $\hat{\boldsymbol{u}}$ and $\hat{\boldsymbol{u}}'$ is that given in studies of dimers with an intrinsic bending angle:[27]

$$E(\hat{\boldsymbol{u}},\hat{\boldsymbol{u}}') = \frac{-2\Omega}{1+\cos(\theta_0)}[(\hat{\boldsymbol{u}}\cdot\hat{\boldsymbol{u}}') + 2\sqrt{1-\cos(\theta_0)}\sqrt{1-(\hat{\boldsymbol{u}}\cdot\hat{\boldsymbol{u}}')}] \tag{3}$$

Examining the conditions we have placed on the energy function, one can see that eq 3 has a minimum at $\hat{\boldsymbol{u}}\cdot\hat{\boldsymbol{u}}' = \cos\theta_0$, satisfying the condition for the average angle. If the angle θ between $\hat{\boldsymbol{u}}$ and $\hat{\boldsymbol{u}}'$ deviates from θ_0 such that $\theta = \theta_0 + \Delta$, we go on to observe that the energy is quadratic in Δ

$$E(\theta_0 + \Delta) = \frac{\Omega}{2}\left[\Delta^2 + \frac{4\cos(\theta_0) - 8}{1+\cos(\theta_0)}\right] \tag{4}$$

which satisfies the second condition.

To derive a continuum version of this chain, let us expand the quantity $(\hat{\boldsymbol{u}}\cdot\hat{\boldsymbol{u}}')$ in the limit of very small θ, such that $(\hat{\boldsymbol{u}}\cdot\hat{\boldsymbol{u}}') = \cos\theta \sim 1 - \theta^2/2 + O(\theta^4)$. Taking $|\Delta\boldsymbol{u}_{\text{i}}| = |\sin\theta| \approx |\theta|$, we expand eq 3 to $O([\Delta\boldsymbol{u}_{\text{i}}]^2)$ and sum over all tangent pairs $\{\hat{\boldsymbol{u}},\hat{\boldsymbol{u}}'\}$. This yields

$$\beta\mathscr{H} = \sum_{i=0}^{N} \frac{\Omega}{(kT)\cos^2[\theta_0/2]}\left[\frac{1}{2}(\Delta\boldsymbol{u}u_i)^2 - 2\left|\sin[\theta_0/2]\right|\left|\Delta\boldsymbol{u}_i\right| - 1\right] \tag{5}$$

Examining Figure 1, one can see that the "radius of curvature" κ_0^{-1} of a pair of links at angle θ_0 is given as $\kappa_0^{-1} \approx b/(2\tan[\theta_0/2])$. Since we are taking the limit of small θ, θ_0 must approach zero as well, but this limit need not result in a straight chain. Rather, we will take $b \to 0$ and $\theta_0 \to 0$ while preserving the ratio κ_0. To finish transforming eq 5 into the Hamiltonian of a continuous chain, let us now simultaneously replace the

sum over i with an integral over a chain length coordinate s, and take the corresponding limits of $\Delta \boldsymbol{u}_i \rightarrow b(\mathrm{d}\boldsymbol{u}/\mathrm{d}s)$ and $N \rightarrow \infty$:

$$\beta\mathscr{H} = \int_0^L \mathrm{d}s\, \frac{\Omega b}{2(kT)}\left[\left(\frac{\mathrm{d}\hat{\boldsymbol{u}}}{\mathrm{d}s}\right)^2 - 2\kappa_0\left|\frac{\mathrm{d}\hat{\boldsymbol{u}}}{\mathrm{d}s}\right|\right] \tag{6}$$

where the chain length L is given as $L = Nb$. We also discard the non-$\boldsymbol{u}$ dependent terms that add an irrelevant constant energy, insofar as we treat the length of the chain as being fixed. Given that the chain curvature $\kappa(s)$ is equal to $|\mathrm{d}\boldsymbol{u}/\mathrm{d}s|$ for $|\boldsymbol{u}(s)| = 1$, we can see that the Hamiltonian of eq 6 relates to a bending energy like that of eq 1, though this energy now penalizes departures from κ_0:

$$E_{\mathrm{bend}} = \int_0^L \mathrm{d}s\, \frac{\epsilon}{2}[\kappa(s) - \kappa_0]^2 \tag{7}$$

where we retain ϵ's use in eq 1 as the local bending modulus; here, $\epsilon = \Omega b$.

One might rightly object that, thus far, our model seems redundant. After all, one would expect that the microscopic model of chain segments with a preferred bending angle that we have presented should only reproduce the results of the freely jointed chain. Admittedly, our formalism results in a slightly different form of the continuum free energy, but the basic vision of independent chain segments joined at an angle is the same as that presented by the freely jointed model. In fact, we need some additional constraint in order to produce anything like a "telephone cord" chain which wraps upon itself. This constraint must act upon the chain's plane of curvature, since if the chain can curl about in all possible directions, the effect will average out to something like an uncurved, wormlike chain.[3] A freely curving chain is also not a fully realistic presentation of a real polymer; after all, steric hindrances and short-range attractive effects mean that monomers do not revolve freely about the bonds to their neighboring monomers, but rest at certain preferred angles of rotation.[28] This again constrains the plane of curvature of the chain, effectively imposing a particular torsion on the chain. We will go on to introduce such a constraint through our use of nonlocal, spatially varying auxiliary fields to treat the absolute value term $\propto |\mathrm{d}\boldsymbol{u}/\mathrm{d}s|$ in eq 6. This constraint will favor zero average torsion, and turns out to be implicit. Before adding this field, we will offer a brief discussion of torsion and introduce a version of the aforementioned auxiliary field model which has a spatially constant auxiliary field and introduces a new change-of-curvature term to effectively constrain the torsion. Such a model proves cumbersome, however, leading us to the simpler version having the spatially varying auxiliary field. We then obtain the results of the theory.

2.2. Curved-Chain Model with Implicit, Mean-Field Torsional Constraint. The torsion $\tau(s)$ of the space curve $\boldsymbol{r}(s)$ is defined by the relation

$$\frac{\mathrm{d}}{\mathrm{d}s}\left(\frac{\boldsymbol{u} \times \frac{\mathrm{d}\boldsymbol{u}}{\mathrm{d}s}}{\left|\boldsymbol{u} \times \frac{\mathrm{d}\boldsymbol{u}}{\mathrm{d}s}\right|}\right) = -\tau(s)\frac{\mathrm{d}\hat{\boldsymbol{u}}}{\mathrm{d}s} \tag{8}$$

In effect, torsion marks the local rate of change of the orientation of the plane of curvature of $\boldsymbol{r}(s)$.[29] For $|\boldsymbol{u}(s)| = 1$ and $|\mathrm{d}\boldsymbol{u}(s)/\mathrm{d}s| = \kappa_0$, the torsion can be written $\tau(s) = \kappa_0^{-2}\, \boldsymbol{u}(s)\cdot(\mathrm{d}\boldsymbol{u}/\mathrm{d}s \times \mathrm{d}^2\boldsymbol{u}/\mathrm{d}s^2)$. As one can see, this "box product" makes torsion difficult to add to a Gaussian Hamiltonian that is quadratic in the tangent variable $\boldsymbol{u}(s)$, as an explicit torsion term will be nonintegrable. Yamakawa accomplishes this in the context of the local "angular velocities" of rotations on a chain.[10] Yet, as we note in the Introduction, extracting results from this formalism is not a transparent process.

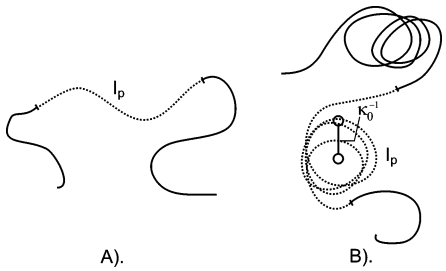

Figure 2. Schematic illustration of persistence length l_p (dashed segments) for (A) uncurved semiflexible and (B) curved chains. For the normal semiflexible chain (A), l_p indicates the length over which the chain remains relatively straight, while in the curved chain (B), l_p now denotes the average chain length that the chain curls up with a radius κ_0^{-1} before it "forgets" to curve and wanders off.

One can introduce an effective implicit torsional constraint by adding a change-of-curvature term $\propto(\mathrm{d}^2\boldsymbol{u}/\mathrm{d}s^2)^2$ to the Hamiltonian of eq 6, which adds a contribution $(\mathrm{d}^2\boldsymbol{u}/\mathrm{d}s^2)^2 = \kappa_0^2\tau(s)^2 + \kappa_0^4$ if the constraints $|\boldsymbol{u}(s)| = 1$ and $|\mathrm{d}\boldsymbol{u}(s)/\mathrm{d}s| = \kappa_0$ hold exactly.[29] This change-of-curvature term is quadratic in $\boldsymbol{u}(s)$ and therefore amenable to Gaussian analysis. We arrive at the following modified Hamiltonian:

$$\beta\mathscr{H}[\boldsymbol{u}(s)] = \int_0^L \mathrm{d}s\left[\frac{\upsilon_p}{4}\left(\frac{\mathrm{d}^2\boldsymbol{u}}{\mathrm{d}s^2}\right)^2 + \frac{l_p}{2}\left(\left|\frac{\mathrm{d}\boldsymbol{u}}{\mathrm{d}s}\right| - \kappa_0\right)^2 + \phi(\boldsymbol{u}^2 - 1)\right] \tag{9}$$

where we have modified eq 6 by adding a change-of-curvature term parametrized by the *compression volume* υ_p. As well, we have included the substitution $l_p = \Omega b/kT$, added an additional energy per unit length of $^1/_2 l_p\kappa_0^2$ in order to complete the square, and incorporated the average length constraint parametrized by ϕ in eq 2. In this model l_p is now an effective *curvature* persistence length over which the curvature should remain roughly constant, as illustrated in Figure 2. Meanwhile, ϕ retains is role as the global inextensibility constraint. Ultimately, the introduction of a preferred curvature into our model should not affect our decision to take a global length constraint, as the basic symmetry that the mean-field model exploited previously—i.e., the interchangeability of chain segments far from the end points—remains the same.

However, we still face difficulties in treating the nonlinearity that arises when we take the absolute value of the local curvature, which appears as a cross-term with κ_0 in eq 7. However, we can still treat this $|\mathrm{d}\boldsymbol{u}/\mathrm{d}s|$ cross-term by introducing a new auxiliary field $\psi(s)$, through the relation[30,31]

$$Z = \mathrm{e}^{\int \mathrm{d}s\,[2\sqrt{x(s)^2}]} = \int \mathrm{d}[\psi(s)]\, \mathrm{e}^{\int \mathrm{d}s\,[x(s)^2\psi^{-2}(s)+\psi^2(s)]} \tag{10}$$

For eq 10, the saddle-point condition that $\partial(\ln Z)/\partial\psi(s) = 0$ leads us to the result $-2x(s)^2/\psi^3(s) + 2\psi = 0$, and thus, $\psi(s)^4 = x(s)^2$. Taking the square root, one recovers $\psi^2(s) = \pm|x(s)|$, where the sign will be fixed by our subsequent choice of the form of $\psi(s)$. We note that our use of ψ^2 for the auxiliary field terms actually improves on previous treatments of exponentiated $|x(s)|$ terms that used only ψ to the first power,[30,31] i.e., $f(x,\psi') = (x^2/\psi' + \psi')$ in $\mathrm{e}^{-\int \mathrm{d}s[2\sqrt{x(s)^2}]} = \int \mathrm{d}[\psi'(s)]\, \mathrm{e}^{f(x,\psi')}$. Taking $f(x,\psi) = (x^2/\psi^2 + \psi^2)$ in $\mathrm{e}^{f(x,\psi)}$, on the other hand, better satisfies the saddle-point approximation's requirement that $|\partial_\psi{}^{2f}(x,\psi)| \gg 1$ at the saddle point. Evaluating this second derivative, we

see $\partial_{\psi^2}(x^2/\psi^2 + \psi^2)|_{\psi^2=|x|} = 4$, whereas $\partial_{\psi'^2}(x^2/\psi' + \psi')|_{\psi'=|x|} = 2/|x|$. Thus, taking ψ to the first power as the auxiliary field is suitable only for small x. Admittedly, we will see that the use of ψ^2 in this version of the Hubbard-Stratonovich transformation does create some additional mathematical work. Nevertheless, the situation illustrates how one can often choose from several different arrangements of auxiliary fields to achieve the same ends, adjusting that choice according to the situation.

We will now apply the auxiliary-field expression eq 10 to the absolute value term in eq 9, taking $2|x(s)| = l_p\kappa_0|\mathrm{d}\boldsymbol{u}/\mathrm{d}s|$. The partition function Z of the chain now becomes

$$Z = \int \mathrm{d}[\psi(s)] \int \mathrm{d}[\boldsymbol{u}(s)]\, \mathrm{e}^{-\beta\mathscr{H}_{\mathrm{mod}}[\mathbf{u}(s)]} \tag{11}$$

with $\beta\mathscr{H}_{\mathrm{mod}}$ given by

$$\beta\mathscr{H}_{\mathrm{mod}}[\boldsymbol{u}(s)] = \int_0^L \mathrm{d}s \left[\frac{\upsilon_p}{4}\left(\frac{\mathrm{d}^2\boldsymbol{u}}{\mathrm{d}s^2}\right)^2 + \left(\frac{l_p}{2} - \frac{l_p^2}{4}\kappa_0^2\psi^{-2}(s)\right)\left(\frac{\mathrm{d}\boldsymbol{u}}{\mathrm{d}s}\right)^2 + \phi(\boldsymbol{u}^2 - 1) - \psi(s)^2\right] \tag{12}$$

The simplest way of implementing an auxiliary field like $\psi(s)$ would be to take it as a constant along the entire length of the chain, $\psi(s) = \psi_0$, a mean field approximation like that found in other auxiliary-field treatments of polymers in the literature.[2,8,32,33] We would then just solve for the saddle point values of ψ_0 and ϕ. However, the resulting pair of saddle point equations is not so easily solved, resulting in an analytically insoluble sixth-order polynomial equation for ϕ. We also must adjust the parameter υ_p to ensure that the chain with the Hamiltonian of eq 13 reproduces the statistics of a semiflexible chain when the intrinsic curvature vanishes at $\kappa_0 = 0$. These complications mean that we ultimately recreate the complexity of earlier treatments of helical polymers, the same complexity which we sought to avoid by introducing the auxiliary field in the first place. As we show below, it is simpler to depart from past treatments of auxiliary fields and remove the mean-field assumption for $\psi(s)$. Instead, we will work with a generally nonlocal, spatially varying auxiliary field $\psi(s - s')$ rather than the constant field ψ_0. We can also discard the change-of-curvature term, as $\psi(s - s')$ will now act to constrain the torsion as well.

2.3. Curved-Chain Model with Spatially Varying Auxiliary Field. Let us return to the continuum bending energy of eq 6, and again incorporate it into the mean-field treatment of eq 2. We obtain

$$\beta\mathscr{H}[\boldsymbol{u}(s)] = \int_0^L \mathrm{d}s \left[\frac{l_p}{2}\left(\left|\frac{\mathrm{d}\boldsymbol{u}}{\mathrm{d}s}\right| - \kappa_0\right)^2 + \phi(\boldsymbol{u}^2 - 1)\right] \tag{13}$$

where ϕ and l_p are as defined earlier in eq 9. We have removed the change-of curvature term $\propto \upsilon_p$, as we will show that the effective torsional constraint this term provided will be replaced by an implicit constraint introduced through the auxiliary field ψ. Let us proceed as we did earlier in moving to eq 13, this time using a nonlocal spatially varying auxiliary field operator $\psi(s - s')$ instead of ψ_0.

As an operator, $\psi(s - s')$ is defined such that

$$\psi^{-1}(x')*\psi(x) = \delta(x - x')$$

x and x' being dummy variables. In order for this to hold, the operation "*" which we have used to apply the inverse can be defined in an operator context by generalizing the functional form $f^2 = f \times f$ to the operator form $\psi^{-2}(s - s') = \psi^{-1}(s)*\psi^{-1}(s') = \int \mathrm{d}s''\ \psi^{-1}(s - s'')\psi^{-1}(s'' - s')$, i.e., a convolution of the two nonlocal operators. This operator approach is well-founded, following that presented previously[30,31] in treating models of semiflexible chains and related quantum phenomena. Recalling the general properties of convolutions, we note $\partial_x(f*g) = (\partial_x f*g) = (f*\partial_x g)$. Though this derivative rule differs from that for the product of simple functions, we can see that is does not affect either the suitability of the auxiliary field approximation discussed in the previous subsection or the advantages of using fields proportional to ψ^2.

We arrive at the modified Hamiltonian

$$\beta\mathscr{H}_{\mathrm{mod}} = \int_0^L \mathrm{d}s\, \mathrm{d}s' \left[\left(\frac{\mathrm{d}\boldsymbol{u}(s)}{\mathrm{d}s}\right)\left[\frac{l_p}{2}\delta(s - s') - \frac{l_p^2}{4L}\kappa_0^2\psi^{-2}(s - s')\right]\left(\frac{\mathrm{d}\boldsymbol{u}(s')}{\mathrm{d}s'}\right) + \left(\frac{l_p}{2}\kappa_0^2 + \phi[\boldsymbol{u}(s)\cdot\boldsymbol{u}(s') - 1]\right)\delta(s - s') - \psi^2(s - s')\right] \tag{14}$$

where we have written out the integration over s and s' to emphasize the nonlocal character of ψ. We will demonstrate how this nonlocal quality acts as a constraint on torsion shortly; for the moment we will simply work through the formalism. Expressed in operator form, this Hamiltonian becomes a quadratic form in the field variable $\{\boldsymbol{u}(s)\}$

$$\beta\mathscr{H}_{\mathrm{mod}} = \int_0^L \mathrm{d}s\, \mathrm{d}s' \left[\left(\frac{l_p}{2}\kappa_0^2 - \phi\right)\delta(s - s') - \psi^2(s - s')\right] + \int_0^L \mathrm{d}s\, \mathrm{d}s'\, (\boldsymbol{u}_s M_{s,s'}\boldsymbol{u}_{s'}) \tag{15}$$

where[8,26]

$$M_{s,s'} = \partial_s\left[\frac{1}{L}\left(\frac{l_p}{2}\delta_{ss'} - \frac{l_p^2}{4}\kappa_0^2\psi^{-2}(s - s')\right)\right]\partial_{s'} + \phi\delta_{ss'} \tag{16}$$

As we have taken ψ to be a function of the length difference $(s - s')$, we analytically extend the operator so that ψ is periodic over L. This is as one would expect for a field that is contingent on the difference between two chain positions and not the absolute chain location. This periodicity also accounts for the L^{-1} factor when performing the double integral over $\mathrm{d}s$ and $\mathrm{d}s'$, and proves necessary for the Fourier analysis we will perform on the matrix $M_{s,s'}$.

The resulting quadratic form can be integrated over the space of configurations $\mathrm{d}[\boldsymbol{u}(s)]$ to obtain the free energy

$$\beta F = -\ln Z = \int_0^L \mathrm{d}s\, \mathrm{d}s' \left(\left[\frac{1}{2}l_p\kappa_0^2 - \phi\right]\delta(s - s') - \psi^2(s - s')\right) \tag{17}$$

$$+ \int_0^L \mathrm{d}s\, \mathrm{d}s'\, \delta(s - s')\frac{1}{2}\mathrm{tr}(\ln M_{s,s'}) \tag{18}$$

where we have used the relation $\ln(\det M) = \int_0^L \mathrm{d}s\, \mathrm{d}s'\, \delta(s - s')\,\mathrm{Tr}(\ln M)$ to eliminate the determinant that would appear in eq 18. We emphasize that we use the trace here to denote a trace along the directional components of the matrix, i.e., $\mathrm{Tr}(M_{s,s'}^{\alpha\beta}) = \Sigma_{\alpha,\beta}\,\delta_{\alpha,\beta}M_{s,s'}^{\alpha\beta}$. This separates out the integrals along s and s' normally understood as part of the trace operation. Let us now take the saddle-point conditions for the auxiliary field ψ and the Lagrange multiplier ϕ, which respectively yield

$$\frac{3}{2}\mathrm{tr}\left(\left[\frac{1}{4L}\partial_s^2 l_p^2\kappa_0^2\psi^{-3}(s'' - s')\right]M^{-1}(s, s')\right) - \psi(s - s''') = 0 \tag{19}$$

for $\partial F/\partial\psi = 0$, and

$$\int_0^L \mathrm{d}s\, \mathrm{d}s'\, \delta(s-s')\frac{3}{2}\mathrm{tr}[M^{-1}(s,s')] - L = 0 \qquad (20)$$

for $\partial F/\partial\phi = 0$. Here s'' is a dummy variable resulting from the derivative, which we later eliminate.

The null value of the derivatives dictates that the left-hand sides of these relations must be equivalent. We can begin to see that this equivalence can be satisfied by multiplying eq 19 through by $L/4$, applying inverse operators to the ψ-dependent term outside of the trace, and integrating. Thus, we can reproduce the isolated $\mathrm{tr}[M^{-1}(s,s')]$ of eq 20 if we establish

$$\delta(s-s') = \psi^{-1}(s-s'')*\left(\frac{1}{4}\partial_s{}^4 l_p{}^2\kappa_0{}^2\psi^{-3}(s''-s')\right) \qquad (21)$$

inside the traces. The application of ψ^{-1} follows directly from our definition of the convolution operation "*" such that $\psi^{-1}(x')*\psi(x) = \delta(x-x')$.

We can now use the convolution property $FT[f(s)*g(s)] = FT[f(s)]\ FT[g(s)]$, where $FT[f(s)]$ is the Fourier transform $FT[f(s)] = \int_{-\infty}^{\infty} \mathrm{d}q\ f(s)\mathrm{e}^{-iqs}$ to resolve the form of $M_{s,s'}$. Returning to eq 21, let us take the Fourier transform of both sides, using $FT[\delta(s-s')] = 1$ and $FT[\partial_s] = iq$. We find that

$$1 = \frac{1}{4}l_p{}^2\kappa_0{}^2(FT[\psi^{-1}(s-s')])^4 q^2 \qquad (22)$$

where we have taken $FT[\psi^4] = (FT[\psi])^4$ as is appropriate for these operators. From the above, we can solve for $FT[\psi^{-1}]$, and upon returning to the real space of chain arc length, obtain $\psi^{-1}(s-s')$ as

$$\psi^{-1}(s-s') = \int_{-\infty}^{\infty}\frac{L}{2\pi}\,\mathrm{d}q\,\frac{\mathrm{e}^{iq(s-s')}}{\left(\frac{1}{2}l_p\kappa_0 q\right)^{1/2}} \qquad (23)$$

and

$$\psi^{-2}(s-s') = \int_{-\infty}^{\infty}\frac{L}{2\pi}\,\mathrm{d}q\,\frac{2\mathrm{e}^{iq(s-s')}}{l_p\kappa_0|\,q|} \qquad (24)$$

Likewise, the condition $\delta(s-s') = \int \mathrm{d}s''\ \psi^2(s-s'')\psi^{-2}(s''-s')$ yields

$$\psi^2(s-s') = \int_{-\infty}^{\infty}\frac{L}{2\pi}\,\mathrm{d}q\,\frac{1}{2}l_p\kappa_0|\,q|\ \mathrm{e}^{iq(s-s')} \qquad (25)$$

Equipped with a form for our auxiliary field, we can substitute ψ into eq 16 to arrive at the effective Fourier-space version of the Hamiltonian of 15:

$$\beta\mathscr{H}_{\mathrm{mod}} = L\frac{l_p}{4}\kappa_0{}^2 - L\phi + \frac{L}{2\pi}\int_{-\infty}^{\infty}\mathrm{d}q\left[-\frac{l_p}{2}\kappa_0\Big|\,q\Big|\right] + \int_{-\infty}^{\infty}\frac{L}{2\pi}\,\mathrm{d}q\,\boldsymbol{u}_q\left[\frac{l_p}{2}\left(q^2 - \kappa_0\frac{q^2}{|\,q|} + \frac{1}{4}\kappa_0{}^2\right) + \phi\right]\boldsymbol{u}_{-q} \qquad (26)$$

Here we have completed the square in q by the substitution $(\phi + {}^1/_8 l_p\kappa_0{}^2) \rightarrow \phi'$. Since the $\int_{-\infty}^{\infty}\mathrm{d}q\,|q|$ integral that stems from the $\psi^2(s-s')$ term is clearly divergent, we discard it from our considerations of the relevant finite part of the excess free energy, which depends on our model parameters.

2.4. Effective Curvature and Torsion. Analyzing the effective Hamiltonian of eq 27, we now appear to have a model which penalizes curvatures that differ from $\kappa_0/2$ rather than κ_0! This rescaling is an unwanted but in this case, unavoidable mathematical effect of our use of the saddle-point approximation. Formally, it emerges from the fact that the $\psi^2(s-s')$ term in the Hamiltonian is independent of $\boldsymbol{u}(s)$, and so does not appear in the matrix $M_{s,s'}$. According to the saddle-point approximation that $(1/2)(x^2/\psi^2 + \psi^2)_{\psi^4=x^2} \approx \sqrt{x^2}$, the dropped ψ^2 term contributes half of the $\sqrt{x^2}$ term, which is the source of our unwanted numerical factor. The change to κ_0 should not come as a complete surprise; for instance, applying the ϕ global length constraint for chain length also rescales the persistence length of the semiflexible chain, l_p, to $2l_p/d$, where d is the dimensionality (hence the familiar $2l_p/3$ in $d = 3$). For simplicity, we will rewrite $\kappa_0/2$ as $\tilde{\kappa}_0$ henceforth, where $\tilde{\kappa}_0$ represents the preferred curvature we actually model in the chain. This is just how $\tilde{l}_p = 2l_p/d$ comes to stand as the *actual* statistical persistence length of a chain in the mean-field semiflexible model. After all, $\tilde{l}_p$ is the length scale over which the chain loses its orientational correlations in that theory, not the original l_p of the Hamiltonian in eq 2. Likewise, $\tilde{\kappa}_0$ stands as the true statistical average of the curvature of the chain in question for eq 14 and not the geometrical parameter κ_0.

Having solved for $\psi^{-2}(s-s')$, we are finally in a position to discuss its action as an implicit torsional constraint. Examining eq 27, we can see that this Hamiltonian penalizes chain states with nonzero values of Fourier components other than $u_{\pm\tilde{\kappa}0}$. The corresponding ground-state space curve that has only these Fourier components is simply a torsion-less circle. If we perturb a section of chain of such that it forms a perfect helix with torsion τ_h, and radius of curvature $\tilde{\kappa}_0{}^{-1}$ this length of chain is now described by a Fourier component triad:

$$|\mathrm{u}_0| = \sqrt{2\pi}\frac{\tau_h}{\tilde{\kappa}'} \qquad (27)$$

$$|\mathrm{u}_{\tilde{\kappa}'}| = \sqrt{\pi}\frac{\tilde{\kappa}_0}{\tilde{\kappa}'} \qquad (28)$$

$$|\mathrm{u}_{-\tilde{\kappa}'}| = \sqrt{\pi}\frac{\tilde{\kappa}_0}{\tilde{\kappa}'} \qquad (29)$$

where $\tilde{\kappa}' = \sqrt{\tilde{\kappa}_0{}^2+\tau_h{}^2}$, as is necessary for the helix's radius of *curvature* to remains $\tilde{\kappa}_0$. Applying these components to eq 27, it is clear that there is an effective torsional penalty, as we have

$$\beta(E_h - E_0) = \frac{l_p L\tilde{\kappa}_{02}(\tau_h{}^2 + [\sqrt{\tilde{\kappa}_0{}^2+\tau_h{}^2} - \tilde{\kappa}_0]^2)}{2(\tilde{\kappa}_{02} + \tau_h{}^2)}$$

where E_h is the energy of the perturbed section and E_0 the energy of the circular ground state. This energy difference clearly has its minimum at τ_h=0, and is quadratic in τ_h for $\tau_h \ll \kappa_0$, as we can see from the expansion

$$\beta(E_h - E_0) \approx (l_p L\tilde{\kappa}_0{}^2+\tau_h{}^2{}_{02}/2)(\tau_h/\tilde{\kappa}_0{}^2+\tau_h{}^2\kappa_0)^2 + O([\tau_h/\tilde{\kappa}_0{}^2+\tau_h{}^2\kappa_0]^4)$$

This result is robust against changes in the radius of curvature of the helix, as might happen if the helix were to keep winding with angular frequency $\tilde{\kappa}$ instead of $\tilde{\kappa}'$. For the small-torsion regime of the expansion, we therefore recover the Yamakawa Hamiltonian for a chain with preferred torsion $\tau_0 = 0$ and preferred curvature $\kappa = \tilde{\kappa}_0$[10]

$$\beta\mathscr{H} = \int_{-\infty}^{\infty} \mathrm{d}s\, \frac{l_p}{2}(\tau^2 + [\kappa - \tilde{\kappa}_0]^2)$$

We therefore conclude that the nonlocal $\psi(s - s')$ field does serve as an implicit torsional constraint, one which arises naturally in the polymer theory after the elimination of the change-of-curvature terms and the mean-field approximation for ψ. Admittedly, the torsional analysis above is only partial, as the conformation of a thermally disordered chain will only very rarely be a perfect helix, and the true Fourier components of such a chain not so neat as in eq 29. Nevertheless, the approximation of a chain made of many local quasi-helical subsections described by eq 29 should be appropriate when the chain is strongly curved, as occurs at high persistence lengths l_p.

3. Results and Discussion

Having resolved the curvature and torsional constraints, we can now move on to evaluate the results of the model. We can begin to do so by replacing the trace over chain length s on $M^{-1}(s, s')$ in eq 20 with a trace over q in the equivalent Fourier-coefficient matrix $M^{-1}(q, q')$ of eq 27 to find

$$\frac{3}{2}\int_{-\infty}^{\infty} \frac{L}{2\pi}\,\mathrm{d}q \left(\frac{1}{\frac{1}{2}l_p(|q| - \tilde{\kappa}_0)^2 + \phi}\right) = L \tag{30}$$

which can be integrated directly to find

$$\frac{3L\sqrt{2}}{2\pi\sqrt{\phi l_p}}\left[\frac{\pi}{2} + \arctan\left(\tilde{\kappa}_0\sqrt{\frac{l_p}{2\phi}}\right)\right] = L \tag{31}$$

Let us now assume $l_p\tilde{\kappa}_0^2 \gg \phi$ such that the $\arctan(\tilde{\kappa}_0\sqrt{l_p/2\phi})$ term depends only weakly on ϕ. We know[8] that $\phi \propto l_p^{-1}$ as $\tilde{\kappa}_0 \to 0$, so for the physically interesting case where $l_p \geq 1$ and $\tilde{\kappa}_0 \geq 1$ this assumption seems appropriate. In fact, we will show it yields a self-consistent solution. If we accept this assumption for the moment, let us replace the arctangent term by a constant such that

$$\arctan\left(\tilde{\kappa}_0\sqrt{\frac{l_p}{2\phi}}\right) = \pi\alpha \quad 0 < \alpha < \frac{1}{2} \tag{32}$$

Formally, the factor α emerges as a result of the presence of the absolute value $|q|$ in the denominator of eq 30; replacing this term with q simply reproduces the semiflexible chain results for ϕ (i.e., $\alpha = 0$). Physically, the α correction suggests that the intrinsic curvature imposes a stress on the length constraint $\boldsymbol{u}^2(s) = 1$, which is larger than that in the ordinary semiflexible case. We therefore require a larger Lagrange multiplier ϕ to enforce the length constraint.

Taking the α approximation of the arctangent as in eq 32, we find the result

$$\phi = \left(\frac{9\left(\frac{1}{2} + \alpha\right)^2}{2l_p}\right) \tag{33}$$

from which we take our subsequent results for the unstretched chain. We see that the presence of α does not greatly modify ϕ, indicating the self-consistence of the approximation in eq 32 for large $l_p\tilde{\kappa}_0^2$. Note that we clearly retain the existing semiflexible result[8,26] of $\phi = 9/(8l_p')$ as $\alpha \to 0$, which corresponds to the uncurved case $\tilde{\kappa}_0 \to 0$.

3.1. Results for the Unstretched Curved Chain.

Equipped with the essential results eqs 23 and 33, we can now derive the tangent−tangent correlator $\langle \boldsymbol{u}(s)\cdot\boldsymbol{u}(s')\rangle$ by standard methods[4,8,34]

$$\langle \boldsymbol{u}(s)\cdot\boldsymbol{u}(s')\rangle = \frac{3L}{4\pi}\int_{-\infty}^{\infty} \mathrm{d}q\, \frac{\mathrm{e}^{iq(s-s')}}{\frac{1}{2}l_p(q^2 - 2\tilde{\kappa}_0|q| + \tilde{\kappa}_0^2) + \phi} \tag{34}$$

By making the substitution $q' = |q| - \tilde{\kappa}_0$, we arrive at

$$\langle \boldsymbol{u}(s)\cdot\boldsymbol{u}(s')\rangle = \frac{3L}{2\pi}\cos(\tilde{\kappa}_0[s - s'])\int_{-\infty}^{\infty}\mathrm{d}q'\, \frac{1}{\frac{1}{2}l_p q'^2 + \phi} \tag{35}$$

which we evaluate to yield the propagator

$$\langle \boldsymbol{u}(s)\cdot\boldsymbol{u}(s')\rangle = \frac{3(1 + 2\alpha)}{4\sqrt{l_p\phi}}\mathrm{e}^{-\sqrt{2\phi l_p^{-1}}|s-s'|}\cos(\tilde{\kappa}_0[s - s']) \tag{36}$$

in the long-range limit as $(s - s') \to \infty$. Note that it is the presence of the absolute value $|q|$ in the denominator of eq 34 that results in the real valued correlator proportional to $\cos(\tilde{\kappa}_0[s - s'])$ that one would desire, as opposed to the $\mathrm{e}^{-i\tilde{\kappa}_0[s-s']}$ dependence that would occur with q alone. Substituting eq 33 into eq 36, we obtain

$$\langle \boldsymbol{u}(s)\cdot\boldsymbol{u}(s')\rangle = \mathrm{e}^{-\Omega|s-s'|}\cos(\tilde{\kappa}_0[s - s']) \tag{37}$$

where $\Omega = 3(1/2 + \alpha)l_p^{-1}$. In the limit of weak or no intrinsic curvature, $\tilde{\kappa}_0 \to 0$, $\alpha \to 0$ and one recovers the mean-field, semiflexible tangential propagator $\langle \boldsymbol{u}(s)\cdot\boldsymbol{u}(s')\rangle = \mathrm{e}^{-3|s-s'|/2l_p'}$.

The mean internal separation $\langle R^2(s - s')\rangle$ follows by integrating the propagator between s and s'

$$\langle R^2(s - s')\rangle = \int_s^{s'}\mathrm{d}\tau \int_s^{s'}\mathrm{d}\tau'\, \mathrm{e}^{-\Omega|\tau-\tau'|}\cos(\tilde{\kappa}_0[\tau - \tau']) \tag{38}$$

Performing the integration, we have

$$\langle R^2(s - s')\rangle = \frac{1}{(\Omega^2 + \tilde{\kappa}_0^2)^2}\Big[(\Omega^2 - \tilde{\kappa}_0^2)[2\mathrm{e}^{-\Omega|s-s'|}\cos(\tilde{\kappa}_0[s - s']) - 2] + 2\Omega(\Omega^2 + \tilde{\kappa}_0^2)\left|s - s'\right| - 4\tilde{\kappa}_0\Omega\mathrm{e}^{-\Omega|s-s'|}\sin(\tilde{\kappa}_0|s - s'|)\Big] \tag{39}$$

If we take the limit where $\tilde{\kappa}_0 \gg \Omega$, i.e., $l_p\tilde{\kappa}_0 \gg 1$, this simplifies to the form

$$\langle R^2(s - s')\rangle = 2\tilde{\kappa}_0^{-2}[1 - \mathrm{e}^{-\Omega|s-s'|}\cos(\tilde{\kappa}_0[s - s']) + \Omega|\, s - s'|] \tag{40}$$

which formally resembles the results given in previous studies of wormlike chains.[8,26] However, the prefactor Ω^{-2} has now been replaced with $\tilde{\kappa}_0^{-2}$, and the damped $\mathrm{e}^{-\Omega(s-s')}$ term now oscillates with a wavelength of $2\pi/\tilde{\kappa}_0$ due to the cosine factor, as shown in Figure 3. The chain still approaches the limit of $\langle R^2(s - s')\rangle \propto (s - s')$ as $(s - s') \to \infty$, but we note that the constant of proportionality is now of order $\Omega/\tilde{\kappa}_0^2$ rather than l_p, indicating that the effective step size of the large-$(s - s')$ random walk is $\sqrt{(\Omega/\tilde{\kappa}_0^2)}$. This dovetails with our suggestion that the chain's spontaneous curvature leads it to wind into torii with a radius $\tilde{\kappa}_0^{-1}$, as illustrated in Figure 2. Examining eq 39, we see that the "effective persistence length" of $\langle R^2(s - s')\rangle/L$ grows with increasing Ω (i.e., increasing thermal disorder) as the chain begins to unwind from a near-disclike state, then contracts once

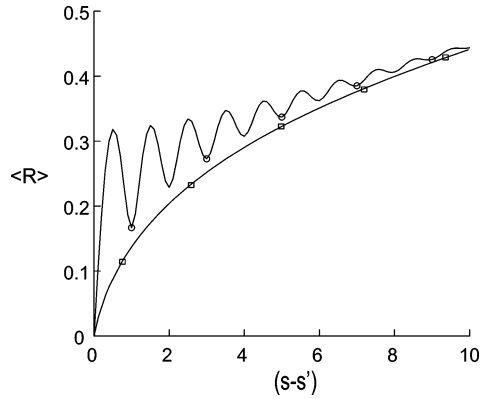

Figure 3. Mean extension ($\bar{R} = \langle R^2(s - s')\rangle$) vs distance along the chain ($s - s'$) for a spontaneously curved chain (circles) with $l_p = 10$ and $\tilde{\kappa}_0 = 2\pi$, and a "semiflexible" chain (squares) with $l_p = 10$. For the semiflexible case, $\tilde{\kappa}_0$ has been set to zero in the oscillating factors of eq 39 but left at 2π in the prefactors so as to scale with the curved chain. As $(s - s') \rightarrow l_p$, the two graphs clearly converge.

again as thermal fluctuations return it to the random coil state, an oscillation seen previously for elastic rods.[22] Ultimately, the internal distance function of eq 40 qualitatively reproduces the distance functions obtained from the calculation of exact analytic results for Yamakawa chains with intrinsic curvature κ_0 and zero torsion,[10] the results for torsion-less elastic rods,[22] as well as Monte Carlo simulations of Yamakawa-like chains[35−38] and chains winding about an external field that induces chain curvature.[39]

Given $\langle R^2(s - s')\rangle$, it is now a simple matter to extract the mean square radius of gyration of the chain, $\langle S^2(L)\rangle$. This quantity follows from

$$\langle S^2(L)\rangle = \frac{1}{L^2}\int_0^L \mathrm{d}s \int_0^L \mathrm{d}s' \langle R^2(s - s')\rangle \tag{41}$$

Applying eq 40 for the quantity $\langle R^2(s - s')\rangle$ and assuming $L \gg 1$ and $L\Omega \gg 1$ so we can drop terms proportional to $e^{-\Omega L}$ and L^{-n} for $n > 0$, we see that

$$\langle S^2(L)\rangle = \frac{2}{3}\frac{L\Omega}{\Omega^2 + \tilde{\kappa}_0^{\,2}} + 2\frac{(\tilde{\kappa}_0^{\,2} - \Omega^2)}{(\Omega^2 + \tilde{\kappa}_0^{\,2})^2} \tag{42}$$

Let us compare this with the known result $\langle S^2(L)\rangle = 1/6\ Nb^2$ for a flexible N-mer with monomer length b. If we remember the chain's preference for zero average torsion, it seems plausible that the chain is bunched into donut-shaped "blobs", as in Figure 2, that each take up a length l_{blob} and have radius r_{blob}. This yields $\langle S^2(L)\rangle = 1/6\ N_{blob}b^2 = 1/6\ Lr_{blob}^2/l_{blob}$.

We so see that

$$\frac{r_{blob}^{\,2}}{l_{blob}} = \frac{4\Omega}{\Omega^2 + \tilde{\kappa}_0^{\,2}} = \frac{12\left(\frac{1}{2} + \alpha\right)l_p}{9\left(\frac{1}{2} + \alpha\right)^2 + \tilde{\kappa}_0^{\,2}l_p^{\,2}} \tag{43}$$

For $l_p^{\,2}\,\tilde{\kappa}_0^{\,2} \gg 1$, we recover $r_{blob}^{\,2}/l_{blob} \sim (l_p\tilde{\kappa}_0^{\,2})$, and assuming that $r_{blob} = \tilde{\kappa}_0^{\,-1}$ on the plausible grounds that the blobs are the product of the spontaneous curvature of the chain, we recover $l_{blob} \sim l_p$ and the interpretation of l_p as a curvature persistence length when $\tilde{\kappa}_0 \neq 0$ (Figure 2).

3.2. Results for the Curved Chain Under an External Force. We now go on to examine the response of an intrinsically curved chain to an externally imposed force $\tilde{\boldsymbol{f}}$, as might be introduced in single-molecule experiments with an AFM or optical-tweezer apparatus operating in the constant-force regime. The presence of this force imposes an additional potential energy term $(\boldsymbol{r}(L) - \boldsymbol{r}(0)) \cdot \tilde{\boldsymbol{f}}$, where $\boldsymbol{r}(s)$ is the position of the chain unit at s. Since $\boldsymbol{r}(L) - \boldsymbol{r}(0) = \int_0^L \mathrm{d}s\ \boldsymbol{u}(s)$, this potential adds an external field term into our Hamiltonian in eq 13, which effectively favors the alignment of each individual segment of the chain with the external field, $\boldsymbol{f}\cdot\boldsymbol{u}(s)$. Note that here we have set $\boldsymbol{f} = \tilde{\boldsymbol{f}}/kT$. While not dynamically accurate, this effect should hold in the equilibrium case treated here. We go on to obtain

$$\beta\mathscr{H} = \int_0^L \mathrm{d}s \left[\frac{l_p}{2}\left(\left(\frac{\mathrm{d}\boldsymbol{u}}{\mathrm{d}s}\right)^2 - 2\tilde{\kappa}_0\left|\frac{\mathrm{d}\boldsymbol{u}}{\mathrm{d}s}\right| + \tilde{\kappa}_0^{\,2}\right) + \phi(\boldsymbol{u}^2 - 1) - \boldsymbol{f}\cdot\boldsymbol{u}(s)\right] \tag{44}$$

We can treat this by first applying the same auxiliary field procedure to the $|\mathrm{d}\boldsymbol{u}/\mathrm{d}s|$ term as we did in eq 13. We then integrate over the configurations $[\boldsymbol{u}(s)]$ by completing the square in Gaussian integration, which generates the relation $\int \mathrm{d}[\boldsymbol{u}]\ e^{-\boldsymbol{u}\zeta\boldsymbol{u} - \beta\cdot\boldsymbol{u}} \propto (\det\zeta)^{-1/2}e^{\beta 2/(4\zeta)}$, where ζ and β are generalized operators. Since we take the zero-frequency limit in our equilibrium analysis, $\boldsymbol{f}$ is constant along the chain. Thus, we take only the $q = 0$ contribution and so arrive at a new relation which modifies eq 20 simply by adding an additional term proportional to f^2.

$$\mathrm{Tr}(M^{-1}(s, s')) + L\frac{f^2}{4(\phi + l_p\tilde{\kappa}_0^{\,2}/2)^2} - L = 0 \tag{45}$$

Following the results of section 2, we evaluate the trace and find

$$\frac{3}{2}\left(\frac{1 + 2\alpha}{\sqrt{2\phi l_p}}\right) = 1 - \frac{f^2}{4\left(\phi + \frac{1}{2}l_p\tilde{\kappa}_0^{\,2}\right)^2} \tag{46}$$

Unfortunately, this algebraic equation is effectively quintic (fifth-order) in ϕ and is no longer exactly soluble. Nonetheless, we can approximate the chain behavior under limiting conditions. Since we do not yet have a solution for $\phi(f)$ as a function of $\boldsymbol{f}$, let us keep ϕ explicit in integrating the propagator $\langle \boldsymbol{u}(s) \cdot \boldsymbol{u}(s')\rangle$ of eq 36 over s and s' to calculate the mean internal separation $\langle R^2(s - s')\rangle$. We so obtain

$$\langle R^2(s - s')\rangle = \frac{f^2(s - s')^2}{4\left(\phi + \frac{1}{2}l_p\tilde{\kappa}_0^{\,2}\right)^2} + \left(\frac{3(1 + 2\alpha)}{4\sqrt{l_p\phi}(\Omega'^2 + \tilde{\kappa}_0^{\,2})^2}\right) \times$$
$$[(\Omega'^2 - \tilde{\kappa}_0^{\,2})(2e^{-\Omega'|s-s'|}\cos(\tilde{\kappa}_0[s - s']) - 2) + 2\Omega'(\Omega'^2 + \tilde{\kappa}_0^{\,2})|s - s'| - 4\tilde{\kappa}_0\,\Omega' e^{-\Omega'|s-s'|}\sin(\tilde{\kappa}_0|s - s'|)] \tag{47}$$

where $\Omega' = \sqrt{2\phi/l_p}$, replacing the Ω used earlier for $\phi(f = 0)$. We plot $R^2(L)$ against the applied force f for chains with and without curvature in Figure 4, using numerically calculated values for ϕ (that is, without the α-approximation).

Looking at the plots, one observes that the most obvious influence of intrinsic curvature is the relatively high force required to extend curved chains to near their full length. This is quite clear when comparing the force scales of the inset ($\tilde{\kappa}_0 = 0$) and full ($\tilde{\kappa}_0 \neq 0$) graphs of Figure 4. Mathematically, this follows from the prefactor $4(\phi + 1/2\ l_p\tilde{\kappa}_0^{\,2})^{-2}$ in the force-dependent part of eq 47, and has a fairly simple physical explanation: a stretched, curved chain will tend to keep its curvature in the plane perpendicular to the applied force $\boldsymbol{f}$ to minimize the energetic term $\boldsymbol{f}\cdot\boldsymbol{u}$, effectively storing length in these oscillations. As f grows large, however, one can imagine

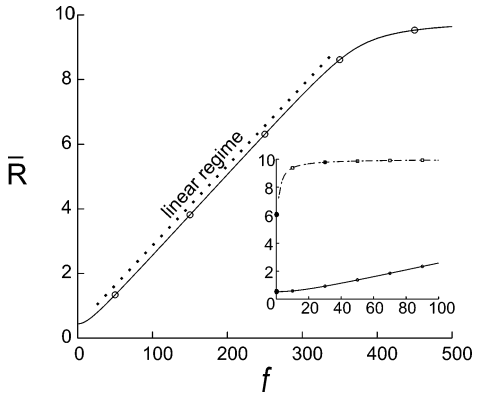

Figure 4. Main graph illustrates mean extension ($\bar{R} = \sqrt{\langle R^2(L)\rangle}$) vs force ($f = \tilde{f}/kT$) for a chain with $l_p = 10$, $\tilde{\kappa}_0 = 2\pi$, and $L = 10$. Note both the very high values of the force f as $\bar{R}$ approaches L, and the nearly constant slope ($d\bar{R}/df \approx 1/50$) of the extension/force response, whose value is in close agreement with our prediction of $d\bar{R}/df \approx L/(l_p\tilde{\kappa}_0^2)$. Meanwhile, the inset compares the force−extension response of the curved chain (circles) against the same plot for a fairly rigid semiflexible chain (squares) with $l_p = 10$, $\tilde{\kappa}_0 = 0$, and $L = 10$. The dots at $f = 0$ on both graphs mark the zero-force equilibrium extension of both chains, which we see is $\approx\tilde{\kappa}_0^{-1}$ for the curved chain and roughly $L/2$ for the semiflexible chain, as one would expect for $l_p \sim L$.

how the chain can only reach its full (straight) extension by "pulling out" the polymer's curves, much as in an over-stretched phone cord. Thus, a nearly taut curved chain should experience an additional force of magnitude $\sim l_p\tilde{\kappa}_0^2$, which is in good agreement with the magnitude of the difference between the forces near full extension seen in Figure 4 for the curved and uncurved chains.

In keeping with previous treatments,[26] we can go on to estimate a tensile screening length scale l_f set by the value of $|s - s'|$ where terms proportional to $(s - s')$ and $(s - s')^2$ are equal, namely

$$l_f = 3(1 + 2\alpha)\frac{1}{f^2}\left(\frac{1}{2}l_p\tilde{\kappa}_0^2 + \phi\right) \tag{48}$$

in this case. For distances along the chain less than l_f, we expect the configuration of the stretched chain to roughly resemble the unperturbed, coiled chain of eq 40, while at larger distances, the chain will appear to be stretched out along the direction of $\boldsymbol{f}$. In a weak-stretching regime where $f \ll l_p\tilde{\kappa}_0^2$, we recover our original result for ϕ from eq 33, and thus find $l_f \sim {}^1/_2 l_p\tilde{\kappa}_0^2/f^2$, indicating that the chain is nearly fully screened. For the intermediate case where $l_f f^2 \lesssim l_p\tilde{\kappa}_0^2$, we arrive at a cubic in ϕ, which we simplify for $\phi \ll l_p\tilde{\kappa}_0^2$ to obtain a self-consistent quadratic solution

$$\phi = \frac{l_p}{2(2l_p^2\tilde{\kappa}_0^2 - 9(1+2\alpha)^2)}\left[\tilde{\kappa}_0^2(-2l_p^2\tilde{\kappa}_0^2 + 9(1+2\alpha)^2) + 4f^2 + \sqrt{16f^4 + 8\tilde{\kappa}_0^2\left(f^2(-2l_p^2\tilde{\kappa}_0^2 + 9(1+2\alpha)^2) + \frac{1}{2}l_p^2\tilde{\kappa}_0^4(l_p^2\tilde{\kappa}_0^2 + 9(1+2\alpha)^2)\right)}\right] \tag{49}$$

Thus, the intermediate regime sees $l_f \approx l_f^{(0)} + l_f^{(1)}$, where $l_f^{(0)}$ is approximately the l_f of eq 48, and

$$l_f^{(1)} = \frac{12l_p(1+2\alpha)}{8l_p^2\tilde{\kappa}_0^2 - 9(1+2\alpha)^2} \approx \frac{3}{l_p\tilde{\kappa}_0^2} \tag{50}$$

is a constant that does not scale with f. We interpret a nonzero value of $l_f^{(1)}$ to mean that extension occurs as lengths $\sim(l_p\tilde{\kappa}_0^2)^{-1}$ of the chain are being rearranged by the force, but that the curvature within these lengths is not yet being "pulled out". In this regime, eq 47 can be approximated as $\langle R^2(s - s')\rangle \sim f^2(s - s')^2/(l_p^2\tilde{\kappa}_0^4)$ due to the condition $\phi \ll l_p\tilde{\kappa}_0^2$, yielding the linear extension-vs-force regime indicated in Figure 4. Note that in the absence of any intrinsic preferred twist, we do not observe any phase-transition-like behavior of the chain curvature, as has been predicted for an intrinsically twisted chain,[23] though extension to a model with intrinsic preferred torsion may yet yield such results.

Finally, the high-stretching regime where $l_f f^2 \gg l_p\tilde{\kappa}_0^2$ yields a complicated, quartic relation for ϕ. While we neglect the exact solution here, the presence of terms in the ratio ϕ/f suggests ϕ scales as $\phi \sim f$, and hence $l_f \sim f^{-1}$. This semiflexible-like scaling of the screening length with the force indicates that the chain is nearly straight in this regime, and that turns of the polymer have been completely "pulled out" by this time.

4. Conclusions

In this paper, we have put forth a simple auxiliary-field theory of polymer chains with zero average torsion and spontaneous curvature. As well, we have provided closed-form results for its tangent-tangent correlator $\langle \boldsymbol{u}(s)\cdot\boldsymbol{u}(s')\rangle$, mean square radius of gyration $\langle S^2(L)\rangle$, and mean square internal separation $\langle R^2(s - s')\rangle$. One should note that this theory will not give exactly correct results for higher moments $\langle S^n(L)\rangle$ and $\langle R^n(s - s')\rangle$ with $n > 2$, like other mean-field treatments of semiflexible polymer chains without a strict Kratky−Porod constraint. Nevertheless, our results should be accurate for the mean square moments and force−extension response, which can be observed experimentally through static light scattering and AFM micromanipulation, among other techniques. Examining our results, curved chains appear to assume contracted conformations at high spontaneous curvature $\tilde{\kappa}_0$ and curvature persistence length l_p. The theory reproduces the results of ordinary semiflexible polymer theory in the limit of $\tilde{\kappa}_0 \to 0$ and hence those of flexible polymer theory as $l_p \to 0$, which roughly confirms the suitability of this treatment. We also examine the force−extension response of these chains, and see that it resembles that of semiflexible chains. We note some significant differences, however, such as a linear force−extension regime, the higher force needed for full extension, and a increased tensile screening length l_f which is strongly dependent on the curvature $\tilde{\kappa}_0$.

Though the similarities in the mathematical treatment and results for semiflexible and intrinsically curved chains suggest that the study of the latter can easily be subsumed in that of semiflexible polymers in general, physically interesting distinctions between the two cases remain, particularly in regards to self-avoidance. In our treatment of curved polymers, we have yet to treat the issue of the steric interactions and excluded volume effects that will occur in a real polymer. Such effects may dominate polymer behavior in the regime where $l_p\tilde{\kappa}_0^2 \gg 1$ and the average separation $\langle R^2(s - s')\rangle$ becomes small over much of the chain. An Edwards-style analysis of the curved chain for the weak-repulsion case should follow in future publications. This problem also seems ripe for Metropolis or multicanonical Monte Carlo simulation, and is a simple generalization of helical-rod studies.

In the present absence of such studies, however, we can already anticipate some of the effects of excluded volume on a curved chain. In particular, steric interactions should lead to the formation of local helical structures rather than torii for chains whose excluded chain "width" r_0 is roughly the radius of curvature, $\tilde{\kappa}_0^{-1}$. Though we already have a torsional constraint, curved polymers with excluded volume must have some local torsion, as the chains cannot interpenetrate. We also

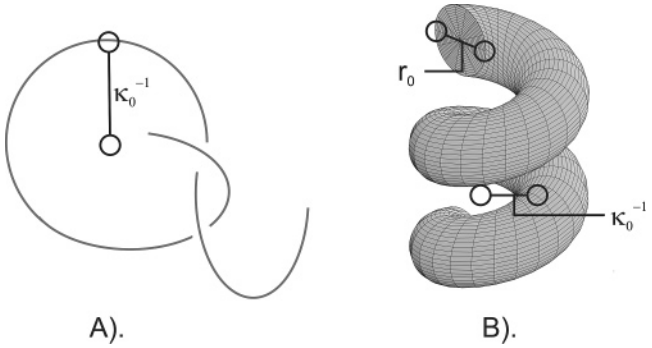

Figure 5. Approximate expected behavior of curved polymers with excluded volume "thicknesses" r_0, such that (A) $r_0 \ll \tilde{\kappa}_0^{-1}$ and (B) $r_0 = 2/3\ \tilde{\kappa}_0^{-1}$. In the A case, the thin curved chain can curl freely without having to over- or under- curl to avoid self-intersection, while the "fat" chain of case B adopts a local, roughly helical conformation to avoid self-intersections.

expect this local torsion to be fairly regular for an appreciable r_0, as the chains cannot easily change the plane of their curvature without their curvature causing them to reintersect the chain. This can be seen in Figure 5, which contrasts the less constrained "A" chain of low r_0 to the thicker "B" case.

For a locally helical, curved polymer, a simple ansatz suggests that the separation resembles the form

$$\langle R^2(s - s')\rangle = \frac{1}{(\Omega^2 + \tilde{\kappa}_0^{\,2})^2}[(\Omega^2 - \tilde{\kappa}_0^{\,2})(1 - p^2)[2e^{-\Omega(s-s')}\cos(\tilde{\kappa}_0[s - s']) - 2] + 2\Omega(\Omega^2 + \tilde{\kappa}_0^{\,2})|s - s'| - 4\tilde{\kappa}_0\Omega e^{-\Omega|s-s'|}\sin(\tilde{\kappa}_0|s - s'|) + p^2(s - s')^2 e^{-\Omega|s-s'|}] \quad (51)$$

where p is an average local torsion determined by the strength of the steric repulsion and size of the excluded volume parameter r_0. Attractive Lennard-Jones-like potentials might also give rise to helical structures with lengths longer than the $\sim l_p$ dependence predicted above, and ultimately reproduce the results of non-conformational models of helix formation.[40−42] Note, however, that for an intrinsically curved chain like those we have described here, any putative helical structures should have no preferred chiral sense and so will produce no net optical rotation on average. This stands in contrast to polypeptides, whose monomers possess an intrinsic chirality which results in a net optical rotation. A conformational theory incorporating chiral effects should resemble Yamakawa's description of helical polymers.[10] Unfortunately, the prospects of producing an explicitly chiral treatment of polymer chains appear to be limited by the fact that torsion is cubic, not quadratic, in the tangent vectors $\boldsymbol{u}(s)$, which raises concerns about integrability. We do note that a Hamiltonian strictly linear in the curvature has a pure helical structure as a ground state,[43] but again, the chirality of this state does not appear to be fixed by the Hamiltonian itself. Unfortunately, the above concerns about the integrability of the torsion term prevent us from developing a theory of a chain with arbitrary, nonzero average torsion like that we have developed for spontaneous curvature, though work continues in this direction.

Self-avoiding, intrinsically curved chains may also show interesting behavior in two dimensions, as in the case of a chain adsorbed on a monolayer interface[44,45] where helix formation is impossible and one expects frustration between the chain's desire to curl upon itself and the need for constant curvature. This competition should result in the formation of "curvature kinks" corresponding to inflection points or straightened segments of the chain, and which to our knowledge have not yet been studied on or off the lattice. Conversely, curved chains in $d > 3$ dimensions should be less sensitive to steric repulsion as there are simply more degrees of freedom available to the chain to satisfy the requirements of constant curvature and self-avoidance.

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