International Journal of Statistics and Applied Mathematics 2023; 8(3): 89-110

International Journal of Statistics and Applied Mathematics

ISSN: 2456-1452
Maths 2023; 8(3): 89-110

https://www.mathsjournal.com
Received: 08-02-2023
Accepted: 11-03-2023

Humbert Philip Kilanowski
Providence College, Department of Mathematics and Computer Science, 1 Cunningham Square, Providence, Rhode Island

Corresponding Author:
Humbert Philip Kilanowski
Providence College, Department of Mathematics and Computer Science, 1 Cunningham Square, Providence, Rhode Island

On the kratky-porod model for semi-flexible polymers in an external force field

Humbert Philip Kilanowski

DOI: https://doi.org/10.22271/maths.2023.v8.i3b.983

Abstract
We prove, by means of matrix-valued stochastic processes, the convergence, in a suitable scaling limit, of the position vectors along a polymer in the discrete freely rotating chain model to that of the continuous Kratky Porod model, building on an earlier result for the original model without a force, and showing that it holds when an external force field is added to the system. In doing so, we also prove that the process of tangent vectors satisfies a stochastic differential equation, showing that it is the sum of a spherical Brownian motion and a projective drift term, and we analyze this equation to derive properties about the polymer in the regimes of high and low values of the force parameter and persistence length, or stiffness parameter of the molecule. If the force is much stronger than the persistence length, the polymer tends toward the rigid rod limit, aligned in the direction of the force; while if the force is much weaker, the polymer is aligned in its original direction, as in the case of the unforced model. The most interesting case occurs when both force and stiffness parameters are very large, in which case the polymer takes on the shape of a deterministic curve that satisfies an ordinary differential equation.

Keywords: Polymer, kratky-porod model, convergence, spherical brownian motion with drift, stochastic differential equation

1. Introduction

The Kratky-Porod model is a basic representation of semi-flexible polymer molecules in which thermal effects, noticeable on small time and length scales, balance the elastic or mechanical effects. This model is particularly useful for representing polymers, which are molecules composed of many copies of the same monomer unit or the same statistical segment, that are immersed in a dilute solution, such as DNA or proteins. The actual model is a secondary result of a 1949 paper by Austrian chemical physicists O. Kratky and G. Porod [15] in which they describe the X-ray scattering of cellulose macromolecules in colloidal suspension.

The foundations for this model date back to the period immediately following the Second World War. In [14], H.A. Kramers in 1946 introduced a bead-rod model, called the *freely rotating chain*, in which all segments have the same length, and the bond angles between successive segments are constant, but the torsional angles are independent and identically distributed. Later, Kirkwood and Riseman introduced another bead-rod model, called the freely jointed chain, where all rods or segments between beads, of a polymer have the same length and are independent, identically distributed random variables [12, 13]. Prince Rouse in 1953 formulated his own model, which involves Gaussian-distributed segments [20]. The Rouse model and Kirkwood-Riseman chain describe flexible polymers, in contrast to the Kramers chain, which models semi-flexible polymers. There are thousands of papers published in the chemical physics literature since the introduction of these models. We make no attempt to survey this vast body of work here, other than to refer to standard reference texts such as [5, 23, 9, 24] and references therein. More recently, Bryant and Lavrentovich have applied a similar stochastic model to biology, namely, to survival probabilities of cell populations, as the branching process can be modeled with a geometric figure that resembles a polymer [1].

Building on the results of [11], which prove the convergence of the freely rotating chain to the Kratky-Porod model and describe its behavior for extreme values of the persistence length, we seek to extend this results to the model with an external force. Here is the first major result of this paper.

Theorem 1.1: Let $R_f^N(s)$ be the forced chain polymer model with parameters (N, a, θ, f), where N is the number of statistical segments, a is the common length of each segment, θ is the angle between each pair of segments, and $f = \|f\|\hat{f}$ is the external force vector, and whose torsional angles follow the Boltzmann-Gibbs distribution of statistical mechanics. Let $R_f(s)$ be the forced.
Kratky-Porod model with parameters $(L, \ell_p, \zeta, \hat{f})$, where L is the total length of the polymer, ℓ_p is its persistence length, ζ is a dimensionless external force parameter, and $\hat{f}$ is the unit vector in the direction of the force, and suppose the parameters satisfy

$$a = \frac{L}{N} \tag{1}$$

$$\theta = \frac{\kappa}{\sqrt{N}} \tag{2}$$

$$\ell_p = \frac{2L}{\kappa^2} \tag{3}$$

Let $\tau = k_B T$ and set

$$\zeta = \frac{L\|\mathbf{f}\|}{\tau} \tag{4}$$

If $R^N(s)$ is the forced chain interpolated linearly, then, as $N \to \infty$, R^N_f converges in distribution to R_f, and the process of tangent vectors T(s) to the polymer is the solution to the stochastic differential equation.

$$d\mathbf{T}(s) = \frac{1}{\sqrt{\ell_p}} d\mathbf{Q}(s) + \frac{\zeta}{\ell_p}(I - \mathbf{T}(s) \otimes \mathbf{T}(s))\hat{\mathbf{f}}\, ds. \tag{5}$$

The tangent vector therefore is an Itˆo process consisting of a diffusion term, the scaled Brownian motion on S^2, and a quadratic drift term, which is proportional to the orthogonal projection of the unit force vector f onto the plane perpendicular to T(s). This means that T is a spherical Brownian motion with a bias towards the direction of the force. While this differential equation cannot be solved explicitly for T(s), the behavior of the polymer can be described fully in several limiting cases.
If we fix the persistence length ℓ_p and consider extreme values of ζ, we expect to see two radically different behaviors. If $\zeta \to 0$, the Brownian motion term dQ(s) dominates equation (5), and the polymer behaves exactly as in the Kratky-Porod model, as described in [11]; while if $\zeta \to \infty$, the drift term dominates, and the polymer becomes a rigid rod pointing in the direction of the force, $\hat{f}$.
The more interesting cases, however, occur when ζ and ℓ_p are proportional and both tend towards infinity. In this case, the Brownian motion can be ignored, but the polymer is stiff enough that it does not point completely in the direction of the force. Rather, it forms a deterministic curve in the plane, whose shape changes with the constant of proportionality between the two large parameters.
Here is the second main result of this article.

Theorem 1.2: The forced Kratky-Porod model has the following behavior:
1. Fix ℓ_p and let $\zeta \to 0$. Then the polymer $R_f(s)$ converges to the Kratky Porod model R(s).
2. Fix ℓ_p and let $\zeta \to \infty$. Then the polymer converges in probability to a rigid rod in the direction of the force: $R_f(s) \to s\hat{f}$.
3. Let $C = \zeta/\ell_p$ be constant, and let $\zeta \to \infty$. Then, $R_f(s)$ converges in probability to the curve.

$$X(s) = \int_0^s \mathbf{x}(\sigma)d\sigma \tag{6}$$

Where x is the solution of the ordinary differential equation $\dot{x} = V(x)$, $x(0) = e_3$, where

$$V(x) = C(I - x \otimes x)\hat{f} \tag{7}$$

This equation can be solved explicitly, leading to an exact formula for X(s).
4. (Trivial Case) Let $C = \zeta/\ell_p$ be constant as above, and let $\zeta \to 0$. Then, in probability, $R_f(s)$ shrinks to a point.

With these results having been stated, the paper is organized according to the following structure.
Section 2 gives some background information on the construction of the freely rotating chain as described in [11] and how the force is added to the system.
Section 3 is concerned with the construction of the forced rotating chain by means of the Boltzmann-Gibbs distribution. Under this probability measure, the segments in the discrete forced model form a Markov chain, and this allows us to compute the driving process $B_f(s)$ of the polymer by its Doob-Meyer decomposition. The main result of this chapter is that the discrete model

converges in distribution to a continuous model and the tangent vector traces a spherical Brownian motion with a drift proportional to the orthogonal projection of the force vector.
Section 4 deals with several limiting cases and proves the behavior of the forced Kratky-Porod model in various regimes, such as the rigid rod and random coil limits. The main result is that as both the force parameter and stiffness increase together, the polymer converges in probability to a deterministic curve that can be described explicitly.

2. Foundations

The freely rotating chain (FRC) models a polymer as a collection of vectors,

$$\mathcal{R}^N = \{\mathbf{R}_0^N, \mathbf{R}_1^N, \cdots, \mathbf{R}_N^N\} \tag{8}$$

Where $\mathbf{R}^N_k$ is the location of the k^{th} bead and

$$\mathrm{Q}_k^N = \mathbf{R}_k^N - \mathbf{R}_{k-1}^N \tag{9}$$

is the k^{th} rod or segment connecting adjacent beads. One can envision this chain as a ball-and-stick model, commonly used to build molecules in chemistry classes. The model depends on a set of parameters (N,a,θ), where $N \in \mathrm{N}$ is the number of segments, $a \in \mathrm{R}^+$ is the common length of each segment, and $\theta \in (0,\pi)$ is the angle supplementary to the common bond angle between any pair of adjoining segments, so that the steric angle between segments is actually $\pi - \theta$. This is chosen so that an angle of $\theta = 0$ corresponds to no bending between segments. Setting

$$\mathcal{Q}^N = \{\mathbf{Q}_1^N, \mathbf{Q}_2^N, \cdots, \mathbf{Q}_N^N\} \tag{10}$$

We have,

$$\|\mathrm{Q}^N_k\| = a \tag{11}$$

$$\mathrm{Q}_k^N \cdot \mathbf{Q}_{k+1}^N = a^2 \cos\theta. \tag{12}$$

Throughout this paper, we choose a specific coordinate system for R^N by specifying the location and orientation of the polymer. We pin the polymer at one end and set $\mathrm{R}_0 = (0,0,0)$ and $\mathrm{R}_1 = (0,0,a)$, so that the first segment $\mathrm{Q}_1 = a\mathrm{e}_3$ points along the positive z-axis. If we describe each segment by its spherical coordinates centered at the base of Q_k, with the north pole in the direction of Q_k, then the radius (a) and polar angle (θ) are determined for the next segment Q_{k+1}, but the azimuthal angle, or *torsional angle*, ϕ_k, remains unspecified. These angles measure the extent to which a given segment twists out of the plane determined by the previous two segments. and they vary randomly with the thermal forces that the solution exerts on the polymer. (Notice, that since Q_1 is determined, the first torsional angle ϕ_1 gives the orientation of Q_2, and the indices of the torsional angles trail those of the immediately affected segments by one.) If we know the set of torsional angles $\Phi = \{\phi_1,..., \phi_{N-1}\}$, then we know the locations of all the segments and beads; since each segment Q_k can be considered as a rotation of the previous segment Q_{k-1} through an angle θ, in a direction determined by the angle ϕ_{k-1}. By convention, the value of $\phi_k = 0$ results in the segments Q_{k-1} and Q_{k+1} on the same side of Q_k, that is, in the *cis* position, while $\phi_k = \pi$ corresponds to the zig-zag, or *trans* position, following the definition of the terms in organic chemistry. Thus, the torsional angles provide coordinates for the polymer, and the randomness inherent in the FRC and its variants is fully reflected in the randomness of the torsional angles.
Since the thermal forces acting on the polymer serve to randomize the torsional angles, we consider these angles to be random variables. The FRC corresponds to the case in which the ϕ_k are independent and identically distributed on the circle $[0,2\pi)$. In this case, if a segment Q_k is known, then the endpoint of the next segment Q_{k+1} is uniformly distributed on the base of a cone with vertex R_k, axis in the direction of Q_k, lateral length a and aperture angle θ. This model is the basis for the other polymer models that we will discuss.
The *Kratky-Porod polymer model*, or wormlike chain, introduced in [15] and expounded upon in [11], is a similar model that can be seen as a continuous analog of the freely rotating chain. Let $\mathrm{Q}(s)$ be a standard Brownian motion process on the unit sphere S^2 and let (L,ℓ_p) be auxiliary parameters. We interpret the time parameter s of $\mathrm{Q}(s)$ as the arc length distance from the fixed end $s = 0$ of the polymer and we let $L > 0$ be the total contour length of the polymer and $\ell_p > 0$ be its persistence length. Letting $\mathrm{R}(s)$ be the position of the segment a distance of arc length s along the polymer, we have

$$\mathrm{R}(s) = \int_0^s \mathbf{Q}(\ell_p^{-1/2}\sigma)\,d\sigma. \tag{13}$$

Recall that the persistence length ℓ_p is a length scale that represents the exponential decay of tangent-tangent correlations; that is, if $\mathrm{T}(s)$ denotes the unit tangent vector to the polymer at an arc length distance of s from the fixed end, then

$$E[\mathrm{T}(0) \cdot \mathrm{T}(s)] \,\tilde{=}\, e^{-s/\ell p} \tag{14}$$

The main result of this dissertation concerns the inclusion of a constant force field to the freely rotating and Kratky-Porod models. The force f, a vector quantity, is first added to the discrete model via a potential energy function:

$$U(\mathrm{Q}^N) = -\alpha \sum_{k=1}^{N} \mathrm{Q}^N_k \cdot \mathrm{f} \tag{15}$$

in which α is a constant that represents the fact that the strength of the electric dipole moment of each segment is constant as $N \to \infty$. (To show this, we must let $\alpha = N$.) This energy is defined as a function of the segment vectors that comprise the polymer. We wish to use this energy to define a probability measure, the Boltzmann-Gibbs distribution with potential U, for the torsional angles $\Phi^N = \{\phi_1^N, \ldots, \phi_{N-1}^N\}$. This is possible because both Q^N and Φ^N can be written as deterministic functions of each other so that knowledge of one set of variables determines the other set. With this in mind, we can write

$$U(\mathrm{Q}^N) = U(\mathrm{Q}^N(\Phi^N)) = U(\Phi^N) \tag{16}$$

Letting $P_0^N(d\Phi)$ represent the uniform product measure on the set $[0,2\pi)^{N-1}$, which is the distribution of the set of angles in the original FRC model, and letting $\tau = k_B T$ be the thermal energy of the system, we define the Gibbs measure for the torsional angles of the forced model as follows:

$$P_f^N(d\Phi) = \exp(-U(\Phi^N)/\tau) P_0^N(d\Phi) \tag{17}$$

As with the freely rotating chain, the forced chain converges in distribution to a continuous model, $\mathrm{R}_f(s)$, which is a forced version of the Kratky-Porod model.

The forced Kratky-Porod model is described in terms of a stochastic differential equation for the tangent process $\mathrm{T}(s)$, that is, the derivative with respect to arc length of $\mathrm{R}_f(s)$, and a set of parameters $(L, \ell_p, \zeta, \hat{\mathrm{f}})$, where ζ is a dimensionless number that measures the relative magnitude of the force, and $\hat{\mathrm{f}}$ is the unit vector in the direction of the force vector f. More precisely, if

$$d\mathbf{T}(s) = \frac{1}{\sqrt{\ell_p}} d\mathbf{Q}(s) + \frac{\zeta}{\ell_p}(\mathbf{I} - \mathbf{T}(s) \otimes \mathbf{T}(s))\hat{\mathbf{f}}\, ds \tag{18}$$

with initial condition

$$\mathrm{T}(0) = e_3 \,(a.s.) \tag{19}$$

Then

$$\mathrm{R}_f(s) = \int_0^s \mathbf{T}(s) d\sigma. \tag{20}$$

In order to add the force, we must consider how it affects the distribution of the torsional angles, which are no longer uniform as in the unforced Kratky Porod model, described in [11]. The distribution will show a bias in the direction that causes the polymer to line up in a single plane, according to the following lemma:

Lemma 2.1: To achieve minimum energy, all segments of the discrete polymer must be coplanar with the force vector f and the initial segment Q_1; that is, for all $k = 2,\ldots,N$,

$$\mathrm{f} \cdot (\mathrm{Q}_1 \times \mathrm{Q}_k) = 0 \tag{21}$$

Proof. Since the vectors f and Q_1 are fixed, Q_2 must be chosen to be in the plane determined by f and Q_1, so that $\mathrm{f} \cdot \hat{\phi}_1 = 0$. Assume that f, $\mathrm{Q}_1,\ldots,\mathrm{Q}_k$ all lie in the same plane. Then in order that $\mathrm{f} \cdot \hat{\phi}_k = 0$, the vector Q_{k+1} must be in the same plane as f and Q_k, meaning that all $k + 2$ segment vectors are in the same plane. Therefore, by induction, in the state of lowest energy, the entire polymer is coplanar, and it sits in the plane defined by the force vector f and the initial direction vector Q_1.

3. Convergence of the Forced Polymer

In [11], we have described the freely rotating chain and Kratky-Porod model of semi-flexible polymers without the external force, and shown that in the scaling limit, the Kramers chain converges to the Kratky-Porod model. Now, let us add the force as a vector that acts equally at all points of the polymer. We wish to show the same results for the polymer in the field, namely, that the force-driven Kramers chain converges to the force-driven Kratky-Porod model. We do this by deriving a stochastic differential equation for the tangent vector, which is no longer simply a scaled Brownian motion as in the unforced model. The equation will now contain a drift term, which introduces a bias in the direction of the force. This is the equation that the tangent vector in the Kratky-Porod model satisfies, and we show that it is the limiting equation for the forced model. This theorem about the forced Kratky-Porod model is the main focus of this section.

Potential Energy and the Boltzmann-Gibbs Distribution

According to Lemma 2.1, the lowest potential energy state for each segment of the discrete polymer corresponds to the case in which the segment points as closely as possible to the direction of the force. Therefore, the energy due to each segment must attain its minimum at the most likely position of each segment; thus, define the energy due to each segment to be a negative constant multiplied by the dot product of the segment with the vector f:

$u_k = -\alpha(Q_k \cdot f)$. (22)

Then, take the sum of all terms for the energy over all segments of the polymer to obtain the total potential energy, since the inner product is linear and the cumulative sum of the Q_k is R_N:

$$U = -\alpha(R_N \cdot f) \tag{23}$$

This definition, in which the energy for each segment is proportional to the inner product of the force and each segment vector, and the total potential energy is proportional to the dot product of f with the position of the free end, is consistent with other sources [22, 6, 17, 19]. In these cases, the energy due to the force is a linear term added to the Hamiltonian.

The most important property, however, of the potential energy formula in [23] is its additivity. This is what facilitates the calculations of the conditional probability distributions for the torsion angles, and in turn, the position of the polymer. In these calculations, the energy of a single segment must be $O(1)$, even as the length of the segment goes to zero. To maintain these properties and to give a physically consistent explanation of the mathematics, suppose that f is the force due to an external electric field, and it induces a potential energy because each segment has a dipole moment proportional to the length. As $N \to \infty$, the length $a = L/N$ of each segment goes to zero, so to keep the proper scaling for the energy, the dipole moment must be kept constant, and this is done by increasing the charge. Thus, we let $\alpha = N$, and the potential energy for one segment Q_k is

$$U_k = -N\mathbf{f} \cdot \mathbf{Q}_k = -L\|\mathbf{f}\| \left(\hat{\mathbf{f}} \cdot \hat{\mathbf{Q}}_k\right) \tag{24}$$

Motivated to define a potential energy for the polymer, we can use this quantity to determine the distribution of the torsional angles, using the *Boltzmann-Gibbs distribution*. If the potential energy U, depending on the configuration of polymer segments, is known for a system, and each state of torsional angles Φ corresponds to a value of U, then the Boltzmann-Gibbs probability measure P for each state is determined thus:

$$P(\Phi \in d\Phi) = \frac{e^{-U(\Phi)/\tau} d\Phi}{Z} \tag{25}$$

Where $\tau = k_B T$ is the thermal energy, and Z is the partition function:

$$Z = \frac{Z}{TN-1} e{-}U(\Phi)/\tau d\Phi \tag{26}$$

While the integral above is over the $N-1$-dimensional torus, the product space of the interval $[0,2\pi)$ with itself $N-1$ times. Since the formula for U is additive, the probability density is multiplicative.

However, in formula (25), the differential is the product measure on the

$N-1$-tuple of angles,

$$d\Phi = d\phi_1 \times d\phi_2 \times \cdots \times d\phi_{N-1} \tag{27}$$

while the exponential factor depends on the segments of the polymer (the exponent is the normalized inner product of the force vector and the position vector of the free end of the polymer, which can be broken up into the segment vectors). Thus, if we wish to use the multiplicativity of the density function, it helps to convert the product measure of torsional angles into the product of transition probabilities of the segments.

This can be done by showing that the sequence of segments in the discrete polymer is a Markov chain; then it becomes possible to calculate conditional expectations of functions of the torsional angles, which are necessary to find the Doob-Meyer decomposition of the driving process of the polymer, by iterated integration. If the measure in the integral is left as the product measure of the torsional angles, then the integral cannot be evaluated segment-wise. By using the Markov property of the segments, the calculations are facilitated, as the positions of the segments can be evaluated as single integrals.

Lemma 3.1: For an N-segment polymer, under the Boltzmann-Gibbs measure on the angles $\Phi = \{\phi_1,\ldots,\phi_{N-1}\}$ corresponding to the potential energy due to a constant force field f, the functions $Q = \{Q_1,\ldots,Q_N\}$ form a Markov chain, and the induced measure is the transition probability π_N^f.

Proof. The full proof appears in the original dissertation, which can be found on-line.

Driving Process of the Forced Kramers Chain

Now that we have established that the segments of the forced Kramers chain form a Markov chain, the next step is to use this property to characterize the matrix-valued driving process, $B^N(s)$, in terms of drift and diffusion. This will lead to the two terms in the differential equation [18] for the tangent vector in the Kratky-Porod model with the added force.

Recall, as in [11], that B^N is given by the formula

$$B^N(s) = \frac{1}{\sqrt{N}} \sum_{k=1}^{[Ns/L]} \mathbf{b}_k(\phi_k) \tag{28}$$

in which the matrices $\mathbf{b}_k$ are infinitesimal rotations, which comprise the segments of the polymer in the following manner:

$$Q^k = \prod_{j=1}^{k-1} \exp\left(\frac{\kappa}{\sqrt{N}} \mathbf{b}_j(\phi_j)\right) \mathbf{Q}_1 \tag{29}$$

Where the product is written so that j increases from left to right, and $\mathbf{Q}_1 = a\mathbf{e}_3$. The formula for each infinitesimal rotation is

$$\mathbf{b}_k(\phi_k) = \begin{pmatrix} 0 & 0 & \sin\phi_k \\ 0 & 0 & -\cos\phi_k \\ -\sin\phi_k & \cos\phi_k & 0 \end{pmatrix}. \tag{30}$$

In the original model without a force, the torsional angles ϕ_k all had a uniform distribution on the circle; therefore, the expected values of the sines and cosines of the angles were all zero. This meant that the mean of each infinitesimal rotation, $E[\mathrm{b}_k(\phi_k)]$, was 0, and so the mean of the driving process $E[\mathrm{B}^N(s)]$ was 0 for all $s \in [0,L]$. In fact, since each increment b_k of the driving process had mean zero, their scaled cumulative sum $\mathrm{B}^N(s)$, or B^N_k with a discrete index, was a martingale.

But now, the distribution of each torsional angle is biased towards a favored value ϕ^0_k, which would make the segment Q_{k+1} line up as closely to the vector of the force field f as possible. Thus, the mean of the driving process will no longer be 0, but instead will show a bias, or a drift, in the direction of the applied external force.

Additionally, the driving process $\mathrm{B}^N(s)$ is no longer a martingale; however, it can be expressed as a semimartingale. To show this, we can write B^N in the form of its Doob-Meyer decomposition. This formulation of B^N will greatly aid us in our proof of the convergence of the discrete forced polymer model to the continuous model.

Lemma 3.2: For an N-segment forced Kramers chain, the driving process $\mathrm{B}^N(s)$ can be expressed as

$$B^N_p(s) = \mathbf{M}^N(s) + \frac{\zeta}{\kappa\ell} \sum_{j=1}^{[Ns/L]} \left((\mathbf{Z}_j^N)^{-1}\hat{\mathbf{f}}\mathbf{e}_3^T - \mathbf{e}_3\hat{\mathbf{f}}^T\mathbf{Z}_j^N\right)\frac{L}{N} \tag{31}$$

where $\mathrm{M}^N(s)$ is a martingale and ζ is a dimensionless parameter. The righthand side of the equation, apart from $\mathrm{M}^N(s)$, constitutes the drift term of the process.

Proof. We will omit most of the details, but touch on the major points of the proof. Let us first re-write B^N in terms of a discrete index k, rather than a continuous parameter s, because the Doob-Meyer decomposition requires a discrete index. Thus B^N_k is given by

$$B^N_k = \frac{1}{\sqrt{N}} \sum_{j=1}^{k} \mathbf{b}_j(\phi_j) \tag{32}$$

and we decompose it as the sum

$$B^N_k = M^N_k + A^N_k \tag{33}$$

Where M^N is a martingale, just like the driving process in the unforced model, and $\mathrm{A}^N_k \in \mathrm{F}_{k-1}$, the σ-field generated by the first $k-1$ segments; that is, A^N is an adapted process. This decomposition can be found by direct calculation, which we can do because of the Markov property of the torsional angles. As an example, let us consider in depth the top-right entry in $E[\mathrm{b}_k(\phi_k)|\mathrm{F}_{k-1}]$, that is, the conditional expectation of $\sin\phi_k$. (The conditional expectation of $\cos\phi_k$ will turn out to be very similar.) This is given by

$$E[\sin\phi_k|\mathcal{F}_{k-1}] = \frac{\int \sin\phi_k\, e^{N\mathbf{f}\cdot\mathbf{Q}_{k+1}/\tau} d\phi_k}{\int e^{N\mathbf{f}\cdot\mathbf{Q}_{k+1}/\tau} d\phi_k} \tag{34}$$

The lower integral in equation (34) equals

$$\int_T e^{\zeta z_{k-1}\cos\theta} \exp(\zeta \sin\theta\, \psi_k)\, d\phi_k$$

Where, for simplicity, we have made the substitutions

$$\zeta = \frac{L\,|\mathbf{f}|}{\tau} \tag{35}$$

And

$$\psi_k(\phi_k) = x_{k-1}\sin\phi_k - y_{k-1}\cos\phi_k. \tag{36}$$

Similarly, for simplicity of notation, let us define

$$\mu = \zeta\sin\theta. \tag{37}$$

Notice that ζ is a dimensionless parameter that measures the magnitude of the force when contour length and temperature are fixed.

Now, the integrand is an exponential that includes trigonometric functions, which is impossible to integrate analytically. However, since the multiplier $\sin\theta$ in the exponent is small, on the order $O(N^{-1/2})$, and we will eventually take the limit as $N \to \infty$ of the discrete model to obtain the continuous model, we can expand the integrand in an asymptotic series, which will allow us to integrate the exponential. Recall that the discrete process $B^N(s)$ is a sum of $[Ns/L]$ infinitesimal rotations, with a factor of $N^{-1/2}$. Therefore, any terms in the asymptotic expansion for $E[b_k(\phi_k)|F_{k-1}]$ that are smaller than $O(N^{-1/2})$ can be ignored, as they will vanish in the limit. This yields the limiting formula:

$$E[\sin\phi_k|\mathcal{F}_{k-1}] = \frac{\mu x_{k-1}}{2} \tag{38}$$

In this formula, the quantities (x_k, y_k, z_k) are the coordinates of the rotated unit force vector, $Z_k^{-1}\hat{f}$. Similar formulas hold for the conditional expectations of the other trigonometric functions of the torsional angles, and these can be used to calculate the Doob-Meyer decomposition of the discrete driving process $B^N(s)$. For example,

$$E[\cos\phi_k|\mathcal{F}_{k-1}] = -\frac{\mu y_{k-1}}{2} \tag{39}$$

From these two conditional expectations, it is now possible to derive the formula for the conditional expectation of each infinitesimal rotation $b_k(\phi_k)$ with respect to the previous σ-field, as such:

$$\bar{\mathbf{b}}_k = E[\mathbf{b}_k(\phi_k)|\mathcal{F}_{k-1}] = \frac{\mu}{2}\begin{pmatrix} 0 & 0 & x_{k-1} \\ 0 & 0 & y_{k-1} \\ -x_{k-1} & -y_{k-1} & 0 \end{pmatrix} \tag{40}$$

To first order. This matrix $\bar{b}_k$ can also be expressed as a difference of tensor products of unit vectors; in each case, the vectors are the initial direction e_3 and the rotated force vector $\hat{\mathbf{f}}_{k-1} = \mathbf{Z}_{k-1}^{-1}\hat{f}$. Therefore, an equivalent formulation of the conditional expectation of the infinitesimal rotation is

$$\bar{\mathbf{b}}_k = \frac{\mu}{2}(\hat{\mathbf{f}}_{k-1}\otimes\mathbf{e}_3 - \mathbf{e}_3\otimes\hat{\mathbf{f}}_{k-1}) \tag{41}$$

or, treating the vectors as matrices,

$$\bar{\mathbf{b}}_k = \frac{\mu}{2}(\mathbf{Z}_{k-1}^T\hat{\mathbf{f}}\mathbf{e}_3^T - \mathbf{e}_3\hat{\mathbf{f}}^T\mathbf{Z}_{k-1}) \tag{42}$$

For a more compact notation, let us denote the outer product commutator of two vectors by the same symbol as the commutator of matrices; that is,

$$[\mathbf{v},\mathbf{w}] = \mathbf{v}\otimes\mathbf{w} - \mathbf{w}\otimes\mathbf{v}. \tag{43}$$

Thus, we can say that

$$\bar{\mathbf{b}}_k = \frac{\mu}{2}[\mathbf{Z}_{k-1}^{-1}\hat{\mathbf{f}}, \mathbf{e}_3] \tag{44}$$

From this conditional expectation, we can calculate the adapted process A^N_k that appears in the Doob-Meyer decomposition of B^N_k and which has the same mean as B^N_k. By summing all the conditional expectations of the infinitesimal √ rotations, and dividing by N, we obtain the following formula for the adapted part of the driving process:

$$A_k^N = \frac{\zeta}{\kappa\ell_p}\frac{L}{N}\sum_{j=1}^{k}[\mathbf{Z}_{j-1}^{-1}\hat{\mathbf{f}}, \mathbf{e}_3] + o \text{ —— — } (1) \tag{45}$$

Thus, returning to our definition of $B^N(s)$ in terms of a continuous parameter (by letting $k = [Ns/L]$), we obtain the desired formula for the Doob-Meyer decomposition.

Once we know the structure of $B^N(s)$, we can use it to define the process of orthonormal frames, $Z^N(s)$, according to a stochastic differential equation:

$$d\mathbf{Z}^N(s) = \mathbf{Z}^N(s)\left(\kappa d\mathbf{B}^N(s) + \frac{1}{2}d[\kappa\mathbf{B}, \kappa\mathbf{B}]_s\right) + \mathbf{r}(N) \tag{46}$$

(Recall here that $\mathbf{r}(N)$ is the increment of the cubic and higher order variations of **B**, which vanish in the limit). This can also be written

$$\partial Z^N(s) = \kappa Z^N(s)\partial B^N(s) + r(N) \tag{47}$$

or in integral form,

$$Z^N(s) = \mathbf{I} + \kappa\int_0^s \mathbf{Z}^N(\sigma)\partial\mathbf{B}^N(\sigma) \tag{48}$$

by the rule relating the Itˆo and Stratonovich derivatives of stochastic processes, since our initial condition is $Z(0) = I$.

Convergence to the Forced Kratky-Porod Model

We can now define the limiting process $B(s)$ by simply taking the pointwise limit of $B^N(s)$ for each fixed s as $N \to \infty$. We will show, in fact, that it is a Brownian motion with a non-linear drift. However, the analogous limiting rotation process, $Z(s)$, can only be defined as the solution to the limiting differential equation, which is the limit of the above discrete equation, if we wish for this relationship between the B and Z processes to continue as the number of the segments of the polymer goes to infinity. The limiting stochastic differential equation is

$$dZ(s) = \kappa Z(s)\partial B(s) \tag{49}$$

and it is often written in integral form:

$$Z(s) = \mathbf{I} + \kappa\int_0^s \mathbf{Z}(\sigma)\partial\mathbf{B}(\sigma) \tag{50}$$

N

We wish to show that the processes Z converge weakly to Z. This is done, as in [11], by means of Theorem 8.1 of Kurtz and Protter [16], which yields the convergence in distribution of processes that are solutions of stochastic differential equations under certain conditions. With the next few lemmas, we will prove that the conditions of the theorem are satisfied. The first step is to prove that the martingale parts M^N converge weakly to a Gaussian limit M, by means of a martingale version of the Central Limit Theorem.

Lemma 3.3: The martingale part $M^N(s)$ of $B^N(s)$ converges in distribution to a Gaussian matrix-valued process.

Proof. Our goal is to show that the martingale part, M^N, when the limit as $N \to \infty$ is taken, is identical to the Gaussian process that governed the motion of the tangent vector along the polymer in the unforced model. To do this, it is necessary to show that the discrete processes satisfies conditions for a version of the Central Limit Theorem, so that as $N \to \infty$, the discrete processes can converge weakly to a continuous Gaussian process. Since the infinitesimal rotation matrices, properly scaled and with the mean subtracted away, are the increments of the martingale part M^N, we must examine the conditional mean and variance of each of these matrices with respect to the previous σ-field. The mean of the matrices has been calculated in equation (44). Now, let us find the second moment:

$$E[\mathbf{b}_k(\phi_k)^2|\mathcal{F}_{k-1}] = E\left[\left(\begin{array}{ccc} -\sin^2\phi_k & \sin\phi_k\cos\phi_k & 0 \\ \sin\phi_k\cos\phi_k & -\cos^2\phi_k & 0 \\ 0 & 0 & -1 \end{array}\right)\middle|\mathcal{F}_{k-1}\right] \tag{51}$$

Therefore, we must compute the conditional expectations of the functions $\sin^2\phi_k$, $\cos^2\phi_k$, and $\sin\phi_k\cos\phi_k$. As before, we will expand the integrand in an asymptotic series and discard all terms that are smaller than $O(N^{-1/2})$. This yields

$$E[\mathbf{b}_k^2(\phi_k)|\mathcal{F}_{k-1}] = \begin{pmatrix} -\frac{1}{2} & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad (52)$$

As before, let us call the matrix on the right-hand side of the above equation
D, since it is a diagonal matrix. Thus, the conditional variance has the form D+$\epsilon_1(N)$, where ϵ_1 is a matrix whose norm is of order $O(N^{-1})$, which will aid in proving that the conditions for the Central Limit Theorem are satisfied.
There are several forms of the Central Limit Theorem for triangular arrays, and even some that apply to conditional expectations. We will use one from [2] p. 333, which employs the Lindeberg-Feller condition. The hypotheses of the theorem are satisfied because the higher-order terms in the expansion of the second moment vanish when summed. Therefore, the theorem applies to the processes, and the limit M(s) is a matrix-valued Gaussian process with mean 0 and variance D(s/L).
Now that we have weak convergence of the martingale part of the driving process B, we must show the same for the entire process, so that we can use the Kurtz-Protter theorem. The next step is to prove relative compactness of both the B^N and the Z^N.

Lemma 3.4: The sequence of pairs of processes $(B^N(s), Z^N(s))_{N\in\mathbb{N}}$ is relatively compact in the Skorohod topology.

Proof. First, consider for each N the Doob-Meyer decomposition of B^N into the sum of a martingale M^N and an adapted process A^N. Recall that

$$A^N(s) = \frac{1}{\sqrt{N}} \sum_{j=1}^{[Ns/L]} E[\mathbf{b}_j|\mathcal{F}_{j-1}] \quad (53)$$

$$M^N(s) = \frac{1}{\sqrt{N}} \sum_{j=1}^{[Ns/L]} \mathbf{b}_j - E[\mathbf{b}_j|\mathcal{F}_{j-1}] \quad (54)$$

Let us first prove relative compactness for the sequence of processes (B^N): this consists of proving both a uniform stochastic boundedness condition and a stochastic equicontinuity condition, according to a theorem of Ethier and Kurtz [8]. First, notice that by Lemma 3.3, the sequence of martingale parts (M^N) is already relatively compact, since it has a weak limit M. In order to place a stochastic bound on B^N and its increments, we can use the bound that we already have for M^N and find one for A^N as well. We know that

$$A^N(s) = \frac{\zeta}{\kappa\ell_p} \frac{L}{N} \sum_{j=1}^{[Ns/L]} [(\mathbf{Z}_j^N)^{-1}\hat{\mathbf{f}}, \mathbf{e}_3] \quad (55)$$

The expression in the sum is the matrix $(\mathbf{Z}_j^N)^T\hat{\mathbf{f}}\mathbf{e}_3^T - \mathbf{e}_3\hat{\mathbf{f}}^T\mathbf{Z}_j^N$, which has norm at most 2, since the vectors whose outer product makes the matrix are unit vectors. Therefore, by the triangle inequality,

$$\|\mathbf{A}^N(s)\| \le \frac{2\zeta s}{\kappa\ell_p}, \quad (56)$$

and since $s \in [0,L]$, the adapted part has a uniform bound of $\kappa\|\mathbf{f}\|L/\tau$. In a similar fashion, we can bound the increment in $\mathbf{A}^N$ between two points s and s' on the curve (here, as before, we take $s < s'$):

$$\|\mathbf{A}^N(s) - \mathbf{A}^N(s')\| = \frac{\zeta}{\kappa\ell_p} \frac{L}{N} \left\| \sum_{j=[Ns/L]+1}^{[Ns'/L]} [(\mathbf{Z}_j^N)^{-1}\hat{\mathbf{f}}, \mathbf{e}_3] \right\| \quad (57)$$

$$\le \frac{2\zeta}{\kappa\ell_p}|s-s'| \quad (58)$$

and thus the aggregate size of the jumps in the adapted process is bounded above by a constant multiple of the increment in the arc length. Therefore, both conditions of relative compactness are satisfied for the adapted part of B^N, and in turn, for all of B^N itself.
Next, we must show that the discrete processes of rotations $Z^N(s)$ are also relatively compact. In terms of the Doob-Meyer decomposition, we can express Z^N by this stochastic differential equation:

$$d\mathbf{Z}^N(s) = \kappa\mathbf{Z}^N(s)d\mathbf{M}^N(s) + \kappa\mathbf{Z}^N(s)d\mathbf{A}^N(s) + \frac{\kappa^2}{2}d[\mathbf{M},\mathbf{M}]_s \quad (59)$$

Recall that since the adapted part A^N has finite variation, the quadratic variation of B^N is precisely that of M^N. The stochastic uniform boundedness of the Z^N is trivial, since all rotations have norm 1. Thus, we must show equicontinuity of each of the three terms on the right side of equation (59). The key to this is another theorem of Ethier and Kurtz [8] which states that a family (Z^N) is stochastically equicontinuous if and only if $\forall \eta > 0$, $L > 0$, $\exists \delta > 0$ such that

$$\sup_N P(w'(\mathbf{Z}^N,\delta,L) \geq \eta) \leq \eta. \tag{60}$$

The quantity w' is a modulus of continuity, and Ethier and Kurtz define it thus:

$$w'(\mathbf{Z}^N,\delta,L) = \inf_{\{s_i\}} \max_i \sup_{s,s'\in[s_{i-1},s_1)} \|\mathbf{Z}^N(s) - \mathbf{Z}^N(s')\| \tag{61}$$

That is, w' is the infimum over all partitions $\{0 = s_0, s_1, ..., s_N = L\}$, of the maximum over intervals in the partition, of the supremum over pairs of points $\{s,s'\}$ within the interval, of the distance between the values of the process at the points s and s'.

We accomplish this by first finding a bound for the modulus of continuity for the two terms involving M^N, then showing that the increment Z^N depending on the adapted part is also stochastically bounded, namely:

$$\kappa \left\| \sum_{j=[Ns/L]+1}^{[Ns'/L]} \mathbf{Z}_j^N(\mathbf{A}_{j+1}^N - \mathbf{A}_j^N) \right\| = \frac{\zeta L}{\ell_p N} \left\| \sum_{j=[Ns/L]+1}^{[Ns'/L]} \mathbf{Z}_j^N [(\mathbf{Z}_j^N)^{-1}\hat{\mathbf{f}}, \mathbf{e}_3] \right\| \tag{62}$$

is bounded above by a constant multiple of $|s - s'|$. But this is true, because we can use the triangle inequality on the increments in the sum: $\|Z^N_j\| = 1$ always, and $\|[(Z^N_j)^{-1}\hat{f}, e_3]\| \leq 2$, since it is the difference of tensor products of unit vectors. Therefore,

$$\kappa \left\| \sum_{j=[Ns/L]+1}^{[Ns'/L]} \mathbf{Z}_j^N(\mathbf{A}_{j+1}^N - \mathbf{A}_j^N) \right\| \leq \frac{2\zeta}{\ell_p}|s - s'| \tag{63}$$

and the relative compactness of $Z^N(s)$ for the forced model follows.

Next, we must show that B^N converges to B weakly, which is the second condition for the Kurtz-Protter theorem. Since we have shown the weak convergence of the martingale part $M^N(s)$ to a Gaussian limit (call it $M(s)$), we must show the same for the adapted part $A^N(s)$. In doing so, we will first show convergence of the A^N and Z^N together along subsequences. Since the processes A^N, M^N, and Z^N satisfy a stochastic differential equation, and the M^N converge weakly to a limit M, we will show that weak convergence of A^N and Z^N will follow, using the next three lemmas. First, notice that existence of a subsequence along which the A^{Nk} converge follows from relative compactness of the A^N (as part of B^N) from Lemma 3.4.

Lemma 3.5: Let (N_k) be the indices of a subsequence along which (B^{Nk}, Z^{Nk}) converges weakly to a limit (B,Z). Then along the same subsequence, the processes $A^{Nk}(s)$ converge weakly to a limit A, satisfying the equation

$$A(s) = \frac{\zeta}{\kappa\ell_p}\int_0^s [\mathbf{Z}(\sigma)^{-1}\hat{\mathbf{f}}, \mathbf{e}_3]\, d\sigma. \tag{64}$$

Proof. First, let (B^{Nk}) be a subsequence which converges to a limit B in distribution. Then, since for all k, $B^{Nk} = M^{Nk} + A^{Nk}$, and $M^{Nk} \Rightarrow M$ by Lemma 3.3 above, it follows that the subsequence (A^{Nk}) converges weakly to a limiting process; call it A.

Recall that if $\Delta s = L/N$, then A^{Nk} and Z^{Nk} satisfy

$$A^{N_k}(s) = \frac{\zeta}{\kappa\ell_p}\sum_{j=1}^{[Ns/L]} [(\mathbf{Z}_j^{N_k})^T\hat{\mathbf{f}}, \mathbf{e}_3]\Delta s. \tag{65}$$

Since the processes A^{Nk} and Z^{Nk} are *c`adl`ag*, the discrete sum can be ex-pressed as the integral of a piecewise constant function. Also, we have replaced Z^{-1} with Z^T, since Z is an orthogonal matrix. This will simplify the next step of the proof.

We now claim that for all k, A^{Nk} is a continuous bounded transformation of Z^{Nk}. The boundedness criterion is immediate from equation (55), so $\|A^N\| \leq \frac{2\zeta s}{\kappa\ell_p}\|\mathbf{Z}^N\|$, and continuity is straightforward as well:

$$\|\mathbf{A}(\mathbf{Z}) - \mathbf{A}(\mathbf{Z}')\| \leq \frac{2\zeta s}{\kappa\ell_p}\|\mathbf{Z} - \mathbf{Z}'\| \tag{66}$$

Since the outer product commutator is bounded above by 2. Therefore, the continuity theorem of weak convergence (Theorem 2.3 of Chapter 2 of [7]) holds, and so equation (64) is true for the subsequential limits A and Z.
Thus, we see that the martingale part M^N of B^N converges weakly to a limit M and the bounded variation part A^N retains its relationship with Z^N along subsequences. There now remains one condition to be proven to use the Kurtz-Protter theorem for subsequences: that the sequence of processes B^N is *good*, in the language of [16]. In the same paper, Kurtz and Protter show that a sequence of stochastic processes is *good* if and only if it is of uniformly controlled variation. This is the condition that we will prove.

Lemma 3.6: The sequence of processes $(B^N)_{N\in N}$ is of uniformly controlled variation (UCV), that is, for all N ∈ N,

$$\sup_N \left\{ E^N[\mathbf{M}^N, \mathbf{M}^N]_s + E^N\left[\int_0^s \|d\mathbf{A}^N(s)\|\right]\right\} < \infty \tag{67}$$

Proof. Note that each of these expressions above, that is, both the quadratic variation of the martingale part and the total variation of the adapted part, can be evaluated. First,

$$E^N[\mathbf{M}^N, \mathbf{M}^N]_s = \frac{1}{N}\sum_{j=1}^{[Ns/L]} \mathrm{Var}[\mathbf{b}_j \tag{68}$$

$$= \frac{s}{L}(\mathbf{D} + \epsilon_1(N)) < \infty \tag{69}$$

Next,

$$E^N\left[\int_0^s \|d\mathbf{A}^N(s)\|\right] = E^N\left[\frac{1}{\sqrt{N}}\sum_{j=1}^{[Ns/L]} \|E[\mathbf{b}_j|\mathcal{F}_{j-1}]\|\right] \tag{70}$$

$$\leq \frac{2s\zeta}{\kappa\ell_n} < \infty. \tag{71}$$

Since these bounds hold for all-natural numbers N, the sequence (B^N) is UCV, as desired.
Therefore, the Kurtz-Protter theorem holds for subsequences. With these lemmas in place, we are now ready to show that convergence of the B^N and Z^N holds along the entire sequence, namely, that all subsequential limits are the same, and that the limiting processes B and Z satisfy the limiting differential equation.

Lemma 3.7: The sequence of processes of orthonormal frames along the polymer in the forced Kramers chain model, $(Z^N)_{N\in N}$, converges weakly to the process of orthonormal frames along the polymer in the forced Kratky-Porod model, Z.

Proof. Let us first describe the Stratonovich differential equation for B^N and Z^N in terms of the Doob-Meyer decomposition:

$$\partial Z^N(s) = \kappa Z^N(s)\partial M^N(s) + \kappa Z^N(s)\partial A^N(s). \tag{72}$$

Let (A_1,Z_1) and (A_2,Z_2) be two subsequential limits of the sequence (A^N,Z^N). Then, by Lemmas 3.3 and 3.5, and by the theorem in [16], these two subsequential limits satisfy the same coupled system of stochastic differential equations, driven by the same process M. But the solutions to stochastic differential equations are unique. Therefore, $(A_1,Z_1) = (A_2,Z_2)$, and it follows that he limiting processes B and Z satisfy the SDE as desired.

$$\partial Z(s) = \kappa Z(s)\partial B(s) \tag{73}$$

Characterization of the tangent vector process
This last lemma (3.7) gives us the convergence of the processes of orthonormal frames (and by projection, of tangent vectors along the molecule) which will greatly aid us in proving the convergence of the discrete forced model to the continuous forced model. As before, the tangent vector to the polymer satisfies a stochastic differential equation. However, since the driving process B(s) is no longer a martingale, but a semi-martingale and its adapted part leads to a drift, the equation governing the tangent vector will include a drift term.
To derive this equation, we must first show that the martingale part M(s) of B(s) defines a Brownian motion. We have already established, in Lemma 3.3, that it is a Gaussian matrix-valued process. Now, we will prove a statement about the entries of the matrix.

Lemma 3.8: The martingale part M(s) of the driving process B(s) has nonzero entries that are scaled independent one-dimensional Brownian motions.

Proof. The key to this proof is to show that the process M is continuous in *s*, and that its entries have the same mean and variance as a Brownian motion. Then, Levy's theorem tells us that the resulting process in each entry of the matrix M is a Brownian motion.

Let us begin by considering the distance between two points of the discrete process $M^N(s)$, and then take the limit as $N \to \infty$. Let $N \in \mathbb{N}$, and $\Delta s = L/N$ as before. Then, the difference between $M^N(s+\Delta s)$ and $M^N(s)$ is bounded as follows:

$$\|\mathbf{M}^N(s+\Delta s) - \mathbf{M}^N(s)\| \le \frac{1}{\sqrt{N}} + \frac{\zeta}{\kappa \ell_p}\Delta s. \tag{74}$$

If Δs is fixed and $N \to \infty$, we have the desired continuity property, which can be seen as follows: let $\epsilon > 0$. Then if we let $\delta = (\kappa\ell_p/\zeta)\epsilon$, if $|s - s'| < \delta$, then $\|M(s) - M(s')\| < \epsilon$. Now, we can find the covariance of the process $M(s)$ and show that it matches that of a Brownian motion. Recall that B(*s*), as well as both of its components in the Doob-Meyer decomposition, is an anti-symmetric matrix whose non-zero entries are in the third row or third column, but not both. Thus M(*s*) can be expressed as follows:

$$\mathrm{M}(s) = \begin{pmatrix} 0 & 0 & \beta_1(s) \\ 0 & 0 & \beta_2(s) \\ -\beta_1(s) & -\beta_2(s) & 0 \end{pmatrix} \tag{75}$$

Where the processes $\beta_i(s)$ for $i = 1,2$ are continuous Gaussian scalar-valued processes, as shown before [11]. We wish to show now that the $\beta_i(s)$ are independent Brownian motions; that is, for some positive constant *C*,

$$E[\beta_i(s)\beta_j(s')] = C\delta_{ij}(s \wedge s'). \tag{76}$$

To prove this claim, we will consider each case of the values of *i* and *j* individually, and without loss of generality, let $s < s'$. If $i = j = 1$, then we will calculate the auto-correlation of β_1, which has the following form:

$$\beta_1(s) = \lim_{N\to\infty} \frac{1}{\sqrt{N}} \sum_{k=1}^{[Ns/L]} \left(\sin\phi_k - \frac{\mu}{2}x_{k-1}\right) \tag{77}$$

Recall that $\mu = O(N^{-1/2})$, and since there is a factor of N^{-1} outside the sum, only the terms inside which are $O(1)$ will have any effect on the total as $N \to \infty$. Such terms only occur when the indices match, as the cross terms have mean zero. Therefore,

$$E[\beta_1(s)\beta_1(s')] = \frac{s}{2L} \tag{78}$$

By a similar argument, the above result holds for $E[\beta_2(s)\beta_2(s')]$ as well; we can apply the same reasoning to the proof above, while replacing β_1 with β_2, $\sin\phi_k$ with $-\cos\phi_k$, and x_{k-1} with y_{k-1}. Thus it remains only to show that $E[\beta_1(s)\beta_2(s')] = 0$. This is true by a similar calculation to the one above, because the terms of matching order are now small enough ($O(N^{-1})$) to vanish in the limit. Therefore, by combining all these cases, we attain the desired result in equation (76), with the constant $C = \frac{1}{2L}$.

Therefore, by L´evy's theorem for martingales, the entries of M(*s*) are multiples of independent Brownian motion processes in the arc length parameter *s*.

We therefore have a formula for the martingale part in terms of one-dimensional Brownian motion processes. We now wish to use this fact to derive a differential equation for the tangent vector process, $T(s) = Z(s)T(0)$ with initial condition $T(0) = e_3$. Since the original, unforced polymer has a tangent vector process equal to a scaled Brownian motion on the sphere, we aim to derive an equation in which one term, the diffusion term, is a scaled spherical Brownian motion. The first step is to isolate the Brownian motion in the driving process, B(*s*).

Lemma 3.9: The driving process B(s) for the forced Kratky-Porod model can be expressed in terms of standard one-dimensional Brownian motions.

Proof. We begin by expressing B(s) as its Doob-Meyer decomposition,

$$\mathrm{B}(s) = \mathbf{M}(s) + \frac{\zeta}{\kappa\ell_p}\int_0^s [\mathbf{Z}(\sigma)^{-1}\hat{\mathbf{f}}, \mathbf{e}_3]\, d\sigma \tag{79}$$

Where M(*s*) is the scaled Gaussian matrix, with entries that are multiples of Brownian motion, as shown in Lemma 3.8. Let us write

$$\mathrm{M}(s) = \frac{1}{\sqrt{2L}}\mathbf{W}(s) \tag{80}$$

And

$$\mathrm{W}(s) = \begin{pmatrix} 0 & 0 & w_1(s) \\ 0 & 0 & w_2(s) \\ -w_1(s) & -w_2(s) & 0 \end{pmatrix} \tag{81}$$

with w_1 and w_2 satisfying

$$E[w_i(s)w_j(s')] = \delta_{ij}(s \wedge s'), \tag{82}$$

Namely, that the w_i are independent one-dimensional Brownian motions. Since the matrix W(s) is standardized, that is, its non-zero entries are normally distributed random processes in s (namely N(0,s)), we will refer to it in future calculations.
Therefore, we have shown in this section that the discrete processes which govern the orientation of the polymer, namely, the driving process B^N and the process of rotation matrices Z^N, converge in distribution to limiting processes B and Z, and the process B satisfies the equation

$$\mathrm{B}(s) = \frac{1}{\sqrt{2L}}\mathbf{W}(s) + \frac{\zeta}{\kappa\ell_p}\int_0^s [\mathbf{Z}(\sigma)^{-1}\hat{\mathbf{f}}, \mathbf{e}_3]\, d\sigma. \tag{83}$$

Now that we have expressed B(s) in terms of the independent standard Brownian motions $w_1(s)$ and $w_2(s)$, let us do the same for the tangent vector process T(s), which will lead to the desired differential equation.

Lemma 3.10: The tangent vector process T(s) for the forced Kratky-Porod model satisfies the following differential equation in terms of the matrices Z(s) and W(s):

$$d\mathbf{T}(s) = \frac{\zeta}{\ell_p}(\mathbf{I} - \mathbf{T}(s) \otimes \mathbf{T}(s))\hat{\mathbf{f}}ds + \frac{1}{\sqrt{\ell_p}}\mathbf{Z}(s)\partial\mathbf{W}(s)\mathbf{e}_3 \tag{84}$$

Proof. Previously, in [11], we defined the Bishop frame to be the unit vector T tangent to the curve representing the polymer, and $\{M_1,M_2\}$ to be its normal development, that is, a pair of orthonormal vectors which span the plane normal to T at any given point on the polymer. The three vectors are mutually orthogonal and have unit length, and together they comprise the matrix-vaued process Z(s), in the order Z = ($M_1|M_2|$T). Together, these vectors satisfy the stochastic differential equation

$$\frac{\partial}{\partial s}\mathbf{Z}(s) = \kappa\mathbf{Z}(s)\frac{\partial}{\partial s}\begin{pmatrix} 0 & 0 & \beta_1(s) \\ 0 & 0 & \beta_2(s) \\ -\beta_1(s) & -\beta_2(s) & 0 \end{pmatrix} \tag{85}$$

With initial conditions
$T(0) = e_3$ (86)
$M_1(0) = e_1$ (87)
$M_2(0) = e_2$ (88)

This shows how the orthonormal frame of vectors moves along the length of the polymer through parallel transport. This differential equation for Z(s) transforms into one for T(s) by simply multiplying each matrix that appears in the equation by the initial direction vector T(0):

$$d\mathbf{T}(s) = \frac{\zeta}{\ell_p}\mathbf{Z}(s)[\mathbf{Z}(s)^{-1}\hat{\mathbf{f}}, \mathbf{e}_3]\mathbf{e}_3 ds + \frac{\kappa}{\sqrt{2L}}\mathbf{Z}(s)\partial\mathbf{W}(s)\mathbf{e}_3 \tag{89}$$

Thus, the Doob-Meyer decomposition expresses the differential of the driving process as the sum of a drift term and a diffusion term (involving the Brownian motion W(s)). The matrix expression involving the outer product commutator in the drift term can be simplified:

$$Z(s)[Z(s)^{-1}\hat{f},e_3]e_3 = (I - T(s) \otimes T(s))\hat{f}. \tag{90}$$

Therefore, the drift term is proportional to the projection of the unit vector in the direction of the force, $\hat{\mathbf{f}}$, onto the plane perpendicular to the current tangent vector. This plane is equal to the normal development, and this yields the following simplified differential equation for T(s):

$$d\mathbf{T}(s) = \frac{\zeta}{\ell_p}(\mathbf{I} - \mathbf{T}(s) \otimes \mathbf{T}(s))\hat{\mathbf{f}}ds + \frac{\kappa}{\sqrt{2L}}Z(s)\partial W(s)e_3 \tag{91}$$

But recall that the persistence length is related to the curvature parameter κ: $\ell_p = 2L/\kappa^2$. Thus, the coefficient on the Brownian motion term is $\ell_p^{-1/2}$, and the equation (91) becomes (84), as desired.
This equation, however, is not self-contained, since Z(s) appears on the right side, and it contains the normal development vectors M_1 and M_2 in addition to T. Also, we wish to express the tangent vector in terms of the spherical Brownian motion Q(s). However,

by an argument of differential geometry, we can show that the part of equation (84) containing the diffusion term is generated by the Laplace-Beltrami operator on the sphere, thereby equaling a spherical Brownian motion in distribution, according to the version of L´evy's theorem for Riemannian manifolds.

Lemma 3.11: The diffusion term in equation (18) is equal in distribution to a scaled spherical Brownian motion.
Proof. We use the Itˆo formula to show that the differential equation for T(s) yields the Laplace-Beltrami operator, which generates the spherical Brownian motion, with drift as the remainder. Let Φ: $S^2 \to$ R be a C^2 function on the unit sphere that extends to a function F : $R^3 \to$ R which is invariant in the distance from the origin; that is, in spherical coordinates, $F(r,\theta,\phi)$ depends only on θ and ϕ. Then if we compose Φ with the vector-valued process T(s) and apply the Itˆo formula, we obtain

$$d\Phi(\mathbf{T}(s)) = \nabla\Phi(\mathbf{T}(s)) \cdot d\mathbf{T}(s) + \frac{1}{2}d\mathbf{T}(s)^T\mathbf{H}\Phi(\mathbf{T}(s))d\mathbf{T}(s) \tag{92}$$

The first term on the right side of (92) is known, since we have a formula (84) for the differential of the tangent vector T(s). The second term can be re-written as the sum of each second-order derivative of Φ, multiplied by each component of the quadratic variation matrix of the vector T:

$$d\mathbf{T}(s)^T\mathbf{H}\Phi(\mathbf{T}(s))d\mathbf{T}(s) = \sum_{i=1}^{3}\sum_{j=1}^{3}\Phi_{i,j}(\mathbf{T}(s))d[\mathbf{T}^i,\mathbf{T}^j]_s \tag{93}$$

This simplifies the second term on the right side of (92), because not every component of the quadratic variation of T is non-zero. First, recall that in equation (84), the differential of T(s) has two terms, one multiplied by the scalar ds, and the other by the matrix dW(s). Since the arc length s is of bounded variation, the only non-zero quadratic variation arises from the square of the dW(s) term. Thus, the differential of the quadratic variation of T(s) is given by

$$d[\mathbf{T},\mathbf{T}]_s = \frac{1}{\ell_p}(\mathbf{M}_1(s)\otimes\mathbf{M}_1(s) + \mathbf{M}_2(s)\otimes\mathbf{M}_2(s))ds. \tag{94}$$

This has an equivalent formulation in terms of the tangent vector:

$$d[\mathbf{T},\mathbf{T}]_s = \frac{1}{\ell_p}(\mathbf{I} - \mathbf{T}(s)\otimes\mathbf{T}(s))\,ds. \tag{95}$$

This matrix must be multiplied component-wise by the Hessian matrix of secondorder partial derivatives of the function Φ(T(s)). These partial derivatives must be directional derivatives with respect to an orthonormal basis; we choose the Bishop frame, which gives a simple result when multiplied entry-wise by the quadratic variation increment, and the entries are summed:

$$\sum_{i=1}^{3}\sum_{j=1}^{3}\Phi_{i,j}(\mathbf{T}(s))d[\mathbf{T}^i,\mathbf{T}^j]_s = \frac{ds}{\ell_p}\left(\Phi_{\mathbf{M}_1\mathbf{M}_1} + \Phi_{\mathbf{M}_2\mathbf{M}_2}\right) \tag{96}$$

This gives us a form for the differential of Φ in which every occurrence of the differential dT(s) has been evaluated:

$$\begin{aligned} d\Phi(\mathbf{T}(s)) \quad &= \quad \nabla\Phi(\mathbf{T}(s))\cdot\left[\frac{\zeta}{\kappa\ell_p}(\mathbf{I}-\mathbf{T}(s)\otimes\mathbf{T}(s))\hat{\mathbf{f}}ds\right. \\ &\left. +\frac{1}{\sqrt{\ell_p}}\mathbf{Z}(s)\partial\mathbf{W}(s)\mathbf{e}_3\right] + \frac{1}{\ell_p}(\Phi_{\mathbf{M}_1\mathbf{M}_1} + \Phi_{\mathbf{M}_2\mathbf{M}_2})ds. \quad (97) \end{aligned}$$

The first term, which contains the first-order derivatives of Φ(T(s)), represents the drift, while the second derivative term represents the diffusion. In order for the tangent vector process to be a Brownian motion with a drift on the sphere, then, the diffusion must be the Laplace-Beltrami operator on the sphere:

$$\Delta_{S^2}\Phi = \frac{1}{\sin\theta}\partial_\theta(\sin\theta\,\partial_\theta\Phi)) + \frac{1}{\sin^2\theta}\partial_\phi^2\Phi \tag{98}$$

This is identical to the Laplacian of F(T) in spherical coordinates, in a neighborhood of the sphere S^2, because $F|_S2$ = Φ and F is constant on rays emanating from the origin (so the radius is always 1, and the radial derivative is 0). Moreover, the Laplace-Beltrami operator on Φ is equivalent to the usual three-dimensional Laplacian of F, whether it is expressed in spherical or Cartesian coordinates. Therefore, $\Delta_S 2\Phi = \Phi_{M1M1} + \Phi_{M2M2}$, and the diffusion term is equal to the generator of a Brownian motion on S^2. Notice that since the coefficient in front of the spherical Laplacian in (97) is $1/\ell_p$, it follows that the -1/2 speed of the Brownian motion is ℓ_p, which is also a multiple of κ as in the original model.

With these facts in place, we are now ready to state and prove the first major result of this paper, namely, the convergence of the discrete force-driven polymer model to the continuous model, and its corresponding stochastic differential equation that describes the tangent vector to the polymer.

Theorem 3.12: (1.1) Let $R^N_f(s)$ be the forced chain polymer model with parameters (N,a,θ,f), where f = ‖f‖ˆf, whose torsional angles follow the Boltzmann Gibbs distribution (17). Let $R_f(s)$ be the forced Kratky-Porod model with parameters $(L,\ell_p,\zeta,\hat{f})$ and suppose the parameters satisfy

$$a = \frac{L}{N} \tag{99}$$

$$\theta = \frac{\kappa}{\sqrt{N}} \tag{100}$$

$$\ell_p = \frac{2L}{\kappa^2}. \tag{101}$$

Let $\tau = k_B T$, and let the dipole moment of each segment remain constant for all N. Set

$$\zeta = \frac{L\|\mathbf{f}\|}{\tau} \tag{102}$$

If $R^N(s)$ is the forced chain interpolated linearly, then, as $N \to \infty$, $\mathbf{R}^N_f$ converges in distribution to R_f, where

$$R_f(s) = \int_0^s \mathbf{T}(\sigma)d\sigma \tag{103}$$

and the unit tangent vector **T**(s) to the polymer is the solution of the stochastic differential equation

$$d\mathbf{T}(s) = \frac{1}{\sqrt{\ell_p}}d\mathbf{Q}(s) + \frac{\zeta}{\ell_p}(\mathbf{I} - \mathbf{T}(s)\otimes\mathbf{T}(s))\hat{\mathbf{f}}\,ds \tag{104}$$

with initial condition

$$\mathbf{T}(0) = \mathbf{e}_3\ (a.s.). \tag{105}$$

Proof. To show the convergence of $R^N_f(s)$ weakly to $R^N(s)$, it is best to consider each vector-valued process in terms of its corresponding matrix-valued process, $Z^N(s)$ and $Z(s)$, respectively, since we have shown in Lemma 3.7 that Z^N converges to Z in distribution. Recall that the position vectors depend on the matrix-valued processes as follows:

$$R^N_f(s) = \sum_{k=1}^{[Ns/L]} Z^N_k e_3\, \Delta s \tag{106}$$

$$R_f(s) = \int_0^s \mathbf{Z}(\sigma)\mathbf{e}_3\, d\sigma. \tag{107}$$

Since the process $\mathbf{Z}^N$ is discrete and piecewise continuous, we can express the sum as an integral:

$$R^N_f(s) = \int_0^s \mathbf{Z}^N(\sigma)\mathbf{e}_3\, d\sigma. \tag{108}$$

Now, fix $s \in [0, L]$, and let $\epsilon > 0$. We wish to show that $R^N_f \Rightarrow R_f$. We know, from Lemma 3.7, that $Z^N \Rightarrow Z$. By the topological definition of weak convergence, for any continuous bounded linear functional F, it follows that $F(Z^N) \to F(Z)$. This is a consequence of the aforementioned continuity theorem (2.3 in Chapter 2 of [7]). Now, the integral $F(\mathbf{X}) = \int_0^s \mathbf{X}(s)\mathbf{e}_3\, ds$ is such a functional, since

$$\|F\| = \max \frac{\|F(\mathbf{X})\|}{\|\mathbf{X}\|} = s \tag{109}$$

So it is bounded, and it is continuous because it is an integral of a bounded function.

Thus, it follows that $F(Z^N) \Rightarrow F(Z)$; that is, $R^N_f \Rightarrow R_f$.

The equation (104) for the tangent vector process T(s) follows directly from
Lemmas 3.10 and 3.11. By L´evy's theorem, the tangent vector process T(s) is a scaled Brownian motion Q(s) on the sphere, plus a drift as given in equation (104). This drift is proportional to the projection of the force vector f onto the normal development of T(s) for any given s, as was to be proven.
Therefore, when the external force is added to the system, the discrete forced Kramers chain converges in distribution to the continuous Kratky-Porod model. The spatial differential equation (104) for the tangent vector can be used to describe the position and orientation of the molecule in this situation, but it cannot be solved explicitly in all cases. The next section concerns several extreme cases, determined by the values of the parameters ζ and ℓ_p, in which an exact solution can be found.

4. Extreme cases of the forced polymer

The stochastic differential equation (18), which we derived for the forced Kratky Porod model, cannot be solved explicitly for T, due to the quadratic drift term. Thus, we cannot formulate an exact expression for the position vector R(s) of the polymer in this model, except in some limiting cases. In our analysis of the unforced model in [11], we discussed the behavior of the Kratky-Porod model for extreme values of the persistence length, and we found that as $\ell_p \to \infty$, the molecule becomes a rigid rod pointing in the initial direction, while as $\ell_p \to 0$, the polymer shrinks to a point.
Now that the force is included in the system, we must also examine the extreme cases for the dimensionless force parameter, ζ, as well as ℓ_p. Investigation of these cases will enable us to divide the space of all possible parameter values ζ and ℓ_p into regimes, in which we expect to observe the polymer in certain states. Some of these are the rigid rod, the compact coil, and a deterministic bent polymer which we call the *K-curve* [1]. This curve is planar, and so the polymer is reduced to a two-dimensional vector-valued function of the parameters $C = \zeta/\ell_p$ and z_0, the cosine of the angle between the initial direction T(0) and the unit force vector ˆf. Several chemical physicists have examined the relationship between force and extension of the wormlike chain in two dimensions [19, 21], often for the case in which the molecule is adsorbed to or embedded in a surface [18]. However, none have considered the case in which both force and persistence length simultaneously go to infinity. Yet, some of the sources give results for small and large forces for fixed ℓ_p: the extension goes to zero proportionally to the force as $\zeta \to 0$, and to the entire polymer length as $\zeta \to \infty$, forming a rigid rod [19]. This type of transition between the coil and rod also appears in polymers of fixed ℓ_p when the nature of the solvent changes [4].
Our goal of this chapter is to characterize the polymer completely, by solving for T(s) and its integral, R(s), in each of these four extreme cases.

Characterization of the K-Curve

Let us begin, then, by considering the case in which the forced worm-like polymer is not affected by any thermal forces (for example, if the temperature is absolute zero). Then, the equation (18) becomes

$$d\mathbf{T}(s) = \frac{\zeta}{\ell_p}(\mathbf{I} - \mathbf{T}(s) \otimes \mathbf{T}(s))\hat{\mathbf{f}}\, ds. \tag{110}$$

Let us assume that the ratio between the force parameter and persistence length is constant: $\zeta/\ell_p = C$. Also, let us denote the tangent vector in this case by x, rather than T, since it is the solution to a deterministic ordinary vector differential equation.

Lemma 4.1: Let x(s) represent the unit tangent vector to the forced polymer in the lowest energy state, so that it satisfies equation (110). Let x(0) be the initial direction of the polymer, ˆf the unit vector in the direction of the force field, and $z_0 = x(0) \cdot \hat{f}$. Then x(s) has the following deterministic formula:

$$x(s) = g(s)\hat{f} + \gamma(s)\hat{f}^{\perp} \tag{111}$$

Where the component functions g and γ are given by

$$g(s) = \tanh\left(Cs + \tanh^{-1} z_0\right) \tag{112}$$

And

$$\gamma(s) = \sqrt{1 - g(s)^2} \tag{113}$$

And the unit vector $\hat{f}^{\perp}$ is given by the Gram-Schmidt process:

$$\hat{f}^{\perp} = \frac{x(0) - z_0\hat{f}}{1 - z_0^2} \tag{114}$$

Proof. Recall, as shown in Lemma 2.1, that in the lowest energy state, the polymer is oriented so that it is completely contained in the plane spanned by the initial direction vector x(0) and the force vector f. In other words, for all $s \in [0,L]$,

[1] The author's doctoral advisor suggested naming it the "Kilanowski curve" after the author himself, but the author prefers the shorter nomenclature.

$x(s) \in S^2 \cap \mathrm{Span}\{X(0), \hat{f}\}$ (115)

Thus, the tangent vector can be written in terms of scalar components, $g(s)$ and $\gamma(s)$, each of which is the projection of $x(s)$ onto one of the unit vectors $\hat{f}$ or $\hat{f}^{\perp}$. Additionally, the locus of possible points for $x(s)$ is a great circle along the sphere, which can be parametrized by a single scalar, so that the behavior for $x(s)$ can be described by a differential equation in one variable only. The fact that $x(s)$ lies on the unit sphere imposes the following restriction on $g(s)$ and $\gamma(s)$:

$$g(s)^2 + \gamma(s)^2 = 1 \tag{116}$$

since $x(s) \cdot x(s) = 1$. We can solve the above equation for γ in terms of g to obtain equation (113). Therefore, the behavior of x can be determined from solving a differential equation for $g(s)$.
Since $x(s)$ obeys equation (110), and since $g(s) = x(s) \cdot \hat{f}$, we can take the inner product of the differential version of equation (110) with the vector $\hat{f}$ to obtain a one-dimensional ordinary differential equation:

$$dg(s) = C(I - x(s) \otimes x(s))\hat{f} \cdot \hat{f}\, ds. \tag{117}$$

This simplifies (by converting every instance of x to g) to

$$dg(s) = C(1 - g(s)^2)ds. \tag{118}$$

This ODE is not linear, but it is separable, so it can be solved explicitly. We find that

$$g(s) = \tanh(Cs + K) \tag{119}$$

An equivalent formulation can also be found using the method of partial fractions. Using the initial condition that $g(0) = T(0) \cdot \hat{f} = z_0$, we find that

$$K = \tanh^{-1} z_0 \tag{120}$$

And so equation (112) is satisfied, completing the proof.
Notice that since for all y, $\tanh^2 y + \mathrm{sech}^2 y = 1$, we have an explicit formula for $\gamma(s)$:

$$\gamma(s) = \mathrm{sech}\left(Cs + \tanh^{-1} z_0\right) \tag{121}$$

This formula for the tangent vector $x(s)$, in terms of its orthogonal components, can be integrated with respect to arc length to obtain the formula for the position vector of the force-driven polymer, in the deterministic stiff limit (the K-curve). This curve will have varying shapes, depending on the constant C and the parameter z_0, which measures the cosine of the angle that the force vector f makes with the initial direction vector $x(0)$, but it can be described by a single formula.

Lemma 4.2: In the low-energy limit, the force-driven Kratky-Porod model depicts a bent chain polymer, whose position $R_f(s)$ satisfies a system of equations similar to those governing $x(s)$.

Proof. We know from Lemma 4.1 that the tangent vector lies in a plane, and its two orthogonal components are described by equations (112) and (121). Thus, we can integrate each component with respect to s, and the result is the components of $R_f(s)$. Again, since the position vector in this case is deterministic, let us denote it by $X(s)$ (so that $dX = x\,ds$). Write the components as

$$X(s) = h(s)\hat{f} + \eta(s)\hat{f}^{\perp} \tag{122}$$

Recall that the initial condition of X is that $X(0) = 0$. Then, h has the following formula:

$$h(s) = \frac{1}{C}\log\left(\frac{\cosh(Cs + \tanh^{-1} z_0)}{\cosh(\tanh^{-1} z_0)}\right) \tag{123}$$

Similarly, η is the integral of γ with $\eta(0) = 0$:

$$\eta(s) = \frac{2}{C}\left[\tan^{-1}\left(\tanh\frac{Cs + \tanh^{-1} z_0}{2}\right) - \frac{2}{C}\tan^{-1}(\tanh((\tanh^{-1} z_0)/2))\right] \tag{124}$$

Therefore, equations (122), (123), and (124) give the definition of the position vector $X(s)$ for each $s \in [0,L]$.
Notice that equation (123) gives a formula for the component of $X(s)$ in the direction of the force equal to 0 when $s = 0$.
This gives a picture of how the polymer, in the deterministic limit, behaves and changes with the direction of the force, expressed as $x(0) \cdot \hat{f}$, and with the ratio of parameters $C = \zeta/\ell_p$. However, this only occurs if there is no Brownian motion in the system, that is, if there are no thermal forces acting on the molecule, or if all thermal forces are negligible. In terms of the parameters of the

polymer, this case occurs when both ζ and ℓ_p grow towards infinity. In other words, $\zeta \to \infty$ means that the system is acted on by an irresistible force, and $\ell_p \to \infty$ means that the polymer is infinitely stiff; that is, it is an immovable object.
Since it is impossible to cool the molecule to absolute zero, or make it infinitely stiff, there will always be some thermal force term, albeit a small one, in equation (18). Thus, if ϵ is a small parameter, we can re-write the equation in this form, where $\mathrm{T}^\epsilon(s)$ is the solution:

$$\sqrt{\_}\, d\mathrm{T}^\epsilon(s) = \epsilon d\mathrm{Q}(s) + C(\mathrm{I} - \mathrm{T}^\epsilon(s) \otimes \mathrm{T}^\epsilon(s))\hat{}\mathrm{f}\, ds \tag{125}$$

and let $\mathrm{T}^0(s)$ be the solution $\mathrm{X}(s)$ to the equation without Brownian motion, namely, the process for which we solved in Lemma 4.1:

$$d\mathrm{T}^0(s) = C(\mathrm{I} - \mathrm{T}^0(s) \otimes \mathrm{T}^0(s))\hat{}\mathrm{f}\, ds. \tag{126}$$

This approach is used in [3] and [10] to examine solutions to perturbed stochastic differential equations. Notice that, in order to keep the perturbed equation (125) consistent with equation (18), we must let $\epsilon = \ell_p^{-1}$. It follows that as $\epsilon \to 0$, $\ell_p \to \infty$ and $\zeta \to \infty$ as well. This corresponds to the extreme case which we are currently examining. Our intention is to show that as $\epsilon \to 0$, the solutions T^ϵ converge in probability to the deterministic solution T^0. This we will show using methods from the theory of large deviations.

Lemma 4.3: For each $\epsilon > 0$, let $\mathrm{T}^\epsilon(s)$ be the solution to equation (125) above, and let $\mathrm{T}^0(s)$ be the solution to the unperturbed equation (126). Then, as $\epsilon \to 0$, in probability.

$$\mathrm{T}^\epsilon \to \mathrm{T}^0 \tag{127}$$

Proof. We prove the assertion by imitating some steps of Theorem 1.1 in Chapter 4 of [10] and filling in the details. Let T^ϵ and T^0 be as above. Define the term $m^\epsilon(s)$, for each $s \in (0,L]$, to be the following measure of the square of the distance between the two processes:

$$m^\epsilon(s) = E\left[\sup_{0\le\sigma\le s} \|\mathbf{T}^\epsilon(\sigma) - \mathbf{T}^0(\sigma)\|^2\right] \tag{128}$$

We find a bound for $m^\epsilon(L)$ in terms of ϵ, in order to obtain convergence in probability, and we do this by Doob's L^2 maximal inequality. This inequality only applies to submartingales, and the quantity $\mathrm{T}^\epsilon(s)$-$\mathrm{T}^0(s)$ is a semimartingale, so we take the Doob-Meyer decompositions for T^ϵ and T^0, and apply the Doob L^2 maximal inequality and parallelogram inequality to the martingale part:

$$m^\epsilon(s) \le 8E[\|\mathrm{T}^\epsilon(s) - \mathrm{T}^0(s)\|^2] + 8E[\|\mathrm{A}^\epsilon(s) - \mathrm{A}^0(s)\|^2] \tag{129}$$

By the same parallelogram inequality,

$$E[\|\mathrm{A}^\epsilon(s) - \mathrm{A}^0(s)\|^2] \le 2E[\|\mathrm{T}^\epsilon(s) - \mathrm{T}^0(s)\|^2] + 2E[\|\mathrm{M}^\epsilon(s)\|^2] \tag{130}$$

And since the driving process is Gaussian, the variance of the martingale part is simple:

$$E[\|\mathrm{M}^\epsilon(s)\|^2] = \epsilon s \tag{131}$$
$\sqrt{\_}$

Since the speed of the Brownian motion is ϵ. Therefore, we have the following bound for the squared difference m^ϵ:

$$m^\epsilon(s) \le 24E[\|\mathrm{T}^\epsilon(s) - \mathrm{T}^0(s)\|^2] + 16\epsilon s. \tag{132}$$

To evaluate this expression, let us consider the processes T^ϵ and T^0 in integral form; then, we obtain this bound for $m^\epsilon(s)$:

$$m^\epsilon(s) \le 24E\left[\left\|\mathbf{Q}(\sqrt{\epsilon}\, s) + C\int_0^s [\mathbf{V}(\mathbf{T}^\epsilon(\sigma)) - \mathbf{V}(\mathbf{T}^0(\sigma))]\, d\sigma\right\|^2\right] + 16\epsilon s \tag{133}$$

Where $\mathrm{V}(\mathrm{T})$ is defined as the right-hand side of the differential equation (110). Using the parallelogram inequality again, we can simplify the above to find

$$m^\epsilon(s) \le 48E\left[\|\mathbf{Q}(\sqrt{\epsilon}\, s)\|^2\right] + 48C^2E\left[\left\|\int_0^s [\mathbf{V}(\mathbf{T}^\epsilon(\sigma)) - \mathbf{V}(\mathbf{T}^0(\sigma))]\, d\sigma\right\|^2\right] + 16\epsilon s. \tag{134}$$

Let us now consider each term on the right-hand side of the above inequality. The first term is the variance of a spherical Brownian motion, with norm ϵs. For the second term, notice that the integrand is bounded: since $\mathrm{V}(\mathrm{T}(s))$ is a unit vector, the integrand has norm at most 2. Recall that for any bounded function F on a compact interval $[a,b]$,

$$\left\| \int_a^b F(x)\,ds \right\|^2 \leq (b-a) \int_a^b \sup_{a \leq x \leq b} \|F(x)\|^2\,dx \tag{135}$$

with equality occurring precisely when $\|F\|$ is constant on $[a,b]$. The boundedness of the integrand also allows us to use Fubini's theorem, so that we can interchange the expected value and the integral. Next, notice that the function V is Lipschitz continuous: for any $x,y \in S^2$,

$$\|V(x) - V(y)\| = \|(I - x \otimes x)\hat{f} - (I - y \otimes y)\hat{f}\| \tag{136}$$

$$\leq 2\|x - y\|. \tag{137}$$

Therefore,

$$E\left[\left\| \int_0^s [\mathbf{V}(\mathbf{T}^\epsilon(\sigma)) - \mathbf{V}(\mathbf{T}^0(\sigma))]\,d\sigma \right\|^2\right] \leq 4s \int_0^s m^\epsilon(s)\,d\sigma. \tag{138}$$

By combining the differences in the drift and diffusion terms, we obtain

$$m^\epsilon(s) \leq 64\epsilon s + 192C^2 s \int_0^s m^\epsilon(\sigma)\,d\sigma \tag{139}$$

and so the bound depends on the integral of m^ϵ itself. This is a common expression in the theory of differential equations. If we divide the above inequality through by s (if $s > 0$), then we find that

$$\frac{m^\epsilon(s)}{s} \leq 64\epsilon + 192C^2 \int_0^s \frac{m^\epsilon(\sigma)}{\sigma}\sigma\,d\sigma \tag{140}$$

which is exactly the condition for Gr¨onwall's lemma with constant coefficients. Applying the lemma yields

$$\frac{m^\epsilon(s)}{s} \leq 64\epsilon \exp\left(192C^2 \int_0^s \sigma\,d\sigma\right) \tag{141}$$

Which, when multiplied back through by s, yields the desired bound for $m^\epsilon(s)$ that depends on ϵ only:

$$m^\epsilon(s) \leq 64se^{96C2s2}\epsilon. \tag{142}$$

To use this bound to show convergence in probability, let $\delta > 0$ be fixed, and consider $m^\epsilon(L)$, so that the whole interval $[0,L]$ is covered. Then, by Chebyshev's inequality, for any $s \in [0,L]$,

$$P(\|\mathbf{T}^\epsilon(s) - \mathbf{T}^0(s)\| > \delta) \leq \frac{m^\epsilon(L)}{\delta^2} = \frac{64Le^{96C^2L^2}}{\delta^2}\epsilon \tag{143}$$

Which yields the conclusion that $T^\epsilon \to T^0$ in probability (moreover, in L^2), as desired.

Results for the Extreme Cases

Thus, the theory of large deviations allows us to prove that the tangent vector diverges from the tangent to the K-curve by only a small amount when ϵ is small, and so when the effect of the thermal forces goes to zero, the stochastic process governing the tangent vector converges to a deterministic limit. This provides us with the theoretical machinery necessary to prove the convergence of the position vector of the polymer in this extreme case. The other extreme cases can be proven by more elementary means. Therefore, we can summarize these results in the following theorem, which is the second main result of this dissertation.

Theorem 4.4: (1.2) The forced Kratky-Porod model has the following behavior:
1. Fix ℓ_p and let $\zeta \to 0$. Then the polymer $R_f(s)$ converges to the Kratky Porod model R(s).
2. Fix ℓ_p and let $\zeta \to \infty$. Then the polymer converges in probability to a rigid rod in the direction of the force: $R_f(s) \to s\hat{f}$.
3. Let $C = \zeta/\ell_p$ be constant, and let $\zeta \to \infty$. Then, $R_f(s)$ converges in probability to the curve

$$X(s) = \int_0^s \mathbf{x}(\sigma)d\sigma \tag{144}$$

Where x is the solution of the ordinary differential equation

$\dot{x} = V(x)$ (145) $x(0) = e_3$ (146)

where

$V(x) = C(I - x \otimes x)\hat{f}.$ (147)

This equation can be solved explicitly, leading to a exact formula for X(s).

4. Let $C = \zeta/\ell_p$ be constant as above and let $\zeta \to 0$. Then, in probability, $R_f(s)$ shrinks to a point.

Proof. We will examine each extreme case, one at a time. First, let $\ell_p \in R^+$ be fixed and let $\zeta \in R^+$ be a variable parameter, for case (1). Denote by $\mathbf{T}(s;\zeta)$ the solution to equation (18) for the chosen value of ζ; that is,

$$d\mathbf{T}(s,\zeta) = \ell_p^{-1/2} d\mathbf{Q}(s) + \frac{\zeta}{\ell_p}(\mathbf{I} - \mathbf{T}(s;\zeta) \otimes \mathbf{T}(s;\zeta))\hat{\mathbf{f}}\, ds. \tag{148}$$

Let $\mathbf{T}(s;0)$ represent the solution to the unforced equation:

$$d\mathbf{T}(s;0) = \ell_p^{-1/2}\mathbf{Q}(s) \tag{149}$$

We therefore wish to show that as $\zeta \to 0$, $\|\mathbf{T}(s,\zeta) - \mathbf{T}(s,0)\| \to 0$ a.s. From the two above equations, we conclude that

$$\|\mathbf{T}(s;\zeta) - \mathbf{T}(s;0)\| = \frac{\zeta}{\ell_p}\left\| \int_0^s (\mathbf{I} - \mathbf{T}(\sigma;\zeta) \otimes \mathbf{T}(\sigma;\zeta))\hat{\mathbf{f}}\, d\sigma \right\| \tag{150}$$

The integrand is bounded above by 1, since it is a projection of a unit vector. This yields a deterministic bound for the difference of solutions:

$$\|\mathbf{T}(s;\zeta) - \mathbf{T}(s;0)\| \leq \frac{\zeta}{\ell_p} s, \ a.s. \tag{151}$$

This shows uniform convergence of $T(s;\zeta)$ to $T(s;0)$. To prove convergence of the position vectors, recall that $R_f(s) = \int_0^s \mathbf{T}(\sigma;\zeta)\, d\sigma$ and $R(s) = \int_0^s \mathbf{T}(\sigma;0)\, d\sigma$.

Thus, the difference between the position vectors satisfies

$$\|\mathbf{R}_f(s) - \mathbf{R}(s)\| \leq \frac{\zeta}{\ell_p}\frac{s^2}{2} \tag{152}$$

and therefore, $R_f \to R$ uniformly, a.s.

For case (2), let ℓ_p still be fixed, but now let $\zeta \to \infty$. Then, the spherical Brownian motion term will become negligible, as it is dwarfed by the drift term. We wish to show that, as $\zeta \to \infty$, $T(s;\zeta) \to \hat{f}$ in probability. Then it will follow, from the Bounded Convergence Theorem, that $R_f(s) \to s\hat{f}$.

We show this by means of a change in the variable s. Let

$$\tilde{T}(s) = T\left(\frac{s}{\zeta}\right) \tag{153}$$

$$\tilde{Q}(s) = Q\left(\frac{s}{\zeta}\right) \tag{154}$$

So, it then follows, by the chain rule, that

$$d\tilde{\mathbf{T}}(s) = \frac{1}{\zeta\sqrt{\ell_p}} d\tilde{\mathbf{Q}}(s) + \frac{1}{\ell_p}\mathbf{V}(\tilde{\mathbf{T}}(s))\, ds. \tag{155}$$

As $\zeta \to \infty$, the Brownian motion term vanishes, and $\tilde{T}(s)$ converges in probability to the deterministic tangent vector, $x(s)$ as in Lemma 4.1, with $C = \ell_p^{-1}$, by a perturbation argument similar to that of Lemma 4.3. Recall the asymptotic behavior of $x(s)$ as $s \to \infty$, by examining the component functions, $g(s)$ in the direction of $\hat{f}$, and $\gamma(s)$ in the perpendicular direction, as given by equations (112) and (113):

$$\lim_{s\to\infty} g(s) = 1 \tag{156}$$

$$\lim \gamma(s) = 0 \tag{157}$$

$s \to \infty$

Regardless of the initial direction parameter z_0, since $C > 0$. Thus it follows that

$$\lim_{s\to\infty} \tilde{T}(s) = \hat{f}, \tag{158}$$

In probability. We complete the proof of this part by returning to the original tangent process, $T(s)$. Let $s \in [0,L]$ be fixed and recall that

$$T(s) = \tilde{T}(s\zeta) \tag{159}$$

Thus as $\zeta \to \infty$, $\tilde{T}(s\zeta) \to \hat{f}$, and therefore, $T(s) \to \hat{f}$ in probability. It follows, by the Bounded Convergence Theorem, that

$$R_f(s) \to s\hat{f} \tag{160}$$

in probability as well.

For case (3), we have shown, in Lemma 4.3, that in the case in which $\zeta/\ell_p = C$ and both parameters go to infinity, the tangent vector process $T^{\epsilon}(s) \to T^0(s)$ in probability. This process $T^0(s)$ is equal in distribution to the solution $x(s)$ of equation (145). Therefore, by the Bounded Convergence Theorem, we can interchange limit and integral again, and as $\epsilon \to 0$, that is, as $\zeta, \ell_p \to \infty$, $R_f(s)$ converges in probability to the deterministic K-curve, described by $X(s)$, the solution to (144). This limit has the formula given by equations (122) and following, as proven in Lemma 4.2.

Finally, case (4) is similar to the result from [11] about the coiled polymer in the limit that $\ell_p \to 0$. In this case, however, we also let $\zeta \to 0$ at the same time, so that $\zeta/\ell_p = C$, a constant. Then, $T(s)$ has the following form:

$$d\mathbf{T}(s) = \frac{1}{\sqrt{\ell_p}} d\mathbf{Q}(s) + C(\mathbf{I} - \mathbf{T}(s) \otimes \mathbf{T}(s))\hat{\mathbf{f}}\, ds. \tag{161}$$

By another change-of-variable argument, similar to the one in case (2), the second term is negligible, and the tangent vector process converges in probability to an infinitely fast Brownian motion on the sphere, with a uniform stationary distribution, as $\ell_p \to 0$. As the speed of the Brownian motion increases, any two tangent vectors along the polymer become uncorrelated, since for all $s < t \in [0,L]$,

$$\lim_{\ell_p\to 0} E[T(s) \cdot T(t)] = \lim_{\ell_p\to 0} e^{-|t-s|/\ell_p} = 0. \tag{162}$$

The mean-square end-to-end length $\bar{R}^2$, which is always non-negative, is the double integral of the tangent-tangent correlation function:

$$\bar{R}^2 = \int_0^L \int_0^L E[\mathbf{T}(s) \cdot \mathbf{T}(t)]\, ds\, dt \tag{163}$$

and since the integrand converges to zero in probability, the double integral does the same, by the Bounded Convergence Theorem. Thus since the average length of the molecule vanishes, for all $s \in [0,L]$, $R(s) \to 0$ a.s., and the polymer shrinks to a point.

This completes our summary of the extreme cases of the forced Kratky-Porod model, for which we can find an approximate solution to the differential equation for the tangent vector process $T(s)$ and the position vector $R_f(s)$. While the equation (18) cannot be solved explicitly and analytically for all values of the parameters ζ and ℓ_p, we can construct the forced wormlike chain by numerical methods, and then compare the results that we obtain for physical characteristics of the polymer, such as mean-square end-to-end distance $\bar{R}^2$ and radius of gyration R_g, to the results for the unforced model, calculated in Section 2. The numerical scheme (calculated in 2010 using MATLAB) appears in the original dissertation and shows the desired results, namely, that the ratio $\bar{R}^2/R_g^2$ approaches 12 in the hard rod limit ($\zeta \gg \ell_p$), 6 in the random coil limit ($\zeta \ll \ell_p$), and an intermediate value depending on the ratio ζ/ℓ_p for the K-curve, as the number of segments in the polymer N increases.

5. Conclusion

The freely rotating chain, combined with its continuous analogue, the Kratky Porod model, is a model for polymer molecules in dilute solution that has been in use for decades, but it was only recently that results about the model, which had been known empirically, were proven using the tools and methods of stochastic calculus and probability theory. These results, such as the fact that the tangent vector along the polymer traces out a Brownian motion along the sphere, are now mathematical truths, and they can be extended to the case in which a uniform force field, in addition to the thermal noise, acts on the polymer. In this case, the stochastic processes that govern the position of the polymer are modified to include the force, and the spherical Brownian motion gains a drift term that reflects the fact that the polymer is being pulled to line up in the direction of the force. The results regarding the physical length scales, such as root-mean-square length and radius of gyration, which were derived for the original Kratky-Porod model, have also been altered to allow for the force. Depending on the strength of the force and the intrinsic stiffness of the polymer, the molecule can be found in the regime of a random coil, a stiff, bent curve, or a rigid rod extending in the direction either of the force or of the initial segment. As we deepen our understanding of these theoretical models, we can apply them to the natural world and gain a greater knowledge of the behavior of long polymer molecules, from proteins to DNA, which form the foundations for all living matter.

6. Acknowledgements

I would like to thank Dr. Peter March, my thesis advisor from my days at The Ohio State University for directing the project, Dr. Marko Samara for working with me on the foundational work for it, and Dr. Lynette Boos for encouraging me at last to turn this dissertation into an article.

7. Statements and Declarations

The author has no relevant financial or non-financial interests to declare.
No funding was received to conduct this study. The original analysis was conducted for a doctoral thesis in 2009-10 when the author's advisor was working for the National Science Foundation.
Data sharing is not applicable to this article as no datasets were generated or analyzed for this study.

8. References

1. Bryant AS, Maxim O. Lavrentovich: Survival in Branching Cellular Populations, Theoretical Population Biology. 2022;144:13-23.
2. Chow YS, Teicher H. Probability Theory: Independence, Interchangeability, Martingales 2nd ed., Springer, New York; c1988.
3. Dembo A, Zeitouni O. Large Deviations: Techniques and Applications, Springer-Verlag, New York; c1998.
4. Dogic Z, Zhang J, Lau AW, Aranda-Espinoza H, Dalhaimer P, Discher DE, *et al*. Elongation and fluctuations of semiflexible polymers in a nematic solvent. Physical review letters. 2004;92(12):125503.
5. Doi M, Edwards SF. The Theory of Polymer Dynamics, Clarendon, New York; c1986.
6. Drozdov AD. Stiffness of Polymer Chains, arXiv:cond-mat/0407716v1
7. Durrett R. Probability: Theory and Examples 2nd ed., Duxbury, Belmont, CA; c1996.
8. Ethier SN, Kurtz TG. Markov Processes: Characterization and Convergence, Wiley, New York; c1986.
9. Flory PJ. Statistical Mechanics of Chain Molecules, Interscience, New York; c1969.
10. Friedlin M. Functional Integration and Partial Differential Equations, Princeton UP, Princeton, NJ; c1985.
11. Kilanowski HP, March P, Samara M. Convergence of the Freelyˇ Rotating Chain to the Kratky-Porod Model of Semi-Flexible Polymers, Journal of Statistical Physics. 2019;174(6):1222-1238.
12. Kirkwood JG, Riseman J. The Intrinsic Viscosities and Diffusion Constants of Flexible Macromolecules in Solution. The Journal of Chemical Physics. 1948;16(6):565-573.
13. Kirkwood JG, Riseman J. The Rotatory Diffusion Constants of Flexible Molecules, The Journal of Chemical Physics. 1949;17(5):442-446.
14. Kramers HA. The Behavior of Macromolecules in Inhomogeneous Flow, J Chem. Phys. 1946;14(7):415-424.
15. Kratky O, Porod G. Diffuse Small-angle Scattering of X-rays in Colloid Systems, Journal of Colloid Science. 1949;4(1):35-70.
16. Kurtz TG, Protter PE. Weak Convergence of Stochastic Integrals and Differential Equations, Lecture Notes in Mathematics. 1995;1627:1-41.
17. Lamura A, Burkhardt TW, Gompper G. Semi-Flexible Polymer in a Uniform Force Field in Two Dimensions, Physical Review E. 2001;64(6):1-30.
18. Podgornik R. Orientational Ordering of Polymers on a Fluctuating Flexible Surface. 1995;52(5):5170-5177
19. Prasad A, Hori Y, Kondev J. Elasticity of Semiflexible Polymers in Two Dimensions. 2005;72(4):419181-419187
20. Rouse PE. A Theory of the Linear Viscoelastic Properties of Dilute Solutions of Coiling Polymers. The Journal of Chemical Physics. 1953;21(7):1272-1280.
21. Seifert U, Wintz W, Nelson P. Straightening of Thermal Fluctuations in Semi-flexible Polymers by Applied Tension, 1996;77(27):5389-5392.
22. Toan NM, Thirumalai D. Theorey of Biopolymer Stretching at High Forces. Macromolecules. 2010;43(9):4394-4400
23. Volkenstein MV. Configurational Statistics of Polymeric Chains, Inter Science, New York; c1963.
24. Yamakawa H. Modern Theory of Polymer Solutions, Harper & Row, New York; c1971.