STATISTICS AND DYNAMICS OF STIFF CHAINS

by

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Abstract

A statistical-mechanical theory of linear elastic polymer chains under constant external force and torque is developed. The general theory takes into account bending, twisting, shearing, and stretching deformations. The theory is found to contain the Kratky-Porod wormlike chain and the Yamakawa-Fujii helical wormlike chain as special cases.

A path integral form of the Green's function defined in the configuration space of a linear elastic chain is proposed. The Fokker-Planck equation for the Green's function is derived from both the general rule of correspondence in quantum mechanics and a purely probabilistic argument using the Chapman-Kolmogorov equation. A simplified $3D$ free-chain (force-free and torque-free) problem and a complete $2D$ free-chain problem are solved. Suppressing the shearing, twisting, and stretching modes in both cases, the solutions are found to agree with respectively the $3D$ and the $2D$ solutions derived by Daniels (1952) for the Kratky-Porod wormlike chain.

The distribution function of the wormlike chain in the short chain (near-rod) limit is solved. Also derived is the asymptotic solution for the mean reciprocal distance $\langle 1/r \rangle (s)$ between two points on the chain in the near-rod limit. The moment $\langle 1/r \rangle$ possesses fundamental significance in the theory of polymer dynamics.

Lastly, the asymptotic distribution of the wormlike chain segments about the center of mass is derived from the moments in conjunction with the known expression derived by Debye and Bueche (1952) for the corresponding distribution in the long chain limiting Gaussian random coil case.

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CONTENTS

§1. Introduction

During the past few years, advances in laser tweezer technology have made it possible to perform experiments on individual biological macromolecules. In this context, much attention has focused on experimental studies of the mechanical and elastic properties of individual double-stranded DNA (dsDNA) molecules and other biopolymers [Bes1,Clu1,Smi1,Str1]. Optical tweezers in general are devices for gripping small objects in a beam of laser light. Since light exerts forces, it is able to trap macromolecules, virus particles, or even bacteria by exerting gradient forces, which propel objects towards the area of maximum light intensity.

Many biologically important processes involving DNA are accompanied by its deformation; for example, dsDNA is stretched by RNA polymerase during RNA synthesis, and a locally underwound DNA strand is necessary for transcriptional activation and recombinational repair. The elastic and mechanical properties of dsDNA affect how DNA bends upon interaction with proteins, wraps around histones, packs into phage heads, and supercoils *in vivo.* A simple way to explore DNA elasticity is to stretch a single macromolecule from both ends, measuring the force exerted on it as a function of its extension (end-to-end distance), thereby establishing the relationship between force and extension [Smi1]. Other elastic properties of dsDNA can be revealed by the relationship of torque vs. winding, which has also been studied recently [Str1]. These results may shed light on biological processes involving DNA deformations.

In the experiments performed by Smith *et al.* [Smi1], single molecules of dsDNA were stretched with force-measuring laser tweezers. These revealed that under a longitudinal stress of 65 picoNewtons (pN), dsDNA molecules in aqueous buffer undergo a highly cooperative transition into a stable form with 5.8 Å rise per base pair, which makes the whole molecule 70% longer than its usual B-form contour length. When the stress was relaxed below 65 pN, the molecules rapidly and reversibly contracted to their normal contour lengths. This transition was affected by changes in the ionic strength of the medium. Individual molecules of single-stranded DNA (ssDNA) were also stretched, yielding a persistence length of 7.5 Å and a stretch modulus of 800 pN. These authors suggested that the overstretched form may play a significant role in the energetics of DNA recombination.

In the experiments of Strick *et al.* [Str1], single dsDNA molecules were first torsionally constrained by binding at multiple sites at one end to a treated glass, and at the other to a magnetic bead. Following this, a magnetic field was used to rotate the beads and thus coil as well as pull the DNA. The elastic behavior of individual dsDNA molecules over- and under-wound by up to 500 turns was studied. The force vs. extension relationship for dsDNA molecules at different degrees of winding was investigated. These authors observed a sharp transition from a low to a high extension state at 0.45 pN for underwound molecules, and at 3 pN for overwound ones. These transitions were suggested to reflect the formation of alternative structures in stretched coiled DNA molecules, and are thus relevant to DNA transcription and replication.

Many theoretical studies have focused on the elastic behavior of linear elastic polymer chains, and in particular of DNA molecules. The statistical properties of flexible polymers are commonly idealized by a discrete random flight model (freely jointed chain), first studied by Lord Rayleigh [Ray1] in the context of random vibrations and random flights. That theory assumes the chain to be so flexible that the directions of successive bonds are uncorrelated. This results in a Gaussian distribution of end-to-end vectors and an extension-force relationship constituted by a sum of Langevin functions over all bonds [Yam1,Sch1]. However, elastic polymer chains like dsDNA do not have such flexibility; rather, they appear to have finite bending elasticity. As such, it is not surprising that the freely jointed chain model does not fit the experimental force-extension data very well, especially at high extensions, where the assumption of freely jointed bonds breaks down [Smi1].

In 1949 Kratky and Porod initiated the concept of the wormlike chain [Kra1], with statistical properties intermediate between the flexible Gaussian random coil and the rigid rod. Their model is based on the limiting behavior of a discrete, freely rotating chain. In 1952 Daniels [Dan1] provided an extensive treatment of the statistical properties of wormlike chains, obtaining an approximate asymptotic distribution of the end-to-end vector in the long chain limit. The discrete model was treated by Daniels as a Markov process. Upon passing to the continuum limit, he was able to obtain and consequently solve the Markov integral equation. Daniels' distribution breaks down in the short chain (near-rod) limit [Hea1]; it also fails to generate exact moments of the end-to-end distribution [Yam1]. Quite independently, in 1952, Hermans and Ullman [Her1] first derived the differential equation governing the wormlike chain distribution function, calculating therefrom exact expressions of up to fourth power moments of the distribution. Later, in 1966, after expressing the conformational partition function of the wormlike chain in a path integral form with elastic bending energy, Saitô *et al.* discovered the analogy existing between the path of a wormlike space curve and the quantum trajectory of a particle in a potential field [Sai1].

The wormlike chain model is by far the most successful elastic chain model from a statistical-mechanical point of view. It agrees with the Gaussian random coil in the long chain limit, whereas it behaves like a rigid rod in the short chain (near-rod) limit. On the other hand, however, it has not been possible to obtain a closed-form solution for the distribution function of the end-to-end vector. Satisfactory asymptotic solutions are only available in the long chain limit [Dan1,Gob1]. Due to the close analogy first developed by Saitô *et al.* [Sai1] between the path of a wormlike space curve and the quantum trajectory of a particle in a potential field, finding the distribution function in the near-rod limit is equivalent to finding the solution of the Schrödinger equation in the classical limit. In 1973, Yamakawa and Fujii [Yam4] worked out a first-order approximation to the distribution in the near-rod limit using the WKB approximation. The wormlike chain model does not agree well with the experimental force-extension relationship because the model assumes constant contour length. As a result of this constraint, a wormlike chain is not able to sustain overstretching, whereas in different experiments [Bes1, Clu1, Smi1, Str1] individual dsDNA molecules were overstretched up to 170% of their original contour length and even longer before the molecules finally ruptured.

Various modifications of the wormlike chain model have been proposed to overcome the analytical difficulties encountered when attempting rigorous mathematical treatment. In 1966, Harris and Hearst [Har1] considered an analytically tractable model for stiff polymer chains. In addition to taking into account the bending stiffness, as in the wormlike chain model, they introduced a Lagrange multiplier, which played the role of a longitudinal stretching modulus. They were able to obtain a closed form solution to the configurational Green's function for the stiff chain.

In 1976, by incorporating both elastic bending and torsional energies, Yamakawa and Fujii [Yam11] initiated the helical wormlike chain model, which is a generalization of the original wormlike chain model. Upon setting the helix parameter to zero, the helical wormlike chain becomes identical to the wormlike chain. Apart from the long chain Gaussian random coil limit and the short chain near-rod limit, with a constant helix parameter the helical wormlike chain is able to adopt a regular helical conformation. This extra feature renders the model applicable to helix-coil transitions of polypeptide chains (proteins). Their investigations of the statistical mechanics and dynamics of helical wormlike chains spanned the past twenty years [Yam11-18,Shm1-4,Yos1-2,Fuj2-4]. In studying this model, Yamakawa *et al.* developed systematic approaches to investigating linear elastic polymer chains. However, the helical wormlike chain is also unstretchable.

Marko and Siggia [Mar1-4] studied DNA supercoiling and overstretching; at quadratic levels in the strains, in addition to the bending and torsional energies appearing in the Kratky-Porod wormlike chain model and the Yamakawa-Fujii helical wormlike chain model, they found a coupling between twisting and bending [Mar1]. In their theory, DNA overstretching is treated as a first-order phase transition [Mar4]. Again, there was no special feature in their model that allowed the contour length to change with the external force.

Recently, Kholodenko [Kho1-6] discovered that a semiflexible linear polymer chain is directly related to the Dirac propagator—the Fourier transform of the configurational Green's function, so that the transition from rigid rod to random coil can be associated with that from the ultrarelativistic to the nonrelativistic limit of the Dirac propagator. Because the Dirac propagator can be obtained in closed form, Kholodenko was able to derive closed-form expressions for various moments; however, these moments are only approximately equal to those of wormlike chain in the long chain limit. The exact relationship between the two models is not yet clear.

A need clearly exists for a generalized theory of linear elastic polymer chains under a constant external force and torque, which experience bending, twisting, shearing and stretching deformations. Such a model is discussed here, being based on numerous models that preceded it. In their book, "Theory of Elasticity", Landau and Lifshitz [Lan2] discuss the quadratic form of the elastic potential energy due to bending and twisting of a rod. Starting from this bending-twisting potential energy function, together with additional potential energy terms resulting from shearing, stretching, and external forces and torques, a differential equation for the configurational Green's function is derived in the present work, and the protocol necessary to obtain asymptotic solutions discussed. The theory is found to contain the Kratky-Porod wormlike chain and the Yamakawa-Fujii helical wormlike chain as special cases. In our analysis we assume θ-solvent conditions and do not take into account the excluded volume effect. For chains overstretched under external forces, or chains in the near-rod limit, this is a particularly well-justified assumption.

In §2 the configuration space of the chain will be shown to be $R^3 \times SO(3)$, requiring *inter alia* a discussion of finite and infinitesimal rotations in $SO(3)$. As such, the underlying structure of our elastic chain problem is closely related to other physical problems, such as an asymmetric top undergoing translational and rotational motion. The material length parameter s in the former corresponds to the time variable t in the latter. Even closer is its relation to a class of stochastic, statistical-mechanical problems involving coupled translational-rotational motions, such as arise during the transport of a rigid orientable (i.e., nonspherical, e.g., ellipsoidal) Brownian particle through a viscous fluid under the action of an external force and/or torque—typified by gravity or centrifugal forces. The diffusion (and hydrodynamic mobility) tensors of such a nonspherical Brownian particle are constant relative to axes fixed in the body and thus require a body-frame characterization, whereas the forces and torques derive from external potentials and thus require a space-frame characterization. In such problems one seeks, in close analogy to the elastic chain problems, a time-dependent Green's function (conditional probability density) in the configuration space $R^3 \times SO(3)$. Convective-diffusive problems of this type have been treated extensively by Brenner *et al.*, and a convenient symbolic mathematical structure developed in detail for characterizing finite and infinitesimal rotations in $SO(3)$ [Bre1-4,Hab1]. In §2, A path integral form of the configurational Green's function is proposed, from which the Fokker-Planck equation for the Green's function is derived from the general rule of correspondence in quantum mechanics, where—starting from the classical Hamiltonian of a system—the correspondence protocol leads to the Schrödinger equation of the corresponding quantum system. The Green's function with constant external force is found to be the force-free Green's function multiplied by a simple Boltzmann factor of the external potential energy.

Since the derivation of the Fokker-Planck equation in §2 is an indirect one, the above differential equation is re-derived in §3 from a purely probabilistic argument. Starting from the path integral form of the Green's function, an identical differential equation is derived from the Chapman-Kolmogorov equation, with the Green's function interpreted as a conditional probability density.

The protocol for asymptotically solving the three-dimensional Green's function is discussed in §4. The exact moments of the elastic chain distribution function are derived therein directly from the Fokker-Planck equation.

In §5, a special case of the general theory—consisting of a force-free and torque-free chain with shearing and stretching moduli approximated by a single mean shearing-stretching modulus—is discussed in detail, and the corresponding Fokker-Planck equation solved asymptotically. Exact solutions for all even-powered moments of the end-to-end vector can be calculated from the asymptotic distribution, provided that enough terms in the asymptotic expansion are retained. Upon suppressing the shearing and stretching modes, the first-order approximation of the solution is found to be identical with Daniels' distribution of the Kratky-Porod wormlike chain. The long chain limits of the moments are identical to those of Gaussian random coils [Yam1], whereas the short chain limits of the moments agree with those for rigid rods.

In §6, the distribution function and, more importantly, the moment $\langle 1/r \rangle$ in the near-rod limit are derived as asymptotic power series in λs. This result is considered to be one of the major results of this thesis. It ends a 40 year long quest in the field of polymer dynamics for the wormlike-chain distribution function and the moment $\langle 1/r \rangle$ in the near-rod limit [Hea1,Yam4].

The protocol for solving the differential equation shown in §4 is practiced in §7 by solving a two-dimensional version of the elastic chain, Fokker-Planck equation. The asymptotic solution and the exact moments in $2D$ are obtained.

In §8 the asymptotic distribution of elastic chain segments about the center of mass is obtained for the special case of the Kratky-Porod wormlike chain without knowledge of the corresponding Fokker-Planck equation. The angular autocorrelation function of the tangent vectors for the wormlike chain is calculated from the differential equation for the angular Green's function. The exact second- and fourth-power moments of the position vector of the chain segments about the center of mass are calculated from the angular autocorrelation function. The long chain and short chain limits of the moments are found to agree respectively with those for Gaussian random coils and rigid rods. The asymptotic form of the distribution function of position vectors about the center of mass is derived from the moments, together with the known expression for the corresponding distribution function in the long chain limiting case of the Gaussian random coil.

Finally, some concluding remarks are given in §9.

§2. Statistical Mechanics of Linear Elastic Polymer Chains

We will study the statistical-mechanical properties of a linear elastic chain with general deformations of bending, twisting, shearing, and stretching. The elastic properties of the chain are characterized by Young's modulus E and shear modulus G. The position of the centerline of the chain is uniquely defined by $\mathbf{r}(s)$, with s being the material length (identical to the arc length when there is no deformation of the chain). However, when the chain is twisted, stretched or sheared under the action of an external force or torque, its material length and arc length will no longer coincide. The total material length L is always constant, independently of the state of deformation, whereas the total arc length depends on the state of deformation.

In the undeformed state (no bending, twisting, shearing, or stretching), the chain is a straight rod with arc length L. We divide the chain into infinitesimal elements, each of which is bounded by two adjacent cross-sections. For each such element we construct body-fixed coordinate systems (termed body-frames in what follows), $\{\hat{\mathbf{a}}_1(s),\ \hat{\mathbf{a}}_2(s),\ \hat{\mathbf{a}}_3(s)\}$, along the chain with origin on the chain centerline. For chains without intrinsic twist, the body-axes are chosen in such a way that in this undeformed state the body-frames are all parallel; explicitly $\{\hat{\mathbf{a}}_3(s) \mid s \in [0, L]\}$ all lie in the tangent direction of the straight rod, while $\hat{\mathbf{a}}_1(s)$ and $\hat{\mathbf{a}}_2(s)$ lie in the plane of cross section at s and there coincide with local principal axes of inertia. For chains with intrinsic twist (for instance, double helix DNA), we first completely untwist the chain while maintaining its shape as a straight rod. We then choose $\hat{\mathbf{a}}_1(s)$ and $\hat{\mathbf{a}}_2(s)$ such that all body-frames are parallel. After body-frames have been erected along the whole chain, we let the chain resume its natural form with intrinsic twist. In this form, while moving along the straight-rod chain, the body-axes $\hat{\mathbf{a}}_1$ and $\hat{\mathbf{a}}_2$ undergo constant rotations about the $\hat{\mathbf{a}}_3$ axis.

We now let the elastic chain in solution deform under the combined action of the thermal agitation and external field. In general, should shearing deformation arise, the body-axis $\hat{\mathbf{a}}_3(s)$ will no longer coincide with the local tangent direction $\mathbf{t}(s) = d\mathbf{r}/ds$, and $\hat{\mathbf{a}}_1(s)$, $\hat{\mathbf{a}}_2(s)$ will not remain within the local cross sectional plane. We denote a space-fixed Cartesian coordinate system (termed space-frame in what follows) by $\{\hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2, \hat{\mathbf{e}}_3\}$. Transformation between the two frames is performed by using the Euler rotational matrix $\mathbf{\Lambda}(\phi(s), \theta(s), \psi(s))$ via the formula

$$\hat{\mathbf{a}}_\alpha(s) = \mathbf{\Lambda}(s) \cdot \hat{\mathbf{e}}_\alpha, \tag{2-1}$$

with elements

$$\Lambda_{\alpha\beta} = \hat{\mathbf{e}}_\alpha \cdot \mathbf{\Lambda} \cdot \hat{\mathbf{e}}_\beta = \hat{\mathbf{e}}_\alpha \cdot \hat{\mathbf{a}}_\beta, \tag{2-2}$$

expressed in the Cartesian space-frame basis. Since $(\hat{\mathbf{e}}_i)_j = \delta_{ij}$, the components of unit vectors along body-axes in terms of the space-frame basis are given by

$$(\hat{\mathbf{a}}_\alpha)_\beta = \Lambda_{\beta\lambda}(\hat{\mathbf{e}}_\alpha)_\lambda = \Lambda_{\beta\lambda}\delta_{\alpha\lambda} = \Lambda_{\beta\alpha}, \tag{2-3}$$

where the summation convention is used. In what follows, the summation convention always applies to Greek suffixes occurring twice in tensor expressions. Adopting the standard $zy'z''$ convention of Euler angles [Edm1 and Sak1], the body-frame is transformed from space-frame first by a rotation of angle $\phi \in (-\pi, \pi]$ about the $\hat{\mathbf{e}}_3$-axis (z), then a rotation of angle $\theta \in [0, \pi]$ about the new $\hat{\mathbf{e}}_2$-axis (y', the line of nodes), and finally a rotation of angle $\psi \in (-\pi, \pi]$ about the $\hat{\mathbf{a}}_3$-axis (z''). If we represent a rotation α about an axis ξ by the operator $D_\xi(\alpha)$, then the above transformation is given by the composite operator $D_{z''}(\psi)D_{y'}(\theta)D_z(\phi)$. However, matrices for rotations about body-axes are rather inconvenient to manipulate. As such, it is desirable to express the body-axis rotations in terms of space-fixed axis rotations.

The Euler rotation operator $D_{z''}(\psi)D_{y'}(\theta)D_z(\phi)$ can be simplified by using the elementary relation $D_{y'}(\theta) = D_z(\phi)D_y(\theta)D_z(-\phi)$. We will prove this relation by demonstrating the effect of a left-hand side single rotation and right-hand side composite rotations on some particular axes. Clearly, the orientation of the line of nodes (y'-axis) is invariant to both rotations. Furthermore, the orientation of $\hat{\mathbf{a}}_3$ (z''-axis) is the same whether we apply $D_{y'}(\theta)$ or $D_z(\phi)D_y(\theta)D_z(-\phi)$. In both cases, $\hat{\mathbf{a}}_3$ makes a polar angle θ with the space-fixed $\hat{\mathbf{e}}_3$-axis (z), and its azimuthal angle in the space-frame is just ϕ. This proves the two rotations to be identical. Similarly, $D_{z''}(\psi)$ is equivalent to $D_{y'}(\theta)D_{z'}(\psi)D_{y'}(-\theta)$. Since z' is identical to z (the z-axis is invariant to the first rotation), $D_{z''}(\psi)$ is equivalent to $D_z(\phi)D_y(\theta)D_z(\psi)D_y(-\theta)D_z(-\phi)$. It follows that $D_{z''}(\psi)D_{y'}(\theta)D_z(\phi) = D_z(\phi)D_y(\theta)D_z(\psi)$. Therefore, the Euler rotation matrix $\mathbf{\Lambda}(\phi, \theta, \psi)$ in the space-frame basis is defined by the product

$$\mathbf{\Lambda} = \begin{pmatrix} \cos\phi & -\sin\phi & 0 \\ \sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{pmatrix} \cdot \begin{pmatrix} \cos\theta & 0 & \sin\theta \\ 0 & 1 & 0 \\ -\sin\theta & 0 & \cos\theta \end{pmatrix} \cdot \begin{pmatrix} \cos\psi & -\sin\psi & 0 \\ \sin\psi & \cos\psi & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad (2\text{-}4)$$

or

$$\begin{aligned}\mathbf{\Lambda} &= \begin{pmatrix} \cos\phi\cos\theta\cos\psi - \sin\phi\sin\psi & -\cos\phi\cos\theta\sin\psi - \sin\phi\cos\psi & \cos\phi\sin\theta \\ \sin\phi\cos\theta\cos\psi + \cos\phi\sin\psi & -\sin\phi\cos\theta\sin\psi + \cos\phi\cos\psi & \sin\phi\sin\theta \\ -\sin\theta\cos\psi & \sin\theta\sin\psi & \cos\theta \end{pmatrix} \\ &= (\,\hat{\mathbf{a}}_1 \quad \hat{\mathbf{a}}_2 \quad \hat{\mathbf{a}}_3\,)\,. \end{aligned} \quad (2\text{-}5)$$

The last equality holds because, from (2-3), $(\hat{\mathbf{a}}_j)_i = \Lambda_{ij}$. Hence, expressed as components in terms of the Cartesian space-frame basis, $\hat{\mathbf{a}}_j$ is just the j^{th} column of the matrix $\mathbf{\Lambda}$.

At each point s on the chain, the position of the point and its local structure are uniquely specified by $\mathbf{r}(s)$ and $\mathbf{\Lambda}(s)$. Since $\mathbf{r}(s) \in \mathcal{R}^3$ and $\mathbf{\Lambda}(s) \in SO(3)$, the configuration space of the elastic chain is $\mathcal{R}^3 \times SO(3)$.

It is interesting to note that with the material length s being identified with the time t, the elastic chain system is similar to the motion of asymmetric tops [Gol1,Lan1,McC1,Par1,Whi1] or of nonspherical Brownian particles [Bre1-4,Hab1]. The configuration space of all these systems is $R^3 \times SO(3)$. As such, it is not surprising to recognize the existence of an analogy between these systems.

Suppose for some unit vector that $\hat{\mathbf{u}} \equiv \hat{\mathbf{e}}_u = (1, \theta, \phi)$ in a space-fixed spherical polar coordinate system; apparently, $\hat{\mathbf{a}}_3 = \hat{\mathbf{e}}_u$ from (2-5). Denote the local orthogonal curvilinear frame at $\hat{\mathbf{e}}_u$ by the set $\{\hat{\mathbf{e}}_u,\ \hat{\mathbf{e}}_\theta,\ \hat{\mathbf{e}}_\phi\}$; thus, expressed as column vectors in the space-frame basis,

$$(\,\hat{\mathbf{e}}_u \quad \hat{\mathbf{e}}_\theta \quad \hat{\mathbf{e}}_\phi\,) = \begin{pmatrix} \cos\phi\sin\theta & \cos\phi\cos\theta & -\sin\phi \\ \sin\phi\sin\theta & \sin\phi\cos\theta & \cos\phi \\ \cos\theta & -\sin\theta & 0 \end{pmatrix}. \tag{2-6}$$

From the above two equations, we have, again in the space-frame basis,

$$(\,\hat{\mathbf{a}}_1 \quad \hat{\mathbf{a}}_2 \quad \hat{\mathbf{a}}_3\,) = (\,\hat{\mathbf{e}}_u \quad \hat{\mathbf{e}}_\theta \quad \hat{\mathbf{e}}_\phi\,)\cdot \begin{pmatrix} 0 & 0 & 1 \\ \cos\psi & -\sin\psi & 0 \\ \sin\psi & \cos\psi & 0 \end{pmatrix}. \tag{2-7}$$

When shearing is absent, $\hat{\mathbf{a}}_3 = \hat{\mathbf{e}}_u = \hat{\mathbf{u}}$ is the unit tangent vector of the chain. This fact will later be used to simplify the related differential equation.

Denote the three Euler angles by the set $\mathbf{\Phi}(s) = (\phi(s), \theta(s), \psi(s))$, and the unit vectors in the directions of rotations ϕ, θ, and ψ respectively by $\hat{\mathbf{a}}_\phi$, $\hat{\mathbf{a}}_\theta$, and $\hat{\mathbf{a}}_\psi$. The vector $\hat{\mathbf{a}}_\phi$ is identical to $\hat{\mathbf{e}}_3$ (z-axis), $\hat{\mathbf{a}}_\theta$ lies on the line of nodes (y'-axis), and $\hat{\mathbf{a}}_\psi$ coincides with $\hat{\mathbf{a}}_3$ (z''-axis). For simplicity we also identify $\mathbf{\Phi}$ with the set $\{\Phi_j\}$, so that $\Phi_1 = \phi$, $\Phi_2 = \theta$, and $\Phi_3 = \psi$. The scalar Φ_j characterizes a rotation about $\hat{\mathbf{a}}_{\Phi_j}$. The frame $\{\hat{\mathbf{a}}_{\Phi_k}\}$ is intrinsically related to the composite rotations characterizing the local structure of a chain; however, unlike the body-frame $\{\hat{\mathbf{a}}_j\}$, it is not an orthogonal frame. Consequently, we have to transform all the infinitesimal rotation vectors into components about the body-frame, for which purpose we need a transformation matrix between the two frames. Explicitly, the base vectors $\hat{\mathbf{a}}_{\Phi_j}$ expressed as column vectors in the space-frame basis adopt the forms

$$(\,\hat{\mathbf{a}}_{\Phi_1} \quad \hat{\mathbf{a}}_{\Phi_2} \quad \hat{\mathbf{a}}_{\Phi_3}\,) \equiv (\,\hat{\mathbf{a}}_\phi \quad \hat{\mathbf{a}}_\theta \quad \hat{\mathbf{a}}_\psi\,) = \begin{pmatrix} 0 & -\sin\phi & \cos\phi\sin\theta \\ 0 & \cos\phi & \sin\phi\sin\theta \\ 1 & 0 & \cos\theta \end{pmatrix} \tag{2-8}$$

and

$$\hat{\mathbf{a}}_{\Phi_\alpha} = \hat{\mathbf{a}}_\beta A_{\beta\alpha}, \tag{2-9}$$

where the transformation matrix $\mathbf{A}$ in the space-frame basis is given by

$$\mathbf{A} = \begin{pmatrix} -\sin\theta\cos\psi & \sin\psi & 0 \\ \sin\theta\sin\psi & \cos\psi & 0 \\ \cos\theta & 0 & 1 \end{pmatrix}. \tag{2-10}$$

Although $\{\hat{\mathbf{a}}_j\}$ is an orthogonal frame, $\{\hat{\mathbf{a}}_{\Phi_k}\}$ is not, whence the transformation matrix $\mathbf{A}$ between the two frames is not an orthogonal matrix.

We denote the set of rotations about the body-axes by $\mathbf{\Omega} = \{\Omega_1, \Omega_2, \Omega_3\}$. The two sets $\mathbf{\Phi}$ and $\mathbf{\Omega}$ represent identical rotations, with $\mathbf{\Phi}$ projected onto $\{\hat{\mathbf{a}}_{\Phi_j}\}$ in terms of $\{\Phi_j\}$, and $\boldsymbol{\Omega}$ projected onto $\{\hat{\mathbf{a}}_k\}$ in terms of $\{\Omega_k\}$. Therefore, the two infinitesimal rotation vectors are identical:

$$d\boldsymbol{\Phi} = d\Phi_\alpha \hat{\mathbf{a}}_{\Phi_\alpha} = d\boldsymbol{\Omega} = d\Omega_\beta \hat{\mathbf{a}}_\beta. \tag{2-11}$$

The triplets $\boldsymbol{\Phi}$ and $\boldsymbol{\Omega}$ constitute vectors only for infinitesimal rotations, but not for finite rotations. Finite rotations cannot be represented by a single vector, inasmuch as finite rotations are not commutative, nor is matrix multiplication commutative. Since $\boldsymbol{\Phi}$ and $\boldsymbol{\Omega}$ are not vectors, any operations performed with them should be regarded as purely symbolic.

When the body-frame at $s+\delta s$ is subjected to a rotation $\delta\boldsymbol{\Phi}(s) = \delta\boldsymbol{\Omega}(s)$ relative to its orientation at s, the generalized angular 'velocity' is

$$\boldsymbol{\omega} = \omega_\alpha \hat{\mathbf{a}}_\alpha = \frac{d\boldsymbol{\Phi}}{ds} = \dot{\Phi}_\beta \hat{\mathbf{a}}_{\Phi_\beta} = \frac{d\boldsymbol{\Omega}}{ds} = \dot{\Omega}_\gamma \hat{\mathbf{a}}_\gamma, \tag{2-12}$$

where Ω_j is the angle of rotation about $\hat{\mathbf{a}}_j$ and the last equality serves as the definition $\omega_j = \dot{\Omega}_j$; an overdot denotes the derivative with respect to s.

The components ω_j in the body-frame can be represented by Euler angles and their derivatives with respect to s. From (2-9) and (2-12), $\omega_\alpha \hat{\mathbf{a}}_\alpha = \dot{\Phi}_\beta \hat{\mathbf{a}}_{\Phi_\beta} = \dot{\Phi}_\beta \hat{\mathbf{a}}_\alpha A_{\alpha\beta}$, where the matrix $\mathbf{A}$ is defined by (2-10). Since the $\hat{\mathbf{a}}_\alpha$'s are completely arbitrary and $\omega_j = \dot{\Omega}_j$, we have that

$$\omega_\alpha = A_{\alpha\beta}\dot{\Phi}_\beta, \tag{2-13}$$

$$d\Omega_\alpha = A_{\alpha\beta} d\Phi_\beta. \tag{2-14}$$

Although the frame $\{\hat{\mathbf{a}}_\phi, \hat{\mathbf{a}}_\theta, \hat{\mathbf{a}}_\psi\}$ is intrinsically related to the infinitesimal rotations and hence to the differential operator in Euler-angle space, it is not an orthogonal frame. The transformation formula (2-9) enables us to express the differential operator in Euler-angle space in terms of components in the body-frame $\{\hat{\mathbf{a}}_1, \hat{\mathbf{a}}_2, \hat{\mathbf{a}}_3\}$. For this purpose, we also need the metric tensors in Φ-space and Ω-space; these two spaces are special in the sense that only infinitesimal vectors are defined in them.

Note that since the body-frame derives from a Cartesian space-frame by a pure rotation, it too is a Cartesian frame. An infinitesimal distance element in $\mathcal{R}^3$ can be expressed as [Ari1,Bri1,Wei1]

$$dl^2 = (d\hat{\mathbf{a}}_\alpha)_\beta (d\hat{\mathbf{a}}_\alpha)_\beta = {}_\Phi g_{\lambda\sigma} d\Phi_\lambda d\Phi_\sigma, \tag{2-15}$$

where the metric tensor in Φ-space is given by

$${}_\Phi g_{\lambda\sigma} = \frac{\partial(\hat{\mathbf{a}}_\alpha)_\beta}{\partial\Phi_\lambda}\frac{\partial(\hat{\mathbf{a}}_\alpha)_\beta}{\partial\Phi_\sigma}. \tag{2-16}$$

Upon performing the summation explicitly over all components of $\hat{\mathbf{a}}_j$ in (2-5) expressed in the space-frame basis, we find that

$${}_\Phi g_{\lambda\sigma} = \begin{pmatrix} 2 & 0 & 2\cos\theta \\ 0 & 2 & 0 \\ 2\cos\theta & 0 & 2 \end{pmatrix}. \tag{2-17}$$

On the other hand, from (2-14), $d\Phi_\alpha = (\mathbf{A}^{-1})_{\alpha\beta} d\Omega_\beta$, with $\mathbf{A}^{-1}$ given explicitly by

$$\mathbf{A}^{-1} = \begin{pmatrix} -\csc\theta\cos\psi & \csc\theta\sin\psi & 0 \\ \sin\psi & \cos\psi & 0 \\ \cot\theta\cos\psi & -\cot\theta\sin\psi & 1 \end{pmatrix}. \tag{2-18}$$

Therefore, by (2-15),

$$dl^2 = {}_\Phi g_{\lambda\sigma} (\mathbf{A}^{-1})_{\lambda\alpha} (\mathbf{A}^{-1})_{\sigma\beta} d\Omega_\alpha d\Omega_\beta = {}_\Omega g_{\alpha\beta} d\Omega_\alpha d\Omega_\beta. \tag{2-19}$$

Expressed explicitly using the expression for $\mathbf{A}^{-1}$ in (2-18) and ${}_\Phi g_{\lambda\sigma}$ in (2-17), the metric tensor in Ω-space is

$${}_\Omega g_{\alpha\beta} = \begin{pmatrix} 2 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{pmatrix} = 2\delta_{\alpha\beta}. \tag{2-20}$$

The gradient operator in Ω-space is therefore

$$\nabla_{\mathbf{\Omega}} = \frac{\hat{\mathbf{a}}_\alpha}{\sqrt{2}} \frac{\partial}{\partial \Omega_\alpha}. \tag{2-21}$$

For an arbitrary scalar function $f(\phi, \theta, \psi)$,

$$df = d\Phi_\alpha \frac{\partial f}{\partial \Phi_\alpha} = d\Omega_\beta \frac{\partial f}{\partial \Omega_\beta}. \tag{2-22a}$$

Since f is arbitrary, it follows from (2-14) that

$$d\Phi_\alpha \frac{\partial}{\partial \Phi_\alpha} = A_{\beta\alpha} d\Phi_\alpha \frac{\partial}{\partial \Omega_\beta}. \tag{2-22b}$$

Again, since the $d\Phi_\alpha$'s are arbitrary, we conclude that

$$\frac{\partial}{\partial \Omega_\alpha} = (\mathbf{A}^{-1})_{\beta\alpha} \frac{\partial}{\partial \Phi_\beta}. \tag{2-23}$$

Upon using the expression for $\mathbf{A}^{-1}$ in (2-18), we find that the gradient operator (2-21) now takes the form

$$\begin{aligned} \nabla_{\mathbf{\Omega}} = \frac{\hat{\mathbf{a}}_\alpha}{\sqrt{2}} \frac{\partial}{\partial \Omega_\alpha} &= \frac{\hat{\mathbf{a}}_1}{\sqrt{2}} \left(-\frac{\cos\psi}{\sin\theta} \frac{\partial}{\partial\phi} + \sin\psi \frac{\partial}{\partial\theta} + \cot\theta\cos\psi \frac{\partial}{\partial\psi} \right) \\ &+ \frac{\hat{\mathbf{a}}_2}{\sqrt{2}} \left(\frac{\sin\psi}{\sin\theta} \frac{\partial}{\partial\phi} + \cos\psi \frac{\partial}{\partial\theta} - \cot\theta\sin\psi \frac{\partial}{\partial\psi} \right) + \frac{\hat{\mathbf{a}}_3}{\sqrt{2}} \left(\frac{\partial}{\partial\psi} \right). \end{aligned} \tag{2-24}$$

The Laplacian in Φ-space or Ω-space is defined by

$$\nabla^2_{\mathbf{\Omega}} = \frac{1}{\sqrt{{}_\Phi g}} \frac{\partial}{\partial \Phi_\alpha} \left[\sqrt{{}_\Phi g}\; {}_\Phi g^{\alpha\beta} \frac{\partial}{\partial \Phi_\beta} \right] = \frac{1}{\sqrt{{}_\Omega g}} \frac{\partial}{\partial \Omega_\alpha} \left[\sqrt{{}_\Omega g}\; {}_\Omega g^{\alpha\beta} \frac{\partial}{\partial \Omega_\beta} \right], \tag{2-25}$$

wherein ${}_{\Phi}g^{\alpha\beta}$ (cf. (3-15)) and ${}_{\Omega}g^{\alpha\beta}$ are the inverses of the respective metric tensors in the two spaces. Using either (2-17) or (2-20) together with (2-24), it is easy to show that

$$\nabla^2_{\Omega} = \frac{1}{2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} - \frac{2\cot\theta}{\sin\theta}\frac{\partial^2}{\partial\phi\partial\psi} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\psi^2}\right]. \quad (2\text{-}26)$$

Note that the first two terms in the parenthesis are exactly the Laplacian $\nabla^2_{\hat{\mathbf{u}}}$ on S^2, the latter denoting the surface of the unit sphere, with $\hat{\mathbf{u}} \equiv \hat{\mathbf{e}}_u = (1, \theta, \phi)$ in the space-fixed spherical polar coordinate system. Therefore, upon operating on a function which does not depend on ψ explicitly, $2\nabla^2_{\Omega}$ reduces to $\nabla^2_{\hat{\mathbf{u}}}$. This fact will be used later to simplify the differential equations for chains with isotropic bending and twisting moduli.

The orthogonality of $\mathbf{\Lambda}$ enables us to show that

$$(\dot{\mathbf{\Lambda}}^T \cdot \mathbf{\Lambda})_{\alpha\beta} = (\mathbf{\Lambda}^T \cdot \dot{\mathbf{\Lambda}})_{\beta\alpha} = -(\mathbf{\Lambda}^T \cdot \dot{\mathbf{\Lambda}})_{\alpha\beta} = \varepsilon_{\alpha\beta\gamma}\omega_\gamma, \quad (2\text{-}27)$$

where $\varepsilon_{\alpha\beta\gamma}$ is the Levi-Civita completely antisymmetric tensor density, and ω_γ is defined in (2-12). This relation together with (2-3) imply that

$$\frac{d(\hat{\mathbf{a}}_\alpha)_\lambda}{ds} = \frac{d\Lambda_{\lambda\alpha}}{ds} = \varepsilon_{\alpha\beta\gamma}\omega_\gamma\Lambda_{\lambda\beta} = \omega_\gamma\varepsilon_{\alpha\beta\gamma}(\hat{\mathbf{a}}_\beta)_\lambda,$$

or $d\hat{\mathbf{a}}_\alpha/ds = \omega_\gamma\varepsilon_{\alpha\beta\gamma}\hat{\mathbf{a}}_\beta = \omega_\gamma\varepsilon_{\gamma\alpha\beta}\hat{\mathbf{a}}_\beta = \omega_\gamma\hat{\mathbf{a}}_\gamma \times \hat{\mathbf{a}}_\alpha$. Therefore, using (2-12), the generalized 'velocity' of the body-axis moving along the chain is given by

$$\frac{d\hat{\mathbf{a}}_\alpha}{ds} = \frac{d\mathbf{\Phi}}{ds} \times \hat{\mathbf{a}}_\alpha. \quad (2\text{-}28)$$

In the space-frame $\mathbf{r} = x_\alpha\hat{\mathbf{e}}_\alpha$, we define the tangent vector $\mathbf{t}$ and its components in the body-frame and space-frame by

$$\mathbf{t} = t_\alpha\hat{\mathbf{a}}_\alpha = \frac{d\mathbf{r}}{ds} = \dot{x}_\alpha\hat{\mathbf{e}}_\alpha. \quad (2\text{-}29)$$

In the case of no shearing and no stretching, $\mathbf{t}$ becomes identical to the unit tangent vector $\hat{\mathbf{u}} \equiv \hat{\mathbf{e}}_u = (1, \theta, \phi)$. Note that the two frames are transformed via the rule $\hat{\mathbf{a}}_j = \mathbf{\Lambda} \cdot \hat{\mathbf{e}}_j$. Hence, given a vector $\mathbf{V}$, its components in the two frames are transformed according to $(V_\alpha)_{\hat{\mathbf{a}}} = \mathbf{V} \cdot \hat{\mathbf{a}}_\alpha = \mathbf{V} \cdot \mathbf{\Lambda} \cdot \hat{\mathbf{e}}_\alpha = (V_\beta)_{\hat{\mathbf{e}}}\, \hat{\mathbf{e}}_\beta \cdot \mathbf{\Lambda} \cdot \hat{\mathbf{e}}_\alpha = \Lambda_{\beta\alpha}(V_\beta)_{\hat{\mathbf{e}}}$, i.e.,

$$(V_\alpha)_{\hat{\mathbf{a}}} = \Lambda_{\beta\alpha}(V_\beta)_{\hat{\mathbf{e}}}, \quad (2\text{-}30a)$$

$$(V_\alpha)_{\hat{\mathbf{e}}} = \Lambda_{\alpha\beta}(V_\beta)_{\hat{\mathbf{a}}}. \quad (2\text{-}30b)$$

Consequently,

$$t_\alpha = \Lambda_{\beta\alpha}\dot{x}_\beta. \quad (2\text{-}31)$$

Following the analogy between the configuration of a wormlike chain and the quantum trajectory of a particle under external field, first established by Saitô *et al.* [Sai1], we now derive the differential equation governing the Green's function $G(\mathbf{r}, \mathbf{\Phi}; s \,|\, \mathbf{r}_0, \mathbf{\Phi}_0; s_0)$, where $\mathbf{r} = \mathbf{r}(s)$, $\mathbf{\Phi} = \{\phi(s), \theta(s), \psi(s)\}$, $\mathbf{r}_0 = \mathbf{r}(s_0)$, and $\mathbf{\Phi}_0 = \{\phi(s_0), \theta(s_0), \psi(s_0)\}$. This approach is similar to those standard rules used in quantum mechanics for transforming the Feynman path integral form of a wave function into the Schrödinger equation it satisfies. For simplicity, in what follows we will set $s_0 = 0$. The Green's function G satisfies the path integral

$$G(\mathbf{r}, \mathbf{\Phi}; s \,|\, \mathbf{r}_0, \mathbf{\Phi}_0; 0; \mathbf{f}; \boldsymbol{\tau}) = \frac{1}{C_0} \int_{\substack{\mathbf{r}(0)=\mathbf{r}_0 \\ \mathbf{\Phi}(0)=\mathbf{\Phi}_0}}^{\substack{\mathbf{r}(s)=\mathbf{r} \\ \mathbf{\Phi}(s)=\mathbf{\Phi}}} e^{i \int_0^s \mathcal{L}(\tau)\, d\tau}\, \mathcal{D}[\mathbf{r}(\tau)]\, \mathcal{D}[\mathbf{\Phi}(\tau)], \qquad (2\text{-}32)$$

where $\mathcal{L} = iU/k_B T$ is the Lagrangian of the system, U is the elastic and external potential energy per material length of the chain, and C_0 is a normalization constant.

From the definitions (2-12) and (2-29), we can easily identify $\{\omega_j\}$ and $\{t_j\}$ with various deformation modes. Explicitly ω_1 and ω_2 are components of the generalized angular 'velocity' in the cross-sectional plane of the chain. Therefore, they represent two modes of bending. On the other hand, ω_3 is the component tangent to the chain, which apparently corresponds to one mode of twisting. Also t_1 and t_2 are components of the generalized linear 'velocity' in the cross-sectional plane of the chain, and should surely be identified with two modes of shearing, whereas t_3, being the component tangent to the chain, must be characterizing by one mode of stretching.

It is easy to see that a constant external force $\mathbf{f} = f_\alpha \hat{\mathbf{e}}_\alpha$ (per $k_B T$) acting on the chain molecule should appear as a term in U of the form $-\mathbf{f} \cdot \mathbf{t} = -f_\alpha \dot{x}_\alpha$, for then the external potential energy is minimized when the chain completely aligns itself with the external field $\mathbf{f}$. Similarly, a constant external torque $\boldsymbol{\tau} = \tau_\alpha \hat{\mathbf{e}}_\alpha$ (per $k_B T$) acting on the chain will appear in U as a term $-\boldsymbol{\tau} \cdot \boldsymbol{\omega} = -\tau_\alpha \Lambda_{\alpha\beta} \omega_\beta$, where (2-30) was used. Note that the components of both the external force $\mathbf{f}$ and torque $\boldsymbol{\tau}$ are naturally chosen to be in the space-frame, since $\mathbf{f}$ and $\boldsymbol{\tau}$ are independent of the local structure of a chain. As a rule, components of variables defined in R^3 (linear variables) are chosen to be space-frame components, whereas those defined in $SO(3)$ (angular variables) are chosen to be body-frame components.

Some elastic chains have a non-zero intrinsic twist even in the relaxed straight-rod state; for instance, the DNA double helix (double-stranded DNA, or dsDNA) has an intrinsic twist of 10.4 basepairs per turn. Since ω_3 is associated with the deformational mode of twist, we denote an intrinsic twist by ω_3^0; (for DNA, $\omega_3^0 = 1.8$ rad/nm). If the parameter s is identified with material length, the intrinsic length scale is $t_3^0 = 1$, rather than zero, for without any deformation the intrinsic tangent vector $\mathbf{t} = \hat{\mathbf{a}}_3$ has a component of unit magnitude along the body-axis $\hat{\mathbf{a}}_3$. However, to maintain the symmetry of the formalism, instead of being replaced by unity, t_3^0 will remain as it is in the following derivation. Note that ω_3^0 and t_3^0 are not the variables ω_3 and t_3 at one end of the chain $s = 0$, but rather characterize the intrinsic twist and intrinsic stretching.

We now proceed to find the explicit form of the Lagrangian $\mathcal{L}$. The infinitesimal chain segment at s has 6 degrees of freedom, in which 3 are translational, characterized by $\mathbf{r}(s)$, and 3 are rotational, characterized by $\mathbf{\Phi}(s)$. Since the Euler angles $\{\Phi_j\}$ are associated with the non-orthogonal curvilinear frame $\{\hat{\mathbf{a}}_\phi, \hat{\mathbf{a}}_\theta, \hat{\mathbf{a}}_\psi\}$, while the set $\{\Omega_j\}$ characterizing the same rotations are associated with the orthogonal body-frame $\{\hat{\mathbf{a}}_1, \hat{\mathbf{a}}_2, \hat{\mathbf{a}}_3\}$, it is natural to choose $\{x_1, x_2, x_3, \Omega_1, \Omega_2, \Omega_3\}$ as the set of generalized coordinates characterizing our system, and $\{\dot{x}_1, \dot{x}_2, \dot{x}_3, \omega_1, \omega_2, \omega_3\}$ as the corresponding generalized 'velocities'; we note that by definition, (2-12), $\omega_j = \dot{\Omega}_j$.

For small deformations, the linear elastic law applies, whence the elastic energy per unit material length is quadratic in the various body-frame components of the deformations ('velocities' and angular 'velocities') [Lan2,LeB1,LeB2,Lov1]. Assuming deformations of the chain to involve bending, twisting, shearing, and stretching, the elastic energy consists of linear combinations of $\omega_i\omega_j$ and t_it_j. It is easy to see that there can be no terms proportional to $\omega_1\omega_3$, $\omega_2\omega_3$, t_1t_3, and t_2t_3. For, since the chain is uniform along its length, all quantities, and in particular the energy, must remain invariant to reversal of the body-axis $\hat{\mathbf{a}}_3$; however, these four terms change sign under such axis-reversal. The other two cross terms, $\omega_1\omega_2$ and t_1t_2, will not appear if the body-axes $\hat{\mathbf{a}}_1$ and $\hat{\mathbf{a}}_2$ are chosen properly [Lan2].

In the interests of the symmetry and generality of the formalism, we assume non-zero intrinsic bending (ω_1^0, ω_2^0), twisting (ω_3^0), shearing (t_1^0, t_2^0), and stretching $(t_3^0 - 1)$. In units of k_BT, the potential energy can be expressed as

$$-i\mathcal{L}(s) = \frac{1}{4}\sum_{k=1}^{3}\frac{1}{A_k(s)}\left[\omega_k(s) - \omega_k^0\right]^2 + \frac{1}{4}\sum_{k=1}^{3}\frac{1}{B_k(s)}\left[t_k(s) - t_k^0\right]^2 - \mathbf{f}\cdot\mathbf{t}(s) - \boldsymbol{\tau}\cdot\boldsymbol{\omega}(s). \tag{2-33}$$

For generality, we have allowed both the A_k's and B_k's to be functions of the material length parameter s. It is apparent that these coefficients are related to the elastic properties of the chain; therefore, in this model, we do not assume elastic homogeneity along the chain. In fact, for double helix DNA molecules, the A_k's and B_k's can be approximated by constants plus small multiples of periodic functions of s. The constants correspond to the first-order approximation of assuming elastic homogeneity, whereas the periodic functions represent the correction terms arising from the unique structure of double helix DNA. As a simple model for double helix DNA, consider an alternating current wire composed of a helical structure of two wires. From common experience we know at a given point on the wire that the bending stiffness in different directions is not isotropic in the local cross-sectional plane; however, the bending stiffness in any given direction is nevertheless periodic along the wire.

From (2-32) we see that $\int_0^s i\mathcal{L}(\tau)\,d\tau$ is dimensionless, whence $\mathcal{L}$ has units of inverse length. By definition (2-12), the ω_k's also have units of inverse length, whereas the t_k's are dimensionless according to (2-29). Therefore, the A_k's have units of inverse length, while the B_k's have units of length.

An important feature of the model emerges as a consequence of the way in which the constant external force $\mathbf{f}$ appears in the potential energy function. Substituting the above Lagrangian into the path integral (2-32), we note that by definition $\int_0^s \mathbf{t}(\tau)d\tau = \mathbf{r} - \mathbf{r}_0$ is independent of the path of the chain between $s = 0$ and s, since $\mathbf{r}$ and $\mathbf{r}_0$ are the upper and lower limits of the integration path. Therefore, the term $e^{\mathbf{f}\cdot(\mathbf{r}-\mathbf{r}_0)}$ can be brought outside of the path integral. However, this is the only term via which the external force $\mathbf{f}$ comes into play in the Green's function; hence, we conclude that

$$G(\mathbf{r}, \mathbf{\Phi}; s \,|\, \mathbf{r}_0, \mathbf{\Phi}_0; 0; \mathbf{f}; \boldsymbol{\tau}) = \frac{1}{C} e^{\mathbf{f}\cdot(\mathbf{r}-\mathbf{r}_0)} G(\mathbf{r}, \mathbf{\Phi}; s \,|\, \mathbf{r}_0, \mathbf{\Phi}_0; 0; \mathbf{0}; \boldsymbol{\tau}), \tag{2-34}$$

where C is some normalization constant, different from C_0 in (2-32). The same argument cannot be applied to $\boldsymbol{\tau}$ since $\boldsymbol{\omega}$ is not integrable. Inasmuch as $\boldsymbol{\omega}$ is not the derivative of any vector, it is a nonholonomic vector, in analogy to the nonintegrable differential constraints. This corresponds to the fact that finite rotations cannot be represented by a single vector.

The intrinsic parameters adopt different numerical values for different models. For instance, if we assume isotropic bending and shearing, then $A_1 = A_2$ and $B_1 = B_2$, whereas zero intrinsic bending and shearing imply that $\omega_1^0 = \omega_2^0 = t_1^0 = t_2^0 = 0$. It can also be shown that this Lagrangian is general, in the sense that it contains the Kratky-Porod wormlike chain and Yamakawa's helix wormlike chain as special cases. For instance, the intrinsic curvature κ_0 and intrinsic torsion τ_0 in Yamakawa's helix wormlike chain model can be identified with $\kappa_0 = \sqrt{(\omega_1^0)^2 + (\omega_2^0)^2}$, and $\tau_0 = \omega_3^0$ in this model. In §5 we will show explicitly in the absence of twisting, shearing, and stretching, that our general elastic chain becomes a wormlike chain.

For isotropic bending and shearing, the A_j's and B_j's are related to Young's modulus E and the shear modulus G of the chain via the formulae [Hag1,Smi1]: $A_1 = A_2 = k_BT/(2EI_1)$, $A_3 = k_BT/(4GI_3)$, $B_1 = B_2 = k_BT/(2G\pi a_c^2)$, $B_3 = k_BT/(2E\pi a_c^2)$. Here a_c is the cross-sectional radius of the chain, whereas I_1 and I_3 are the two principal moments of inertia, with $I_3 = 2I_1 = \pi a_c^4/4$. Poisson's ratio, which characterizes the elastic property of the chain, is given by $\sigma = E/(2G) - 1$. For double helix DNA the numerical values of these elastic constants are listed at the end of §4.

By definition, the linear 'momentum' $\mathbf{P}$ and angular 'momentum' $\mathbf{J}$ are given by

$$\mathbf{P} = P_\alpha \hat{\mathbf{e}}_\alpha, \tag{2-35a}$$

$$\mathbf{J} = J_\alpha \hat{\mathbf{a}}_\alpha. \tag{2-35b}$$

Since all the linear variables are defined in $\mathcal{R}^3$ and all the angular variables are defined in $SO(3)$, we have let the components of the linear 'momentum' $\mathbf{P}$ be those in the space-frame basis and let the components of the angular 'momentum' $\mathbf{J}$ be those in the body-frame basis. These components are obtained from the Lagrangian

$$P_\alpha = \frac{\partial \mathcal{L}}{\partial \dot{x}_\alpha} = b_\alpha + M_{\alpha\beta}\dot{x}_\beta, \tag{2-36a}$$

$$J_k = \frac{\partial \mathcal{L}}{\partial \omega_k} = \frac{i(\omega_k - \omega_k^0)}{2A_k} - i\tau_\alpha \Lambda_{\alpha k}, \tag{2-36b}$$

where

$$b_\alpha = -\frac{i}{2}\sum_{k=1}^{3}\frac{\Lambda_{\alpha k}t_k^0}{B_k} - if_\alpha, \tag{2-37}$$

$$M_{\alpha\beta} = \frac{i}{2}\sum_{k=1}^{3}\frac{\Lambda_{\alpha k}\Lambda_{\beta k}}{B_k}. \tag{2-38}$$

Using the orthogonality of $\mathbf{\Lambda}$ it is easy to show that $\det(\mathbf{M}) = 1/(8iB_1B_2B_3)$ and

$$(\mathbf{M}^{-1})_{\alpha\beta} = -2i\sum_{k=1}^{3} B_k\Lambda_{\alpha k}\Lambda_{\beta k}. \tag{2-39}$$

Equations (2-36a,b) enable us to express $\dot{x}_\alpha$ in terms of P_β, and ω_k in terms of J_k:

$$\omega_k - \omega_k^0 = -2iA_k(J_k + i\tau_\alpha\Lambda_{\alpha k}), \tag{2-40a}$$

$$\dot{x}_\alpha = \left(\mathbf{M}^{-1}\right)_{\alpha\beta}(P_\beta - b_\beta), \tag{2-40b}$$

where the summation convention is not applied to repeated Latin suffixes (A_j and B_j are not components of vectors).

Using (2-31), (2-39), and (2-40b), we obtain $t_k = -2iB_k\Lambda_{\alpha k}(P_\alpha - b_\alpha)$, or

$$t_k - t_k^0 = -2iB_k\Lambda_{\alpha k}(P_\alpha + if_\alpha). \tag{2-41}$$

The Hamiltonian $\mathcal{H} = \sum_k p_k\dot{q}_k - \mathcal{L}$ for our particular choice of generalized 'velocity', angular 'velocity', 'momentum', and angular 'momentum', is

$$\mathcal{H} = \omega_\alpha J_\alpha + \dot{x}_\alpha P_\alpha - \mathcal{L}. \tag{2-42}$$

Upon substituting (2-40) into (2-42), with $\mathbf{M}^{-1}$ given by (2-39), and making use of identities like $P_\alpha\Lambda_{\alpha\beta} = P_\alpha\hat{\mathbf{e}}_\alpha \cdot \mathbf{\Lambda} \cdot \hat{\mathbf{e}}_\beta = \mathbf{P} \cdot \hat{\mathbf{a}}_\beta$, we obtain, after a long derivation,

$$i\mathcal{H} = \sum_{k=1}^{3}\Big[A_k[\hat{\mathbf{a}}_k\cdot(\mathbf{J}+i\boldsymbol{\tau})]^2 + B_k[\hat{\mathbf{a}}_k\cdot(\mathbf{P}+i\mathbf{f})]^2 + i\omega_k^0[\hat{\mathbf{a}}_k\cdot(\mathbf{J}+i\boldsymbol{\tau})] + it_k^0[\hat{\mathbf{a}}_k\cdot(\mathbf{P}+i\mathbf{f})]\Big]. \tag{2-43}$$

Using the general rule for forming the Schrödinger equation by correspondence operations [Mes1], given the explicit form of a Hamiltonian the path integral form of a wave function can be transformed into the Schrödinger equation it satisfies: $(\hbar\partial/\partial s + i\mathcal{H})\psi = 0$. The conversion procedure, $\mathbf{P} \Rightarrow -i\hbar\nabla_{\mathbf{r}}$ and $\mathbf{J} \Rightarrow -i\hbar\nabla_{\mathbf{\Omega}}$ with $\nabla_{\mathbf{\Omega}}$ given by (2-24), leads to the desired differential equation for the Green's function ($\hbar \equiv 1$ for our purposes):

$$\left(\frac{\partial}{\partial s} + \Xi\right)G(\mathbf{r}, \mathbf{\Phi}; s \,|\, \mathbf{r}_0, \mathbf{\Phi}_0; 0) = \delta(s)\delta(\mathbf{r} - \mathbf{r}_0)\delta(\mathbf{\Phi} - \mathbf{\Phi}_0), \tag{2-44a}$$

where

$$\Xi = -(\nabla_{\Omega} - \boldsymbol{\tau}) \cdot \boldsymbol{\Theta} \cdot (\nabla_{\Omega} - \boldsymbol{\tau}) - (\nabla_{\mathbf{r}} - \mathbf{f}) \cdot \mathbf{D} \cdot (\nabla_{\mathbf{r}} - \mathbf{f}) + \Xi_0 \tag{2-44b}$$

and

$$\Xi_0 = \omega_\alpha^0 [\hat{\mathbf{a}}_\alpha \cdot (\nabla_{\Omega} - \boldsymbol{\tau})] + t_\alpha^0 [\hat{\mathbf{a}}_\alpha \cdot (\nabla_{\mathbf{r}} - \mathbf{f})]. \tag{2-44c}$$

The translational and rotational diffusion tensors $\mathbf{D}$ and $\boldsymbol{\Theta}$ are given by

$$\boldsymbol{\Theta} = \sum_{j=1}^{3} A_j \hat{\mathbf{a}}_j \hat{\mathbf{a}}_j, \tag{2-44d}$$

$$\mathbf{D} = \sum_{j=1}^{3} B_j \hat{\mathbf{a}}_j \hat{\mathbf{a}}_j, \tag{2-44e}$$

while the delta function in Euler-angle space is

$$\delta(\boldsymbol{\Phi} - \boldsymbol{\Phi}_0) = \frac{1}{\sin\theta} \delta(\phi - \phi_0)\, \delta(\theta - \theta_0)\, \delta(\psi - \psi_0). \tag{2-44f}$$

Observe that the external force $\mathbf{f}$ enters the differential equation in terms of the group entity $\nabla_{\mathbf{r}} - \mathbf{f}$, whereas the external torque $\boldsymbol{\tau}$ enters in terms of $\nabla_{\Omega} - \boldsymbol{\tau}$. This fact is consistent with (2-34). Suppose, for simplicity, that we let the Green's function with constant external force f and constant external torque $\boldsymbol{\tau}$ be denoted by $G(\mathbf{r}; \mathbf{f}; \boldsymbol{\tau})$, whereas that for the force-free case is $G(\mathbf{r}; \mathbf{0}; \boldsymbol{\tau})$. Then, from (2-34), we have $G(\mathbf{r}; \mathbf{0}; \boldsymbol{\tau}) = Ce^{-\mathbf{f}\cdot(\mathbf{r}-\mathbf{r}_0)} G(\mathbf{r}; \mathbf{f}; \boldsymbol{\tau})$. Upon applying the operator $\nabla_{\mathbf{r}}$ to both sides of the latter we obtain

$$\nabla_{\mathbf{r}} G(\mathbf{r}; \mathbf{0}; \boldsymbol{\tau}) = Ce^{-\mathbf{f}\cdot(\mathbf{r}-\mathbf{r}_0)} (\nabla_{\mathbf{r}} - \mathbf{f}) G(\mathbf{r}; \mathbf{f}; \boldsymbol{\tau}).$$

Since the differential equation (2-44) is homogeneous, the factor $Ce^{-\mathbf{f}\cdot(\mathbf{r}-\mathbf{r}_0)}$ can be dropped in the equation. Hence upon replacing $\nabla_{\mathbf{r}}$ by $\nabla_{\mathbf{r}} - \mathbf{f}$ everywhere in the differential equation for the force-free ($\mathbf{f} = \mathbf{0}$) Green's function, what we obtain is exactly the differential equation for the Green's function with an external force (and torque).

By examining the derivation leading to (2-44) we notice that the path integral (2-32) was not used explicitly to derive the differential equation (2-44). Rather, we made use of the general rule for forming the Schrödinger equation by correspondence.

The correspondence rule states that to a classical system with Hamiltonian $\mathcal{H}(\{q_j\}; \{p_j\}; t)$ there corresponds a quantum system whose dynamic state is represented by a wave function $\Psi(\{q_j\}; t)$ defined in configuration space, one whose wave equation can be obtained by performing on both sides of the equation $\mathcal{E} = \mathcal{H}(\{q_j\}; \{p_j\}; t)$ (arising from the homogeneity of the system in t) the substitutions $\mathcal{E} \Rightarrow i\hbar\partial/\partial t$, $p_\alpha \Rightarrow -i\hbar\partial/\partial q_\alpha$, and by observing that these two quantities, considered as operators, give identical results when acting on Ψ. The equation thus obtained is the Schrödinger equation of the corresponding quantum system : $i\hbar\partial\Psi(\{q_j\};t)/\partial t = \mathcal{H}(\{q_j\};\{-i\hbar\partial/\partial q_j\};t)\Psi(\{q_j\};t)$.

However, the correspondence rule stated above does not define the Schrödinger equation uniquely [Mes1]. Rather, there exist two sources of ambiguity. The first arises from the fact that this rule is not invariant to a change of coordinates parameterizing the configuration space. The second stems from the fact that operators do not necessarily commute with each other due to the finite, non-zero character of $\hbar$. As a consequence, different quantum Hamiltonians may correspond to equivalent forms of the classical Hamiltonian.

Consequently (2-44) needs to be confirmed by using direct approaches, especially because $\mathbf{\Omega}$ is not a vector owing to its failure to obey the commutative law under addition. In the next section we will use a probabilistic approach to confirm the differential equation (2-44). Because the differential equation governing Green's function in the presence of external forces and torques can be obtained from that of the free chain simply by replacing $\nabla_{\mathbf{r}}$ by $\nabla_{\mathbf{r}} - \mathbf{f}$ and $\nabla_{\mathbf{\Omega}}$ by $\nabla_{\mathbf{\Omega}} - \boldsymbol{\tau}$, we need only find the free chain ($\mathbf{f} = \mathbf{0}$ and $\boldsymbol{\tau} = \mathbf{0}$) differential equation.

§3. A Probabilistic Approach to the Elastic Chain Distribution

In the preceding section we derived the differential equation for the elastic chain Green's function by using the correspondence rule from quantum mechanics. This approach, although simple and elegant, is an indirect one. We now re-examine the elastic free chain ($\mathbf{f} = \mathbf{0}$, $\boldsymbol{\tau} = \mathbf{0}$) Green's function using a purely probabilistic approach which makes explicit use of the path integral (2-32). Consider a differentiable space curve with constant material length L. We now set up body-frames everywhere along the chain, the same way as in §2. The configuration of the infinitesimal chain segment at any given point s is characterized by its linear coordinates $\mathbf{r}(s)$ and angular coordinates $\boldsymbol{\Phi}(s)$ (the set of Euler angles). We are interested in the differential equation governing the Green's function $G(\mathbf{r}, \boldsymbol{\Phi}; s \,|\, \mathbf{r}_0, \boldsymbol{\Phi}_0; 0; \mathbf{f} = \mathbf{0}; \boldsymbol{\tau} = \mathbf{0})$, which can be viewed as a conditional probability function. Since the free chain Green's function is used exclusively in this section, the explicit notation $\mathbf{f} = \mathbf{0}$ and $\boldsymbol{\tau} = \mathbf{0}$ that would otherwise appear in the argument will be suppressed. For a given Δs, $G(\mathbf{r}, \boldsymbol{\Phi}; s + \Delta s \,|\, \mathbf{r}_0, \boldsymbol{\Phi}_0; 0)$ satisfies the Chapman-Kolmogorov equation

$$G(\mathbf{r}, \boldsymbol{\Phi}; s + \Delta s \,|\, \mathbf{r}_0, \boldsymbol{\Phi}_0; 0) = \int G(\mathbf{r}, \boldsymbol{\Phi}; s+\Delta s \,|\, \mathbf{r}-\Delta\mathbf{r}, \boldsymbol{\Phi}-\Delta\boldsymbol{\Phi}; s)\, G(\mathbf{r}-\Delta\mathbf{r}, \boldsymbol{\Phi}-\Delta\boldsymbol{\Phi}; s \,|\, \mathbf{r}_0, \boldsymbol{\Phi}_0; 0)\, d^3(\Delta\mathbf{r})\, d^3(\Delta\boldsymbol{\Phi}). \tag{3-1}$$

Expand $G(\mathbf{r}, \boldsymbol{\Phi}; s + \Delta s \,|\, \mathbf{r}_0, \boldsymbol{\Phi}_0; 0)$ and $G(\mathbf{r} - \Delta\mathbf{r}, \boldsymbol{\Phi} - \Delta\boldsymbol{\Phi}; s \,|\, \mathbf{r}_0, \boldsymbol{\Phi}_0; 0)$ into Taylor series to obtain:

$$\begin{aligned} G(\mathbf{r}, \boldsymbol{\Phi}; s \,|\, \mathbf{r}_0, \boldsymbol{\Phi}_0; 0) + \Delta s \frac{\partial G}{\partial s} + O\big((\Delta s)^2\big) = \\ \int \Big[G - \Delta\mathbf{r} \cdot \nabla_{\mathbf{r}} G - \Delta\boldsymbol{\Phi} \cdot \nabla_{\boldsymbol{\Phi}} G + \frac{1}{2} \Delta\mathbf{r}\Delta\mathbf{r} : \nabla_{\mathbf{r}}\nabla_{\mathbf{r}} G + \frac{1}{2} \Delta\boldsymbol{\Phi}\Delta\boldsymbol{\Phi} : \nabla_{\boldsymbol{\Phi}}\nabla_{\boldsymbol{\Phi}} G \\ + \Delta\mathbf{r}\Delta\boldsymbol{\Phi} : \nabla_{\mathbf{r}}\nabla_{\boldsymbol{\Phi}} G + \dots \Big] G(\mathbf{r}, \boldsymbol{\Phi}; s + \Delta s \,|\, \mathbf{r} - \Delta\mathbf{r}, \boldsymbol{\Phi} - \Delta\boldsymbol{\Phi}; s)\, d^3(\Delta\mathbf{r})\, d^3(\Delta\boldsymbol{\Phi}). \end{aligned} \tag{3-2}$$

For an arbitrary function $M(\Delta\mathbf{r}, \Delta\boldsymbol{\Phi})$, we define the expectation value

$$\langle M \rangle = \int M(\Delta\mathbf{r}, \Delta\boldsymbol{\Phi})\, G(\mathbf{r}, \boldsymbol{\Phi}; s + \Delta s \,|\, \mathbf{r} - \Delta\mathbf{r}, \boldsymbol{\Phi} - \Delta\boldsymbol{\Phi}; s)\, d^3(\Delta\mathbf{r})\, d^3(\Delta\boldsymbol{\Phi}), \tag{3-3}$$

where the transition probability $G(\mathbf{r}, \boldsymbol{\Phi}; s + \Delta s \,|\, \mathbf{r} - \Delta\mathbf{r}, \boldsymbol{\Phi} - \Delta\boldsymbol{\Phi}; s)$ is properly normalized: $\int G\, d^3(\Delta\mathbf{r})\, d^3(\Delta\boldsymbol{\Phi}) = 1$. Equation (3-2) thereby becomes

$$\begin{aligned} \Delta s \frac{\partial G}{\partial s} + O\big((\Delta s)^2\big) = -\langle \Delta\mathbf{r} \rangle \cdot \nabla_{\mathbf{r}} G - \langle \Delta\boldsymbol{\Phi} \rangle \cdot \nabla_{\boldsymbol{\Phi}} G + \frac{1}{2} \langle \Delta\mathbf{r}\Delta\mathbf{r} \rangle : \nabla_{\mathbf{r}}\nabla_{\mathbf{r}} G \\ + \frac{1}{2} \langle \Delta\boldsymbol{\Phi}\Delta\boldsymbol{\Phi} \rangle : \nabla_{\boldsymbol{\Phi}}\nabla_{\boldsymbol{\Phi}} G + \langle \Delta\mathbf{r}\Delta\boldsymbol{\Phi} \rangle : \nabla_{\mathbf{r}}\nabla_{\boldsymbol{\Phi}} G + \dots . \end{aligned} \tag{3-4}$$

The properties of the Green's function $G(\mathbf{r}, \boldsymbol{\Phi}; s+\Delta s \,|\, \mathbf{r}-\Delta\mathbf{r}, \boldsymbol{\Phi}-\Delta\boldsymbol{\Phi}; s)$ (a transition probability) for an elastic chain can be used to simplify the above equation.

We have assumed that any Green's function takes the path integral form (2-32), which in this particular case becomes

$$G(\mathbf{r},\mathbf{\Phi};s+\Delta s\,|\,\mathbf{r}-\Delta\mathbf{r},\mathbf{\Phi}-\Delta\mathbf{\Phi};s)=\frac{1}{C_0}\int_{\substack{\mathbf{r}-\Delta\mathbf{r}\\ \mathbf{\Phi}-\Delta\mathbf{\Phi}}}^{\mathbf{r},\mathbf{\Phi}} e^{i\int_s^{s+\Delta s}\mathcal{L}(\tau)\,d\tau}\,\mathcal{D}[\mathbf{r}(\tau)]\,\mathcal{D}[\mathbf{\Phi}(\tau)]. \tag{3-5}$$

For infinitesimal Δs, the path integral of the infinitesimal transition probability extends over an almost unique path, whence the path integration disappears and the transition probability becomes simply $e^{i\mathcal{L}\Delta s}$. The explicit form of the Lagrangian is given by (2-33). Note that $\Delta\mathbf{r}/\Delta s=\mathbf{t}=t_\alpha\hat{\mathbf{a}}_\alpha\equiv(\Delta r_\alpha/\Delta s)\hat{\mathbf{a}}_\alpha$ (summation convention on repeated Greek suffixes), where the last equality serves as the definition of Δr_α. This makes $\omega_k=\Delta\Omega_k/\Delta s, t_k=\Delta r_k/\Delta s$. Aside from a normalization constant, the transition probability becomes the product of two independent Gaussian distribution Boltzmann factors:

$$\begin{aligned}&G(\mathbf{r},\mathbf{\Phi};s+\Delta s\,|\,\mathbf{r}-\Delta\mathbf{r},\mathbf{\Phi}-\Delta\mathbf{\Phi};s)\\ &\qquad=\frac{1}{C}e^{-\sum_k[4\Delta sA_k]^{-1}(\Delta\Omega_k-\omega_k^0\Delta s)^2}\,e^{-\sum_k[4\Delta sB_k]^{-1}(\Delta r_k-t_k^0\Delta s)^2}.\end{aligned} \tag{3-6}$$

Since, for infinitesimal transitions the Green's function becomes a Gaussian distribution, the expectation values of different quantities can easily be obtained by explicit integration. However, since the angular variable in the Gaussian distribution is Ω_k rather than Φ_k, we need therefore to transform (3-4) into an equivalent form, namely

$$\begin{aligned}\Delta s\frac{\partial G}{\partial s}+O((\Delta s)^2)&=-\langle\Delta\mathbf{r}\rangle\cdot\nabla_{\mathbf{r}}G-\langle\Delta\mathbf{\Omega}\rangle\cdot\nabla_{\mathbf{\Omega}}G+\frac{1}{2}\langle\Delta\mathbf{r}\Delta\mathbf{r}\rangle:\nabla_{\mathbf{r}}\nabla_{\mathbf{r}}G\\ &\quad+\frac{1}{2}\langle\Delta\mathbf{\Omega}\Delta\mathbf{\Omega}\rangle:\nabla_{\mathbf{\Omega}}\nabla_{\mathbf{\Omega}}G+\langle\Delta\mathbf{r}\Delta\mathbf{\Omega}\rangle:\nabla_{\mathbf{r}}\nabla_{\mathbf{\Omega}}G+\ldots.\end{aligned} \tag{3-7}$$

We have systematically changed the angular coordinates of our system from those of Φ-space to those of Ω-space; for intuitively, the Taylor expansion (3-2), (3-4) and the desired differential equation must each be invariant to coordinate transformation. The equivalence of (3-4) and (3-7) will be proved explicitly at the end of this section.

In Ω-space, (3-3) now takes the form

$$\begin{aligned}\langle M\rangle=\frac{(A_1A_2A_3B_1B_2B_3)^{-1/2}}{64\sqrt{8}(\Delta s)^3\pi^3}&\int M(\Delta\mathbf{r},\Delta\mathbf{\Omega})\,e^{-\sum_k[4\Delta sA_k]^{-1}(\Delta\Omega_k-\omega_k^0\Delta s)^2}\\ &\times e^{-\sum_k[4\Delta sB_k]^{-1}(\Delta r_k-t_k^0\Delta s)^2}\,d^3(\Delta\mathbf{r})\,d^3(\Delta\mathbf{\Omega}).\end{aligned} \tag{3-8}$$

An extra factor $\sqrt{8}$ appears in the normalization constant because, from (2-20), the determinant of the metric tensor ${}_\Omega g_{ij}$ in Ω-space is ${}_\Omega g=8$. As such, the infinitesimal volume element is $d^3(\Delta\mathbf{\Omega})=\sqrt{8}\,d(\Delta\Omega_1)\,d(\Delta\Omega_2)\,d(\Delta\Omega_3)$.

Since the Gaussian distributions over linear coordinates Δr_k (with mean $t_k^0 \Delta s$) and over angular coordinates $\Delta \Omega_j$ (with mean $\omega_j^0 \Delta s$) are independent, we have that

$$\langle \Delta \mathbf{r} \rangle = \Delta s\, t_\alpha^0\, \hat{\mathbf{a}}_\alpha, \tag{3-9a}$$

$$\langle \Delta \mathbf{\Omega} \rangle = \Delta s\, \omega_\alpha^0\, \hat{\mathbf{a}}_\alpha, \tag{3-9b}$$

$$\langle \Delta \mathbf{r} \Delta \mathbf{r} \rangle = \sum_{j,k=1}^{3} \left[2\Delta s B_k \delta_{j,k} + (\Delta s)^2 t_j^0 t_k^0 \right] \hat{\mathbf{a}}_j \hat{\mathbf{a}}_k, \tag{3-9c}$$

$$\langle \Delta \mathbf{\Omega} \Delta \mathbf{\Omega} \rangle = \sum_{j,k=1}^{3} \left[2\Delta s A_k \delta_{j,k} + (\Delta s)^2 \omega_j^0 \omega_k^0 \right] \hat{\mathbf{a}}_j \hat{\mathbf{a}}_k, \tag{3-9d}$$

$$\langle \Delta \mathbf{r} \Delta \mathbf{\Omega} \rangle = \langle \Delta \mathbf{r} \rangle \langle \Delta \mathbf{\Omega} \rangle = (\Delta s)^2\, t_\alpha^0 \omega_\beta^0\, \hat{\mathbf{a}}_\alpha \hat{\mathbf{a}}_\beta. \tag{3-9e}$$

Substitution of (3-9) into (3-7) yields

$$\begin{aligned} \frac{\partial G}{\partial s} + O(\Delta s) = & -t_\alpha^0 (\hat{\mathbf{a}}_\alpha \cdot \nabla_{\mathbf{r}}) G - \omega_\alpha^0 (\hat{\mathbf{a}}_\alpha \cdot \nabla_{\mathbf{\Omega}}) G + \sum_{k=1}^{3} A_k (\hat{\mathbf{a}}_k \cdot \nabla_{\mathbf{\Omega}})^2 G \\ & + \sum_{k=1}^{3} B_k (\hat{\mathbf{a}}_k \cdot \nabla_{\mathbf{r}})^2 G + \frac{\Delta s}{2} t_\alpha^0 t_\beta^0 (\hat{\mathbf{a}}_\alpha \cdot \nabla_{\mathbf{r}})(\hat{\mathbf{a}}_\beta \cdot \nabla_{\mathbf{r}}) G \\ + \frac{\Delta s}{2} \omega_\alpha^0 \omega_\beta^0 & (\hat{\mathbf{a}}_\alpha \cdot \nabla_{\mathbf{\Omega}})(\hat{\mathbf{a}}_\beta \cdot \nabla_{\mathbf{\Omega}}) G + (\Delta s) t_\alpha^0 \omega_\beta^0 (\hat{\mathbf{a}}_\alpha \cdot \nabla_{\mathbf{r}})(\hat{\mathbf{a}}_\beta \cdot \nabla_{\mathbf{\Omega}}) G + \ldots. \end{aligned} \tag{3-10}$$

Upon deleting terms of order $O(\Delta s)$ and higher in the above equation we obtain the differential equation of the free chain ($\mathbf{f} = \mathbf{0}$, $\boldsymbol{\tau} = \mathbf{0}$) Green's function:

$$\frac{\partial G}{\partial s} - \sum_{k=1}^{3} A_k (\hat{\mathbf{a}}_k \cdot \nabla_{\mathbf{\Omega}})^2 G - \sum_{k=1}^{3} B_k (\hat{\mathbf{a}}_k \cdot \nabla_{\mathbf{r}})^2 G + t_\alpha^0 (\hat{\mathbf{a}}_\alpha \cdot \nabla_{\mathbf{r}}) G + \omega_\alpha^0 (\hat{\mathbf{a}}_\alpha \cdot \nabla_{\mathbf{\Omega}}) G = 0. \tag{3-11}$$

For chains with constant external force $\mathbf{f}$ and torque $\boldsymbol{\tau}$, the corresponding differential equation is obtained upon replacing $\nabla_{\mathbf{r}}$ and $\nabla_{\mathbf{\Omega}}$ in above with $\nabla_{\mathbf{r}} - \mathbf{f}$ and $\nabla_{\mathbf{\Omega}} - \boldsymbol{\tau}$ respectively. Furthermore, upon taking into account the source terms by placing delta functions on the right-hand side of the resulting equation, the differential equation thereby obtained is identical to (2-44). Consequently, a purely probabilistic approach with explicit use of the path integral confirms the result obtained in §2 by alternative arguments.

To conclude this section, we now prove the equivalence of (3-4) and (3-7). In particular, we will show explicitly that

$$\Delta \mathbf{\Phi} \cdot \nabla_{\mathbf{\Phi}} G = \Delta \mathbf{\Omega} \cdot \nabla_{\mathbf{\Omega}} G, \tag{3-12a}$$

$$\Delta \mathbf{\Phi} \Delta \mathbf{\Phi} : \nabla_{\mathbf{\Phi}} \nabla_{\mathbf{\Phi}} G = \Delta \mathbf{\Omega} \Delta \mathbf{\Omega} : \nabla_{\mathbf{\Omega}} \nabla_{\mathbf{\Omega}} G. \tag{3-12b}$$

As $\Delta \mathbf{\Phi}$ and $\Delta \mathbf{\Omega}$ approach infinitesimal rotations, (3-12a) becomes identical to (2-22a) since the covariant derivative of a scalar is identical to the ordinary gradient.

Therefore, we need only prove (3-12b). Expressed alternatively, the operator on the left-hand side of the latter becomes

$$d\Phi_\alpha d\Phi_\beta \frac{\partial}{\partial \Phi_\alpha}\frac{\partial}{\partial \Phi_\beta} = d\Phi_\alpha d\Phi_\beta \left[\frac{\partial^2}{\partial \Phi_\alpha \partial \Phi_\beta} - {}_\Phi\Gamma^\gamma_{\alpha\beta}\frac{\partial}{\partial \Phi_\gamma}\right], \tag{3-13}$$

where ${}_\Phi\Gamma^\gamma_{\alpha\beta}$ is the Christoffel symbol of the second kind (the affine connection) in Φ-space. Its definition, independent of choice of coordinate system, is

$$\Gamma^\gamma_{\alpha\beta} = \frac{1}{2} g^{\gamma\lambda}\left[\frac{\partial g_{\lambda\beta}}{\partial x^\alpha} + \frac{\partial g_{\lambda\alpha}}{\partial x^\beta} - \frac{\partial g_{\alpha\beta}}{\partial x^\lambda}\right]. \tag{3-14}$$

Use of the metric tensor (2-17) and its inverse in Φ-space gives

$${}_\Phi g^{\alpha\beta} = \begin{pmatrix} \frac{1}{2}\csc^2\theta & 0 & -\frac{1}{2}\csc^2\theta\cos\theta \\ 0 & \frac{1}{2} & 0 \\ -\frac{1}{2}\csc^2\theta\cos\theta & 0 & \frac{1}{2}\csc^2\theta \end{pmatrix}. \tag{3-15}$$

Consequently, the only non-vanishing components of $\partial g_{ij}/\partial\Phi_k$ are $\partial g_{13}/\partial\Phi_2 = \partial g_{31}/\partial\Phi_2 = -2\sin\theta$. This yields,

$${}_\Phi\Gamma^\gamma_{11} = {}_\Phi\Gamma^\gamma_{22} = {}_\Phi\Gamma^\gamma_{33} = 0 \qquad (\gamma = 1,2,3), \tag{3-16a}$$

$${}_\Phi\Gamma^\gamma_{12} = {}_\Phi\Gamma^\gamma_{21} = (\, \tfrac{1}{2}\cot\theta \quad 0 \quad -\tfrac{1}{2}\csc\theta\,), \tag{3-16b}$$

$${}_\Phi\Gamma^\gamma_{13} = {}_\Phi\Gamma^\gamma_{31} = (\,0 \quad \tfrac{1}{2}\sin\theta \quad 0\,), \tag{3-16c}$$

$${}_\Phi\Gamma^\gamma_{23} = {}_\Phi\Gamma^\gamma_{32} = (\,-\tfrac{1}{2}\csc\theta \quad 0 \quad \tfrac{1}{2}\cot\theta\,). \tag{3-16d}$$

From (3-13), this furnishes the expression,

$$\begin{bmatrix} \frac{\partial^2}{\partial\phi^2} & \frac{\partial^2}{\partial\phi\partial\theta} - \frac{\cot\theta}{2}\frac{\partial}{\partial\phi} + \frac{\csc\theta}{2}\frac{\partial}{\partial\psi} & \frac{\partial^2}{\partial\phi\partial\psi} - \frac{\sin\theta}{2}\frac{\partial}{\partial\theta} \\ \frac{\partial^2}{\partial\phi\partial\theta} - \frac{\cot\theta}{2}\frac{\partial}{\partial\phi} + \frac{\csc\theta}{2}\frac{\partial}{\partial\psi} & \frac{\partial^2}{\partial\theta^2} & \frac{\partial^2}{\partial\theta\partial\psi} + \frac{\csc\theta}{2}\frac{\partial}{\partial\phi} - \frac{\cot\theta}{2}\frac{\partial}{\partial\psi} \\ \frac{\partial^2}{\partial\phi\partial\psi} - \frac{\sin\theta}{2}\frac{\partial}{\partial\theta} & \frac{\partial^2}{\partial\theta\partial\psi} + \frac{\csc\theta}{2}\frac{\partial}{\partial\phi} - \frac{\cot\theta}{2}\frac{\partial}{\partial\psi} & \frac{\partial^2}{\partial\psi^2} \end{bmatrix}$$

$$= \frac{\partial}{\partial\Phi_\alpha}\frac{\partial}{\partial\Phi_\beta} = \frac{\partial^2}{\partial\Phi_\alpha\partial\Phi_\beta} - {}_\Phi\Gamma^\gamma_{\alpha\beta}\frac{\partial}{\partial\Phi_\gamma} \tag{3-17}$$

for the second-order covariant differential operator in Φ-space.

As an excursion, note that in addition to the definition (2-25) of the Laplacian in Φ-space, we also have, equivalently,

$$\nabla^2_\Omega = {}_\Phi g^{\alpha\beta}\frac{\partial}{\partial\Phi_\alpha}\frac{\partial}{\partial\Phi_\beta}. \tag{3-18}$$

Here ${}_\Phi g^{\alpha\beta}$, given by (3-15), is the inverse of the metric tensor (2-17). Upon using (3-18) and taking the tensor contraction of (3-15) and (3-17), one indeed recovers (2-26).

Use of (2-14), (2-20), and (2-24), enables the right-hand side of (3-12b) to be evaluated, albeit involving a tedious and lengthy calculation. We first note that

$$d\Omega_\mu d\Omega_\nu \frac{\partial}{\partial\Omega_\mu}\frac{\partial}{\partial\Omega_\nu} = A_{\mu\alpha}A_{\nu\beta}d\Phi_\alpha d\Phi_\beta\left[\frac{\partial^2}{\partial\Omega_\mu\partial\Omega_\nu} - {}_\Omega\Gamma^\gamma_{\mu\nu}\frac{\partial}{\partial\Omega_\gamma}\right]. \tag{3-19}$$

Because the metric tensor in Ω-space is ${}_\Omega g_{\alpha\beta} = 2\delta_{\alpha\beta}$, all components of ${}_\Omega\Gamma^\gamma_{\alpha\beta} = 0$. The covariant derivatives in Ω-space are thus identical to the ordinary derivatives.

The three components of $\partial/\partial\Omega_k$ given by (2-24) enable us to calculate all the second derivatives $(\partial/\partial\Omega_i)(\partial/\partial\Omega_j)$. If, for simplicity of notation we write $\partial_i\partial_j \equiv (\partial/\partial\Omega_i)(\partial/\partial\Omega_j)$, then

$$\begin{aligned}\partial_1\partial_1 = {}& \frac{\cos^2\psi}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \sin^2\psi\frac{\partial^2}{\partial\theta^2} + \cot^2\theta\cos^2\psi\frac{\partial^2}{\partial\psi^2} - 2\frac{\sin\psi\cos\psi}{\sin\theta}\frac{\partial^2}{\partial\phi\partial\theta}\\ &- 2\frac{\cos\theta\cos^2\psi}{\sin^2\theta}\frac{\partial^2}{\partial\phi\partial\psi} + 2\cot\theta\sin\psi\cos\psi\frac{\partial^2}{\partial\theta\partial\psi} + \cot\theta\cos^2\psi\frac{\partial}{\partial\theta}\\ &+ 2\frac{\cos\theta\sin\psi\cos\psi}{\sin^2\theta}\frac{\partial}{\partial\phi} - (1+2\cot^2\theta)\sin\psi\cos\psi\frac{\partial}{\partial\psi},\end{aligned} \tag{3-20a}$$

$$\begin{aligned}\partial_2\partial_2 = {}& \frac{\sin^2\psi}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \cos^2\psi\frac{\partial^2}{\partial\theta^2} + \cot^2\theta\sin^2\psi\frac{\partial^2}{\partial\psi^2} + 2\frac{\sin\psi\cos\psi}{\sin\theta}\frac{\partial^2}{\partial\phi\partial\theta}\\ &- 2\frac{\cos\theta\sin^2\psi}{\sin^2\theta}\frac{\partial^2}{\partial\phi\partial\psi} - 2\cot\theta\sin\psi\cos\psi\frac{\partial^2}{\partial\theta\partial\psi} + \cot\theta\sin^2\psi\frac{\partial}{\partial\theta}\\ &- 2\frac{\cos\theta\sin\psi\cos\psi}{\sin^2\theta}\frac{\partial}{\partial\phi} + (1+2\cot^2\theta)\sin\psi\cos\psi\frac{\partial}{\partial\psi},\end{aligned} \tag{3-20b}$$

$$\partial_3\partial_3 = \frac{\partial^2}{\partial\psi^2}, \tag{3-20c}$$

$$\begin{aligned}\partial_1\partial_2 = {}& -\frac{\sin\psi\cos\psi}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \sin\psi\cos\psi\frac{\partial^2}{\partial\theta^2} - \cot^2\theta\sin\psi\cos\psi\frac{\partial^2}{\partial\psi^2}\\ &+ \frac{\sin^2\psi-\cos^2\psi}{\sin\theta}\frac{\partial^2}{\partial\phi\partial\theta} + 2\frac{\cos\theta\sin\psi\cos\psi}{\sin^2\theta}\frac{\partial^2}{\partial\phi\partial\psi}\\ &+ \cot\theta(\cos^2\psi-\sin^2\psi)\frac{\partial^2}{\partial\theta\partial\psi} + \frac{\cos\theta(\cos^2\psi-\sin^2\psi)}{\sin^2\theta}\frac{\partial}{\partial\phi}\\ &- \cot\theta\sin\psi\cos\psi\frac{\partial}{\partial\theta} + \frac{\sin^2\psi-\cos^2\theta\cos^2\psi}{\sin^2\theta}\frac{\partial}{\partial\psi},\end{aligned} \tag{3-20d}$$

$$\begin{aligned}\partial_2\partial_1 = {}& -\frac{\sin\psi\cos\psi}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \sin\psi\cos\psi\frac{\partial^2}{\partial\theta^2} - \cot^2\theta\sin\psi\cos\psi\frac{\partial^2}{\partial\psi^2}\\ &+ \frac{\sin^2\psi-\cos^2\psi}{\sin\theta}\frac{\partial^2}{\partial\phi\partial\theta} + 2\frac{\cos\theta\sin\psi\cos\psi}{\sin^2\theta}\frac{\partial^2}{\partial\phi\partial\psi}\\ &+ \cot\theta(\cos^2\psi-\sin^2\psi)\frac{\partial^2}{\partial\theta\partial\psi} + \frac{\cos\theta(\cos^2\psi-\sin^2\psi)}{\sin^2\theta}\frac{\partial}{\partial\phi}\\ &- \cot\theta\sin\psi\cos\psi\frac{\partial}{\partial\theta} + (\cot^2\theta\sin^2\psi-\csc^2\theta\cos^2\psi)\frac{\partial}{\partial\psi},\end{aligned} \tag{3-20e}$$

$$\partial_1\partial_3 = -\frac{\cos\psi}{\sin\theta}\frac{\partial^2}{\partial\phi\partial\psi} + \sin\psi\frac{\partial^2}{\partial\theta\partial\psi} + \cot\theta\cos\psi\frac{\partial^2}{\partial\psi^2}, \tag{3-20f}$$

$$\partial_2\partial_3 = \frac{\sin\psi}{\sin\theta}\frac{\partial^2}{\partial\phi\partial\psi} + \cos\psi\frac{\partial^2}{\partial\theta\partial\psi} - \cot\theta\sin\psi\frac{\partial^2}{\partial\psi^2}, \tag{3-20g}$$

$$\begin{aligned}\partial_3\partial_1 = &-\frac{\cos\psi}{\sin\theta}\frac{\partial^2}{\partial\phi\partial\psi} + \sin\psi\frac{\partial^2}{\partial\theta\partial\psi} + \cot\theta\cos\psi\frac{\partial^2}{\partial\psi^2}\\ &+\frac{\sin\psi}{\sin\theta}\frac{\partial}{\partial\phi} + \cos\psi\frac{\partial}{\partial\theta} - \cot\theta\sin\psi\frac{\partial}{\partial\psi},\end{aligned} \tag{3-20h}$$

$$\begin{aligned}\partial_3\partial_2 = &\frac{\sin\psi}{\sin\theta}\frac{\partial^2}{\partial\phi\partial\psi} + \cos\psi\frac{\partial^2}{\partial\theta\partial\psi} - \cot\theta\sin\psi\frac{\partial^2}{\partial\psi^2}\\ &+\frac{\cos\psi}{\sin\theta}\frac{\partial}{\partial\phi} - \sin\psi\frac{\partial}{\partial\theta} - \cot\theta\cos\psi\frac{\partial}{\partial\psi}.\end{aligned} \tag{3-20i}$$

Recall that $\nabla^2_{\mathbf{\Omega}} = {}_{\Omega}g^{\alpha\beta}(\partial/\partial\Omega_\alpha)(\partial/\partial\Omega_\beta) = {}_{\Omega}g^{\alpha\beta}\partial_\alpha\partial_\beta$, and also that the inverse of metric tensor in Ω-space ${}_{\Omega}g^{\alpha\beta} = \delta_{\alpha\beta}/2$ from (2-20). Hence, $\nabla^2_{\mathbf{\Omega}} = (1/2)\partial_\alpha\partial_\alpha$. Using (3-20a) to (3-20c), we recover (2-26).

From (3-20) we recognize that the covariant derivatives in Ω-space do not commute. In fact, we have the commutator

$$\frac{\partial}{\partial\Omega_\alpha}\frac{\partial}{\partial\Omega_\beta} - \frac{\partial}{\partial\Omega_\beta}\frac{\partial}{\partial\Omega_\alpha} = \left[\frac{\partial}{\partial\Omega_\alpha}, \frac{\partial}{\partial\Omega_\beta}\right] = \varepsilon_{\alpha\beta\lambda}\frac{\partial}{\partial\Omega_\lambda}, \tag{3-21}$$

which defines the Lie bracket of $\partial/\partial\Omega_j$.

Using (3-19) with matrix $\mathbf{A}$ given by (2-10), a lengthy and tedious calculation eventually yields

$$\begin{aligned}&\begin{pmatrix} \frac{\partial^2}{\partial\phi^2} & \frac{\partial^2}{\partial\phi\partial\theta} & \frac{\partial^2}{\partial\phi\partial\psi} \\ \frac{\partial^2}{\partial\phi\partial\theta} - \cot\theta\frac{\partial}{\partial\phi} + \csc\theta\frac{\partial}{\partial\psi} & \frac{\partial^2}{\partial\theta^2} & \frac{\partial^2}{\partial\theta\partial\psi} \\ \frac{\partial^2}{\partial\phi\partial\psi} - \sin\theta\frac{\partial}{\partial\theta} & \frac{\partial^2}{\partial\theta\partial\psi} + \csc\theta\frac{\partial}{\partial\phi} - \cot\theta\frac{\partial}{\partial\psi} & \frac{\partial^2}{\partial\psi^2} \end{pmatrix}\\ &= A_{\mu\alpha}A_{\nu\beta}\frac{\partial}{\partial\Omega_\mu}\frac{\partial}{\partial\Omega_\nu} = A_{\mu\alpha}A_{\nu\beta}\left[\frac{\partial^2}{\partial\Omega_\mu\partial\Omega_\nu} - {}_{\Omega}\Gamma^\gamma_{\mu\nu}\frac{\partial}{\partial\Omega_\gamma}\right].\end{aligned} \tag{3-22}$$

Although matrix (3-22) is different from (3-17), the respective tensor contractions of the two matrices with $d\Phi_\alpha d\Phi_\beta$ are identical. Indeed, we have

$$d\Phi_\alpha d\Phi_\beta\left[\frac{\partial^2}{\partial\Phi_\alpha\partial\Phi_\beta} - {}_{\Phi}\Gamma^\gamma_{\alpha\beta}\frac{\partial}{\partial\Phi_\gamma}\right] = d\Omega_\alpha d\Omega_\beta\left[\frac{\partial^2}{\partial\Omega_\alpha\partial\Omega_\beta} - {}_{\Omega}\Gamma^\gamma_{\alpha\beta}\frac{\partial}{\partial\Omega_\gamma}\right], \tag{3-23}$$

which proves the equivalence of (3-4) and (3-7). Whereas it may seem that (3-23) is a proven fact, a proof was in fact necessary, because in angular space (Φ-space or Ω-space) finite rotations do not commute (cf., for example, the commutation relation (3-21)). Q.E.D.

§4. Moments of Linear Elastic Polymer Chains in 3D

In §2 and §3, we concluded that the Green's function of a linear elastic chain under a constant external force $\mathbf{f}$ and constant external torque $\boldsymbol{\tau}$ satisfies the following differential equation:

$$\left[\frac{\partial}{\partial s} - \sum_{j=1}^{3} A_j[\hat{\mathbf{a}}_j \cdot (\nabla_{\Omega} - \boldsymbol{\tau})]^2 - \sum_{j=1}^{3} B_j[\hat{\mathbf{a}}_j \cdot (\nabla_{\mathbf{r}} - \mathbf{f})]^2 + \sum_{j=1}^{3} \omega_j^0[\hat{\mathbf{a}}_j \cdot (\nabla_{\Omega} - \boldsymbol{\tau})] + \sum_{j=1}^{3} t_j^0[\hat{\mathbf{a}}_j \cdot (\nabla_{\mathbf{r}} - \mathbf{f})]\right] G = \delta(s)\delta(\mathbf{r} - \mathbf{r}_0)\delta(\boldsymbol{\Phi} - \boldsymbol{\Phi}_0). \quad (4\text{-}1)$$

Although the A_j's and B_j's are generally functions of material length s, for simplicity in what follows they will be assumed to be constants. This amounts to assuming homogeneous elasticity along the chain.

Taking the Laplace transform with respect to s and the Fourier transform with respect to $\mathbf{r}$, $\nabla_{\mathbf{r}} - \mathbf{f}$ becomes $-i(\mathbf{k} - i\mathbf{f})$. If we denote the Fourier transform of $G(\mathbf{r}, \boldsymbol{\Phi}; s \,|\, \mathbf{r}_0, \boldsymbol{\Phi}_0; 0; \mathbf{f}; \boldsymbol{\tau})$ by $F(\mathbf{k}, \boldsymbol{\Phi}; s \,|\, \mathbf{r}_0, \boldsymbol{\Phi}_0; 0; \mathbf{f}; \boldsymbol{\tau})$ and the Laplace-Fourier transform of G by $I(\mathbf{k}, \boldsymbol{\Phi}; p \,|\, \mathbf{r}_0, \boldsymbol{\Phi}_0; 0; \mathbf{f}; \boldsymbol{\tau})$, then I satisfies

$$\left[p - \sum_{j=1}^{3} A_j[\hat{\mathbf{a}}_j \cdot (\nabla_{\Omega} - \boldsymbol{\tau})]^2 + \sum_{j=1}^{3} B_j[\hat{\mathbf{a}}_j \cdot (\mathbf{k} - i\mathbf{f})]^2 + \sum_{j=1}^{3} \omega_j^0[\hat{\mathbf{a}}_j \cdot (\nabla_{\Omega} - \boldsymbol{\tau})] - i\sum_{j=1}^{3} t_j^0[\hat{\mathbf{a}}_j \cdot (\mathbf{k} - i\mathbf{f})]\right] I = \delta(\boldsymbol{\Phi} - \boldsymbol{\Phi}_0). \quad (4\text{-}2)$$

From (4-2), the Fourier transform of the Green's function $G(\mathbf{r}; \mathbf{f}; \boldsymbol{\tau})$ with external force $\mathbf{f}$ (and external torque $\boldsymbol{\tau}$) can be obtained simply by replacing vector $\mathbf{k}$ by $\mathbf{k} - i\mathbf{f}$ in the expression for the force-free Green's function ($\mathbf{f} = \mathbf{0}$). If we denote the force-free chain Green's function and its Fourier transform by $G(\mathbf{r}; \mathbf{0}; \boldsymbol{\tau})$ and $F(\mathbf{k}; \mathbf{0}; \boldsymbol{\tau})$ respectively, then

$$F(\mathbf{k}, \boldsymbol{\Phi}; s \,|\, \mathbf{r}_0, \boldsymbol{\Phi}_0; 0; \mathbf{f}; \boldsymbol{\tau}) = \frac{1}{C} F(\mathbf{k} - i\mathbf{f}, \boldsymbol{\Phi}; s \,|\, \mathbf{r}_0, \boldsymbol{\Phi}_0; 0; \mathbf{0}; \boldsymbol{\tau}), \quad (4\text{-}3)$$

where C is some constant chosen to ensure that the F functions on both sides are properly normalized. Upon taking the inverse Fourier transform of both sides of (4-3), with simplified arguments, and assuming $\mathbf{f}$ to be a constant external force, we obtain

$$\begin{aligned} G(\mathbf{r}; \mathbf{f}; \boldsymbol{\tau}) &= \frac{1}{(2\pi)^3} \int e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}_0)} F(\mathbf{k}; \mathbf{f}; \boldsymbol{\tau})\, d^3\mathbf{k} \\ &= \frac{1}{C(2\pi)^3} \int e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}_0)} F(\mathbf{k} - i\mathbf{f}; \mathbf{0}; \boldsymbol{\tau})\, d^3\mathbf{k} \\ &= \frac{e^{\mathbf{f}\cdot(\mathbf{r}-\mathbf{r}_0)}}{C(2\pi)^3} \int e^{-i(\mathbf{k}-i\mathbf{f})\cdot(\mathbf{r}-\mathbf{r}_0)} F(\mathbf{k} - i\mathbf{f}; \mathbf{0}; \boldsymbol{\tau})\, d^3(\mathbf{k} - i\mathbf{f}) \\ &= \frac{e^{\mathbf{f}\cdot(\mathbf{r}-\mathbf{r}_0)}}{C} G(\mathbf{r}; \mathbf{0}; \boldsymbol{\tau}), \end{aligned} \quad (4\text{-}4)$$

which is identical to (2-34), as expected. Assuming G_0 to be normalized, the constant C is necessary to ensure that G is also properly normalized. Since the Green's function with constant external force is just a force-free Green's function multiplied by $e^{\mathbf{f}\cdot(\mathbf{r}-\mathbf{r}_0)}$, we will only discuss the force-free Green's function in what follows.

The eigen-functions of the differential operator $\nabla_{\mathbf{\Omega}}$ in Euler angle space are the Wigner functions defined by [Edm1,Dav1]

$$\mathcal{D}^l_{m,n}(\phi,\theta,\psi)$$
$$= c_l\sqrt{\frac{(l+n)!(l-n)!}{(l+m)!(l-m)!}}[\cos(\theta/2)]^{n+m}[\sin(\theta/2)]^{n-m}P^{(n-m,n+m)}_{l-n}(\cos\theta)\,e^{im\phi+in\psi}, \tag{4-5}$$

where

$$c_l=\sqrt{\frac{2l+1}{8\pi^2}}, \tag{4-6}$$

and $P^{(\alpha,\beta)}_n(x)$ is the Jacobi polynomial defined by

$$P^{(\alpha,\beta)}_n(x)=\frac{(-1)^n}{2^n n!}(1-x)^{-\alpha}(1+x)^{-\beta}\frac{d^n}{dx^n}[(1-x)^{\alpha+n}(1+x)^{\beta+n}]. \tag{4-7}$$

If we denote $c^n_l=\sqrt{(l-n)(l+n+1)}$ and $i=\sqrt{-1}$, then the eigen-equations are

$$(\hat{\mathbf{a}}_1\cdot\nabla_{\mathbf{\Omega}})\mathcal{D}^l_{m,n}=\frac{i}{2}[c^n_l\mathcal{D}^l_{m,n+1}+c^{-n}_l\mathcal{D}^l_{m,n-1}], \tag{4-8a}$$

$$(\hat{\mathbf{a}}_2\cdot\nabla_{\mathbf{\Omega}})\mathcal{D}^l_{m,n}=-\frac{1}{2}[c^n_l\mathcal{D}^l_{m,n+1}-c^{-n}_l\mathcal{D}^l_{m,n-1}], \tag{4-8b}$$

$$(\hat{\mathbf{a}}_3\cdot\nabla_{\mathbf{\Omega}})\mathcal{D}^l_{m,n}=in\mathcal{D}^l_{m,n}. \tag{4-8c}$$

The orthogonality property of Wigner functions is such that

$$\int\mathcal{D}^l_{m,n}\mathcal{D}^{l'*}_{m',n'}\sin\theta d\theta\,d\phi\,d\psi=\delta_{ll'}\delta_{mm'}\delta_{nn'}. \tag{4-9}$$

One can thus expand the Laplace-Fourier transform I appearing in (4-2) in a series of Wigner functions and thereby obtain a system of algebraic equations satisfied by the expansion coefficients. Thus, an infinite series representation of the free-chain Green's function can in principal be obtained. However, since the differential equation (4-1) satisfied by the Green's function is known, all the positive power moments of the distribution (i.e., the Green's function) can be calculated without knowing the functional form of the distribution itself. We now calculate the first few moments of the distribution.

For simplicity we will use DNA as a model system, and suppose the chain has no intrinsic bending ($\omega^0_1=\omega^0_2=0$), no intrinsic shearing ($t^0_1=t^0_2=0$), and that the bending and shearing are isotropic ($A_1=A_2$, $B_1=B_2$). Upon multiplying (4-1) by any function $M(\mathbf{r},\mathbf{\Phi};s)$ which does not depend explicitly on s (i.e., $\partial M/\partial s=0$), and integrating with respect to $d^3\mathbf{r}\, d^3\mathbf{\Phi}\, d^3\mathbf{r}_0\, d^3\mathbf{\Phi}_0$, we obtain the dimensionless Laplace transform,

$$\begin{aligned}\langle N\rangle_p &= p\int_0^\infty \langle M\rangle_s\, e^{-ps} ds \\ &= p\int_0^\infty e^{-ps} ds \int M(\mathbf{r},\mathbf{\Phi};s)\, G(\mathbf{r},\mathbf{\Phi};s\,|\,\mathbf{r}_0,\mathbf{\Phi}_0;0)\, d^3\mathbf{r}\, d^3\mathbf{\Phi}\, d^3\mathbf{r}_0\, d^3\mathbf{\Phi}_0,\end{aligned} \tag{4-10}$$

which satisfies the following equation:

$$\begin{aligned}p\langle N\rangle_p - p\langle M\rangle_{s=0} &= \sum_{k=1}^{3} A_k\langle(\hat{\mathbf{a}}_k\cdot\nabla_\Omega)^2 N\rangle_p + \sum_{k=1}^{3} B_k\langle(\hat{\mathbf{a}}_k\cdot\nabla_\mathbf{r})^2 N\rangle_p \\ &\quad + \omega_3^0\langle(\hat{\mathbf{a}}_3\cdot\nabla_\Omega)N\rangle_p + t_3^0\langle(\hat{\mathbf{a}}_3\cdot\nabla_\mathbf{r})N\rangle_p.\end{aligned} \tag{4-11}$$

Using (4-11), all moments of the form $\langle N^{(k)}_{l_1,l_2,l_3}\rangle_p \equiv \langle r^k(\mathbf{r}\cdot\hat{\mathbf{a}}_1)^{l_1}(\mathbf{r}\cdot\hat{\mathbf{a}}_2)^{l_2}(\mathbf{r}\cdot\hat{\mathbf{a}}_3)^{l_3}\rangle$ can be calculated if each of $\{k,l_1,l_2,l_3\}$ is non-negative and at least one is positive (to ensure that $\langle M^{(k)}_{l_1,l_2,l_3}\rangle_{s=0}\to 0$ as $s\to 0$). Using (2-24) and (2-26) it is easy to show that

$$(\hat{\mathbf{a}}_\alpha\cdot\nabla_\Omega)\hat{\mathbf{a}}_\beta = \frac{1}{\sqrt{2}}\varepsilon_{\alpha\beta\gamma}\hat{\mathbf{a}}_\gamma, \tag{4-12}$$

$$\nabla_\Omega^2\hat{\mathbf{a}}_\beta = -\hat{\mathbf{a}}_\beta. \tag{4-13}$$

Using these identities, we obtain the recurrence formula

$$\begin{aligned}p\langle N^{(k)}_{l_1,l_2,l_3}\rangle_p &= A_1\Big[l_2(l_2-1)\langle N^{(k)}_{l_1,l_2-2,l_3+2}\rangle_p + l_3(l_3-1)\langle N^{(k)}_{l_1,l_2+2,l_3-2}\rangle_p \\ &\quad - (l_2+l_3+2l_2l_3)\langle N^{(k)}_{l_1,l_2,l_3}\rangle_p\Big] + A_2\Big[l_3(l_3-1)\langle N^{(k)}_{l_1+2,l_2,l_3-2}\rangle_p \\ &\quad + l_1(l_1-1)\langle N^{(k)}_{l_1-2,l_2,l_3+2}\rangle_p - (l_1+l_3+2l_1l_3)\langle N^{(k)}_{l_1,l_2,l_3}\rangle_p\Big] \\ &\quad + A_3\Big[l_1(l_1-1)\langle N^{(k)}_{l_1-2,l_2+2,l_3}\rangle_p + l_2(l_2-1)\langle N^{(k)}_{l_1+2,l_2-2,l_3}\rangle_p \\ &\quad - (l_1+l_2+2l_1l_2)\langle N^{(k)}_{l_1,l_2,l_3}\rangle_p\Big] + B_1\Big[k(k-2)\langle N^{(k-4)}_{l_1+2,l_2,l_3}\rangle_p \\ &\quad + k(2l_1+1)\langle N^{(k-2)}_{l_1,l_2,l_3}\rangle_p + l_1(l_1-1)\langle N^{(k)}_{l_1-2,l_2,l_3}\rangle_p\Big] \\ &\quad + B_2\Big[k(k-2)\langle N^{(k-4)}_{l_1,l_2+2,l_3}\rangle_p + k(2l_2+1)\langle N^{(k-2)}_{l_1,l_2,l_3}\rangle_p \\ &\quad + l_2(l_2-1)\langle N^{(k)}_{l_1,l_2-2,l_3}\rangle_p\Big] + B_3\Big[k(k-2)\langle N^{(k-4)}_{l_1,l_2,l_3+2}\rangle_p \\ &\quad + k(2l_3+1)\langle N^{(k-2)}_{l_1,l_2,l_3}\rangle_p + l_3(l_3-1)\langle N^{(k)}_{l_1,l_2,l_3-2}\rangle_p\Big]\end{aligned}$$

$$+\omega_3^0\left[l_1\langle N^{(k)}_{l_1-1,l_2+1,l_3}\rangle_p - l_2\langle N^{(k)}_{l_1+1,l_2-1,l_3}\rangle_p\right]$$

$$+ t_3^0\left[k\langle N^{(k-2)}_{l_1,l_2,l_3+1}\rangle_p + l_3\langle N^{(k)}_{l_1,l_2,l_3-1}\rangle_p\right]. \quad (4\text{-}14)$$

Using the recurrence formulae and taking the inverse Laplace transform, allows one to obtain all positive-power moments. The first few moments thereby obtained are as follows:

$$\langle \mathbf{r}\rangle = \frac{t_3^0(1-e^{-2A_1 s})}{2A_1}\hat{\mathbf{a}}_3^0, \quad (4\text{-}15a)$$

$$\begin{pmatrix}\langle\hat{\mathbf{a}}_1\rangle\\ \langle\hat{\mathbf{a}}_2\rangle\\ \langle\hat{\mathbf{a}}_3\rangle\end{pmatrix} = e^{-(A_1+A_3)s}\begin{pmatrix}\cos(\omega_3^0 s) & \sin(\omega_3^0 s) & 0\\ -\sin(\omega_3^0 s) & \cos(\omega_3^0 s) & 0\\ 0 & 0 & e^{-(A_1-A_3)s}\end{pmatrix}\cdot\begin{pmatrix}\hat{\mathbf{a}}_1^0\\ \hat{\mathbf{a}}_2^0\\ \hat{\mathbf{a}}_3^0\end{pmatrix}, \quad (4\text{-}15b)$$

$$\langle \mathbf{r}\cdot\hat{\mathbf{a}}_1\rangle = \langle \mathbf{r}\cdot\hat{\mathbf{a}}_2\rangle = 0, \quad (4\text{-}15c)$$

$$\langle \mathbf{r}\cdot\hat{\mathbf{a}}_3\rangle = \frac{t_3^0(1-e^{-2A_1 s})}{2A_1}, \quad (4\text{-}15d)$$

$$\langle r^2\rangle = -\frac{(t_3^0)^2(1-e^{-2A_1 s})}{2A_1^2} + \left(\frac{(t_3^0)^2}{A_1} + 4B_1 + 2B_3\right)s, \quad (4\text{-}15e)$$

$$\langle R_g^2\rangle = \left(\frac{(t_3^0)^2}{6A_1} + \frac{2}{3}B_1 + \frac{1}{3}B_3\right)L - \frac{2A_1^2L^2 - 2A_1L + 1 - e^{-2A_1L}}{8A_1^4L^2}(t_3^0)^2, \quad (4\text{-}15f)$$

where $\hat{\mathbf{a}}_j^0 \equiv \hat{\mathbf{a}}_j(s=0)$, and $\langle R_g^2\rangle = (1/L^2)\int_0^L ds\int_0^s dt\langle r^2(s-t)\rangle$ is the mean square radius of gyration. Note that (4-15) is derived assuming $\omega_1^0 = \omega_2^0 = 0$ (no intrinsic bending), $t_1^0 = t_2^0 = 0$ (no intrinsic shearing). Should these conditions be suppressed, (4-15c) would become a diffent expression. The non-vanishing of $\langle \mathbf{r}\cdot\hat{\mathbf{a}}_j\rangle$ for all $j(=1,2,3)$ indeed leads to a persistence vector.

Setting $A_1 = A_2 = \lambda$ (isotropic bending), $A_3 = 0$ (no twisting), $B_1 = B_2 = B_3 = 0$ (no shearing and stretching), $t_3^0 = 1$ (no intrinsic stretching and identifying s as identical to arc length), and $\omega_3^0 = 0$ (no intrinsic twisting), the resulting moments become identical to those of classical Kratky-Porod wormlike chain.

From (4-15) we notice that the deformations of shearing and stretching (associated with $\{B_1, B_2, B_3\}$ and t_3^0) contribute terms linear in s (or L) to $\langle r^2\rangle$ (or $\langle R^2\rangle$). We now list various limiting behaviors of $\langle r^2\rangle$ for deformable chains (choosing $t_3^0 = 1$):

(1) Random coil limit: When $s \gg A_1^{-1}$, $\langle r^2\rangle = (4B_1 + 2B_3 + A_1^{-1})s$.

(2) Near-rod limit: When $A_1^{-1} \gg s \gg 4B_1 + 2B_3$, $\langle r^2\rangle = s^2$. The chain is too rigid to sustain each of all four types of deformations (bending, twisting, shearing and stretching).

(3) Rigid-spring limit: When $A_1^{-1} \ll s \ll 4B_1 + 2B_3$, $\langle r^2\rangle = (4B_1 + 2B_3)s \gg s^2$. The chain is shearable and stretchable, yet too rigid to sustain bending and twisting. This resembles a rigid spring.

We can estimate the above various elastic constants using double helix DNA as the model system. We take the radius of DNA cross section to be $a_c = 1\,\mathrm{nm}$, temperature $T = 300\,\mathrm{K}$. According to experimental data for DNA bending and twisting elasticity [Hag1,Smi1], Young's modulus is $E = (3.46 \pm 0.3) \times 10^8\,\mathrm{Pa}$, with Poisson's ratio $E/(2G) - 1 = \sigma = 0.32$. Hence the shear modulus is $G = 1.31 \times 10^8\,\mathrm{Pa}$. One of the principal moments of inertia in the cross-sectional plane is given by $I_1 = \pi a_c^4/8 = 3.93 \times 10^{-37}\,\mathrm{m}^4$, whereas the one in the tangent direction is $I_3 = 2I_1$ [Lan2]. Bending rigidity is $\kappa = 2EI_1 = 2.72 \times 10^{-28}\,\mathrm{J{\cdot}m}$. From these data, we readily find $A_1^{-1} = A_2^{-1} = \kappa/k_BT = 56.5$ nm (the same as the persistence length of DNA), $A_3^{-1} = 4GI_3/k_BT = 99\,\mathrm{nm}$, $B_1 = B_2 = k_BT/(2G\pi a_c^2) = 0.005\,\mathrm{nm}$, and $B_3 = k_BT/(2E\pi a_c^2) = 0.002\,\mathrm{nm}$. Recall that various deformations are associated with A_j and B_j via $\{A_1, A_2\} \Leftrightarrow$ bending; $A_3 \Leftrightarrow$ twisting; $\{B_1, B_2\} \Leftrightarrow$ shearing; $B_3 \Leftrightarrow$ stretching. We thus see that bending and twisting are the dominant types of deformation for DNA without external forces and torques. However, this is no longer true when external forces and torques are applied to overstretch and overtwist single DNA molecules.

§5. Distribution Function of a Typical Linear Elastic Chain

In this section we solve the Green's function for a chain characterized by some particular choices of deformation moduli and without external force ($\mathbf{f} = \mathbf{0}$) or torque ($\boldsymbol{\tau} = \mathbf{0}$).

From the numerical data for DNA elasticity shown at the end of §4, we notice that the shearing constants $B_1 = B_2$ are of the same magnitude as the stretching constant B_3. Suppose that in fact the shearing and stretching constants are equal: $B_j = \mu$ $(j = 1, 2, 3)$. From (3-11), the term $\sum_k B_k(\hat{\mathbf{a}}_k \cdot \nabla_{\mathbf{r}})^2 G$ then becomes $\mu \nabla_{\mathbf{r}}^2 G$, which drastically simplifies the differential equation governing the Green's function.

In this simplified linear elastic chain model, μ can be thought of as a mean shearing-stretching constant. This picture is not too far removed from physical reality. However, even more important is the fact that the mathematical structure of the resulting model is very close to that of the Kratky-Porod wormlike chain. Recall from §1 that it has not been possible to find the exact asymptotic solution for the wormlike chain distribution function. Here "exact" asymptotic solution is defined in the sense that it is one which generates exact moments. Recall also from §4 that exact moments can be obtained directly from the differential equation without solving the latter; therefore, it is always possible to confirm approximate solutions of the distribution function to establish that the resulting moments derived from the solution agree with the exact ones obtained directly from the differential equation. Daniels' distribution for the wormlike chain is but an approximate solution, valid only in the long chain limit, and hence one which does not give exact moments (cf. [Yam1] p. 56, for example; compare his equations (9.86) through (9.88) with (9.113)). With the newly introduced shearing-stretching mode, it becomes possible to obtain the exact asymptotic solution in the sense that exact moments can be obtained directly from the solution, provided that enough terms are included in the asymptotic expansion—each of the remaining asymptotic terms contributing exactly zero to the moments. Recall upon suppressing the shearing and stretching modes, our simplified linear elastic chain reduces to the Kratky-Porod wormlike chain. Upon setting $\mu = 0$ in the moments thereby obtained, we arrive at the exact moments of the Kratky-Porod wormlike chain.

It is reasonable to assume isotropic bending, $A_1 = A_2 = 2\lambda$. We further assume the chain either has no twisting mode (unable to sustain twist) or has vanishing twisting elasticity (twist does not cost elastic potential energy). The factor of 2 is consistent with conventional notation. At the end of §4 it is seen that for DNA $A_1^{-1} = A_2^{-1}$ are the same as the persistence length, which is half of the Kuhn's statistical segment length, λ^{-1}. Note from §2 that ψ is the angle of twist about body-axis $\hat{\mathbf{a}}_3$ (tangent direction of the chain in case of no shearing). Therefore, for a chain without twisting, G is independent of ψ: $\partial G/\partial \psi = 0$. Let us also suppose that the chain has no intrinsic bending or twisting ($\forall j$, $\omega_j^0 = 0$), and no intrinsic shearing or stretching ($t_j^0 = \delta_{j,3}$). These parameters correspond to some typical state of deformation for elastic chains in the absence of external force or torque.

Now, since $\partial G/\partial \psi = 0$, the operator $2\nabla_{\Omega}^2$ reduces to the first two terms in (2-26)—which is identical to $\nabla_{\hat{\mathbf{u}}}^2$, the Laplacian on S^2, where $\hat{\mathbf{u}} = (1, \theta, \phi)$ in a space-fixed spherical coordinate frame. Similarly, it is easy to show that under the same circumstances, the term $\sum_k A_k(\hat{\mathbf{a}}_k \cdot \nabla_{\mathbf{\Omega}})^2 G$ reduces to $\lambda\nabla^2_{\hat{\mathbf{u}}}G$.

The configuration space for this chain is confined to a subspace of $\mathcal{R}^3 \times SO(3)$. Since the Euler angles θ and ϕ are respectively identical to the polar angle θ and azimuthal angle ϕ of $\hat{\mathbf{a}}_3$ in a space-fixed spherical coordinate system, and since $\hat{\mathbf{a}}_3(s) \in S^2$, the configuration space of this particular chain is $\mathcal{R}^3 \times S^2$. For isotropic shearing, $\hat{\mathbf{a}}_3$ is on average identical to the unit tangent vector $\hat{\mathbf{u}}$. For simplicity, let the origin of the space-frame be coincident with one end of the chain ($\mathbf{r}_0 = 0$), and let the initial tangent vector of the chain at this end lie in the $\hat{\mathbf{e}}_z$ direction. In such circumstances the Green's function becomes $G(\mathbf{r}, \hat{\mathbf{u}}; s \,|\, \mathbf{0}, \hat{\mathbf{e}}_z; 0)$, and the differential equation (3-11) reduces to

$$\frac{\partial G}{\partial s} + \hat{\mathbf{u}} \cdot \nabla_{\mathbf{r}} G - \mu\nabla^2_{\mathbf{r}}G - \lambda\nabla^2_{\hat{\mathbf{u}}}G = \delta(s)\delta^3(\mathbf{r})\delta^2(\hat{\mathbf{u}} - \hat{\mathbf{e}}_z). \tag{5-1}$$

Upon setting $\mu = 0$ in (5-1) the resulting differential equation becomes identical with the classical Kratky-Porod chain (no twisting, shearing, or stretching). To gain some physical insight into (5-1), note that $\hat{\mathbf{u}} \cdot \nabla_{\mathbf{r}} G$ constitutes a convection term; that is, the chain has the tendency to persist in its original direction (a stiff chain, in contrast to the random-flight model of a Gaussian coil [Ray1,Wax1,Yam1]). On the other hand, the chain is not rigid; rather, its tangent vector is able to diffuse from its initial direction of $\hat{\mathbf{e}}_z$ to everywhere on the unit sphere surface S^2, as demonstrated by the presence of the term $\lambda\nabla^2_{\hat{\mathbf{u}}}G$. The term $\mu\nabla^2_{\mathbf{r}}G$, representing diffusion in $\mathcal{R}^3$ space, arises from the fact that the chain is capable of shearing and stretching.

The number of independent variables characterizing the Green's function G is 5, namely three from $\mathbf{r}$ and two from $\hat{\mathbf{u}}$. However, since the system is statistically invariant to rotation of the space-frame, the number of independent variables of G can be reduced by two. The absolute orientations of $\mathbf{r}$ and $\hat{\mathbf{u}}$ are irrelevant to G; rather, G depends only on their relative orientation. In order to make use of the rotational invariance of the system and consequently to reduce the number of independent variables, we need two sets of coordinate systems—one space-frame and one body-frame. Let the body-axis $\hat{\mathbf{a}}_3(s) = \hat{\mathbf{e}}'_z(s) = \hat{\mathbf{u}}(s)$ point in the direction of the local tangent at s. Then $\hat{\mathbf{e}}_z$ and $\hat{\mathbf{u}}$ are both tangent vectors of the chain, the former being at one end of the chain, the latter at point s. Assuming that the statistical behavior of any part of the chain is the same as that of the whole chain, we can ignore the effect of the free end. Point s can then be thought of as simply another end of the chain. Therefore, the space-frame at $s = 0$ and body-frame at s can be viewed as located at two ends of the chain, with the corresponding z axis directed in the local tangent directions. Since the chain possesses head-tail symmetry, the two coordinates are statistically equivalent. Let (α, β) be spherical polar variables specifying $\hat{\mathbf{u}}$ in the space-frame, so that

$$\nabla^2_{\hat{\mathbf{u}}} = \frac{1}{\sin\alpha}\frac{\partial}{\partial\alpha}\left(\sin\alpha\frac{\partial}{\partial\alpha}\right) + \frac{1}{\sin^2\alpha}\frac{\partial^2}{\partial\beta^2}. \tag{5-2a}$$

Additionally let the spherical polar form of $\mathbf{r}$ in the body-frame be (r, θ, ϕ), and that of its Fourier conjugate $\mathbf{k}$ be (k, ψ, χ), also in the body-frame. For a chain with isotropic bending and with initial tangent in the $\hat{\mathbf{e}}_z$ direction, we expect G to be independent of the azimuthal angle of $\mathbf{r}$ in the space-frame. Since the two frames are equivalent, G must be independent of the azimuthal angle ϕ of $\mathbf{r}$ in the body-frame. This fact can be used to further reduce the number of independent variables from 3 to 2 (Recall that the system's invariance to rotations of the space-frame can be used to reduce the number of independent variables from 5 to 3). A transformation of independent variables from (α, β) to (θ, ϕ), coupled with the fact that G is independent of ϕ, transforms (5-2a) into

$$\nabla^2_{\hat{\mathbf{u}}} G = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial G}{\partial\theta}\right). \tag{5-2b}$$

Let $\Phi(\mathbf{k}, \hat{\mathbf{u}}; s)$ be the Fourier transform of $G(\mathbf{r}, \hat{\mathbf{u}}; s)$ (the arguments of G and of Φ will be simplified in what follows):

$$\Phi(\mathbf{k}, \hat{\mathbf{u}}; s) = \int G(\mathbf{r}, \hat{\mathbf{u}}; s)\, e^{i\mathbf{k}\cdot\mathbf{r}}\, d^3\mathbf{r}, \tag{5-3a}$$

$$G(\mathbf{r}, \hat{\mathbf{u}}; s) = \frac{1}{(2\pi)^3}\int \Phi(\mathbf{k}, \hat{\mathbf{u}}; s)\, e^{-i\mathbf{k}\cdot\mathbf{r}}\, d^3\mathbf{k}. \tag{5-3b}$$

Substitution into (5-1) shows that Φ satisfies the differential equation

$$\frac{\partial\Phi}{\partial s} - i\Phi\hat{\mathbf{u}}\cdot\mathbf{k} = -\mu k^2\Phi + \lambda\nabla^2_{\hat{\mathbf{u}}}\Phi. \tag{5-4}$$

By definition, we have that

$$\begin{aligned}
&\Phi(\mathbf{k}, \hat{\mathbf{u}}; s)\\
&\quad = \int G(r, \theta, \hat{\mathbf{u}}; s) \exp\big[irk(\sin\theta\sin\psi\cos(\phi-\chi) + \cos\theta\cos\psi)\big] r^2 dr \sin\theta d\theta d\phi\\
&\quad = 2\pi\int G(r, \theta, \hat{\mathbf{u}}; s) e^{irk\cos\theta\cos\psi} J_0(rk\sin\theta\sin\psi) r^2 dr \sin\theta d\theta,
\end{aligned} \tag{5-5}$$

where the dependence of Φ on χ is only through the combination $(\phi - \chi)$, which in turn disappears upon integration with respect to ϕ; (note that G is independent of ϕ). Φ is therefore independent of χ. Fourier transformation of (5-2b) gives

$$\nabla^2_{\hat{\mathbf{u}}}\Phi = \frac{1}{\sin\psi}\frac{\partial}{\partial\psi}\left(\sin\psi\frac{\partial\Phi}{\partial\psi}\right)$$

in the body-frame. Since $\mathbf{k} = (k, \psi, \chi)$ in the body-frame, and $\hat{\mathbf{u}} = \hat{\mathbf{e}}'_z$ lies along the local z-axis of the body-frame, it follows that $\hat{\mathbf{u}}\cdot\mathbf{k} = k\cos\psi$. Thus, (5-4) simplifies to the form

$$\frac{\partial\Phi}{\partial s} - i\Phi k\cos\psi = -\mu k^2\Phi + \lambda\frac{1}{\sin\psi}\frac{\partial}{\partial\psi}\left(\sin\psi\frac{\partial\Phi}{\partial\psi}\right), \tag{5-6}$$

whose differential operators do not involve $\hat{\mathbf{u}}$ explicitly. As such, we can integrate Φ with respect to $\hat{\mathbf{u}}$. For simplicity, however, we still denote by Φ the new function $\Phi = \Phi(\mathbf{k}; s) = \Phi(k, \psi; s) = \int \Phi(\mathbf{k}, \hat{\mathbf{u}}; s)\, d^2\hat{\mathbf{u}}$, with only two independent variables. That we have painstakingly used two coordinate systems (the space-frame and the body-frame) at the same time is only to permit taking full advantage of the head-tail symmetry of the chain and the rotational invariance of the system so as to reduce the number of independent variables from five to two. This in turn, renders an asymptotic solution possible.

Let

$$F(k, \psi; p) = p \int_0^\infty \Phi(k, \psi; s)\, e^{-ps}\, ds$$

be the dimensionless Laplace transform of Φ. An extra p is introduced so that both Φ and F are properly normalized. Upon setting $x \equiv \cos\psi$ and noting that $\Phi(\mathbf{k}; s = 0) = 1$ from the delta function source of G at $s = 0$, we find upon taking the Laplace transform of both sides of above equation that

$$(p - ikx + \mu k^2)F = p + \lambda \frac{\partial}{\partial x}\left[(1 - x^2)\frac{\partial F}{\partial x}\right]. \tag{5-7}$$

Upon expanding F in Legendre polynomials,

$$F(k, x; p) = \sum_{n=0}^{\infty} g_n(k; p) P_n(x),$$

we obtain a sequence of equations for the g_n's:

$$(p + \mu k^2) g_0 - \frac{ik}{3} g_1 = p, \tag{5-8a}$$

$$-\frac{ikn}{2n-1} g_{n-1} + \left[p + \mu k^2 + \lambda n(n+1)\right] g_n - \frac{ik(n+1)}{2n+3} g_{n+1} = 0. \tag{5-8b}$$

These can be conveniently expressed as $\mathbf{A}\mathbf{g} = p\mathbf{b}$, where $\mathbf{g}$ is a vector whose entries are $g_0, g_1, \ldots$; $\mathbf{b}$ is a constant vector whose i^{th} component is δ_{i0}, and $\mathbf{A}$ is the semi-infinite matrix (setting $p + \mu k^2 \equiv q$)

$$\mathbf{A} = \begin{pmatrix} q & \frac{-ik}{3} & 0 & 0 & 0 & 0 & \cdots \\ -ik & q + 2\lambda & \frac{-2ik}{5} & 0 & 0 & 0 & \cdots \\ 0 & \frac{-2ik}{3} & q + 6\lambda & \frac{-3ik}{7} & 0 & 0 & \cdots \\ 0 & 0 & \frac{-3ik}{5} & q + 12\lambda & \frac{-4ik}{9} & 0 & \cdots \\ 0 & 0 & 0 & \frac{-4ik}{7} & q + 20\lambda & \frac{-5ik}{11} & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \ddots & \end{pmatrix}. \tag{5-9a}$$

Unlike conventional notation, the matrix $\mathbf{A}$ starts with the zeroth row (column); g_0 is the Fourier transform of the isotropic part, $G(r; s)/(4\pi r^2)$, of $G(\mathbf{r}; s)$ in its expansion in Legendre polynomials. Denote by $\mathbf{A}^{k,m}$ the submatrix of $\mathbf{A}$ which starts with the k^{th} row/column and ends with the m^{th} row/column. Then $\mathbf{A} \equiv \mathbf{A}^{0,\infty}$. Upon inversion, $\mathbf{g}/p = \mathbf{A}^{-1}\mathbf{b}$. Since $b_i = \delta_{i0}$, $g_0/p = (\mathbf{A}^{-1})_{00}$ is the first entry of $\mathbf{A}^{-1}$. If $a_{k,m} = \det(\mathbf{A}^{k,m})$, then

$$\frac{g_0}{p} = (\mathbf{A}^{-1})_{00} = \lim_{m\to\infty} \frac{a_{1,m}}{a_{0,m}}. \tag{5-9b}$$

In general, we have

$$\frac{g_j}{p} = \lim_{m\to\infty} \frac{(2ik)^j\,(j!)^2\,a_{j+1,m}}{(2j)!\,a_{0,m}} \qquad (j \geq 0). \tag{5-9c}$$

Note that $a_{k,m}$ can be expressed as a sum of $a_{j,m}$'s ($j = k+1, k+2, \ldots$); for instance, $a_{0,m} = (p+\mu k^2)a_{1,m} + (k^2/3)a_{2,m}$. Therefore, g_j/p can be expressed in the form of a continued fraction. In particular, setting $p + \mu k^2 \equiv q$, we obtain

$$\frac{g_0}{p} = \cfrac{1}{q + \cfrac{k^2/3}{q+2\lambda + \cfrac{4k^2/15}{q+6\lambda + \cfrac{9k^2/35}{q+12\lambda + \cfrac{16k^2/63}{q+20\lambda + \cfrac{25k^2/99}{q+30\lambda + \cfrac{36k^2/143}{q+42\lambda + \cfrac{49k^2/195}{\cdots}}}}}}}}. \tag{5-10}$$

Rearrange g_0/p into a power series of $[p + \mu k^2 + j(j+1)\lambda]^{-1}, (j = 0, 1, 2, \ldots)$, and for simplicity set $q_n \equiv p + \mu k^2 + n\lambda$. This yields

$$\begin{aligned} \frac{g_0}{p} = \frac{1}{q_0} &- \left(\frac{k^2}{3}\right)\frac{1}{q_0^2 q_2} + \left(\frac{k^2}{3}\right)^2 \frac{1}{q_0^3 q_2^2} + \left(\frac{4k^2}{15}\right)\left(\frac{k^2}{3}\right)\frac{1}{q_0^2 q_2^2 q_6} \\ &- \left(\frac{k^2}{3}\right)^3 \frac{1}{q_0^4 q_2^3} - 2\left(\frac{4k^2}{15}\right)\left(\frac{k^2}{3}\right)^2 \frac{1}{q_0^3 q_2^3 q_6} - \left(\frac{4k^2}{15}\right)^2\left(\frac{k^2}{3}\right)\frac{1}{q_0^2 q_2^3 q_6^2} \\ &- \left(\frac{9k^2}{35}\right)\left(\frac{4k^2}{15}\right)\left(\frac{k^2}{3}\right)\frac{1}{q_0^2 q_2^2 q_6^2 q_{12}} + \ldots, \end{aligned} \tag{5-11}$$

with similar expressions for the other g_n/p's.

Define $h_n(k;s)$ by the expressions

$$\Phi(\mathbf{k};s) = \Phi(k,\psi;s) = \sum_{n=0}^{\infty} h_n(k;s) P_n(\cos\psi), \tag{5-12a}$$

$$g_n(k;p) = p\int_0^{\infty} h_n(k;s)\,e^{-ps}\,ds; \tag{5-12b}$$

that is, the inverse dimensionless Laplace transform of $g_n(k;p)$ is $h_n(k;s)$. Note also from the above that the inverse dimensionless Laplace transform of a function

$f(p)$ is identical to the inverse conventional Laplace transform of $f(p)/p$. Taking the inverse dimensionless Laplace transformation of g_0 given by (5-11), we find that

$$h_0(k;s) = e^{-\mu k^2 s}\left[1 + k^2\left(\frac{1-e^{-2\lambda s}}{12\lambda^2} - \frac{s}{6\lambda}\right) + k^4\left(\frac{1-e^{-2\lambda s}}{60\lambda^4} - \frac{s(26+9e^{-2\lambda s})}{1080\lambda^3} + \frac{s^2}{72\lambda^2} - \frac{1-e^{-6\lambda s}}{6480\lambda^4}\right) + \dots\right], \tag{5-13a}$$

$$h_1(k;s) = e^{-\mu k^2 s}\, ik\left[\left(\frac{1-e^{-2\lambda s}}{2\lambda}\right) + k^2\left(\frac{26-27e^{-2\lambda s}+e^{-6\lambda s}}{360\lambda^3} + \frac{s(-5-3\,e^{-2\lambda s})}{60\lambda^2}\right) + \dots\right], \tag{5-13b}$$

$$h_2(k;s) = e^{-\mu k^2 s}\left[k^2\left(\frac{-2+3e^{-2\lambda s}-e^{-6\lambda s}}{36\lambda^2}\right) + k^4\left(\frac{-85-5e^{-6\lambda s}}{9072\lambda^4} + \frac{83e^{-2\lambda s}}{8400\lambda^4} + \frac{s(10+9e^{-2\lambda s})}{1080\lambda^3} - \frac{s\,e^{-6\lambda s}}{1512\lambda^3} + \frac{e^{-12\lambda s}}{25200\lambda^4}\right) + \dots\right], \tag{5-13c}$$

with similar expressions for the other h_n's. This, in turn, furnishes $\Phi(\mathbf{k};s)$ via (5-12a). Upon taking the inverse Fourier transform of $\Phi(\mathbf{k};s)$ we thereby obtain $G(\mathbf{r};s)$.

Recall that with the mean shearing-stretching constant $\mu = 0$, the current model reduces to the Kratky-Porod wormlike chain model. Setting $\mu = 0$ in (5-13), the inverse Fourier transform of h_0 becomes a sum of delta function and its derivatives, with similar results for the inverse Fourier transforms of the other h_n's. This is the primary reason why Daniels' distribution for a wormlike chain does not give exact moments. Moreover, it represents only the first-order approximation of the exact asymptotics in the long chain limit.

The asymptotic series for $G(\mathbf{r};s\,|\,\mathbf{0},\hat{\mathbf{e}}_z;0) = \int G(\mathbf{r},\hat{\mathbf{u}};s\,|\,\mathbf{0},\hat{\mathbf{e}}_z;0)\,d^2\hat{\mathbf{u}}$ is

$$\begin{aligned}
&G(\mathbf{r};s\,|\,\mathbf{0},\hat{\mathbf{e}}_z;0)\\
&= \left(\frac{1}{4\pi\mu s}\right)^{3/2} e^{-\frac{r^2}{4\mu s}}\Bigg\{\Bigg[1 + \left(\frac{3}{2\mu s} - \frac{r^2}{4\mu^2 s^2}\right)\left(\frac{1-e^{-2\lambda s}}{12\lambda^2} - \frac{s}{6\lambda}\right) + \left(\frac{15}{4\mu^2 s^2} - \frac{5r^2}{4\mu^3 s^3}\right.\\
&\quad \left.+ \frac{r^4}{16\mu^4 s^4}\right)\left(\frac{1-e^{-2\lambda s}}{60\lambda^4} - \frac{s(26+9e^{-2\lambda s})}{1080\lambda^3} + \frac{s^2}{72\lambda^2} - \frac{1-e^{-6\lambda s}}{6480\lambda^4}\right) + \dots\Bigg]\\
&\quad + P_1(\cos\theta)\Bigg[\frac{r(1-e^{-2\lambda s})}{4\lambda\mu s} + \left(\frac{26-27e^{-2\lambda s}+e^{-6\lambda s}}{360\lambda^3} + \frac{s(-5-3e^{-2\lambda s})}{60\lambda^2}\right)\\
&\quad \times\left(\frac{5r}{4\mu^2 s^2} - \frac{r^3}{8\mu^3 s^3}\right) + \dots\Bigg]\\
&\quad + P_2(\cos\theta)\Bigg[\frac{r^2(2-3e^{-2\lambda s}+e^{-6\lambda s})}{144\lambda^2\mu^2 s^2} + \left(\frac{r^4}{16\mu^4 s^4} - \frac{7r^2}{8\mu^3 s^3}\right)\left(\frac{-85-5e^{-6\lambda s}}{9072\lambda^4}\right.\\
&\quad \left.+ \frac{83e^{-2\lambda s}}{8400\lambda^4} + \frac{s(10+9e^{-2\lambda s})}{1080\lambda^3} - \frac{se^{-6\lambda s}}{1512\lambda^3} + \frac{e^{-12\lambda s}}{25200\lambda^4}\right) + \dots\Bigg] + \dots\Bigg\}.
\end{aligned} \tag{5-14}$$

The first few moments of the distribution function G can be easily obtained as

$$\langle \mathbf{r}\cdot\hat{\mathbf{u}}\rangle = \langle \mathbf{r}\cdot\hat{\mathbf{e}}_z\rangle = \frac{1-e^{-2\lambda s}}{2\lambda}, \tag{5-15a}$$

$$\langle \hat{\mathbf{u}}\rangle = e^{-2\lambda s}\hat{\mathbf{e}}_z, \tag{5-15b}$$

$$\langle r^2\rangle = s\left(6\mu + \frac{1}{\lambda}\right) - \frac{1-e^{-2\lambda s}}{2\lambda^2}, \tag{5-15c}$$

$$\langle (\mathbf{r}\cdot\hat{\mathbf{u}})^2\rangle = 2\mu s + \frac{s}{3\lambda} - \frac{1-e^{-6\lambda s}}{18\lambda^2}, \tag{5-15d}$$

$$\langle r^4\rangle = \frac{s^2(180\lambda^2\mu^2+60\lambda\mu+5)}{3\lambda^2} + \frac{se^{-2\lambda s}(10\lambda\mu-1)}{\lambda^3} + \frac{e^{-6\lambda s}}{54\lambda^4} - \frac{s(90\lambda\mu+26)}{9\lambda^3} - \frac{2e^{-2\lambda s}}{\lambda^4} + \frac{107}{54\lambda^4}. \tag{5-15e}$$

The equality $\langle \mathbf{r}\cdot\hat{\mathbf{u}}\rangle = \langle \mathbf{r}\cdot\hat{\mathbf{e}}_z\rangle$ is, as expected, a consequence of the head-tail symmetry of the chain. Since μ is the mean shearing-stretching constant, we note that shearing and stretching affect $\langle r^2\rangle$ in a manner linear in s when no external force and torque act.

From (5-15c), one can readily obtain the mean-square radius of gyration $\langle R_g^2\rangle = (1/L^2)\int_0^L dy \int_0^y dx \langle r^2(|x-y|)\rangle$ of the chain whose total material length is L:

$$\langle R_g^2\rangle = L\left(\mu + \frac{1}{6\lambda}\right) - \frac{1}{4\lambda^2} + \frac{1}{4\lambda^3 L} - \frac{1-e^{-2\lambda L}}{8\lambda^4 L^2}. \tag{5-15f}$$

To show that (5-15) constitute the correct moments, we return to the original partial differential equation (5-1). Multiplication of the latter by any function $M(\mathbf{r},\hat{\mathbf{u}};s)$ which does not depend explicitly on s (i.e., $\partial M/\partial s = 0$), followed by integration of both sides of the resulting equation with respect to $\mathbf{r}$ and $\hat{\mathbf{u}}$ yields

$$\frac{\partial\langle M\rangle}{\partial s} = \langle \hat{\mathbf{u}}\cdot\nabla_{\mathbf{r}} M\rangle + \mu\langle \nabla_{\mathbf{r}}^2 M\rangle + \lambda\langle \nabla_{\hat{\mathbf{u}}}^2 M\rangle, \tag{5-16}$$

with the expectation value defined by

$$\langle y\rangle = \int y(\mathbf{r},\hat{\mathbf{u}};s) G(\mathbf{r},\hat{\mathbf{u}};s\,|\,\mathbf{0},\hat{\mathbf{e}}_z;0) d^3\mathbf{r}\, d^2\hat{\mathbf{u}}.$$

Define the dimensionless Laplace transform:

$$\langle N(\mathbf{r},\hat{\mathbf{u}};p)\rangle_p = p\int_0^\infty \langle M(\mathbf{r},\hat{\mathbf{u}};s)\rangle_s e^{-ps} ds,$$

and take the transform of the above equation to obtain

$$p\langle N\rangle_p - p\langle M\rangle_{s=0} = \langle \hat{\mathbf{u}}\cdot\nabla_{\mathbf{r}} N\rangle_p + \mu\langle \nabla_{\mathbf{r}}^2 N\rangle_p + \lambda\langle \nabla_{\hat{\mathbf{u}}}^2 N\rangle_p. \tag{5-17}$$

Choose M successively as $\mathbf{r}\cdot\hat{\mathbf{u}}$, $\hat{\mathbf{u}}$, r^2, $(\mathbf{r}\cdot\hat{\mathbf{u}})^2$, and r^4, respectively, solve the corresponding systems of equations, and take the inverse Laplace transform only to recover equations (5-15). This shows (5-14) to be an exact asymptotic solution, in the sense that this solution generates exact moments provided that enough terms are included in the asymptotic expansion. This exactness is a consequence of the fact that each remaining term in the expansion contributes zero when calculating the moments. For instance, adding two more terms to (5-14) will give a correct $\langle r^6\rangle$ moment. This is different from Daniels' distribution, which is a first-order approximation to the asymptotic solution only in long chain limit.

In general, moments of arbitrary order can be expressed by the relation $C_{m,n} \equiv \langle(\mathbf{r}\cdot\hat{\mathbf{u}})^m r^n\rangle$. Using (5-17) we obtain a recurrence formula for the moments:

$$(p+\lambda m^2+\lambda m)C_{m,n} = nC_{m+1,n-2}+mC_{m-1,n}+\lambda m(m-1)C_{m-2,n+2} + \mu m(m-1)C_{m-2,n}+\mu(n^2+n+2nm)C_{m,n-2}. \quad (5\text{-}18)$$

Note when m is set to be zero, the recurrence of $\langle r^n\rangle$ changes the index from j to $j-2$ for each recurrence. This renders all positive even-powered moments $\langle r^{2k}\rangle$ solvable in closed form. For odd powered moments, $\langle r^{2k+1}\rangle$, the recurrence formula will eventually pass the zero power threshold and generate infinitely many negative-powered moments, which would have to be solved for first in order to obtain $\langle r^{2k+1}\rangle$. Thus, it is impossible using (5-18) to obtain closed-form solutions for positive odd-powered moments and for any negative-powered moments. One of the most important moments in polymer dynamics is $\langle 1/r\rangle$, which unfortunately is negatively powered. We will discuss its asymptotic solution in next section.

It can be shown that the leading order approximation of (5-14) in the long chain limit is identical to Daniels' distribution. To do this, set $\lambda s \gg 1$ and rearrange the summation in (5-13) (a resummation approach). Since the dominant terms, $1+(-k^2s/6\lambda)+(1/2!)(-k^2s/6\lambda)^2+\ldots$, can be grouped into $\exp(-k^2s/6\lambda)$, h_0 then becomes

$$h_0(k;s) = e^{-(\mu+\frac{1}{6\lambda})k^2 s}\left[1+k^2\left(\frac{1-e^{-2\lambda s}}{12\lambda^2}\right) + k^4\left(\frac{1-e^{-2\lambda s}}{60\lambda^4}-\frac{s(11+24e^{-2\lambda s})}{1080\lambda^3}-\frac{1-e^{-6\lambda s}}{6480\lambda^4}\right)+\ldots\right], \quad (5\text{-}19)$$

with similar expressions for the other h_n's. Note that (5-19) is a resummation of (5-13). The two alternate asymptotic expressions approximate identical functions, but manifest different asymptotic behavior in different limiting cases. For instance, (5-19) is only valid in the long chain limit (approaching Gaussian random coil). Upon forming the inverse Fourier transform of h_0 and setting $\mu = 0$, we readily obtain an asymptotic expression for the isotropic part, $G(r;s\,|\,\mathbf{0},\hat{\mathbf{e}}_z;0)$, of the distribution

$G(\mathbf{r}; s \,|\, \mathbf{0}, \hat{\mathbf{e}}_z; 0)$:

$$
\begin{aligned}
G(r; s) = 4\pi r^2 \left(\frac{3\lambda}{2\pi s}\right)^{\frac{3}{2}} e^{-\frac{3\lambda r^2}{2s}} \Bigg[1 &- \frac{5 + 30e^{-2\lambda s}}{8\lambda s} + \frac{107 - 108e^{-2\lambda s} + e^{-6\lambda s}}{48\lambda^2 s^2} \\
&+ r^2 \left(\frac{8 + 27e^{-2\lambda s}}{4s^2} - \frac{107 - 108e^{-2\lambda s} + e^{-6\lambda s}}{24\lambda s^3}\right) \\
&+ r^4 \left(-\frac{3\lambda(11 + 24e^{-2\lambda s})}{40s^3} + \frac{107 - 108e^{-2\lambda s} + e^{-6\lambda s}}{80s^4}\right) + \dots\Bigg].
\end{aligned}
\tag{5-20}
$$

This represents the first term of an infinite asymptotic expansion in Legendre polynomials. The other coefficients in the Legendre polynomial expansion can easily be obtained using the same approach. The leading-order approximation of the resulting distribution $G(\mathbf{r}; s)$ is identical to Daniels' distribution. To show this explicitly we note in the long chain limit, $e^{-n\lambda s} \to 0$ $(n = 2, 6)$, dropping all the exponential terms in the parenthesis in (5-20), we recover the isotropic part of the Daniels' distribution. The distribution function (5-20) is an exact asymptotic solution of the Green's function for the Kratky-Porod wormlike chain. The moments $\langle r^2 \rangle$ and $\langle r^4 \rangle$ obtained from the distribution (5-20) are identical to the exact moments obtained via other methods [Kra1,Ull1,Sai1].

§6. Distribution of the Wormlike Chain in the Near-Rod Limit

Upon taking explicit account of hydrodynamic interactions among segments of polymer molecules by using the Oseen tensor, Kirkwood and Riseman in 1948 [Kir1] developed a theory of polymer dynamics. Their theory of the frictional properties (intrinsic viscosity, frictional coefficient, and sedimentation coefficient) of polymers in solution has since become a classical work. According to their theory, the frictional properties of polymer molecules can be derived from the mean reciprocal distance $\langle 1/r\rangle(s)$ (inverse of the distance between two points on the chain averaged over all possible configurations as a function of arc length s between the two points). In 1956 Zimm [Zim1] proposed his famous dynamic model of flexible polymer chains, which approximates the hydrodynamic interactions among chain segments by preaveraging the Oseen tensor. The dynamical properties of the polymer chains can be calculated from the equilibrium mean reciproal distance $\langle 1/r\rangle(s)$. The Kirkwood-Riseman theory of frictional properties of polymer chains [Kir1] and Zimm's dynamic model of polymer chains [Zim1] make $\langle 1/r\rangle$ the most important moment in polymer dynamics. Unfortunately, it is a negative-powered moment. As such, closed-form solutions cannot be derived directly from the differential equation governing the distribution function.

The long chain (Gaussian random coil) limit of $\langle 1/r\rangle$ can readily be obtained from the exact expansion (5-14) with $\mu = 0$, or directly from (5-20). Recall that Daniels' distribution $P(\mathbf{r}; s \,|\, \mathbf{0}, \hat{\mathbf{e}}_z; 0)$ characterizes the behavior of a polymer chain very successfully in the long chain limit; in this limit $\langle 1/r\rangle$ has been obtained from Daniels' distribution by Hearst and Stockmayer [Hea1]. However, over the past 40 years, there has not been a satisfactory solution of the Green's function $G(\mathbf{r}, \hat{\mathbf{u}}; s \,|\, \mathbf{0}, \hat{\mathbf{e}}_z; 0)$, or the distribution $P(\mathbf{r}; s \,|\, \mathbf{0}, \hat{\mathbf{e}}_z; 0) = \int G(\mathbf{r}, \hat{\mathbf{u}}; s \,|\, \mathbf{0}, \hat{\mathbf{e}}_z; 0)\, d^2\hat{\mathbf{u}}$, in the short chain (near-rod) limit. Hearst and Stockmayer [Hea1] estimated the near-rod solution of $\langle 1/r\rangle$ by extrapolating it from both the corresponding long chain solution derived from Daniels' distribution, and the exact expression of $\langle r^2\rangle$ valid for all chain length. Recall the analogy between the path of a wormlike space curve and the quantum trajectory of a particle in a potential field. Thus finding the distribution function in the near-rod limit is equivalent to finding the solution of the Schrödinger equation in the classical limit. In 1973, Yamakawa and Fujii [Yam4] worked out a first-order approximation to the distribution in the near-rod limit by applying the WKB approximation to the path integral form of the distribution. However, only the first order approximation of the distribution can be derived from this approach. As such, only the first correction term to the leading order approximation $1/s$ of $\langle 1/r\rangle$ was obtained: $\langle 1/r\rangle = 1/s + \lambda/3 + \ldots$.

In this section, we will derive the distribution function and the moment $\langle 1/r\rangle$ for a wormlike chain in the near-rod limit. We start from equation (5-8) and set $\mu = 0$ in what follows; that is, we will study the near-rod limiting behavior of the Kratky-Porod wormlike chain, which is a special case of our general elastic chain. Note that the matrix $\mathbf{A}$ in (5-9a) has p appearing throughout its diagonal entries ($\mu = 0$ for our purpose here; hence $q \equiv p + \mu k^2 = p$). Since p is the Laplace variable conjugate to s, in the short chain limit $s \to 0$ and $p \to \infty$. Decompose $\mathbf{A}$ into two matrices and write $\mathbf{A} = p\mathbf{I} + \mathbf{B}$, where $\mathbf{I}$ is the identity matrix and $\mathbf{B}$ given by

$$\mathbf{B} = \begin{pmatrix} 0 & \frac{-ik}{3} & 0 & 0 & 0 & 0 & \cdots \\ -ik & 2\lambda & \frac{-2ik}{5} & 0 & 0 & 0 & \cdots \\ 0 & \frac{-2ik}{3} & 6\lambda & \frac{-3ik}{7} & 0 & 0 & \cdots \\ 0 & 0 & \frac{-3ik}{5} & 12\lambda & \frac{-4ik}{9} & 0 & \cdots \\ 0 & 0 & 0 & \frac{-4ik}{7} & 20\lambda & \frac{-5ik}{11} & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \ddots & \end{pmatrix}. \tag{6-1}$$

Recall that g_0 is the Fourier transform of the isotropic part, $G(r;s)/(4\pi r^2)$ of $G(\mathbf{r};s) = \int G(\mathbf{r},\hat{\mathbf{u}};s\,|\,\mathbf{0},\hat{\mathbf{e}}_z;0)\,d^2\hat{\mathbf{u}}$ in its expansion in Legendre polynomials. Hence, knowledge of g_0 suffices to calculate $\langle 1/r\rangle$. Since from (5-9b) $g_0/p = (\mathbf{A}^{-1})_{00}$, we have that

$$\frac{g_0}{p} = \frac{1}{p}\left[\left(\mathbf{I} + \frac{\mathbf{B}}{p}\right)^{-1}\right]_{00} = \sum_{j=0}^{\infty} \frac{(-1)^j(\mathbf{B}^j)_{00}}{p^{j+1}}. \tag{6-2}$$

Form the inverse Laplace transform and observe that the highest-order terms in the resulting expression can be exactly grouped into $\sin(sk)/sk$. Thus, we obtain

$$\begin{aligned} h_0(k;s) &= \sum_{j=0}^{\infty} \frac{(-s)^j(\mathbf{B}^j)_{00}}{j!} \\ &= \frac{\sin(sk)}{sk}\left[1 + (sk)^2\left(\frac{\lambda s}{9} - \frac{(\lambda s)^2}{18} + \frac{(\lambda s)^3}{45} - \frac{(\lambda s)^4}{135} + \ldots\right)\right. \\ &\qquad \left. + (sk)^4\left(\frac{\lambda s}{135} + \frac{(\lambda s)^2}{675} + \ldots\right) + \ldots\right]. \end{aligned} \tag{6-3}$$

The isotropic distribution $G(r;s\,|\,\mathbf{0},\hat{\mathbf{e}}_z;0)/(4\pi r^2) \equiv \mathcal{F}^{-1}(h_0)$—the inverse Fourier transform of h_0—can thus be obtained. It is well known that the characteristic function of a rigid rod distribution is $\sin(sk)/sk$. Accordingly, (6-3) gives the first pair of corrections to the rigid rod characteristic function for our short chain (near-rod) limit. Since k is the Fourier variable conjugate to r (r has the same order of magnitude as s in the near-rod limit), it follows that sk is of order 1. Moreover, in the near-rod limit, s is much smaller than the Kuhn's statistical segment length $1/\lambda$, i.e., $\lambda s \to 0$. Consequently, (6-3) represents an asymptotic expansion of the Fourier transform of $G(r;s\,|\,\mathbf{0},\hat{\mathbf{e}}_z;0)$ in the near-rod limit.

We have pointed out that knowledge of $h_0(k;s)$ suffices to calculate the moment $\langle 1/r\rangle$. To show this explicitly, note that

$$\begin{aligned} \left\langle \frac{1}{r} \right\rangle &= \int \frac{1}{r} G(\mathbf{r};s)\,d^3\mathbf{r} = \frac{1}{(2\pi)^3}\int \frac{1}{r} e^{-i\mathbf{k}\cdot\mathbf{r}}\,d^3\mathbf{r} \int \Phi(\mathbf{k};s)\,d^3\mathbf{k} \\ &= \frac{1}{\pi}\int_0^{\infty} dk \int_0^{\pi} \sin\psi\,d\psi \sum_{n=0}^{\infty} h_n(k;s)P_n(\cos\psi). \end{aligned}$$

Upon performing the integration with respect to ψ we obtain the desired expression, namely,

$$\langle \frac{1}{r} \rangle = \frac{2}{\pi} \int_0^\infty h_0(k;s)\,dk. \tag{6-4}$$

From (6-3) we observe that the leading order term of h_0 is $\sin(sk)/(sk)$. Upon substituting this term into (6-4), we find the leading order term of $\langle 1/r \rangle$ is $1/s$ which is correct for a chain in the near-rod limit. However, substitution of the remaining terms of (6-3) into (6-4) gives rise to an infinite sum of terms, each of which is divergent. Accordingly, we need to perform a resummation on (6-3). That a resummation may resolve the convergence problem is easy to understand. For instance, (5-19) is a resummation of (5-13), as is (6-3). They all derive from equation (5-8), with h_n being the inverse dimensionless Laplace transform of g_n. The three asymptotic expressions (5-13), (5-19), and (6-3) approximate the same identical function, but represent different asymptotic behavior in different limiting cases. Substituting (5-19) into (6-4) and setting $\mu = 0$ yields a well behaved asymptotic function of $\langle 1/r \rangle$ in the long chain limit. However, substituting (5-13) into (6-4) and setting $\mu = 0$, or else substituting (6-3) into (6-4) both lead to an infinite sum of terms, each of which is divergent.

We now perform the resummation of h_0. Observe that if we set $sk \equiv \kappa$ and $\lambda s \equiv t$ for simplicity, h_0 can be expressed as the sum

$$\begin{aligned}
h_0 = &\left[1 - \frac{\kappa^2}{3!} + \frac{\kappa^4}{5!} - \frac{\kappa^6}{7!} + \frac{\kappa^8}{9!} - \frac{\kappa^{10}}{11!} + \frac{\kappa^{12}}{13!} - \frac{\kappa^{14}}{15!} + \frac{\kappa^{16}}{17!} - \frac{\kappa^{18}}{19!} + \frac{\kappa^{20}}{21!} + \dots\right] \\
&+ t^1\left[\frac{2\kappa^2}{3\times 3!} - \frac{4\kappa^4}{3\times 5!} + \frac{2\kappa^6}{7!} - \frac{8\kappa^8}{3\times 9!} + \frac{10\kappa^{10}}{3\times 11!} - \frac{4\kappa^{12}}{13!} + \frac{14\kappa^{14}}{3\times 15!} - \frac{16\kappa^{16}}{3\times 17!} + \dots\right] \\
&+ t^2\left[-\frac{4\kappa^2}{3\times 4!} + \frac{116\kappa^4}{15\times 6!} - \frac{344\kappa^6}{15\times 8!} + \frac{152\kappa^8}{3\times 10!} - \frac{284\kappa^{10}}{3\times 12!} + \frac{476\kappa^{12}}{3\times 14!} - \frac{1232\kappa^{14}}{5\times 16!} + \dots\right] \\
&+ t^3\left[\frac{8\kappa^2}{3\times 5!} - \frac{224\kappa^4}{5\times 7!} + \frac{1808\kappa^6}{7\times 9!} - \frac{58784\kappa^8}{63\times 11!} + \frac{54184\kappa^{10}}{21\times 13!} - \frac{17984\kappa^{12}}{3\times 15!} + \dots\right] \\
&+ t^4\left[-\frac{16\kappa^2}{3\times 6!} + \frac{3952\kappa^4}{15\times 8!} - \frac{103344\kappa^6}{35\times 10!} + \frac{1824944\kappa^8}{105\times 12!} - \frac{212576\kappa^{10}}{3\times 14!} + \frac{227424\kappa^{12}}{16!} + \dots\right] \\
&+ t^5\left[\frac{32\kappa^2}{3\times 7!} - \frac{23488\kappa^4}{15\times 9!} + \frac{3603424\kappa^6}{105\times 11!} - \frac{329472\kappa^8}{13!} + \frac{21767616\kappa^{10}}{11\times 15!} + \dots\right] \\
&+ t^6\left[-\frac{64\kappa^2}{3\times 8!} + \frac{46784\kappa^4}{5\times 10!} - \frac{14132992\kappa^6}{35\times 12!} + \frac{1997595392\kappa^8}{315\times 14!} - \frac{64864938112\kappa^{10}}{1155\times 16!} + \dots\right] \\
&+ t^7\left[\frac{128\kappa^2}{3\times 9!} - \frac{840704\kappa^4}{15\times 11!} + \frac{167633408\kappa^6}{35\times 13!} - \frac{12966519808\kappa^8}{105\times 15!} + \dots\right] \\
&+ t^8\left[-\frac{256\kappa^2}{3\times 10!} + \frac{5040896\kappa^4}{15\times 12!} - \frac{171270400\kappa^6}{3\times 14!} + \frac{254642959616\kappa^8}{105\times 16!} + \dots\right] \\
&+ t^9\left[\frac{512\kappa^2}{3\times 11!} - \frac{10079232\kappa^4}{5\times 13!} + \frac{23887130112\kappa^6}{35\times 15!} - \frac{15092048115712\kappa^8}{315\times 17!} + \dots\right]
\end{aligned}$$

$$+t^{10}\left[-\frac{1024\kappa^2}{3\times 12!}+\frac{181408768\kappa^4}{15\times 14!}-\frac{286040827904\kappa^6}{35\times 16!}+\frac{14256379553792\kappa^8}{15\times 18!}+\dots\right]$$
$$+t^{11}\left[\frac{2048\kappa^2}{3\times 13!}-\frac{1088413696\kappa^4}{15\times 15!}+\frac{10285496946688\kappa^6}{105\times 17!}-\frac{397035221426176\kappa^8}{21\times 19!}+..\right]$$
$$+t^{12}\left[-\frac{4096\kappa^2}{3\times 14!}+\frac{435359744\kappa^4}{16!}-\frac{5873695133696\kappa^6}{5\times 18!}+\frac{23738481491021824\kappa^8}{63\times 20!}+.\right]$$
$$+t^{13}\left[\frac{8192\kappa^2}{3\times 15!}-\frac{39182188544\kappa^4}{15\times 17!}+\frac{98644120215552\kappa^6}{7\times 19!}+\dots\right]$$
$$+t^{14}\left[-\frac{16384\kappa^2}{3\times 16!}+\frac{235092721664\kappa^4}{15\times 18!}-\frac{2536092905111552\kappa^6}{15\times 20!}+\dots\right]$$
$$+t^{15}\left[\frac{32768\kappa^2}{3\times 17!}-\frac{470185148416\kappa^4}{5\times 19!}+\frac{71003548561965056\kappa^6}{35\times 21!}+\dots\right]$$
$$+t^{16}\left[-\frac{65536\kappa^2}{3\times 18!}+\frac{8463330770944\kappa^4}{15\times 20!}-\frac{851997444970184704\kappa^6}{35\times 22!}+\dots\right]. \qquad (6\text{-}5)$$

Substitution of (6-5) into (6-4) leads to a sum of terms, each of which is divergent. However, it is easy to see that the first line of (6-5) can be grouped into $(\sin\kappa)/\kappa$ and the second line into $(-\lambda s/3)\,\kappa\,(d/d\kappa)[(\sin\kappa)/\kappa]$. Upon integrating these two terms from $k=0$ to ∞ (cf. (6-4)), we obtain $\langle 1/r\rangle = 1/s+\lambda/3+\dots$, in exact agreement with the result obtained by Hearst and Stockmayer [Hea1,1962], and by Yamakawa and Fujii [Yam4,1973]. Were we able to find the first two terms in the expansion of $\langle 1/r\rangle$, our approach would be no better than the previous two. However, while their approaches are limited to furnishing only the first two leading order terms, our method provides a systematic approach for calculating $\langle 1/r\rangle$ in terms of an infinite expansion in powers of λs. λs is the dimensionless arc length of the wormlike chain measured in units of Kuhn's statistical segment length $1/\lambda$. In the near-rod limit, the wormlike chain is much shorter than $1/\lambda$. Therefore, $\lambda s \ll 1$. After a careful and tedious inspection, the hidden rule within the seemingly random sum in (6-5) was revealed. In fact, we can show that ($t\equiv\lambda s,\ \kappa\equiv sk$)

$$h_0 = \frac{\sin\kappa}{\kappa}-\frac{t}{3}\kappa\frac{d}{d\kappa}\frac{\sin\kappa}{\kappa}+\frac{t^2}{90}\left[8\kappa\frac{d}{d\kappa}\frac{\sin\kappa}{\kappa}+7\kappa^2\frac{d^2}{d\kappa^2}\frac{\sin\kappa}{\kappa}\right]$$
$$-\frac{t^3}{1890}\left[30\kappa\frac{d}{d\kappa}\frac{\sin\kappa}{\kappa}+96\kappa^2\frac{d^2}{d\kappa^2}\frac{\sin\kappa}{\kappa}+31\kappa^3\frac{d^3}{d\kappa^3}\frac{\sin\kappa}{\kappa}\right]$$
$$+\frac{t^4}{37800}\left[96\kappa\frac{d}{d\kappa}\frac{\sin\kappa}{\kappa}+744\kappa^2\frac{d^2}{d\kappa^2}\frac{\sin\kappa}{\kappa}\right.$$
$$\left.+720\kappa^3\frac{d^3}{d\kappa^3}\frac{\sin\kappa}{\kappa}+127\kappa^4\frac{d^4}{d\kappa^4}\frac{\sin\kappa}{\kappa}\right]+\dots. \qquad (6\text{-}6)$$

Upon substituting (6-6) into (6-4) we readily obtain the asymptotic solution to $\langle 1/r\rangle$ in near-rod limit:

$$\langle\frac{1}{r}\rangle=\frac{1}{s}\left[1+\frac{\lambda s}{3}+\frac{(\lambda s)^2}{15}+\frac{4(\lambda s)^3}{315}+\frac{(\lambda s)^4}{315}+\dots\right]. \qquad (6\text{-}7)$$

The distribution function $G(\mathbf{r};s)$ can be calculated by taking the inverse Fourier transform of $\Phi(\mathbf{k};s) = \sum_0^\infty h_n(k;s)P_n(\cos\psi)$. As an illustration, we now calculate the asymptotic expansion of the isotropic (independent of the polar angle θ of $\mathbf{r}$) distribution $G(r;s)$ in the near-rod limit. Write the full distribution $G(\mathbf{r};s) = \sum_0^\infty q_n(r;s)P_n(\cos\theta)$ as an expansion in Legendre polynomials. Then, $q_0(r;s)$ is the inverse Fourier transform of $h_0(k;s)$. The isotropic distribution $G(r;s)$ is related to q_0 via $G(r;s) = 4\pi r^2 q_0(r;s)$. It is easy to show that the inverse Fourier transform of $h_0(k;s)$ is given by

$$q_0(r;s) = \mathcal{F}^{-1}[h_0(k;s)] = \frac{1}{2\pi^2 r}\int_0^\infty k\,\sin(kr)\,h_0(k;s)\,dk. \tag{6-8}$$

We can also demonstrate the inverse Fourier transform

$$\mathcal{F}^{-1}\left[(sk)^n \frac{d^n}{d\,(sk)^n}\left(\frac{\sin(sk)}{sk}\right)\right] = \frac{(-1)^n}{4\pi r s}\sum_{j=0}^{n} C_n^j C_{n+1}^j\, j!\, r^{n-j}\frac{d^{n-j}}{dr^{n-j}}\,\delta(r-s), \tag{6-9}$$

with C_p^q being the binomial coefficients.

With use of the relationship (6-9), substitution of (6-6) into (6-8) leads to the desired asymptotic expansion of the isotropic distribution $G(r;s)$ in the near-rod limit:

$$\begin{aligned} G(r;s) = \frac{r}{s}\Bigg[1 &+ \frac{\lambda s}{3}\left(r\frac{d}{dr}+2\right) + \frac{(\lambda s)^2}{90}\left(7\,r^2\frac{d^2}{dr^2} + 34\,r\frac{d}{dr} + 26\right) \\ &+ \frac{(\lambda s)^3}{1890}\left(31\,r^3\frac{d^3}{dr^3} + 276\,r^2\frac{d^2}{dr^2} + 570\,r\frac{d}{dr} + 228\right) \\ &+ \frac{(\lambda s)^4}{37800}\Bigg(127\,r^4\frac{d^4}{dr^4} + 1820\,r^3\frac{d^3}{dr^3} + 7344\,r^2\frac{d^2}{dr^2} \\ &\qquad + 8928\,r\frac{d}{dr} + 2232\Bigg) + \dots\Bigg]\,\delta(r-s). \end{aligned} \tag{6-10}$$

The distribution (6-10) together with the simple relation

$$\int_0^\infty r^n \frac{d^n}{dr^n}\,\delta(r-s)\,dr = (-1)^n\, n!$$

and the definition $\langle 1/r\rangle = \int_0^\infty G(r;s)/r\,dr$ lead again to (6-7).

Similarly, the relationship

$$\int_0^\infty r^{n+3}\frac{d^n}{dr^n}\,\delta(r-s)\,dr = (-1)^n\,\frac{(n+3)!}{3!}\,s^3$$

and the definition $\langle r^2\rangle = \int_0^\infty r^2\,G(r;s)\,dr$ enable us to derive the moment $\langle r^2\rangle$ in the near-rod limit

$$\langle r^2\rangle = s^2\left[1 - \frac{2\lambda s}{3} + \frac{(\lambda s)^2}{3} - \frac{2(\lambda s)^3}{15} + \frac{2(\lambda s)^4}{45} + \dots\right], \tag{6-11}$$

which is identical to the correct $\langle r^2\rangle$ in the near-rod limit derivable from the exact expression of $\langle r^2\rangle$ for the wormlike chain. For example, setting $\mu = 0$ in (5-15c) and expanding $e^{-2\lambda s}$ in power series of λs, we recover (6-11). This fact demonstrates that (6-10) is indeed the correct wormlike chain distribution function in the near rod limit.

§7. Distribution Function of Elastic Polymer Chains in $2D$

Chains stiff enough, or short enough, or chains stretched by external forces possess configurations close to that for rigid rods, in which case the corresponding Green's functions in $3D$ will not be drastically different from those in $2D$. Therefore, it is desirable to obtain the asymptotic Green's function in $2D$.

Equation (4-1) also applies to the $2D$ case if we make appropriate changes in notation and set specific rules for the parameters. In $2D$, $x_1\hat{\mathbf{e}}_1 + x_2\hat{\mathbf{e}}_2 = \mathbf{r} \in \mathcal{R}^2$. The transformation matrix between the body-frame and the space-frame depends only on one variable, namely ϕ, the angle between the x-axes of the space-frame and body-frame. Since, $\phi \in S^1$, the configuration space of a $2D$ chain is of type $\mathcal{R}^2 \times S^1$. The rotation matrix in $2D$ is

$$\mathbf{\Lambda}\big(\phi(s)\big) = \begin{pmatrix} \cos\phi & -\sin\phi \\ \sin\phi & \cos\phi \end{pmatrix}, \tag{7-1}$$

$$(\hat{\mathbf{a}}_\alpha)_\beta(s) = \Lambda_{\beta\gamma}(\hat{\mathbf{e}}_\alpha)_\gamma = \Lambda_{\beta\gamma}\delta_{\alpha\gamma} = \Lambda_{\beta\alpha}, \tag{7-2}$$

where summation over repeated Greek suffixes is again implied.

Since a chain cannot sustain twist or torque in $2D$, a $2D$ chain is only capable of bending, shearing, or stretching, each with a single mode. Referring to (4-1) in $3D$, we set $\boldsymbol{\tau} = \mathbf{0}$, $A_2 = A_3 = 0$ and $\omega_2 = \omega_3 = 0$, which correspond to the vanishing of one bending mode and the twisting mode. Since these modes do not appear at all in $2D$, their corresponding intrinsic variables are meaningless. Thus, $\omega_2^0 = \omega_3^0 = 0$; we also set $B_2 = 0$, $t_2 = t_2^0 = 0$ (vanishing of one mode of shearing), $t_1^0 = 0$ (no intrinsic shearing for the remaining one shearing mode). For simplicity in notation, we define $A_1 = \lambda$, $B_1 = \nu$, $B_3 = \mu$. Previously, we chose the undeformed $\hat{\mathbf{a}}_3$ to lie in the tangent direction of the chain in $3D$. For convenience, here we will choose $\hat{\mathbf{a}}_1$ to lie in that direction. Then, corresponding to (2-33) in $3D$, we have in $2D$ that

$$-i\mathcal{L} = \frac{1}{4\lambda}(\omega - \omega^0)^2 + \frac{1}{4\mu}(t_1 - t_1^0)^2 + \frac{1}{4\nu}(t_2 - t_2^0)^2 - \mathbf{f}\cdot\mathbf{t}. \tag{7-3}$$

The Hamiltonian is

$$\begin{aligned} i\mathcal{H} = \lambda J^2 + i\omega^0 J + \mu[\hat{\mathbf{a}}_1\cdot(\mathbf{P}+i\mathbf{f})]^2 + \nu[\hat{\mathbf{a}}_2\cdot(\mathbf{P}+i\mathbf{f})]^2 \\ + i[\hat{\mathbf{a}}_1\cdot(\mathbf{P}+i\mathbf{f})]t_1^0 + i[\hat{\mathbf{a}}_2\cdot(\mathbf{P}+i\mathbf{f})]t_2^0. \end{aligned} \tag{7-4}$$

Converting operators $J \Rightarrow -i\partial/\partial\phi$ and $\mathbf{P} \Rightarrow -i\nabla_{\mathbf{r}}$, we obtain the differential equation for the Green's function. For a $2D$ bendable, shearable, stretchable chain without intrinsic bending and intrinsic shearing, we identify $\omega^0 = 0$, $t_1^0 = 1$, $t_2^0 = 0$. Therefore, the Green's function satisfies

$$\begin{aligned} \Big[\frac{\partial}{\partial s} + \hat{\mathbf{a}}_1\cdot(\nabla_{\mathbf{r}} - \mathbf{f}) - \mu[\hat{\mathbf{a}}_1\cdot(\nabla_{\mathbf{r}} - \mathbf{f})]^2 - \nu[\hat{\mathbf{a}}_2\cdot(\nabla_{\mathbf{r}} - \mathbf{f})]^2 \\ - \lambda\frac{\partial^2}{\partial\phi^2}\Big] G(\mathbf{r},\phi;s\,|\,\mathbf{r}_0,\phi_0;0) = \delta(s)\delta(\mathbf{r}-\mathbf{r}_0)\delta(\phi-\phi_0). \end{aligned} \tag{7-5}$$

Let the Laplace-Fourier transform of $G(\mathbf{r},\phi;s\,|\,\mathbf{r}_0,\phi_0;0)$ be $I(\mathbf{k},\phi;p\,|\,\mathbf{r}_0,\phi_0;0)$. Then I satisfies the following equation:

$$\Big[p - i\hat{\mathbf{a}}_1\cdot(\mathbf{k}-i\mathbf{f}) + \mu[\hat{\mathbf{a}}_1\cdot(\mathbf{k}-i\mathbf{f})]^2 + \nu[\hat{\mathbf{a}}_2\cdot(\mathbf{k}-i\mathbf{f})]^2 - \lambda\frac{\partial^2}{\partial\phi^2}\Big]I(\mathbf{k},\phi;p\,|\,\mathbf{r}_0,\phi_0;0) = \delta(\phi-\phi_0), \quad (7\text{-}6)$$

from which we again recognize that the Fourier transform of the Green's function for a chain with external force is obtained from that of a force-free Green's function simply by replacing $\mathbf{k}$ by $\mathbf{k}-i\mathbf{f}$. Therefore, a solution for the free-chain Green's function can be used to obtain that of a chain with external force by using (2-34), with $\mathbf{\Phi}$ and $\mathbf{\Phi}_0$ being replaced by ϕ and ϕ_0 in the argument. A $2D$ chain is not capable of sustaining torque in the first place. In what follows we assume $\mathbf{f}=\mathbf{0}$ and $\boldsymbol{\tau}=\mathbf{0}$.

Since exact solutions for all positive-even-power moments can be obtained without knowing the explicit form of the Green's function, we first solve for some moments of a free chain, and then derive the asymptotic solution of the Green's function in the long chain limit (Daniels' approximation). Given any function $M(\mathbf{r},\phi;s)$ which does not depend on s explicitly, again let the Laplace transform of $\langle M\rangle_s$ be $\langle N\rangle_p$. Then $\langle N\rangle_p$ satisfies

$$p\langle N\rangle_p - p\langle M\rangle_{s=0} = \langle(\hat{\mathbf{a}}_1\cdot\nabla_{\mathbf{r}})N\rangle_p + \mu\langle(\hat{\mathbf{a}}_1\cdot\nabla_{\mathbf{r}})^2N\rangle_p + \nu\langle(\hat{\mathbf{a}}_2\cdot\nabla_{\mathbf{r}})^2N\rangle_p + \lambda\langle\frac{\partial^2}{\partial\phi^2}N\rangle_p. \quad (7\text{-}7)$$

Generic moments in $2D$ have the form $\langle N^{(k)}_{l_1,l_2}\rangle \equiv \langle r^k(\mathbf{r}\cdot\hat{\mathbf{a}}_1)^{l_1}(\mathbf{r}\cdot\hat{\mathbf{a}}_2)^{l_2}\rangle$. Using a recurrence formula similar to (4-14), we are able to obtain all positive-power moments, with a few listed below as follows:

$$\langle\mathbf{r}\rangle = \frac{1-e^{-\lambda s}}{\lambda}\hat{\mathbf{a}}_1^0, \quad (7\text{-}8a)$$

$$\langle\hat{\mathbf{a}}_j\rangle = e^{-\lambda s}\hat{\mathbf{a}}_j^0 \qquad (j=1,2), \quad (7\text{-}8b)$$

$$\langle\mathbf{r}\cdot\hat{\mathbf{a}}_1\rangle = \frac{1-e^{-\lambda s}}{\lambda}, \quad (7\text{-}8c)$$

$$\langle\mathbf{r}\cdot\hat{\mathbf{a}}_2\rangle = 0, \quad (7\text{-}8d)$$

$$\langle r^2\rangle = 2\left(\mu+\nu+\frac{1}{\lambda}\right)s - \frac{2(1-e^{-\lambda s})}{\lambda^2}, \quad (7\text{-}8e)$$

$$\langle(\mathbf{r}\cdot\hat{\mathbf{a}}_1)^2\rangle = \left(\mu+\nu+\frac{1}{\lambda}\right)s - \frac{2(1-e^{-\lambda s})}{3\lambda^2} + \frac{3\lambda(\mu-\nu)-1}{12\lambda^2}\left(1-e^{-4\lambda s}\right), \quad (7\text{-}8f)$$

$$\langle(\mathbf{r}\cdot\hat{\mathbf{a}}_2)^2\rangle = \left(\mu+\nu+\frac{1}{\lambda}\right)s - \frac{4(1-e^{-\lambda s})}{3\lambda^2} - \frac{3\lambda(\mu-\nu)-1}{12\lambda^2}\left(1-e^{-4\lambda s}\right), \quad (7\text{-}8g)$$

$$\langle(\hat{\mathbf{a}}_j\cdot\hat{\mathbf{a}}_j^0)^2\rangle = \frac{1+e^{-4\lambda s}}{2} \qquad (j=1,2), \quad (7\text{-}8h)$$

$$\langle(\hat{\mathbf{a}}_1\cdot\hat{\mathbf{a}}_2^0)^2\rangle = \langle(\hat{\mathbf{a}}_2\cdot\hat{\mathbf{a}}_1^0)^2\rangle = \frac{1-e^{-4\lambda s}}{2}, \quad (7\text{-}8i)$$

$$\langle r^4\rangle = \left[8\left(\mu+\nu+\frac{1}{\lambda}\right)^2\right]s^2 + \left[\frac{-4\mu-28\nu-\frac{30}{\lambda}+2\lambda(\mu-\nu)^2}{\lambda^2}\right]s$$
$$+\left[\frac{\frac{87}{\lambda^2}-\frac{42}{\lambda}(\mu-\nu)-(\mu-\nu)^2}{2\lambda^2}\right]+\left[\frac{8(3\mu+\nu-\frac{5}{3\lambda})}{\lambda^2}\right]se^{-\lambda s}$$
$$+\left[\frac{64\mu-64\nu-\frac{392}{3\lambda}}{3\lambda^3}\right]e^{-\lambda s}+\left[\frac{(\mu-\nu-\frac{1}{3\lambda})^2}{2\lambda^2}\right]e^{-4\lambda s}. \tag{7-8j}$$

Next, we proceed to solve the $2D$ free-chain Green's function using (7-6). We first note that p (conjugate to s) and $\mathbf{k}$ (conjugate to $\mathbf{r}$) both have the units of inverse length. Therefore, μ and ν have the units of length, while λ has the units of inverse length. Recall that $1/\lambda$ is Kuhn's statistical segment length. Denote this length by $h \equiv 1/\lambda$. Now, we have from (7-6) with $\mathbf{f}=\mathbf{0}$ that

$$[p - i\hat{\mathbf{a}}_1\cdot\mathbf{k} + \mu(\hat{\mathbf{a}}_1\cdot\mathbf{k})^2 + \nu(\hat{\mathbf{a}}_2\cdot\mathbf{k})^2 - \frac{1}{h}\frac{\partial^2}{\partial\phi^2}]I(\mathbf{k},\phi;p\,|\,\mathbf{r}_0,\phi_0;0) = \delta(\phi-\phi_0). \tag{7-9}$$

Recall that ϕ is the angle between the $\hat{\mathbf{a}}_1$-axis in the body-frame and the $\hat{\mathbf{e}}_1$-axis in the space-frame. Let $\mathbf{k} = (k, \phi_k)$ in the space-fixed polar coordinate system; explicitly, $\mathbf{k} = \hat{\mathbf{e}}_1 k\cos\phi_k + \hat{\mathbf{e}}_2 k \sin\phi_k$. Upon defining $\alpha = \phi - \phi_k$ and $\alpha_0 = \phi_0 - \phi_k$, we can rewrite the above equation as

$$[p - ik\cos\alpha + \frac{\mu+\nu}{2}k^2 + \frac{\mu-\nu}{2}k^2\cos 2\alpha - \frac{1}{h}\frac{\partial^2}{\partial\phi^2}]I(\mathbf{k},\phi;p\,|\,\mathbf{r}_0,\phi_0;0) = \delta(\alpha-\alpha_0). \tag{7-10}$$

Expand the functions $\delta(\alpha-\alpha_0)$ and I as the Fourier series

$$\delta(\alpha-\alpha_0) = \frac{1}{2\pi}\sum_{m=-\infty}^{\infty} e^{im(\alpha-\alpha_0)} = \frac{1}{2\pi}\sum_{m,n=-\infty}^{\infty}\delta_{m,n}e^{im(\alpha-\alpha_0)}, \tag{7-11}$$

$$I(\mathbf{k},\phi;p\,|\,\mathbf{r}_0,\phi_0;0) = \frac{1}{2\pi}\sum_{m,n=-\infty}^{\infty} g_{m,n}(k;p)e^{im\alpha - in\alpha_0}. \tag{7-12}$$

Substitute $\cos(k\alpha) = (1/2)[e^{ik\alpha}+e^{-ik\alpha}]$ and the above Fourier expansions respectively into the two sides of (7-10) to obtain the following relation (which can be used to solve for the expansion coefficients $g_{m,n}$):

$$[p + \frac{\mu+\nu}{2}k^2 + \frac{1}{h}m^2]g_{m,n} - \frac{ik}{2}[g_{m-1,n}+g_{m+1,n}] + \frac{\mu-\nu}{4}k^2[g_{m-2,n}+g_{m+2,n}] = \delta_{m,n}, \tag{7-13}$$

or, expressed alternatively,

$$\Big[(p + \frac{\mu+\nu}{2}k^2 + \frac{1}{h}m^2)\delta_{m,\beta} - \frac{ik}{2}(\delta_{m-1,\beta}+\delta_{m+1,\beta})$$
$$+ \frac{\mu-\nu}{4}k^2(\delta_{m-2,\beta}+\delta_{m+2,\beta})\Big]g_{\beta,n} = \delta_{m,n}. \tag{7-14}$$

In matrix notion, if we introduce the matrix entries $(\mathbf{A})_{ij} = g_{ij}$, the above equation can be put in the form

$$\mathbf{N} \cdot \mathbf{A} = \mathbf{I}. \tag{7-15}$$

where **N** is a symmetric matrix whose entries are all terms inside the large parenthesis in (7-14), and where **I** is the identity matrix. Therefore,

$$\mathbf{A} = \mathbf{N}^{-1}, \tag{7-16}$$

$$g_{m,n} = (\mathbf{N}^{-1})_{m,n}. \tag{7-17}$$

Note that **N** is symmetric, as too is its inverse. Therefore, $g_{m,n}$ is symmetric with respect to m and n.

We now recognize that solving the $2D$ free chain Green's function amounts to inverting a matrix, which incidently is an infinite by infinite matrix. Therefore, only an asymptotic solution can be obtained. Note that **N** is the sum of a diagonal matrix and two subdiagonal matrices, with the two subdiagonal matrices being proportional to k and k^2 respectively (cf. (7-14)). Since k is the Fourier variable conjugate to r, as k decreases with increasing r, the submatrices will be subdominant compared with the diagonal one. Thus, the asymptotic solution is one valid in the long chain (random coil) limit. We will invert a $(2M+1)$–by–$(2M+1)$ matrix with $M = 2$.

Let the inverse Laplace transform of $I(\mathbf{k}, \alpha; p \,|\, \mathbf{r}_0, \alpha_0; 0)$ be $K(\mathbf{k}, \alpha; s \,|\, \mathbf{r}_0, \alpha_0; 0)$ and that of $g_{m,n}(k;p)$ be $h_{m,n}(k;s)$. The symmetry of $g_{m,n}$ guarantees the symmetry of $h_{m,n}$. By definition, K is the Fourier transform of the Green's function G:

$$G(\mathbf{r}, \phi; s \,|\, \mathbf{r}_0, \phi_0; 0) = \frac{1}{(2\pi)^2} \int e^{-i\mathbf{k}\cdot\mathbf{r}} K(\mathbf{k}, \alpha; s \,|\, \mathbf{r}_0, \alpha_0; 0)\, d^2\mathbf{k}$$

$$= \frac{1}{(2\pi)^2} \sum_{m,n=-\infty}^{\infty} e^{im\phi - in\phi_0} \int_0^\infty h_{m,n}(k;s)\, k\, dk \int_0^{2\pi} d\phi_k e^{i(n-m)\phi_k} e^{-ikr\cos(\phi_k - \phi_r)}, \tag{7-18}$$

where we have written $\mathbf{r} = (r, \phi_r)$ in the space-fixed polar coordinate system. Integrating with respect to ϕ_k, yields

$$G(\mathbf{r}, \phi; s \,|\, \mathbf{r}_0, \phi_0; 0) = \frac{1}{(2\pi)^2} \sum_{m,n=-\infty}^{\infty} e^{im(\phi-\phi_r) - in(\phi_0 - \phi_r)} G_{m,n}(r;s), \tag{7-19}$$

where

$$G_{m,n}(r;s) = i^{n-m} \int_0^\infty h_{m,n}(k;s)\, J_{n-m}(kr)\, k\, dk. \tag{7-20}$$

The Green's function G is a conditional probability distribution. Since the freedom of choosing the origin of the space-frame is still at our disposal, the condition $\mathbf{r}_0$ becomes $\mathbf{0}$ once we let the origin of the space-frame coincide with one end of the chain. The distribution $P(\mathbf{r}, \phi; s)$ (with one end of the chain fixed at the origin and local tangent at the end in the $\hat{\mathbf{e}}_z$ direction being implicitly implied), in which $\mathbf{r}$ is the position vector of point s on the chain, and ϕ the polar angle of $\hat{\mathbf{a}}_1$ in the space-frame, can therefore be obtained by integrating G with respect to ϕ_0:

$$P(\mathbf{r}, \phi; s) = \int G(\mathbf{r}, \phi; s \,|\, \phi_0; 0)\, d\phi_0 = \frac{1}{2\pi} \sum_{m=-\infty}^{\infty} e^{im(\phi-\phi_r)} G_{m,0}. \tag{7-21}$$

The distribution $P(\mathbf{r}; s)$ irrespective of the body-frame direction at s can be obtained by integrating over the range of ϕ:

$$P(\mathbf{r}; s) = \int_0^{2\pi} P(\mathbf{r}, \phi; s)\, d\phi = G_{0,0}(r; s). \tag{7-22}$$

Note that the distribution $P(\mathbf{r}; s)$, equivalent to the isotropic function $G_{0,0}(r; s)$, does not have an angular dependence. This is evident from the fact that we have integrated over the polar angle ϕ_0 of the initial body-frame $\hat{\mathbf{a}}_1$(s=0), i.e., in the distribution $P(\mathbf{r}; s)$ the initial tangent direction of the chain is not specified—in which case $P(\mathbf{r}; s)$ must, of course, be isotropic.

Suppose we are interested in the distribution $P(\mathbf{r}; s \,|\, \phi_0; 0)$, representing the conditional distribution of $\mathbf{r}$ at s given that the polar angle of initial body-frame $\hat{\mathbf{a}}_1(s = 0)$ is ϕ_0. Then we have that

$$P(\mathbf{r}; s \,|\, \phi_0; 0) = \int G(\mathbf{r}, \phi; s \,|\, \phi_0; 0)\, d\phi = \frac{1}{2\pi} \sum_{n=-\infty}^{\infty} e^{in(\phi_r-\phi_0)} G_{0,n}, \tag{7-23}$$

which depends only on the angle $(\phi_r - \phi_0)$ between $\mathbf{r}$ and the initial body-frame $\hat{\mathbf{a}}_1(s = 0)$, as expected (since the system is invariant under a rotation of the space-frame). We also note another interesting feature which is intrinsically related to the symmetry of Green's function. From the head-tail symmetry of the chain, and the fact that ϕ is the polar angle of $\hat{\mathbf{a}}_1(s)$ at s in the space-frame, whereas ϕ_0 is that of the initial $\hat{\mathbf{a}}_1(s = 0)$ in the space-frame, we intuitively expect that the functional forms of $P(\mathbf{r}; s \,|\, \phi_0; 0)$ and $P(\mathbf{r}, \phi; s)$ will be identical. From equations (7-21) and (7-23) we therefore expect $G_{m,n}$ to be symmetrical with respect to m and n. This is indeed true, since from (7-20) the symmetry of $G_{m,n}$ is implied by the symmetry of $h_{m,n}$, whereas the symmetry of $h_{m,n}$ is guaranteed by that of $g_{m,n}$.

We now calculate the asymptotic solutions for $g_{m,n}(k; p)$ and $G_{m,n}(r; s)$ following Daniels [Dan1]. From the $2D$ moments (7-8e) we find as s increases that $\langle r^2 \rangle$ approaches s linearly. We now define

$$h = \frac{1}{\lambda}, \tag{7-24}$$

$$\hbar = h + \mu + \nu. \tag{7-25}$$

Both h and $\hbar$ possess the units of length. The usual meaning of $\hbar$ as Planck's constant will not cause confusion since we will never use Planck's constant in what follows. From the moment equation (7-8e), $\lim_{s\to\infty}\langle r^2\rangle = 2\hbar s$. If $\mu = \nu = 0$, then $\hbar = 1/\lambda$ is the Kuhn's statistical segment length. Hence, $\hbar$ can be thought of as the effective Kuhn's statistical segment length for the $2D$ bendable, shearable, stretchable chain. Therefore, in the long chain (Gaussian random coil) limit one expects intuitively that the distribution will approach the circular normal form with $r^2 = O(s)$ over the effective range of s. It is therefore reasonable to investigate approximations to $g_{m,n}(k;p)$ for small p and k with $p = O(k^2)$. To indicate the order of the approximations, let S denote a typical value of s. Terms which are $O(p^\tau)$ or $O(k^{2\tau})$ are taken to be $O(S^{-\tau})$ in the sense that after the change of scale, $s = s'S$, $r = r'S^{\frac{1}{2}}$, $S^{-\tau}$ appears explicitly as a factor of such terms—the corresponding variables p', k' and the elastic moduli μ, ν, λ being of $O(1)$ in S.

Set $M = 2$. We will: (*i*) first invert the 5-by-5 matrix $\mathbf{N}$; (*ii*) expand the resulting entries of $\mathbf{N}^{-1}$ into a series with respect to the small expansion parameter $S^{-\frac{1}{2}}$ up to S^{-1}; (*iii*) ignore terms that are subdominant; and (*iv*) finally change the scale back to the original one by using $p' = pS$, $k' = kS^{\frac{1}{2}}$. The results are listed as follows, with all g's possessing the argument $(k;p)$:

$$g_{0,0} = \big(1 + \frac{1}{2}h^2k^2\big)\frac{p}{p+\frac{1}{2}\hbar k^2} - \frac{1}{32}h(h-\mu+\nu)(7h+\mu+\nu)k^4\frac{p}{(p+\frac{1}{2}\hbar k^2)^2} + O(s^{-\frac{3}{2}}), \tag{7-26a}$$

$$g_{0,1} = g_{1,0} = g_{-1,0} = g_{0,-1} = \frac{i}{32}hk[5hk^2(3h-2\mu+2\nu)+16]\frac{p}{p+\frac{1}{2}\hbar k^2} - \frac{i}{64}h^2(h-\mu+\nu)(7h+\mu-\nu)k^5\frac{p}{(p+\frac{1}{2}\hbar k^2)^2} + O(s^{-\frac{3}{2}}), \tag{7-26b}$$

$$g_{1,1} = g_{-1,1} = g_{1,-1} = g_{-1,-1} = -\frac{1}{4}h^2k^2\frac{p}{p+\frac{1}{2}\hbar k^2} + O(s^{-\frac{3}{2}}), \tag{7-26c}$$

$$g_{0,2} = g_{2,0} = g_{-2,0} = g_{0,-2} = -\frac{1}{16}h(h+\mu-\nu)k^2\frac{p}{p+\frac{1}{2}\hbar k^2} + O(s^{-\frac{3}{2}}), \tag{7-26d}$$

$$g_{1,2} = g_{2,1} = g_{-1,2} = g_{2,-1} = g_{1,-2} = g_{-2,1} = g_{-2,-1} = g_{-1,-2} = -\frac{i}{16}h^2(h+\mu-\nu)k^3\frac{p}{p+\frac{1}{2}\hbar k^2} + O(s^{-\frac{3}{2}}), \tag{7-26e}$$

$$g_{m,n} \le O(s^{-\frac{3}{2}}) \qquad (|m| \text{ or } |n| \ge 3). \tag{7-26f}$$

In deriving the above expressions we have omitted terms associated with factors like $(p+\frac{1}{2}\hbar k^2)^j$ (with $j = 0, 1, 2, \dots$) since they do not contribute to the inverse Laplace transform. The inverse Laplace transform of $g_{m,n}(k;p)$ is $h_{m,n}(k;s)$, wherein

$$h_{0,0} = e^{-\frac{1}{2}\hbar k^2 s}\big[1 + \frac{1}{2}h^2k^2 - \frac{1}{32}h(h-\mu+\nu)(7h+\mu-\nu)k^4 s\big], \tag{7-27a}$$

$$h_{1,1} = h_{-1,1} = h_{1,-1} = h_{-1,-1} = -\frac{1}{4}h^2k^2e^{-\frac{1}{2}\hbar k^2 s}, \tag{7-27b}$$

$$h_{0,1} = h_{1,0} = h_{-1,0} = h_{0,-1} = e^{-\frac{1}{2}\hbar k^2 s}\left[\frac{i}{32}hk[5hk^2(3h - 2\mu + 2\nu) + 16]\right.$$

$$\left. - \frac{i}{64}h^2(h - \mu + \nu)(7h + \mu - \nu)k^5 s\right], \qquad \text{(7-27c)}$$

$$h_{0,2} = h_{2,0} = h_{-2,0} = h_{0,-2} = -\frac{1}{16}h(h + \mu - \nu)k^2 e^{-\frac{1}{2}\hbar k^2 s}, \qquad \text{(7-27d)}$$

$$h_{1,2} = h_{2,1} = h_{-1,2} = h_{2,-1} = h_{1,-2} = h_{-2,1} = h_{-2,-1} = h_{-1,-2}$$

$$= -\frac{i}{16}h^2(h + \mu - \nu)k^3 e^{-\frac{1}{2}\hbar k^2 s}. \qquad \text{(7-27e)}$$

Upon performing the integration in (7-20) for the $h_{m,n}(k;s)$'s, we obtain the desired expression for the $G_{m,n}(r;s)$'s:

$$G_{0,0} = \frac{1}{\hbar s}e^{-\frac{r^2}{\hbar s}}\left[[1 + \frac{h^2}{\hbar s} - \frac{1}{4\hbar^2 s}h(h - \mu + \nu)(7h + \mu - \nu)] - [\frac{h^2}{2\hbar s} - \frac{1}{4\hbar^2 s}h\right.$$

$$\times (h - \mu + \nu)(7h + \mu - \nu)]\left(\frac{r^2}{\hbar s}\right)$$

$$\left. - [\frac{1}{32\hbar^2 s}h(h - \mu + \nu)(7h + \mu + \nu)]\left(\frac{r^2}{\hbar s}\right)^2\right], \qquad \text{(7-28a)}$$

$$G_{1,0} = G_{0,1} = G_{-1,0} = G_{0,-1} = \frac{1}{\hbar s}\left(\frac{rh}{2\hbar s}\right)e^{-\frac{r^2}{\hbar s}}\left[[1 + \frac{5}{4\hbar s}h(3h - \mu + \nu)\right.$$

$$- \frac{3}{4\hbar^2 s}h(h - \mu + \nu)(7h + \mu - \nu)] - [\frac{5h}{16\hbar s}(3h - \mu + \nu) - \frac{3}{8\hbar^2 s}h(h - \mu + \nu)$$

$$\left. \times (7h + \mu - \nu)]\left(\frac{r^2}{\hbar s}\right) - [\frac{1}{32\hbar^2 s}h(h - \mu + \nu)(7h + \mu - \nu)]\left(\frac{r^2}{\hbar s}\right)^2\right], \qquad \text{(7-28b)}$$

$$G_{1,1} = G_{-1,1} = G_{1,-1} = G_{-1,-1} = \frac{1}{\hbar s}\left(-\frac{h^2}{4\hbar s}\right)\left(2 - \frac{r^2}{\hbar s}\right)e^{-\frac{r^2}{\hbar s}}, \qquad \text{(7-28c)}$$

$$G_{0,2} = G_{2,0} = G_{-2,0} = G_{0,-2} = \frac{1}{\hbar s}\left(\frac{h(h + \mu - \nu)}{16\hbar s}\right)\left(\frac{r^2}{\hbar s}\right)e^{-\frac{r^2}{\hbar s}}, \qquad \text{(7-28d)}$$

$$G_{1,2} = G_{2,1} = G_{-1,-2} = G_{-2,-1} = -\frac{1}{\hbar s}\left(\frac{h^2(h + \mu - \nu)r}{32\hbar^3 s^3}\right)\left(4 - \frac{r^2}{\hbar s}\right)e^{-\frac{r^2}{\hbar s}}, \qquad \text{(7-28e)}$$

$$G_{1,-2} = G_{-2,1} = G_{-1,2} = G_{2,-1} = \frac{1}{\hbar s}\left(\frac{h^2(h + \mu - \nu)r^3}{32\hbar^3 s^3}\right)e^{-\frac{r^2}{2\hbar s}}. \qquad \text{(7-28f)}$$

The Green's function $G(\mathbf{r}, \phi; s \,|\, \phi_0; 0)$ is obtained as

$$G(\mathbf{r}, \phi; s \,|\, \phi_0; 0) = \frac{1}{(2\pi)^2}[G_{0,0} + 2G_{0,1}(\cos\beta + \cos\beta_0) + 2G_{1,1}\cos(\beta - \beta_0)$$

$$+ 2G_{0,2}(\cos 2\beta + \cos 2\beta_0) + 2G_{1,2}[\cos(2\beta - \beta_0) + \cos(2\beta_0 - \beta)]$$

$$+ 2G_{1,-2}[\cos(2\beta + \beta_0) + \cos(2\beta_0 + \beta)] + O(s^{-\frac{3}{2}}), \qquad \text{(7-29)}$$

where $\beta = \phi - \phi_r$ and $\beta_0 = \phi_0 - \phi_r$. The Green's function G is invariant under the interchange of β and β_0; hence, it is also invariant under the interchange of ϕ and ϕ_0. This is a clear demonstration of both the symmetry of Green's function and the head-tail symmetry of the physical system involved. Integrating G with respect to ϕ_0 over its full range of 2π yields the unconditional distribution $P(\mathbf{r}, \phi; s)$:

$$P(\mathbf{r}, \phi; s) = \frac{1}{2\pi}[G_{0,0} + 2G_{0,1}\cos(\phi - \phi_r) + 2G_{0,2}\cos(2\phi - 2\phi_r) + \ldots]. \qquad (7\text{-}30)$$

The distribution $P(\mathbf{r}; s)$ is obtained by integrating $P(\mathbf{r}, \phi; s)$ with respect to ϕ over 2π:

$$P(\mathbf{r}; s) = G_{0,0}. \qquad (7\text{-}31)$$

Finally, the conditional distribution $P(\mathbf{r}; s \mid \phi_0; 0)$, which is the distribution function studied by Daniels, is obtained by integrating G with respect to ϕ over 2π (or, taking advantage of the head-tail symmetry, by simply replacing ϕ in (7-30) by ϕ_0):

$$P(\mathbf{r}; s \mid \phi_0; 0) = \frac{1}{2\pi}[G_{0,0} + 2G_{0,1}\cos(\phi_0 - \phi_r) + 2G_{0,2}\cos(2\phi_0 - 2\phi_r) + \ldots]. \quad (7\text{-}32)$$

If we set $\mu = \nu = 0$ (without shearing and extension), then $\hbar = h = 1/\lambda$ is the Kuhn's statistical segment length, and $\phi_0 - \phi_r$ becomes the angle between the initial tangent of the chain and the position vector $\mathbf{r}$ at s (which is the same as θ in Daniels' classical paper [Dan1]). In the special no-shearing, no-extension case, $P(\mathbf{r}; s \mid \phi_0; 0)$ becomes identical with Daniels' $2D$ distribution.

§8. Distribution of Chain Segments About the Center of Mass

Thus far, all of the distributions or Green's functions obtained have been exclusively those of the end-to-s vector, or of the end-to-end vector if we set $s = L$. These represent distributions of chain segments about one end of the chain. However, it is sometimes equally desirable to obtain the corresponding distribution of chain segments about the center of mass. In this section we derive an asymptotic expression for the distribution function of chain segments about the center of mass and also calculate the exact moments.

Denote the distribution in question by $P(\mathbf{W}(s); s)$, where $\mathbf{W}(s)$ is a position vector measured from the center of mass (rather than from one end of chain) to the point with material length s. Since a free chain (both force-free $\mathbf{f} = \mathbf{0}$ and torque-free $\boldsymbol{\tau} = \mathbf{0}$) can be modeled quite successfully by the Kratky-Porod wormlike chain model [Kra1], and since our bendable, shearable, twistable, stretchable elastic chain model contains the Kratky-Porod wormlike chain model as a special case, we here assume the chain to be a wormlike chain (without twist, shear, and extension), lending simplicity to the formalism. Generalization to the case of a general elastic chain is straightforward.

Some special features arise from the nature of the problem. First, unlike the end of a chain, the center of mass of a chain is not generally located on the chain itself. Second, an infinitesimal movement of any segment of the chain will change the position of the center of mass. Therefore, under thermal agitation the position of the center of mass is a stochastic variable. As the chain has infinitely-many degrees of freedom, the position of its center of mass necessarily depends on the structure of the chain in a quite complicated way. Yet the nature of our problem demands that the origin of our space-frame be fixed at the center of mass. Finally, the particular way in which the position vector between the center of mass and point s is related to the structure of the chain renders it difficult to find the differential equation satisfied by the distribution of chain segments about the center of mass.

These circumstances create a problem that demands an entirely different approach from previous ones, wherein we have always started from a differential equation and then subsequently obtained the moments and the asymptotic solutions of the distribution functions. In the present problem we have to start from the exact moments of the distribution and then proceed to obtain the corresponding distribution itself. However, the moments themselves are insufficient to ensure a unique distribution. Fortunately we have one more piece of information at our disposal. For highly flexible Gaussian random coils the bond distribution is Gaussian and each bond is independent of all others, since linear functions of independent Gaussian distributions are also Gaussian. Uhlenbeck's Theorem [Yam1] for a linear Gaussian chain states that, in general, the multivariate distribution function of the chain, and in particular the distribution of chain segments about the center of mass, is obtainable so long as the variables are linear functions of independent Gaussian bond vectors. For the Gaussian random coil, the position vector about the center of mass can be put in the form of a linear function of bond vectors. Uhlenbeck's Theorem therefore allows the distribution about the center of mass to be easily obtained, and is indeed found to be of Gaussian form. For discrete Gaussian random coil, the corresponding distribution about the center of mass was derived by Debye and Bueche [Deb1] (cf. [Yam1], p. 21)

$$P(\mathbf{W}_j) = \left(\frac{9n}{2\pi a^2[n^2 - 3j(n-j)]}\right)^{3/2} e^{-\frac{9nW_j^2}{2a^2[n^2-3j(n-j)]}}.$$

For wormlike chains, due to finite elasticity the bond vectors (unit tangent vectors) are not independent of each other. Hence, Uhlenbeck's Theorem is not applicable. However, it is clear that the limiting behavior of the wormlike chain in the long chain limit must be identical to that of the Gaussian random coil. This known leading behavior of the distribution, together with the exact moments, enables us to obtain the unique asymptotic solution to the chain distribution about the center of mass, which is exactly the route we will follow in bring the calculation to fruition.

Although the unit tangent vectors on a wormlike chain are not independent of one other, we are nevertheless able to obtain their autocorrelation functions, which will then be used to obtain the exact moments of the distribution. For this purpose, we first find the autocorrelation function of the unit tangent vector (angular autocorrelation function). The differential equation for the distribution function $Q(\hat{\mathbf{u}}; s) = \int G(\mathbf{r}, \hat{\mathbf{u}}; s \,|\, \mathbf{0}, \hat{\mathbf{u}}_0; 0)\, d^3\mathbf{r}\, d^2\hat{\mathbf{u}}_0$ can be obtained by integrating (5-1) with respect to $\mathbf{r}$ and $\hat{\mathbf{e}}_z (= \hat{\mathbf{u}}_0)$, with $\mu = 0$ for wormlike chain. This yields

$$\frac{\partial Q}{\partial s} = \lambda \nabla^2_{\hat{\mathbf{u}}} Q, \tag{8-1}$$

with a delta function source term being implicitly employed as an initial condition. This is a diffusion equation on S^2, for which the general solution is well known (cf. [Yam1], p. 55, or [Sai1]). If we let the latitudinal and azimuthal angles of $\hat{\mathbf{u}}$ be α and β respectively, then

$$\frac{\partial Q}{\partial s} = \lambda \left[\frac{1}{\sin\alpha}\frac{\partial}{\partial\alpha}\left(\sin\alpha\frac{\partial Q}{\partial\alpha}\right) + \frac{1}{\sin^2\alpha}\frac{\partial^2 Q}{\partial\beta^2}\right]. \tag{8-2}$$

The general solution of (8-2) can be expanded in terms of even and odd spherical harmonics, Y^e_{mn} and Y^o_{mn}:

$$Q(\hat{\mathbf{u}}; s) = \int Q(\hat{\mathbf{u}}'; s') G(\hat{\mathbf{u}}; s|\hat{\mathbf{u}}'; s') d^2\hat{\mathbf{u}}', \tag{8-3}$$

with the Green's function $G(\hat{\mathbf{u}}; s|\hat{\mathbf{u}}'; s')$ given by the infinite series,

$$\begin{aligned} G(\alpha, \beta; s|\alpha', \beta'; s') &= \frac{1}{4\pi}\sum_{n=0}^{\infty}\sum_{m=0}^{n}(2n+1)\epsilon_m\frac{(n-m)!}{(n+m)!}e^{-n(n+1)\lambda|s-s'|} \\ &\quad \times \left(Y^e_{mn}(\alpha,\beta)Y^e_{mn}(\alpha',\beta') + Y^o_{mn}(\alpha,\beta)Y^o_{mn}(\alpha',\beta')\right) \\ &= \frac{1}{4\pi}\sum_{n=0}^{\infty}(2n+1)e^{-n(n+1)\lambda|s-s'|} \\ &\quad \times \sum_{m=0}^{n}\epsilon_m\frac{(n-m)!}{(n+m)!}P_n^m(\cos\alpha)P_n^m(\cos\alpha')\cos[m(\beta-\beta')], \end{aligned} \tag{8-4}$$

with $\epsilon_0 = 1$ and $\epsilon_m = 2$ for $m = 1, 2, 3, \ldots$. Suppose that we set up a coordinate system on the chain with $\hat{\mathbf{e}}_z$ in the $\hat{\mathbf{u}}'$ direction. Using the identities $P_n^0(x) = P_n(x)$, $P_n(\pm 1) = (\pm 1)^n$, and $P_n^m(1) = \delta_{m0}$, we obtain

$$G(\hat{\mathbf{u}}; s|\hat{\mathbf{e}}_z; s') = \frac{1}{4\pi} \sum_{n=0}^{\infty} (2n+1) e^{-n(n+1)\lambda|s-s'|} P_n(\cos\alpha). \tag{8-5}$$

From (8-5) we can calculate the autocorrelation function $\langle \hat{\mathbf{u}}(s) \cdot \hat{\mathbf{u}}(s') \rangle$:

$$\langle \hat{\mathbf{u}}(s) \cdot \hat{\mathbf{u}}(s') \rangle = \int \hat{\mathbf{u}} \cdot \hat{\mathbf{e}}_z G(\hat{\mathbf{u}}; s|\hat{\mathbf{e}}_z; s') d^2\hat{\mathbf{u}} = e^{-2\lambda|s-s'|}, \tag{8-6}$$

where $\int_{-1}^{+1} x P_n(x) dx = (2/3)\delta_{n1}$ was used in the last equality. Actually, (8-6) can easily be obtained without knowing the explicit functional form of the Green's function (8-4) or (8-5). Without loss of generality, set $s' = 0$, and note that the Green's function $G(\hat{\mathbf{u}}_s|\hat{\mathbf{u}}_0)$ satisfies (8-1), i.e., $\partial G/\partial s = \lambda \nabla^2_{\hat{\mathbf{u}}_s} G$. It is then easy to prove for the Laplacian in S^2 that

$$\nabla^2_{\hat{\mathbf{u}}} \hat{\mathbf{u}} = -2\hat{\mathbf{u}}, \tag{8-7}$$

with its counterpart in $SO(3)$ being (4-13). Using these relationships we find that

$$\begin{aligned} \frac{\partial \langle \hat{\mathbf{u}}_s \cdot \hat{\mathbf{u}}_0 \rangle}{\partial s} &= \int \hat{\mathbf{u}}_s \cdot \hat{\mathbf{u}}_0 \frac{\partial G}{\partial s} d^2\hat{\mathbf{u}}_s = \lambda \int \hat{\mathbf{u}}_s \cdot \hat{\mathbf{u}}_0 \nabla^2_{\hat{\mathbf{u}}_s} G d^2\hat{\mathbf{u}}_s = \lambda \int G \nabla^2_{\hat{\mathbf{u}}_s} (\hat{\mathbf{u}}_s \cdot \hat{\mathbf{u}}_0) d^2\hat{\mathbf{u}}_s \\ &= -2\lambda \int \hat{\mathbf{u}}_s \cdot \hat{\mathbf{u}}_0 G d^2\hat{\mathbf{u}}_s = -2\lambda \langle \hat{\mathbf{u}}_s \cdot \hat{\mathbf{u}}_0 \rangle. \end{aligned}$$

Solving the ODE subject to the initial condition $\langle \hat{\mathbf{u}}_{s=0} \cdot \hat{\mathbf{u}}_0 \rangle = 1$ enables us to recover (8-6).

The identity

$$\int_{-1}^{+1} P_m(x) P_n(x) dx = \frac{2\delta_{mn}}{2n+1}, \tag{8-8}$$

together with the expression for Green's function (8-5) leads to

$$\langle P_n\big(\hat{\mathbf{u}}(s) \cdot \hat{\mathbf{u}}(s')\big) \rangle = e^{-\lambda n(n+1)|s-s'|}. \tag{8-9}$$

It is interesting to note that (8-6) furnishes an alternative definition for the inverse Kuhn's statistical segment length λ in terms of the integral of the unit tangent autocorrelation function of arc length. This may be compared with the usual Brownian self-diffusion coefficient D expressed in terms of the integral of the velocity autocorrelation function of time:

$$\frac{1}{\lambda} = 2 \int_0^{\infty} \langle \hat{\mathbf{u}}(s) \cdot \hat{\mathbf{u}}(0) \rangle ds, \tag{8-10a}$$

$$D = \frac{1}{3} \int_0^{\infty} \langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle dt. \tag{8-10b}$$

By definition, the position of the center of mass of a chain whose total arc length is L is $\mathbf{r}_c = (1/L)\int_0^L \mathbf{r}(s)ds$. Using (5-15a), we obtain

$$\langle \mathbf{r}_c \rangle = \hat{\mathbf{e}}_z \left(\frac{1}{2\lambda} - \frac{1 - e^{-2\lambda L}}{4\lambda^2 L} \right). \tag{8-11}$$

The position vector $\mathbf{W}(s)$ from center of mass to point s can be expressed as a linear function of the unit tangent vector:

$$\begin{aligned}\mathbf{W}(s) = \mathbf{r}(s) - \mathbf{r}_c &= \int_0^s \hat{\mathbf{u}}(\tau)d\tau - \frac{1}{L}\int_0^L \int_0^s \hat{\mathbf{u}}(\tau)d\tau ds \\ &= \int_0^L \left[\frac{\tau}{L} - H(\tau - s) \right] \hat{\mathbf{u}}(\tau)d\tau, \end{aligned} \tag{8-12}$$

with Heaviside's unit step function H.

We now use (8-6) and (8-12) to calculate the second moment of the distribution function $\langle W^2 \rangle$:

$$\langle W^2 \rangle = \int_0^L \int_0^L \left[\frac{x}{L} - H(x - s) \right] \left[\frac{y}{L} - H(y - s) \right] \langle \hat{\mathbf{u}}(x) \cdot \hat{\mathbf{u}}(y) \rangle \, dx \, dy. \tag{8-13}$$

Upon subdividing the L by L square integration region into six subregions : $s > y > x$, $s > x > y$,$x > s > y$, etc., and using (8-6), we obtain, after a lengthy calculation,

$$\begin{aligned}\langle W^2 \rangle = \frac{1}{8\lambda^4 L^2} \Big[& 1 + 2\lambda L(1 - e^{-2\lambda s}) - e^{-2\lambda L} - 2\lambda L e^{-2\lambda(L-s)} \\ & + \frac{8\lambda^3 L^3}{3} - 2\lambda^2 L^2 + 8\lambda^3 L s^2 - 8\lambda^3 L^2 s \Big]. \end{aligned} \tag{8-14}$$

An alternative definition of the mean-square radius of gyration is $R_g^2 = \overline{\langle W^2 \rangle} = (1/L)\int_0^L \langle W^2 \rangle ds$, where the angular brackets $\langle \ldots \rangle$ denotes the average over all possible configurations of the chain, and the overbar denotes the average over arc length. Upon using (8-14) and performing the average over arc length, we recover (5-15f) with $\mu = 0$.

For respectively very long ($\lambda L \gg 1$) and very short ($\lambda L \ll 1$) chains, (8-14) becomes

$$\lim_{\lambda L \to \infty} \langle W^2 \rangle = \frac{L}{3\lambda} \left[1 - \frac{3s(L - s)}{L^2} \right], \tag{8-15a}$$

$$\lim_{\lambda L \to 0} \langle W^2 \rangle = \left(\frac{L}{2} - s \right)^2. \tag{8-15b}$$

If we replace λ by $1/a$, where a is the Kuhn's statistical segment length, then in the long chain limit (8-15a) is in exact agreement with that for the Gaussian random coil [Yam1]. On the other hand, when the chain becomes very short it behaves like a straight rod with center of mass situated at the middle of the chain (arc length $L/2$). The average (over all possible configurations) distance squared from the center of mass to point s is expected to be $(L/2-s)^2$, in exact conformity with (8-15b).

The exact expression for the mean square distance from the center of mass to either end of the chain is given by

$$\langle W_{s=0}^2\rangle = \langle W_{s=L}^2\rangle = \frac{1}{8\lambda^4 L^2}\left[1 - e^{-2\lambda L} - 2\lambda L e^{-2\lambda L} + \frac{8\lambda^3 L^3}{3} - 2\lambda^2 L^2\right], \quad (8\text{-}16)$$

which serves as a measure of the linear dimension of the chain. Letting $L \to \infty$ in both (5-15f) (with $\mu = 0$) and (8-16), we obtain the mean square radius of gyration, $\langle R_g^2\rangle \to L/6\lambda$, and $\langle W_0^2\rangle = \langle W_L^2\rangle \to L/3\lambda$, which is twice $\langle R_g^2\rangle$.

The fourth moment $\langle W^4\rangle$ can be obtained as follows:

$$\begin{aligned}\langle W^4\rangle &= \int_0^L\int_0^L\int_0^L\int_0^L \prod_{i=1}^{4}\left[dx_i\left[\frac{x_i}{L} - H(x_i - s)\right]\right]\langle[\hat{\mathbf{u}}(x_1)\cdot\hat{\mathbf{u}}(x_2)]\,[\hat{\mathbf{u}}(x_3)\cdot\hat{\mathbf{u}}(x_4)]\rangle \\ &= 8\int_0^L dx_4\int_0^{x_4} dx_3\int_0^{x_3} dx_2\int_0^{x_2} dx_1 \prod_{i=1}^{4}\left[\frac{x_i}{L} - H(x_i - s)\right] \\ &\quad\times\left[\langle[\hat{\mathbf{u}}_1\cdot\hat{\mathbf{u}}_2]\,[\hat{\mathbf{u}}_3\cdot\hat{\mathbf{u}}_4]\rangle + \langle[\hat{\mathbf{u}}_1\cdot\hat{\mathbf{u}}_3]\,[\hat{\mathbf{u}}_2\cdot\hat{\mathbf{u}}_4]\rangle + \langle[\hat{\mathbf{u}}_1\cdot\hat{\mathbf{u}}_4]\,[\hat{\mathbf{u}}_2\cdot\hat{\mathbf{u}}_3]\rangle\right],\end{aligned} \quad (8\text{-}17)$$

where we have written $\hat{\mathbf{u}}_i \equiv \hat{\mathbf{u}}(x_i)$ for simplicity. By definition,

$$\langle(\hat{\mathbf{u}}_1\cdot\hat{\mathbf{u}}_2)(\hat{\mathbf{u}}_3\cdot\hat{\mathbf{u}}_4)\rangle_{1234} = \frac{1}{4\pi}\int G(\hat{\mathbf{u}}_4|\hat{\mathbf{u}}_3)G(\hat{\mathbf{u}}_3|\hat{\mathbf{u}}_2)G(\hat{\mathbf{u}}_2|\hat{\mathbf{u}}_1)[\hat{\mathbf{u}}_1\cdot\hat{\mathbf{u}}_2][\hat{\mathbf{u}}_3\cdot\hat{\mathbf{u}}_4]\prod_{i=1}^{4} d^2\hat{\mathbf{u}}_i, \quad (8\text{-}18)$$

where the subscript $\langle\ldots\rangle_{1234}$ specifies that points x_1, x_2, x_3, and x_4 are in increasing order of arc length, as required by the setting of the integral in the second half of equation (8-17). The other two moments, $\langle(\hat{\mathbf{u}}_1\cdot\hat{\mathbf{u}}_3)(\hat{\mathbf{u}}_2\cdot\hat{\mathbf{u}}_4)\rangle$ and $\langle(\hat{\mathbf{u}}_1\cdot\hat{\mathbf{u}}_4)(\hat{\mathbf{u}}_2\cdot\hat{\mathbf{u}}_3)\rangle$, have similar forms. The Green's function $G(\hat{\mathbf{u}}_i|\hat{\mathbf{u}}_j)$ is the infinite expansion in spherical harmonics given by (8-4).

Choosing the spherical angles of $\hat{\mathbf{u}}_k$ to be (θ_k, ϕ_k) in (8-4), we find that

$$G(\hat{\mathbf{u}}_i|\hat{\mathbf{u}}_j) = \sum_{n=0}^{\infty}\sum_{m=0}^{n} A_{nm}P_n^m(\cos\theta_i)P_n^m(\cos\theta_j)\cos[m(\phi_i - \phi_j)], \quad (8\text{-}19)$$

where

$$A_{nm} = \frac{1}{4\pi}(2n+1)e^{-n(n+1)\lambda|s_i - s_j|}\epsilon_m\frac{(n-m)!}{(n+m)!}. \quad (8\text{-}20)$$

Expressed explicitly in terms of spherical angles,

$$\begin{aligned}(\hat{\mathbf{u}}_1\cdot\hat{\mathbf{u}}_2)(\hat{\mathbf{u}}_3\cdot\hat{\mathbf{u}}_4) &= [\sin\theta_1\sin\theta_2\cos(\phi_1 - \phi_2) + \cos\theta_1\cos\theta_2] \\ &\quad\times[\sin\theta_3\sin\theta_4\cos(\phi_3 - \phi_4) + \cos\theta_3\cos\theta_4].\end{aligned} \quad (8\text{-}21)$$

Therefore, $\langle(\hat{\mathbf{u}}_1 \cdot \hat{\mathbf{u}}_2)(\hat{\mathbf{u}}_3 \cdot \hat{\mathbf{u}}_4)\rangle_{1234}$ is the sum of four configurational averages, the first of which is

$$S_1 \equiv \langle \cos(\phi_1 - \phi_2)\cos(\phi_3 - \phi_4)\prod_{k=1}^{4}\sin\theta_k\rangle_{1234} = \frac{1}{4\pi}\int\prod_{k=1}^{4}[\sin^2\theta_k d\theta_k d\phi_k]\times$$
$$\sum_{nm,ij,pq} A_{nm}A_{ij}A_{pq}P_n^m(\cos\theta_1)P_n^m(\cos\theta_2)P_i^j(\cos\theta_2)P_i^j(\cos\theta_3)P_p^q(\cos\theta_3)P_p^q(\cos\theta_4)$$
$$\times \cos(\phi_1 - \phi_2)\cos(\phi_3 - \phi_4)\cos[m(\phi_1 - \phi_2)]\cos[j(\phi_2 - \phi_3)]\cos[q(\phi_3 - \phi_4)].$$

The integration with respect to the ϕ_k's can easily be performed:

$$\int\prod_{k=1}^{4} d\phi_k \cos(\phi_1 - \phi_2)\cos[m(\phi_1 - \phi_2)]\cos[j(\phi_2 - \phi_3)]\cos(\phi_3 - \phi_4)\cos[q(\phi_3 - \phi_4)]$$
$$= 4\pi^4\delta_{m1}\delta_{j0}\delta_{q1}.$$

Consequently, the first configurational average, S_1, is

$$S_1 = \pi^3\sum_{n,i,p} A_{n1}A_{i0}A_{p1}\int_0^\pi P_n^1(\cos\theta_1)\sin^2\theta_1 d\theta_1\int_0^\pi P_p^1(\cos\theta_4)\sin^2\theta_4 d\theta_4$$
$$\times\int_0^\pi P_n^1(\cos\theta_2)P_i^0(\cos\theta_2)\sin^2\theta_2 d\theta_2\int_0^\pi P_i^0(\cos\theta_3)P_p^1(\cos\theta_3)\sin^2\theta_3 d\theta_3.$$

Using the identities

$$\int_0^\pi P_k^1(\cos\theta)\sin^2\theta d\theta = \frac{4}{3}\delta_{k,1}, \tag{8-22a}$$
$$\int_0^\pi P_k^1(\cos\theta)P_j^0(\cos\theta)\sin^2\theta d\theta = \frac{2k^2+2k}{4k^2-1}\delta_{j,k-1} - \frac{2k^2+2k}{(2k+1)(2k+3)}\delta_{j,k+1}, \tag{8-22b}$$

S_1 and other S_j's are found to be

$$S_1 \equiv \langle \sin\theta_1\sin\theta_2\sin\theta_3\sin\theta_4\cos(\phi_1 - \phi_2)\cos(\phi_3 - \phi_4)\rangle$$
$$= \frac{4}{9}e^{-2\lambda(x_4 - x_3 + x_2 - x_1)} + \frac{4}{45}e^{-2\lambda(x_4 + 2x_3 - 2x_2 - x_1)},$$
$$S_2 \equiv \langle \sin\theta_1\sin\theta_2\cos\theta_3\cos\theta_4\cos(\phi_1 - \phi_2)\rangle$$
$$= S_3 \equiv \langle \cos\theta_1\cos\theta_2\sin\theta_3\sin\theta_4\cos(\phi_3 - \phi_4)\rangle$$
$$= \frac{2}{9}e^{-2\lambda(x_4 - x_3 + x_2 - x_1)} - \frac{4}{45}e^{-2\lambda(x_4 + 2x_3 - 2x_2 - x_1)},$$
$$S_4 \equiv \langle \cos\theta_1\cos\theta_2\cos\theta_3\cos\theta_4\rangle = \frac{1}{9}e^{-2\lambda(x_4 - x_3 + x_2 - x_1)} + \frac{4}{45}e^{-2\lambda(x_4 + 2x_3 - 2x_2 - x_1)}.$$

Upon noticing that $\langle(\hat{\mathbf{u}}_1 \cdot \hat{\mathbf{u}}_2)(\hat{\mathbf{u}}_3 \cdot \hat{\mathbf{u}}_4)\rangle_{1234} = \sum_{j=1}^{4} S_j$, and using similar approaches to calculate the other moments, we finally obtain

$$\langle(\hat{\mathbf{u}}_1 \cdot \hat{\mathbf{u}}_2)(\hat{\mathbf{u}}_3 \cdot \hat{\mathbf{u}}_4)\rangle_{1234} = e^{-2\lambda(x_4-x_3+x_2-x_1)}, \tag{8-23a}$$

$$\begin{aligned}\langle(\hat{\mathbf{u}}_1 \cdot \hat{\mathbf{u}}_3)(\hat{\mathbf{u}}_2 \cdot \hat{\mathbf{u}}_4)\rangle_{1234} &= \langle(\hat{\mathbf{u}}_1 \cdot \hat{\mathbf{u}}_4)(\hat{\mathbf{u}}_2 \cdot \hat{\mathbf{u}}_3)\rangle_{1234} \\ &= \frac{1}{3}e^{-2\lambda(x_4-x_3+x_2-x_1)} + \frac{2}{3}e^{-2\lambda(x_4+2x_3-2x_2-x_1)}.\end{aligned} \tag{8-23b}$$

Combining (8-17), (8-23a), and (8-23b) allows $\langle W^4\rangle$ to be expressed as

$$\begin{aligned}\langle W^4\rangle = &\\ &\frac{40}{3L^4}\int_0^L dx_4 \int_0^{x_4} dx_3 \int_0^{x_3} dx_2 \int_0^{x_2} dx_1 \prod_{i=1}^{4}\Big[x_i - LH(x_i-s)\Big] e^{-2\lambda(x_4-x_3+x_2-x_1)} \\ &+ \frac{32}{3L^4}\int_0^L dx_4 \int_0^{x_4} dx_3 \int_0^{x_3} dx_2 \int_0^{x_2} dx_1 \prod_{i=1}^{4}\Big[x_i - LH(x_i-s)\Big] e^{-2\lambda(x_4+2x_3-2x_2-x_1)}.\end{aligned} \tag{8-24}$$

After a rather lengthy and tedious calculation, $\langle W^4\rangle$ is obtained. In particular, if we define

$$\begin{aligned}A(s) = &\frac{s^6}{72\lambda^2} - \frac{11s^5}{240\lambda^3} + \frac{11s^4}{128\lambda^4} - \frac{5s^3}{48\lambda^5} + \frac{5s^2}{64\lambda^6} - \frac{21}{256\lambda^8} \\ &+ e^{-2\lambda s}\left(\frac{s^4}{48\lambda^4} + \frac{11s^3}{192\lambda^5} + \frac{11s^2}{128\lambda^6} + \frac{21s}{128\lambda^7} + \frac{21}{256\lambda^8}\right),\end{aligned} \tag{8-25a}$$

$$\begin{aligned}B(s) = &\left[e^{-2\lambda s}\left(\frac{s^3}{24\lambda^3} + \frac{s^2}{32\lambda^4} + \frac{5}{32\lambda^6}\right) - \frac{s^4}{12\lambda^2} + \frac{11s^3}{48\lambda^3} - \frac{11s^2}{32\lambda^4} + \frac{5s}{16\lambda^5} - \frac{5}{32\lambda^6}\right] \\ &\times \left(\frac{L-s}{2\lambda} + \frac{e^{-2\lambda(L-s)}-1}{4\lambda^2}\right),\end{aligned} \tag{8-25b}$$

$$C(s) = \frac{s^3}{6\lambda} - \frac{s^2}{8\lambda^2} + \frac{1}{16\lambda^4} - \frac{se^{-2\lambda s}}{8\lambda^3} - \frac{e^{-2\lambda s}}{16\lambda^4}, \tag{8-25c}$$

$$\begin{aligned}D(s) = &\frac{s^5}{120\lambda^3} - \frac{7s^4}{288\lambda^4} + \frac{89s^3}{2592\lambda^5} - \frac{89s^2}{3456\lambda^6} + \frac{4781}{186624\lambda^8} \\ &+ e^{-2\lambda s}\left(-\frac{s^4}{96\lambda^4} - \frac{13s^3}{768\lambda^5} - \frac{13s^2}{512\lambda^6} - \frac{105s}{2048\lambda^7} - \frac{105}{4096\lambda^8}\right) \\ &+ e^{-6\lambda s}\left(\frac{7s^2}{41472\lambda^6} + \frac{49s}{497664\lambda^7} + \frac{49}{2985984\lambda^8}\right),\end{aligned} \tag{8-25d}$$

$$\begin{aligned}E(s) = &\left(\frac{L-s}{2\lambda} + \frac{e^{-2\lambda(L-s)}-1}{4\lambda^2}\right)\Bigg[-\frac{s^3}{24\lambda^3} + \frac{7s^2}{72\lambda^4} - \frac{89s}{864\lambda^5} + \frac{89}{1728\lambda^6} + e^{-2\lambda s} \\ &\times \left(-\frac{s^3}{48\lambda^3} + \frac{s^2}{128\lambda^4} - \frac{53}{1024\lambda^6}\right) + e^{-6\lambda s}\left(\frac{7s}{6912\lambda^5} + \frac{7}{27648\lambda^6}\right)\Bigg],\end{aligned} \tag{8-25e}$$

$$F(s) = \frac{s^2}{12\lambda^2} - \frac{5s}{72\lambda^3} + \frac{5}{432\lambda^4} + \frac{7e^{-6\lambda s}}{1728\lambda^4} + \frac{se^{-2\lambda s}}{16\lambda^3} - \frac{e^{-2\lambda s}}{64\lambda^4}, \tag{8-25f}$$

then the exact expression for the fourth moment is given by

$$\langle W^4(s)\rangle = \frac{40}{3L^4}\left[A(s)+A(L-s)+B(s)+B(L-s)+C(s)C(L-s)\right] + \frac{32}{3L^4}\left[D(s)+D(L-s)+E(s)+E(L-s)+F(s)F(L-s)\right]. \tag{8-26}$$

Observe that $\langle W^4(s)\rangle = \langle W^4(L-s)\rangle$, as expected from the head-tail symmetry of the chain.

The leading-order approximation can be obtained as

$$\langle W^4(s)\rangle = \frac{5}{27\lambda^2 L^4}(L^6+15L^4s^2+9L^2s^4-6L^5s-18L^3s^3) - \frac{1}{90\lambda^3L^4}(47L^5-185L^4s+295L^3s^2-220L^2s^3+110Ls^4)+\dots. \tag{8-27}$$

The exact mean fourth power distance from the center of mass to either end of chain is

$$\langle W^4(0)\rangle = \langle W^4(L)\rangle = \frac{5L^2}{27\lambda^2} - \frac{47L}{90\lambda^3} + \frac{383}{432\lambda^4} - \frac{497}{486\lambda^5 L} + \frac{497}{648\lambda^6L^2} - \frac{57421}{69984\lambda^8L^4} + e^{-2\lambda L}\left(\frac{1}{6\lambda^4}+\frac{7}{12\lambda^5L}+\frac{7}{8\lambda^6L^2}+\frac{105}{64\lambda^7L^3}+\frac{105}{128\lambda^8L^4}\right) + e^{-6\lambda L}\left(\frac{7}{3888\lambda^6L^2}+\frac{49}{46656\lambda^7L^3}+\frac{49}{279936\lambda^8L^4}\right). \tag{8-28}$$

In the limits of both very long and very short chains, $\langle W^4\rangle$ is given by

$$\lim_{\lambda L\to\infty}\langle W^4\rangle = \frac{5L^2}{27\lambda^2}\left[1-6\frac{s}{L}+15\frac{s^2}{L^2}-18\frac{s^3}{L^3}+9\frac{s^4}{L^4}+\dots\right], \tag{8-29a}$$

$$\lim_{\lambda L\to 0}\langle W^4\rangle = \left(\frac{L}{2}-s\right)^4. \tag{8-29b}$$

The latter is in exact conformity with the expected $\langle W^4\rangle$ expression for a rod-like short chain.

Although the first few moments are insufficient to specify the distribution function uniquely, we nevertheless have yet one more piece of information at our disposal. Recall that in the long chain limit a wormlike chain behaves like a Gaussian random coil. Hence, the leading order approximation of the desired distribution function approaches that for the Gaussian random coil, which is well known [Yam1]. Since the distribution of a linear combination of independent Gaussian distributions is also Gaussian, whereas for the Gaussian random coil the position vector from the center of mass to point s can be expressed in terms of a linear combination of independent Gaussian bond vectors. Hence, it is easy to obtain the corresponding distribution for the Gaussian random coil. The first few moments, together with the known leading order behavior of the desired distribution, enable us to calculate the unique asymptotic distribution $P(W;s)$ of chain segments about the center of mass.

To do this, we first note that for discrete Gaussian random coil, the corresponding distribution about the center of mass is given by [Deb1] (cf. [Yam1], p. 21)

$$P(\mathbf{W}_j) = \left(\frac{9n}{2\pi a^2[n^2 - 3j(n-j)]}\right)^{3/2} e^{-\frac{9nW_j^2}{2a^2[n^2-3j(n-j)]}}.$$

The general rule of correspondence between the wormlike chain and the Gaussian random coil states that, upon replacing $1/\lambda$ by a, L by na, the wormlike chain distribution function of any kind valid in the long chain limit must be identical to the corresponding distribution for Gaussian coil. This rule of correspondence and the above expression define the leading behavior of the wormlike chain distribution about the center of mass uniquely. Secondly, we note that the distribution must be isotropic because it is invariant to rotation of the space-frame. This fact implies that in the asymptotic expansion, only even powers of W will appear. Suppose we let the distribution be the above leading term (with a replaced by $1/\lambda$, na replaced by L) multiplied by $(A + BW^2 + CW^4 + \cdots)$. Then the requirement that the resulting $\langle W^2 \rangle$ and $\langle W^4 \rangle$ should at least asymptotically match (4-8) and (4-11), and that the leading term of A is 1, suffice to determine uniquely the desired distribution,

$$P(W;s) = 4\pi W^2 \left(\frac{9\lambda L^2}{2\pi\left[(L-s)^3 + s^3\right]}\right)^{\frac{3}{2}} e^{-\frac{(9\lambda L^2)W^2}{2[(L-s)^3+s^3]}} \left[\left(1 - \frac{27}{20\lambda L} + \frac{9s}{10\lambda L^2} + \ldots\right)\right.$$
$$\left. + W^2\left(\frac{459}{40L^2} + \frac{783s}{20L^3} + \ldots\right) + W^4\left(-\frac{2673\lambda}{200L^3} - \frac{18711\lambda s}{200L^4} + \ldots\right) + \ldots\right]. \quad (8\text{-}30)$$

§9. Concluding Remarks

In this thesis we proposed a theory of linear elastic polymer chains under constant external force and torque. The general theory takes into account bending, twisting, shearing, and stretching deformations. The theory, which is novel, is found to contain the Kratky-Porod wormlike chain and the Yamakawa-Fujii helical wormlike chain as special cases. We derived the Fokker-Planck equation governing the Green's function both from the rule of correspondence in quantum mechanics and from a purely probabilistic approach. The model in its most general form is versatile in the sense that it does not assume isotropic bending or shearing (in the cross-sectional plane); neither does it assume homogeneous (along the chain) bending, twisting, shearing, and stretching. Additionally, no assumption was made regarding the ratio of chain length to diameter of the chain, whereas in all previous models slender chains were always assumed. This is partly because we have incorporated shearing and stretching into the model; the model is therefore applicable to materials whose length is of the same order of magnitude as its diameter so long as the elastic potential energy function of the material satisfies the quadratic form of the elastic energy function we proposed (cf. eqn (2-33)). We consider the model as one of the major results of the thesis. In terms of solving the differential equation governing the Green's function, we solved a simplified $3D$ problem and a complete $2D$ problem.

The distribution function of the wormlike chain in the short chain (near-rod) limit is solved. Also derived is the asymptotic solution for the mean reciprocal distance $\langle 1/r \rangle(s)$ between two points on the chain in the near-rod limit. The two leading terms in the asymptotic expansion of the moment $\langle 1/r \rangle$ were derived by Hearst and Stockmayer [Hea1] in 1962, and by Yamakawa and Fujii [Yam4] in 1973. However, due to the mathematical difficulty arising from their approaches, their methods were able to supply only the two leading terms in the expansion. In this thesis we have developed a method which can be used to systematically generate all the terms in the expansion of $\langle 1/r \rangle(s)$. This constitutes another major result of the thesis.

The asymptotic form of the distribution function of the wormlike chain segments about the center of mass was derived from the first few moments in conjunction with the known expression for the corresponding distribution in the long chain limiting Gaussian random coil case derived by Debye and Bueche [Deb1] in 1952.

The elastic chain model we proposed in the thesis does not take into account the coupling of twisting and stretching which arises, for example, in the context of stretching individual double helix DNA molecules, where the extension of the chain is achieved at the cost of partially unwinding the double helix. It is easy to incorporate this feature into the model by adding to the quadratic form of the Lagrangian (2-33) the cross term $(\omega_3 - \omega_3^0)(t_3 - t_3^0)$ multiplied by a new elasticity parameter, say $C(s)$.

Although our model in its most general form contains a (constant) external force and torque, in the thesis we only solved the Green's functions and the moments for the free-chain (force-free and torque-free) problems. The natural next step is to find the moments of the distribution in the presence of a constant external force and torque. It would be more complete were we able to find the asymptotic solution of the Green's function in the presence of the constant external force and torque. On the other hand, since the model is proposed in a complete form with differential equations derived, those interested in the problem can find ways to solve different simplified versions of the complete problem to suit their own research interest on elastic materials (which may not necessarily be polymer chains). This fact also demonstrates that our model is useful not only to the polymer community but also to a wider audience.

Lastly, a few comments about the title of this thesis. Although part of the thesis dealt with the general elastic chain model, we chose the title "Statistics and Dynamics of Stiff Chains" because we also included much work on new perspectives of the wormlike chain. In the polymer community, The "stiff chain" is a more well established name than is the "elastic chain". The name "stiff chain" is widely used in contrast to the name "random coil" for highly flexible discrete Gaussian chain. In this context, stiff chain contains the framework of of both our novel general elastic chain and the Kratky-Porod wormlike chain.

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