Conformational statistics of stiff macromolecules as solutions to partial differential equations on the rotation and motion groups

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Partial differential equations (PDE's) for the probability density function (PDF) of the position and orientation of the distal end of a stiff macromolecule relative to its proximal end are derived and solved. The Kratky-Porod wormlike chain, the Yamakawa helical wormlike chain, and the original and revised Marko-Siggia models are examples of stiffness models to which the present formulation is applied. The solution technique uses harmonic analysis on the rotation and motion groups to convert PDE's governing the PDF's of interest into linear algebraic equations which have mathematically elegant solutions.

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I. INTRODUCTION

A quantity of importance in polymer science is the probability density function describing the relative occurrence of positions and orientations of the distal end of the chain for a given position and orientation of the proximal end [1–4]. For flexible chains, the orientation distribution quickly reaches its limiting form, which is a constant over all orientations [2]. Hence, the distribution of end positions (without regard to orientation) has been the subject of intensive study over the past half century (see, e.g., [5,3,6] for complete reviews of the literature), and remains of interest to the present day [7,8].

In the case of stiff chains (e.g., DNA), a much greater length is required for the orientation distribution of the distal end relative to the proximal one to reach its limiting form, and it cannot be considered constant when considering relatively small segments of the chain. Hence, it is important to characterize the evolution of a joint positional and orientational probability density function in such cases.

The statistical mechanics of DNA and other stiff (wormlike) chains has received much attention in the literature (see, e.g., [9–29]). In particular, stiff polymer theories based on diffusion processes and path integral techniques can be found in [30–33]

Experimental measurements of DNA stiffness parameters have been reported in [34–38,4]. Efforts to characterize integrals of the joint positional and orientational probability density function (PDF) over many of its arguments can be found in [25,39], and the whole distribution in the case of the helical wormlike chain can be found in [4]. DNA elastic properties and experimental measurements of DNA elastic twist/stretch coupling have also been reported in [40–44].

The approach presented here solves the most general inextensible case, and draws on a number of group-theoretical notations. The utility of our approach is that it is so general that it is valid for any second-order stiffness and chirality model. As an example of this generality, we show later in the paper how the Kratky-Porod [45–47], Yamakawa [4], and Marko-Siggia [48] models all fit within our framework. We note that while our model is applicable to DNA, it is not limited to this case. In analogy with the way the Kratky-Porod (KP) model for stiff polymers was introduced prior to the discovery of DNA, we expect our model to be applicable to numerous manmade stiff molecules to be invented in the twenty-first century.

Orientations are described as elements of the rotation group, SO(3) [the set of 3×3 real matrices satisfying $A^TA=I$ and $\det(A)=1$]. Translations (and positions) are described as elements of three-space: $\mathbf{a}\in\mathbb{R}^3$. The Euclidean motion group (or special Euclidean group), SE(3), is the semidirect product of $\mathbb{R}^3$ with the special orthogonal group, SO(3). We denote elements of SE(3) as $g=(\mathbf{a},A)\in\mathrm{SE}(3)$, where $A\in\mathrm{SO}(3)$ and $\mathbf{a}\in\mathbb{R}^3$. The group law is written as $g_1\circ g_2=(\mathbf{a}_1+A_1\mathbf{a}_2,A_1A_2)$ and $g^{-1}=(-A^T\mathbf{a},A^T)$. Any element of SE(3) can be written as the product of a pure translation and pure rotation as $(\mathbf{a},A)=(\mathbf{a},I)\circ(\mathbf{0},A)$.

One may represent any element of SE(N) as an $(N+1)\times(N+1)$ homogeneous transformation matrix of the form

$$H(g)=\begin{pmatrix} A & \mathbf{a} \\ \mathbf{0}^T & 1 \end{pmatrix}.$$

Clearly, $H(g_1)H(g_2)=H(g_1\circ g_2)$ and $H(g^{-1})=H^{-1}(g)$, and the mapping $g\rightarrow H(g)$ is an isomorphism between SE(N) and the set of homogeneous transformation matrices, and so we henceforth make no distinction between g and $H(g)$.

When describing a frame of reference or motion [which are both elements of SE(3)], the translations (or positions) will be parametrized in either Cartesian or spherical coordinates,

$$\mathbf{a}=\begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix}=\begin{pmatrix} a\sin\theta\cos\phi \\ a\sin\theta\sin\phi \\ a\cos\theta \end{pmatrix}.$$

Rotations (or orientations) are parametrized using ZXZ Euler angles,

$$A(\alpha,\beta,\gamma)=\Omega_{\mathrm{rot}}[\mathbf{e}_3,\alpha]\Omega_{\mathrm{rot}}[\mathbf{e}_1,\beta]\Omega_{\mathrm{rot}}[\mathbf{e}_3,\gamma],$$

where $\Omega_{\mathrm{rot}}[\mathbf{e}_i,\varphi]$ denotes the rotation matrix describing counterclockwise rotation by φ about the natural basis vector $\mathbf{e}_i$ which has elements $(\mathbf{e}_i)_j=\delta_{ij}$.

II. MODEL FORMULATION

As is often the case in theoretical polymer science, analogies between the motion of a particle along a path and the motion of an observer traversing a polymer chain allow for tools from classical and quantum mechanics to be applied.

In particular, a number of authors have derived potential energies of bending and/or twisting of a stiff chain that are of the form

$$E=\int_0^L U[\boldsymbol{\omega}(s)]ds,$$

where L is the length of the macromolecule and

$$U=\frac{1}{2}\boldsymbol{\omega}^T B\boldsymbol{\omega}-\mathbf{b}^T\boldsymbol{\omega}+\beta'. \tag{1}$$

Here $B=B^T\in\mathbb{R}^{3\times 3}$ is a positive semidefinite matrix, $\mathbf{b}\in\mathbb{R}^3$, and $\beta'\in\mathbb{R}$. $\boldsymbol{\omega}$ is the "angular velocity" of a frame of reference which traverses the macromolecule, coinciding with each frame $[\mathbf{a}(s),A(s)]$ affixed to the backbone of the molecule for each value of arclength s. This "angular velocity" is the dual vector of the skew symmetric matrix $A^T\dot{A}$, where the overdot denotes d/ds. That is, $\boldsymbol{\omega}\times\mathbf{x}=A^T\dot{A}\mathbf{x}$ for all $\mathbf{x}\in\mathbb{R}^3$. This is completely analogous to the definition of angular velocity of a rigid body as seen in the body fixed frame with s taking the place of time. Henceforth, we will use the notation $U=U(\boldsymbol{\omega})=U(A,\dot{A})$ to denote the fact that the bending energy is a function of the rotation matrix and its derivative through of the definition of $\boldsymbol{\omega}$.

As well-known examples of Eq. (1) from the polymer science literature, consider the following.

The Kratky-Porod model [1,45]:

$$B=\begin{pmatrix}\alpha_0 & 0 & 0\\ 0 & \alpha_0 & 0\\ 0 & 0 & 0\end{pmatrix},\quad \mathbf{b}=\begin{pmatrix}0\\0\\0\end{pmatrix},\quad \beta'=0.$$

The Yamakawa model [4]:

$$B=\begin{pmatrix}\alpha_0 & 0 & 0\\ 0 & \alpha_0 & 0\\ 0 & 0 & \beta_0\end{pmatrix},\quad \mathbf{b}=\begin{pmatrix}0\\ \alpha_0\kappa_0\\ \beta_0\tau_0\end{pmatrix},$$

$$\beta'=\frac{1}{2}(\beta_0\tau_0^2+\alpha_0\kappa_0^2).$$

The Marko-Siggia DNA model [48]:

$$B=\begin{pmatrix}A' & 0 & B\\ 0 & A & 0\\ B & 0 & C\end{pmatrix},\quad \mathbf{b}=\begin{pmatrix}B\omega_0\\ 0\\ C\omega_0\end{pmatrix},\quad \beta'=\frac{1}{2}C\omega_0^2.$$

The revised Marko-Siggia model [49]:

$$B=\begin{pmatrix}A+B^2/C & 0 & B\\ 0 & A & 0\\ B & 0 & C\end{pmatrix},\quad \mathbf{b}=\begin{pmatrix}B\omega_0\\ 0\\ C\omega_0\end{pmatrix},$$

$$\beta'=\frac{1}{2}C\omega_0^2.$$

Other modifications of these models may be made to include stretching effects [50], though the current presentation is restricted to the inextensible case.

We now generate the diffusion equation that governs the evolution of the positional and orientation probability density function $F(\mathbf{a},A;s)$ for all values of $0\leqslant s\leqslant L$. Assuming that the proximal end is fixed at the frame $(\mathbf{0},I)$, then $F(\mathbf{a},A;0)=\delta(\mathbf{a})\delta(A)$. Here the Dirac delta function on the motion group is written as the product of those for $\mathbb{R}^3$ and SO(3).

Under the constraint that the molecule is inextensible, and all the frames of reference are attached to the backbone with their local z axis pointing in the direction of the next frame, one observes

$$\mathbf{a}(L)=\int_0^L \mathbf{u}(s)ds \quad\text{and}\quad \mathbf{u}(s)=A(s)\mathbf{e}_3. \tag{2}$$

Hence, the PDF of interest can be formulated as the following path integral over the rotation group:

$$F(\mathbf{a},A;L)=\int_{A(0)=I}^{A(L)=A}\delta\left(\mathbf{a}(L)-\int_0^L\mathbf{u}(s)ds\right)\times\exp\left[-\int_0^L U(A,\dot{A})ds\right]\mathcal{D}[A(s)], \tag{3}$$

where it is assumed that the bending energy U is measured in units of k_BT. Path integration over the rotation group has been studied extensively in the literature in the context of quantum mechanics (see [51–54] and references therein). Our notation and formulation follows that in [4].

Using the classical Fourier transform pair

$$\hat{f}(\mathbf{k})=\int_{\mathbb{R}^3}f(\mathbf{a})e^{-i\mathbf{k}\cdot\mathbf{a}}d^3a$$

$$f(\mathbf{a})=\frac{1}{(2\pi)^3}\int_{\mathbb{R}^3}\hat{f}(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{a}}d^3k, \tag{4}$$

one writes

$$\hat{F}(\mathbf{k},A;L)=\int_{A(0)=I}^{A(L)=A}\exp\left[-\int_0^L(i\mathbf{k}\cdot\mathbf{u}+U)ds\right]\mathcal{D}[A(s)].$$

Treating the innermost integrand as i times a Lagrangian with kinetic and potential energies,

$$T=\frac{1}{2}i\boldsymbol{\omega}^T B\boldsymbol{\omega}$$

and

$$V=i[\mathbf{b}\cdot\boldsymbol{\omega}-\beta']+\mathbf{k}\cdot\mathbf{u}$$

(the constant β' can be ignored) one calculates the momenta and Hamiltonian in the usual way, which for this case means

$$p_k = \frac{\partial L}{\partial \omega_k} \rightarrow H = -i\left[\frac{1}{2}\mathbf{p}^T B^{-1}\mathbf{p}\right] + \mathbf{b}^T B^{-1}\mathbf{p} + \mathbf{k}\cdot\mathbf{u}. \quad (5)$$

Here and henceforth B is assumed to be positive definite (and hence invertible).

The quantization

$$p_i = -iX_i^R \quad (6)$$

is used, where the differential operators X_i^R acting on functions on the rotation group are defined as

$$X_i^R f(A) = \left.\frac{df(A\cdot\Omega_{\mathrm{rot}}[\mathbf{e}_i,t])}{dt}\right|_{t=0} = \left.\frac{df[A(I+tX_i)]}{dt}\right|_{t=0}, \quad (7)$$

where

$$X_1 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix},$$

$$X_2 = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{pmatrix},$$

$$X_3 = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}.$$

The superscript R in X_i^R denotes the fact that the infinitesimal rotation $I+tX_i$ is applied on the right of the argument of the function. This corresponds to an infinitesimal motion relative to the body-fixed frame in a rigid body.

Using the ZXZ Euler angles (α,β,γ) these operators have the explicit form

$$X_1^R = -\cot\beta\sin\gamma\frac{\partial}{\partial\gamma} + \frac{\sin\gamma}{\sin\beta}\frac{\partial}{\partial\alpha} + \cos\gamma\frac{\partial}{\partial\beta},$$

$$X_2^R = -\cot\beta\cos\gamma\frac{\partial}{\partial\gamma} + \frac{\cos\gamma}{\sin\beta}\frac{\partial}{\partial\alpha} - \sin\gamma\frac{\partial}{\partial\beta}, \quad (8)$$

$$X_3^R = \frac{\partial}{\partial\gamma}.$$

The Schrödinger-like equation corresponding to the Hamiltonian (5) and quantization (6) is

$$i\frac{\partial\hat{F}}{\partial L} = H\hat{F}.$$

This takes the explicit form

$$\left(\frac{\partial}{\partial L} - \frac{1}{2}\sum_{k,l=1}^{3}(B_{lk}^{-1}X_l^R X_k^R - 2B_{lk}^{-1}b_k X_l^R) + i\mathbf{k}\cdot\mathbf{u}\right)\hat{F} = 0. \quad (9)$$

Henceforth we will use the quantities $D = B^{-1}$ and $\mathbf{d} = -B^{-1}\mathbf{b}$.

The classical Fourier inversion formula (4) then converts (9) to

$$\left(\frac{\partial}{\partial L} - \frac{1}{2}\sum_{k,l=1}^{3} D_{lk}X_l^R X_k^R - \sum_{l=1}^{3} d_l X_l^R + \mathbf{u}\cdot\nabla_{\mathbf{a}}\right)F = 0, \quad (10)$$

which is a partial differential equation (PDE) on the motion group, SE(3). The initial conditions are $F(\mathbf{a},A;0) = \delta(\mathbf{a})\,\delta(A)$.

Integrating F over all positions, $\mathbf{a}\in\mathbb{R}^3$, results in a purely orientational density function:

$$f(A;s) = \int_{\mathbb{R}^3} F(\mathbf{a},A;s)d^3a.$$

Performing this integration over the initial conditions and Eq. (10) results in the SO(3)-diffusion equation

$$\left(\frac{\partial}{\partial L} - \frac{1}{2}\sum_{k,l=1}^{3} D_{lk}X_l^R X_k^R - \sum_{l=1}^{3} d_l X_l^R\right)f = 0 \quad (11)$$

with initial conditions $f(A;0) = \delta(A)$.

Equation (11) is a partial differential equation that governs the evolution of the function f on the rotation group SO(3). It is solved in series form in Sec. III using techniques from noncommutative harmonic analysis. Equations similar to Eq. (11) have been derived in, e.g., [36,37]. Our goal in this paper is to solve both Eq. (11) and (10) in a numerically efficient and mathematically elegant way.

III. HARMONIC ANALYSIS ON THE ROTATION GROUP

The matrix elements of the irreducible unitary representations IUR's of SO(3) are given to within an arbitrary unitary transformation by [55–57]:

$$U_{mn}^l(g(\alpha,\beta,\gamma)) = (-1)^{n-m}e^{-i(m\alpha+n\gamma)}P_{mn}^l(\cos\beta) \quad (12)$$

where

$$P_{mn}^l(\cos\beta) = \left[\frac{(l-m)!(l+m)!}{(l-n)!(l+n)!}\right]^{1/2} \times \sin^{m-n}\frac{\beta}{2}\cos^{m+n}\frac{\beta}{2}P_{l-m}^{(m-n,m+n)}(\cos\beta) \quad (13)$$

and $P_l^{m,n}(\cdot)$ are the Jacobi polynomials.

The matrices U^l with entries U_{mn}^l are $(2l+1)\times(2l+1)$ dimensional, and the indicies take the range of values $-l \le m,n \le l$. These representation matrices posess the homomorphism and orthogonality properties

$$U^l(A_1A_2)=U^l(A_1)U^l(A_2) \tag{14}$$

and

$$\int_{SO(3)} \overline{U^{l'}_{m'n'}(A)}U^l_{mn}(A)\,dA=\frac{\delta_{m'm}\,\delta_{n'n}\,\delta_{l'l}}{(2l+1)}. \tag{15}$$

Any square-integrable function on SO(3) can be expanded in a Fourier series as

$$f(A)=\sum_{l=0}^{\infty}(2l+1)\sum_{m=-l}^{l}\sum_{n=-l}^{l}\hat{f}^l_{mn}U^l_{nm}(A)$$
$$=\sum_{l=0}^{\infty}(2l+1)\mathrm{Tr}(\hat{f}^lU^l), \tag{16}$$

where the entries of the Fourier transform matrix $\mathcal{F}(f)^l=\hat{f}^l$ are defined as

$$\hat{f}^l_{mn}=\int_{SO(3)} f(A)U^l_{mn}(A^{-1})dA. \tag{17}$$

Here $dA=(1/8\pi^2)\sin\beta d\alpha d\beta d\gamma$ is the invariant integration measure for SO(3) normalized so that $\int_{SO(3)}dA=1$. Hence, by expanding the PDF in the PDE in Eq. (11) into a Fourier series on SO(3), the solution can be obtained once one knows how the differential operators X_i^R transform the matrix elements $U^l_{m,n}(A)$. In fact, this is well known, and can be found in [55,56] (adjusted for the differing definitions of U^l_{mn}) as

$$X_1^RU^l_{mn}=\frac{1}{2}c^l_{-n}U^l_{m,n-1}-\frac{1}{2}c^l_nU^l_{m,n+1}, \tag{18}$$

$$X_2^RU^l_{mn}=\frac{1}{2}ic^l_{-n}U^l_{m,n-1}+\frac{1}{2}ic^l_nU^l_{m,n+1}, \tag{19}$$

$$X_3^RU^l_{mn}=-inU^l_{mn}, \tag{20}$$

where $c^l_n=\sqrt{(l-n)(l+n+1)}$ for $l\geqslant|n|$ and $c^l_n=0$ otherwise. From this definition it is clear that $c^k_k=0, c^l_{-(n+1)}=c^l_n, c^l_{n-1}=c^l_{-n}$, and $c^l_{n-2}=c^l_{-n+1}$. Equations (18)–(20) follow from Eq. (14) and the fact that

$$\frac{d}{dt}U^l_{mn}(\Omega_{\mathrm{rot}}(\mathbf{e}_1,t))|_{t=0}=\frac{1}{2}c^l_{-n}\delta_{m+1,n}-\frac{1}{2}c^l_n\delta_{m-1,n}, \tag{21}$$

$$\frac{d}{dt}U^l_{mn}(\Omega_{\mathrm{rot}}(\mathbf{e}_2,t))|_{t=0}=\frac{i}{2}c^l_{-n}\delta_{m+1,n}+\frac{i}{2}c^l_n\delta_{m-1,n}, \tag{22}$$

$$\frac{d}{dt}U^l_{mn}(\Omega_{\mathrm{rot}}(\mathbf{e}_3,t))|_{t=0}=-in\,\delta_{m,n}. \tag{23}$$

By repeated application of these rules one finds

$$(X_1^R)^2U^l_{mn}=\frac{1}{4}c^l_{-n}c^l_{-n+1}U^l_{m,n-2}-\frac{1}{4}(c^l_{-n}c^l_{n-1}+c^l_nc^l_{-n-1})U^l_{mn}+\frac{1}{4}c^l_nc^l_{n+1}U^l_{m,n+2},$$

$$(X_2^R)^2U^l_{mn}=-\frac{1}{4}c^l_{-n}c^l_{-n+1}U^l_{m,n-2}-\frac{1}{4}(c^l_{-n}c^l_{n-1}+c^l_nc^l_{-n-1})U^l_{mn}-\frac{1}{4}c^l_nc^l_{n+1}U^l_{m,n+2},$$

$$(X_3^R)^2U^l_{mn}=-n^2U^l_{mn},$$

$$X_1^RX_2^RU^l_{m,n}=\frac{i}{4}c^l_{-n}c^l_{-n+1}U^l_{m,n-2}+\frac{i}{4}(-c^l_{-n}c^l_{n-1}+c^l_nc^l_{-n-1})U^l_{m,n}-\frac{i}{4}c^l_nc^l_{n+1}U^l_{m,n+2},$$

$$X_2^RX_1^RU^l_{m,n}=\frac{i}{4}c^l_{-n}c^l_{-n+1}U^l_{m,n-2}+\frac{i}{4}(c^l_{-n}c^l_{n-1}-c^l_nc^l_{-n-1})U^l_{m,n}-\frac{i}{4}c^l_nc^l_{n+1}U^l_{m,n+2},$$

$$X_1^RX_3^RU^l_{m,n}=i\frac{n}{2}(-c^l_{-n}U^l_{m,n-1}+c^l_nU^l_{m,n+1}),$$

$$X_3^RX_1^RU^l_{m,n}=-i\frac{n-1}{2}c^l_{-n}U^l_{m,n-1}+i\frac{n+1}{2}c^l_nU^l_{m,n+1},$$

$$X_3^RX_2^RU^l_{m,n}=\frac{(n-1)}{2}c^l_{-n}U^l_{m,n-1}+\frac{(n+1)}{2}c^l_nU^l_{m,n+1},$$

$$X_2^RX_3^RU^l_{m,n}=\frac{n}{2}(c^l_{-n}U^l_{m,n-1}+c^l_nU^l_{m,n+1}).$$

As a direct result of the definition of the SO(3)-Fourier inversion formula (16), one observes that if a differential operator X transforms U^l_{mn} as

$$XU^l_{m,n}=x(n)U^l_{m,n+p},$$

then there is a corresponding operational property of the Fourier transform

$$\mathcal{F}(Xf)^l_{m,n}=x(m-p)\hat{f}^l_{m-p,n}. \tag{24}$$

We use this to write

$$\mathcal{F}(X_1^Rf)^l_{mn}=\frac{1}{2}c^l_{-m-1}\hat{f}^l_{m+1,n}-\frac{1}{2}c^l_{m-1}\hat{f}^l_{m-1,n},$$

$$\mathcal{F}(X_2^Rf)^l_{mn}=\frac{1}{2}ic^l_{-m-1}\hat{f}^l_{m+1,n}+\frac{1}{2}ic^l_{m-1}\hat{f}^l_{m-1,n},$$

$$\mathcal{F}(X_3^Rf)^l_{mn}=-im\hat{f}^l_{mn},$$

$$\mathcal{F}((X_1^R)^2 f)^l_{mn} = \frac{1}{4} c^l_{m+1} c^l_{-m-1} \hat{f}^l_{m+2,n} - \frac{1}{4}(c^l_{-m} c^l_{m-1} + c^l_m c^l_{-m-1}) \hat{f}^l_{mn} + \frac{1}{4} c^l_{-m+1} c^l_{m-1} \hat{f}^l_{m-2,n},$$

$$\mathcal{F}((X_2^R)^2 f)^l_{mn} = -\frac{1}{4} c^l_{m+1} c^l_{-m-1} \hat{f}^l_{m+2,n} - \frac{1}{4}(c^l_{-m} c^l_{m-1} + c^l_m c^l_{-m-1}) \hat{f}^l_{mn} - \frac{1}{4} c^l_{-m+1} c^l_{m-1} \hat{f}^l_{m-2,n},$$

$$\mathcal{F}((X_3^R)^2 f)^l_{mn} = -m^2 \hat{f}^l_{mn},$$

$$\mathcal{F}((X_1^R X_2^R + X_2^R X_1^R) f)^l_{m,n} = \frac{i}{2} c^l_{m+1} c^l_{-m-1} \hat{f}^l_{m+2,n} - \frac{i}{2} c^l_{-m+1} c^l_{m-1} \hat{f}^l_{m-2,n},$$

$$\mathcal{F}((X_1^R X_3^R + X_1^R X_3^R) f)^l_{m,n} = -i \frac{2m+1}{2} c^l_{-m-1} \hat{f}^l_{m+1,n} + i \frac{2m-1}{2} c^l_{m-1} \hat{f}^l_{m-1,n},$$

$$\mathcal{F}((X_3^R X_2^R + X_2^R X_3^R) f)^l_{m,n} = \frac{(2m+1)}{2} c^l_{-m-1} \hat{f}^l_{m+1,n} + \frac{(2m-1)}{2} c^l_{m-1} \hat{f}^l_{m-1,n}.$$

Collecting everything together we have

$$\mathcal{F}\left(\left(\frac{1}{2} \sum_{i,j=1}^{3} D_{ij} X_i^R X_j^R + \sum_{i=1}^{3} d_i X_i^R\right) f\right)^l_{mn} = \sum_{k=\max(-l,m-2)}^{\min(l,m+2)} \mathcal{A}^l_{m,k} \hat{f}^l_{k,n},$$

where

$$\mathcal{A}^l_{m,m+2} = \left[\frac{(D_{11}-D_{22})}{8} + \frac{i}{4} D_{12}\right] c^l_{m+1} c^l_{-m-1},$$

$$\mathcal{A}^l_{m,m+1} = \left[\frac{(2m+1)}{4}(D_{23} - iD_{13}) + \frac{1}{2}(d_1 + id_2)\right] c^l_{-m-1},$$

$$\mathcal{A}^l_{m,m} = \left[-\frac{(D_{11}+D_{22})}{8}(c^l_{-m} c^l_{m-1} + c^l_m c^l_{-m-1}) - \frac{D_{33} m^2}{2} - i d_3 m\right],$$

$$\mathcal{A}^l_{m,m-1} = \left[\frac{(2m-1)}{4}(D_{23} + iD_{13}) + \frac{1}{2}(-d_1 + id_2)\right] c^l_{m-1},$$

$$\mathcal{A}^l_{m,m-2} = \left[\frac{(D_{11}-D_{22})}{8} - \frac{i}{4} D_{12}\right] c^l_{-m+1} c^l_{m-1}.$$

Hence, application of the SO(3)-Fourier transform to Eq. (11) and corresponding intial conditions reduces (11) to a set of linear time-invariant ODE's of the form

$$\frac{d\hat{f}^l}{dL} = \mathcal{A}^l \hat{f}^l \quad \text{with} \quad \hat{f}^l(0) = I_{2l+1}. \tag{25}$$

Here I_{2l+1} is the $(2l+1)\times(2l+1)$ identity matrix and the banded matrix $\mathcal{A}^l$ are of the following form for $l=0,1,2,3$:

$$\mathcal{A}^0 = \mathcal{A}^0_{0,0} = 0, \quad \mathcal{A}^1 = \begin{pmatrix} \mathcal{A}^1_{-1,-1} & \mathcal{A}^1_{-1,0} & \mathcal{A}^1_{-1,1} \\ \mathcal{A}^1_{0,-1} & \mathcal{A}^1_{0,0} & \mathcal{A}^1_{0,1} \\ \mathcal{A}^1_{1,-1} & \mathcal{A}^1_{1,0} & \mathcal{A}^1_{1,1} \end{pmatrix},$$

$$\mathcal{A}^2 = \begin{pmatrix} \mathcal{A}^2_{-2,-2} & \mathcal{A}^2_{-2,-1} & \mathcal{A}^2_{-2,0} & 0 & 0 \\ \mathcal{A}^2_{-1,-2} & \mathcal{A}^2_{-1,-1} & \mathcal{A}^2_{-1,0} & \mathcal{A}^2_{-1,1} & 0 \\ \mathcal{A}^2_{0,-2} & \mathcal{A}^2_{0,-1} & \mathcal{A}^2_{0,0} & \mathcal{A}^2_{0,1} & \mathcal{A}^2_{0,2} \\ 0 & \mathcal{A}^2_{1,-1} & \mathcal{A}^2_{1,0} & \mathcal{A}^2_{1,1} & \mathcal{A}^2_{1,2} \\ 0 & 0 & \mathcal{A}^2_{2,0} & \mathcal{A}^2_{2,1} & \mathcal{A}^2_{2,2} \end{pmatrix},$$

$$\mathcal{A}^3=\begin{pmatrix} \mathcal{A}^3_{-3,-3} & \mathcal{A}^3_{-3,-2} & \mathcal{A}^3_{-3,-1} & 0 & 0 & 0 & 0 \\ \mathcal{A}^3_{-2,-3} & \mathcal{A}^3_{-2,-2} & \mathcal{A}^3_{-2,-1} & \mathcal{A}^3_{-2,0} & 0 & 0 & 0 \\ \mathcal{A}^3_{-1,-3} & \mathcal{A}^3_{-1,-2} & \mathcal{A}^3_{-1,-1} & \mathcal{A}^3_{-1,0} & \mathcal{A}^3_{-1,1} & 0 & 0 \\ 0 & \mathcal{A}^3_{0,-2} & \mathcal{A}^3_{0,-1} & \mathcal{A}^3_{0,0} & \mathcal{A}^3_{0,1} & \mathcal{A}^3_{0,2} & 0 \\ 0 & 0 & \mathcal{A}^3_{1,-1} & \mathcal{A}^3_{1,0} & \mathcal{A}^3_{1,1} & \mathcal{A}^3_{1,2} & \mathcal{A}^3_{1,3} \\ 0 & 0 & 0 & \mathcal{A}^3_{2,0} & \mathcal{A}^3_{2,1} & \mathcal{A}^3_{2,2} & \mathcal{A}^3_{2,3} \\ 0 & 0 & 0 & 0 & \mathcal{A}^3_{3,1} & \mathcal{A}^3_{3,2} & \mathcal{A}^3_{3,3} \end{pmatrix}.$$

As is well known in systems theory, the solution to Eq. (25) is of the form of a matrix exponential,

$$\hat{f}^l(L)=e^{L\mathcal{A}^l}. \tag{26}$$

Since $\mathcal{A}^l$ is a band-diagonal matrix for $l>1$, the matrix exponential can be calculated much more efficiently (either numerically or symbolically) for large values of l than for general matrices of dimension $(2l+1)\times(2l+1)$. One also gains efficiencies in computing the matrix exponential of LA^l by observing the symmetry

$$\mathcal{A}^l_{m,n}=(-1)^{m-n}\overline{\mathcal{A}^l_{-m,-n}}.$$

Matrices with this kind of symmetry have eigenvalues that occur in conjugate pairs, and if x_m are the components of the eigenvector corresponding to the complex eigenvalue λ, then $(-1)^m\bar{x}_{-m}$ will be the components of the eigenvector corresponding to $\bar{\lambda}$ [58].

In general, the numerically calculated values of $\hat{f}^l(L)$ may be substituted back into the Fourier inversion formula (16) to yield the solution for $f(A;L)$ to any desired accuracy. In the specific case of the Kratky-Porod model, the analytical expressions for the Fourier transform matrices $\hat{f}^l(L)$ are of a simple enough form to write analytically by inspection. I.e., since $D_{11}=D_{22}=1/\alpha_0$, $D_{33}\to\infty$, and every other parameter in D and $\mathbf{d}$ is zero, the matrices $\mathcal{A}^l$ are all diagonal. This implies that the nonzero Fourier coefficients are of the form $\hat{f}^l_{m,m}(L)=\exp(L\mathcal{A}^l_{m,m})$. However, for $m\neq 0$ the value of D_{33} causes $\hat{f}^l_{m,m}(L)$ to be zero and what remains is a series in l with $m=0$:

$$f_{KP}(A;L)=\sum_{l=0}^{\infty}(2l+1)e^{-l(l+1)L/2\alpha_0}U^l_{0,0}(A)$$
$$=\sum_{l=0}^{\infty}(2l+1)e^{-l(l+1)L/2\alpha_0}P_l(\cos\beta).$$

A technique analogous to that presented here is presented in Sec. IV for solving Eq. (10).

IV. HARMONIC ANALYSIS ON THE MOTION GROUP

We now develop the tools required to solve Eq. (10) in an elegant way. The differential operators analogous to those in the case of pure rotation take the form

$$\tilde{X}^R_i f(H)=\left.\frac{df(H\cdot(\mathbf{1}+t\tilde{X}_i))}{dt}\right|_{t=0} \tag{27}$$

for the motion group where $H=H(g)\in \mathrm{SE}(3)$ and

$$\tilde{X}_1=\begin{pmatrix}0&0&0&0\\0&0&-1&0\\0&1&0&0\\0&0&0&0\end{pmatrix},\quad \tilde{X}_2=\begin{pmatrix}0&0&1&0\\0&0&0&0\\-1&0&0&0\\0&0&0&0\end{pmatrix},$$

$$\tilde{X}_3=\begin{pmatrix}0&-1&0&0\\1&0&0&0\\0&0&0&0\\0&0&0&0\end{pmatrix},\quad \tilde{X}_4=\begin{pmatrix}0&0&0&1\\0&0&0&0\\0&0&0&0\\0&0&0&0\end{pmatrix},$$

$$\tilde{X}_5=\begin{pmatrix}0&0&0&0\\0&0&0&1\\0&0&0&0\\0&0&0&0\end{pmatrix},\quad \tilde{X}_6=\begin{pmatrix}0&0&0&0\\0&0&0&0\\0&0&0&1\\0&0&0&0\end{pmatrix}.$$

These correspond to infinitesimal rotations and translations about the 1,2, and 3 axes.

In Appendix A we show that

$$\tilde{X}^R_i=\begin{cases} X^R_i & \text{for } i=1,2,3\\ (A^T\nabla_{\mathbf{a}})_{i-3} & \text{for } i=4,5,6\end{cases} \tag{28}$$

where X^R_i is defined in Eq. (8), and $(\nabla_{\mathbf{a}})_i=\partial/\partial a_i$. Observing the definition of $\mathbf{u}$ in Eq. (2), it is easy to see that $\mathbf{u}\cdot\nabla_{\mathbf{a}}=\tilde{X}^R_6$, and hence Eq. (10) can be written as

$$\left(\frac{\partial}{\partial L}-\frac{1}{2}\sum_{k,l=1}^{3}D_{lk}\tilde{X}^R_l\tilde{X}^R_k-\sum_{l=1}^{3}d_l\tilde{X}^R_l+\tilde{X}^R_6\right)F=0. \tag{29}$$

With an appropriate concept of Fourier transform, the differential operators $\tilde{X}^R_i$ acting on functions on the group SE(3) may be transformed to linear algebraic operations in Fourier space [59], and hence in principle Eq. (29) can be solved using matrix methods. The remainder of this section is devoted to the details of this calculation.

The unitary representations $U^s(\mathbf{a},A)$ of SE(3), which act on functions $\phi(\mathbf{p})\in L^2(S^2)$ with the usual inner product, are defined by [60,59]

$$[U^s(\mathbf{a},A)\phi](\mathbf{p})=e^{-i\mathbf{p}\cdot\mathbf{a}}\,\Delta_s(R_{\mathbf{p}}^{-1}A\,R_{A^{-1}\mathbf{p}})\,\phi(A^{-1}\mathbf{p}), \tag{30}$$

where $A\in\mathrm{SO}(3), R_{\mathbf{p}}$ is the rotation matrix which converts $(0,0,p)^T$ to any $\mathbf{p}\in\mathbb{R}^3$ with $|\mathbf{p}|=p$, and Δ_s are representations of $SO(2)$ enumerated by $s=0,\pm1,\pm2,\ldots$. (See Appendix B for a detailed explanation of these quantities.)

Each representation, characterized by $p=|\mathbf{p}|$ and s is irreducible [they, however, become reducible if we restrict SE(3) to SO(3), i.e., when $|\mathbf{a}|=0$]. They are unitary, because $(U^s(\mathbf{a},A)\phi_1,U^s(\mathbf{a},A)\phi_2)=(\phi_1,\phi_2)$. The set of all such representations is also complete.

Representations (30), which we denote below by $U^s(g,p)$, satisfy the homomorphism properties

$$U^s(g_1\circ g_2,p)=U^s(g_1,p)\cdot U^s(g_2,p),$$

where $\circ$ is the motion group operation and $\cdot$ denotes the composition of linear operators.

A. Matrix elements

To obtain the matrix elements of the unitary representations we use the group property

$$U^s(\mathbf{a},A)=U^s(\mathbf{a},I)\cdot U^s(\mathbf{0},A). \tag{31}$$

The basis eigenfunctions of the irreducible representations (30) of SE(3) may be enumerated by the integer numbers l,m (for each s and p). The range for the l,m,s indices are $l\geqslant|s|;l\geqslant|m|$.

The basis functions may be expressed in the form [56,60]

$$h^l_{m\,s}(\theta,\phi)=Q^l_{s,m}(\cos\theta)\,e^{i(m+s)\phi} \tag{32}$$

where

$$Q^l_{-s,m}(\cos\theta)=(-1)^{l-s}\sqrt{\frac{2l+1}{4\pi}}P^l_{s\,m}(\cos\theta),$$

and generalized Legendre functions $P^l_{m\,s}(\cos\theta)$ are given in Eq. (13).

It may be shown that these basis functions are transformed under rotations $h^l_{m\,s}(\mathbf{p})\to\Delta_s(Q(\mathbf{p},A))\,h^l_{m\,s}(A^{-1}\mathbf{p})$ as [59]

$$(U^s(0,A)\,h^l_{m\,s})(\mathbf{p})=\sum_{n=-l}^{l}U^l_{n\,m}(A)h^l_{n\,s}(\mathbf{p}), \tag{33}$$

where $U^l_{n\,m}(A)$ are matrix elements of the transposed SO(3) IUR's in Eq. (12).

The translation matrix elements are given by the integral [60]

$$\begin{aligned}(h^{l'}_{m'\,s},U^s(\mathbf{a},I)h^l_{m\,s})&=[l',m'\,|\,p,s|l,m](\mathbf{a})\\&=\int_0^{\pi}\int_0^{2\pi}Q^{l'}_{s,m'}(\cos\theta)\\&\quad\times e^{-i(m'+s)\phi}\,e^{-i\mathbf{p}\cdot\mathbf{a}}\,Q^l_{s,m}(\cos\theta)\\&\quad\times e^{i(m+s)\phi}\sin\theta\,d\theta\,d\phi.\end{aligned} \tag{34}$$

Finally, using the group property (31), the matrix elements of the unitary representation $U^s(g,p)$ (30) (for $s=0,\pm1,\pm2,\ldots$) are expressed as

$$U^s_{l',m';l,m}(\mathbf{a},A;p)=\sum_{j=-l}^{l}[l',m'\,|\,p,s\,|\,l,j](\mathbf{a})U^l_{j\,m}(A). \tag{35}$$

B. Fourier transform

Here we review the definition of the Fourier transform of functions $F(\mathbf{a},A)\in L^2(\mathrm{SE}(3))$. To define an invertible Fourier transform for functions on SE(3) we have to use a complete orthogonal basis for functions on the motion group. Proofs for the completeness and orthogonality of matrix elements (35) can be found in [60,59]. Hence, using the unitary representations $U(g,p)$ (30) (for $s=0,\pm1,\pm2\ldots$), the Fourier transform of functions on the motion group may be defined as follows.

Definition. Given a complex-valued function $F(\mathbf{a},A)$ on SE(3), the Fourier transform is the matrix-valued function

$$\mathcal{F}(F)=\hat{f}(p)=\int_{\mathrm{SE}(3)}F(g)U(g^{-1};p)dg,$$

where $g=(\mathbf{a},A)\in\mathrm{SE}(3), dg=dA\,d^3a$, and $U(g;p)$ is the unitary matrix with elements (35).

The matrix elements of the transform are given in terms of matrix elements (35) as

$$\hat{F}^s_{l',m';l,m}(p)=\int_{\mathrm{SE}(3)}F(\mathbf{a},A)\overline{U^s_{l,m;l',m'}(\mathbf{a},A;p)}\,dA\,d^3a, \tag{36}$$

where we have used the unitary property.

The inverse Fourier transform recovers $F(g)$ from $\hat{F}(p)$ as [59]

$$F(g)=\mathcal{F}^{-1}(\hat{F})=\frac{1}{2\pi^2}\int_0^{\infty}\mathrm{Tr}[\hat{F}(p)U(g,p)]\,p^2\,dp. \tag{37}$$

In component form this is written as

$$\begin{aligned}F(\mathbf{a},A)=\frac{1}{2\pi^2}\sum_{s=-\infty}^{\infty}\sum_{l'=|s|}^{\infty}\sum_{l=|s|}^{\infty}\sum_{m'=-l'}^{l'}\sum_{m=-l}^{l}\int_0^{\infty}p^2dp\\\times\hat{F}^s_{l,m;l',m'}(p)U^s_{l',m';l,m}(\mathbf{a},A;p).\end{aligned} \tag{38}$$

We note that as a direct result of Eqs. (14), (35), and the above inversion formula,

$$\int_{\mathrm{SO}(3)} F(\mathbf{a},A)\,dA = \frac{1}{2\pi^2}\sum_{l'=0}^{\infty}\sum_{m'=-l'}^{l'}\int_0^{\infty} p^2\,dp \times \hat{F}^0_{0,0;l',m'}(p)[l',m'\,|p,0|\,0,0](\mathbf{a}).$$

If this distribution of end positions is then integrated over the surface of a sphere with radius $a=|\mathbf{a}|$, the result is the end-to-end distance distribution:

$$\frac{a^2}{2\pi^2}\int_{S^2}\int_{\mathrm{SO}(3)} F(a\mathbf{u},A)\,d\mathbf{u}\,dA = \frac{2}{\pi}a^2\int_0^{\infty} p^2\,dp\,\hat{F}^0_{0,0;0,0}(p)[0,0\,|p,0|\,0,0](\mathbf{a}). \tag{39}$$

It is easy to verify that $[0,0\,|p,0|\,0,0](\mathbf{a}) = J_{1/2}(pa) = \sin(pa)/pa$. These expressions provide a means of addressing PDF's of end-to-end relative position and end-to-end distance when knowledge of orientation is not critical.

C. Operational Properties and Solutions of PDE's

By the definition of the SE(3)Fourier transform $\mathcal{F}[\,\cdot\,]$ and operators $\tilde{X}_i^R$ reviewed in earlier subsections of this section, one observes that

$$\mathcal{F}[\tilde{X}_i^R F] = \int_{\mathrm{SE}(3)} \frac{d}{dt}[F(g\circ\exp(t\tilde{X}_i))]|_{t=0}U^s(g^{-1},p)\,dg. \tag{40}$$

Here g can be thought of as $H(g)$ and $\exp(t\tilde{X}_i)$ is an element of the subgroup of SE(3) generated by $\tilde{X}_i$, which for small values of t is approximated as $I+t\tilde{X}_i$. By performing the change of variables $h=g\circ\exp(t\tilde{X}_i)$ and using the homomorphism property of the representations $U^s(\cdot)$, one finds

$$\mathcal{F}[\tilde{X}_i^R F] = \int_{\mathrm{SE}(3)} F(h)\frac{d}{dt}[U^s(\exp(t\tilde{X}_i)\circ h^{-1},p)]|_{t=0}\,dh \tag{41}$$

$$= \frac{d}{dt}[U^s(\exp(t\tilde{X}_i),p)]|_{t=0} \times \int_{\mathrm{SE}(3)} F(h)U^s(h^{-1},p)\,dh. \tag{42}$$

By defining

$$u^s(\tilde{X}_i,p) = \frac{d}{dt}[U^s(\exp(t\tilde{X}_i),p)]|_{t=0},$$

we write

$$\mathcal{F}[\tilde{X}_i^R F] = u^s(\tilde{X}_i,p)\hat{F}^s(p).$$

Hence, Eq. (29) can be transformed to the infinite system of linear differential equations.

$$\frac{d\hat{F}^s}{dL} = \mathcal{B}^s\hat{F}^s, \tag{43}$$

where

$$\mathcal{B}^s = \frac{1}{2}\sum_{k,l=1}^{3} D_{lk}u^s(\tilde{X}_l,p)u^s(\tilde{X}_k,p) + \sum_{l=1}^{3} d_l u^s(\tilde{X}_l,p) - u^s(\tilde{X}_6,p).$$

In principle, $F(\mathbf{a},A;L)$ is then found by simply substituting $\hat{F}^s(p;L) = \exp(L\mathcal{B}^s)$ into the SE(3) Fourier inversion formula (38). In practice, however, exponentiation of a nondiagonal infinite-dimensional matrix poses some difficulties that need to be addressed. This is the subject of the next section.

Explicitly, for $i=1,2,3$ we have

$$u^s(\tilde{X}_i,p) = \frac{d}{dt}U^s_{l',m';l,m}(\mathbf{0},\exp[tX_i];p)|_{t=0} = \delta_{l,l'}\frac{d}{dt}U^l_{m',m}(\exp[tX_i])|_{t=0},$$

where $\exp[tX_i] = \Omega_{\mathrm{rof}}[\mathbf{e}_i,t]$. The second equality above follows easily from the structure of the matrix elements $U^s_{l',m';l,m}$, and $d/dt\,U^l_{m,n}(\exp[tX_i])|_{t=0}$ are given explicitly in Eq. (23). This, together with the fact that [59]

$$u^s_{l',m';l,m}(\tilde{X}_6,p) = \frac{d}{dt}U^s_{l',m';l,m}(t\mathbf{e}_3,I;p)|_{t=0} = ip\kappa^s_{l',m'}\delta_{l'-1,l}\delta_{m',m} + ip\frac{m's}{l'(l'+1)}\delta_{l'l}\delta_{m',m} + ip\kappa^s_{l,m}\,\delta_{l',l-1}\delta_{m',m},$$

where

$$\kappa^s_{l',m'} = \left(\frac{(l'^2-m'^2)\,(l'^2-s^2)}{(2l'+1)(2l'-1)l'^2}\right)^{1/2}$$

allows us to write the elements of $\mathcal{B}^s(p)$ as

$$\mathcal{B}^s_{l',m';l,m} = \mathcal{A}^l_{m',m}\delta_{l',l} - ip\kappa^s_{l',m'}\delta_{l'-1,l}\delta_{m',m} - ip\frac{m's}{l'(l'+1)}\delta_{l'l}\delta_{m',m} - ip\,\kappa^s_{l,m}\,\delta_{l',l-1}\delta_{m',m}.$$

V. NUMERICAL RESULTS

From a theoretical point of view, the solution to Eq. (43) subject to the initial conditions $\hat{F}^s(p;0)=I$ is simply $\hat{F}^s = \exp[L\mathcal{B}^s(p)]$. This may then be substituted into the motion-group Fourier transform to find the PDF $F(g;L)$ for any value of L.

In practice, however, we must truncate $\mathcal{B}^s(p)$ at finite values of s,l, and p. When the end-to-end distance PDF is of interest, Eq. (39) suggests that we need only consider $s=0$.

We truncate at $l=L_B$ and $p=P_B$, and denote the corresponding finite matrix as $[\mathcal{B}^0(p)]_{L_B}$ for $0\leq p\leq P_B$. In the numerical results that follow, we exponentiate $L[\mathcal{B}^0(p)]_{L_B}$, and examine the convergence of the 00;00 element of $\exp(L[\mathcal{B}^0]_{L_B})$ and the behavior of the PDF found by substituting this truncated solution into Eq. (39).

In the numerical results that follow, all stiffness and length parameters are normalized by persistence length as in [4]. The parameter α_0 is related to the temperature, Boltzmann constant and persistence length as

$$\alpha_0=\frac{k_B T}{2\lambda}.$$

In our numerical results, we take $\lambda=1$, and assume units such that $k_B T=1$. For the helical wormlike chain model Yamakawa defines [4]:

$$\beta_0=\alpha_0(1+\sigma)^{-1}$$

where σ is the Poisson ratio. As in [4], we take $\alpha_0=0.5$ and $\sigma=0$. In [4] the following moment of end-to-end distance was calculated:

$$\langle R^2\rangle=c_\infty L-\frac{\tau_0^2}{2\nu^2}-\frac{2\kappa_0^2(4-\nu^2)}{\nu^2 r^4}+\frac{e^{-2L}}{\nu^2}\times\left(\frac{\tau_0^2}{2}+\frac{2\kappa_0^2}{r^4}[(4-\nu^2)\cos(\nu L)-4\nu\sin(\nu L)]\right), \quad (44)$$

where

$$c_\infty=\frac{4+\tau_0^2}{4+\kappa_0^2,+\tau_0^2} \quad (45)$$

$$\nu=(\kappa_0^2+\tau_0^2)^{1/2}$$

and

$$r=(4+\nu^2)^{1/2}.$$

Here κ_0 and τ_0 are the unperturbed values of curvature and torsion of the helix. In our notation, $\langle R^2\rangle=\langle|\mathbf{a}|^2\rangle$.

Figure 1 shows our technique used to find the end-to-end distance PDF for the KP model with $L=1$ and $\alpha_0=0.5$. (This is the Yamakawa model with $\beta_0=\kappa_0=\tau_0=0$.) In this numerical implementation we chose $\beta_0=10^{-13}$ and $\kappa_0=\tau_0=0$ in order to use our method (which was derived with nonsingular stiffness and flexibility matrices). We show how the form of the PDF converges for different values of truncation parameters.

Figure 2 shows the end-to-end distance PDF for the Kratky-Porod model with $L=1$ for several of its parameters and the truncation values L_B and P_B. We set L_B and P_B by choosing successively higher values until the shape of the PDF converged. For the $\alpha_0=2$ case (which is very stiff) small oscillations are still present. If we choose L_B and P_B large enough, these oscillations can be made negligibly small (in the L^2 sense), but this requires a greater computational burden.

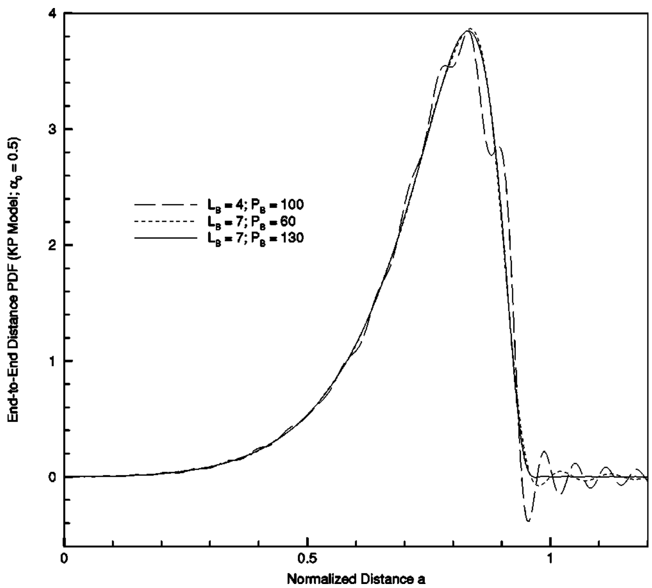

FIG. 1. End-to-end distance PDF for the KP model: successive approximations for one stiffness value.

In Figs. 3–5 we show the end-to-end distance PDF's for the Yamakawa helical wormlike chain model for several parameters and compare it with the KP model for various values of normalized length L. Following [4]: For HW1, $\kappa_0=2.5$ and $\tau_0=0.5$; for HW2, $\kappa_0=5.0$ and $\tau_0=1.0$; for HW3, $\kappa_0=1.0$ and $\tau_0=1.0$; for HW5, $\kappa_0=30.0$ and $\tau_0=8.0$. Clearly for smaller L, the chain is effectively stiffer, and our Fourier method exhibits some Gibbs-type oscillations.

Figure 6 shows how the moments of the end-to-end distance PDF generated using our technique at discrete values of L matches with the closed-form result (44) presented in Fig. 4.14 of [4] .

The benefit of our approach is that the PDF contains all the information to generate any desired moment. While we have demonstrated the compatability of our method with theKP and helical wormlike models, our method is valid for

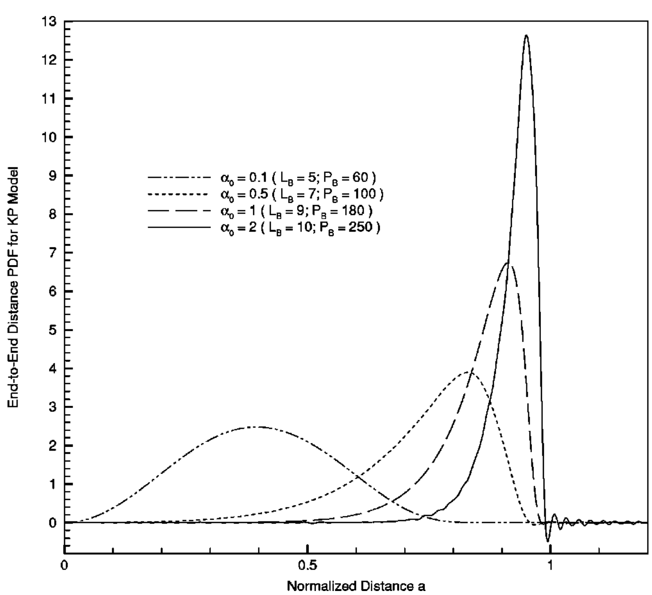

FIG. 2. End-to-end distance PDF's for the KP model for several different stiffness values.

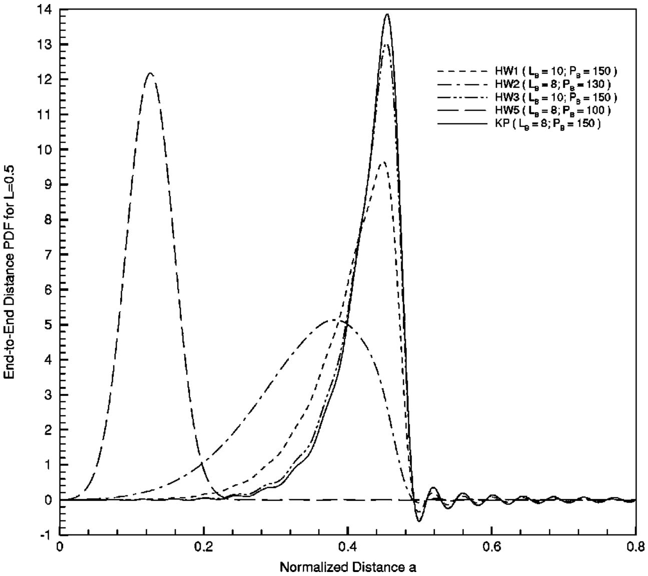

FIG. 3. End-to-end distance PDF for the HW and KP models with $L=0.5$.

any second-order stiffness model (with arbitrary linear chirality term).

VI. CONCLUSION

This paper contributes three ideas to the understanding of the conformational statistics of stiff macromolecules. First, a PDE governing the PDF's for inextensible stiff macromolecules with arbitrary (though uniform) local stiffness and chirality characteristics is derived. This PDE describes a process that evolves on the Euclidean motion group. Second, analytical tools for the solution of this PDE are presented. Third, we show how this analytical framework can be used to numerically generate PDF's of interest in polymer science, the moments of which match with moments generated using other techniques.

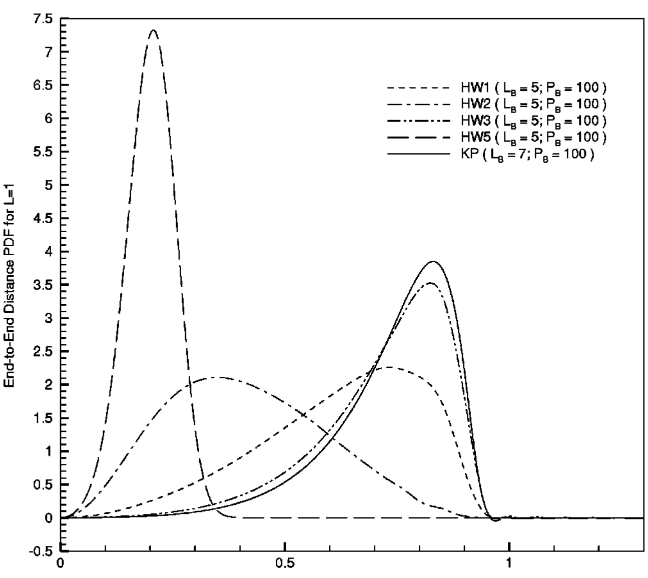

FIG. 4. End-to-end distance PDF for the HW and KP models with $L=1$.

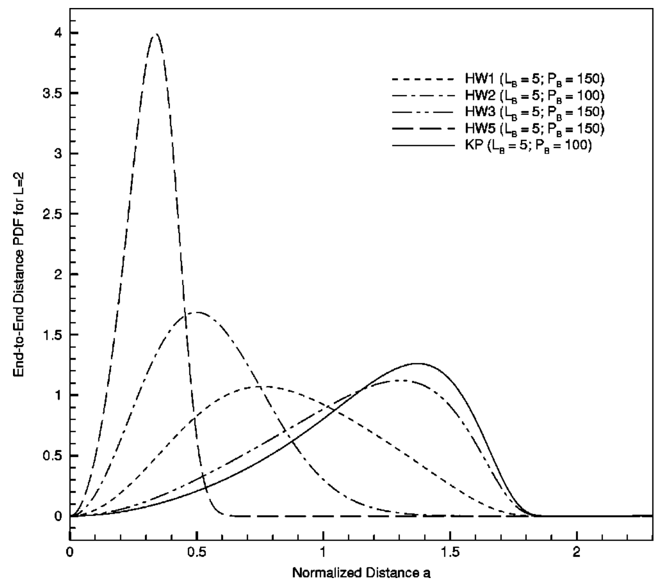

FIG. 5. End-to-end distance PDF for the HW and KP models with $L=2$.

ACKNOWLEDGMENTS

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APPENDIX A: THE OPERATORS $\tilde{X}_i^R$

In this appendix it will be helpful to associate each matrix $\tilde{X}_i$ defined in Sec. IV with a vector $(\tilde{X}_i)^\vee$ in the following way:

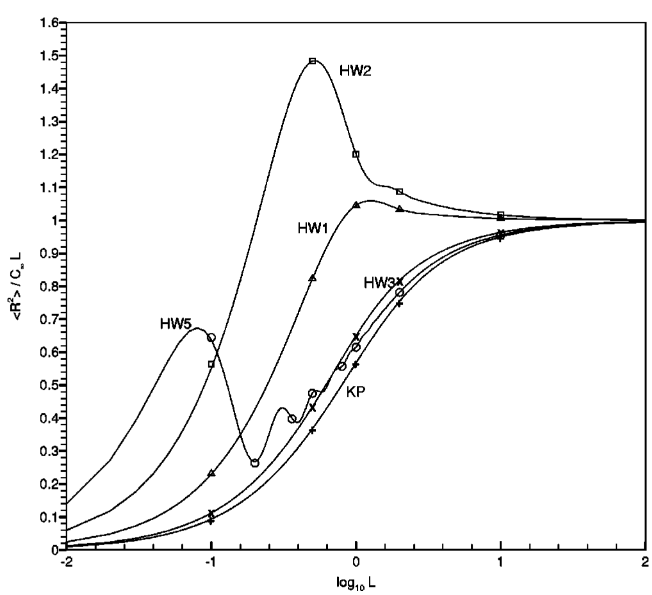

FIG. 6. Comparison of moments generated numerically and analytically.

$$(\tilde{X}_1)^\vee = \begin{pmatrix}1\\0\\0\\0\\0\\0\end{pmatrix}, \quad (\tilde{X}_2)^\vee = \begin{pmatrix}0\\1\\0\\0\\0\\0\end{pmatrix}, \quad (\tilde{X}_3)^\vee = \begin{pmatrix}0\\0\\1\\0\\0\\0\end{pmatrix},$$

$$(\tilde{X}_4)^\vee = \begin{pmatrix}0\\0\\0\\1\\0\\0\end{pmatrix}, \quad (\tilde{X}_5)^\vee = \begin{pmatrix}0\\0\\0\\0\\1\\0\end{pmatrix}, \quad (\tilde{X}_6)^\vee = \begin{pmatrix}0\\0\\0\\0\\0\\1\end{pmatrix}.$$

Given elements of SE(3) parametrized as $H=H(\mathbf{q})$, the differential operators $\tilde{X}_i^R$ are calculated as

$$\tilde{X}_i^R f(H) = \left.\frac{df(H\cdot(I+t\tilde{X}_i))}{dt}\right|_{t=0}. \tag{A1}$$

By defining $\mathbf{q}^{R,i}$ such that $H(\mathbf{q}+t\mathbf{q}^{R,i})=H(\mathbf{q})(I+t\tilde{X}_i)$, and expanding both sides in a Taylor series in t, one observes that

$$H+tH\tilde{X}_i = H+t\sum_{j=1}^{6}\frac{\partial H}{\partial q_j}q_j^{R,i}+O(t^2)$$

since

$$q_j^{R,i}=\frac{d}{dt}(q_j+tq_j^{R,i})|_{t=0}.$$

Differentiating with respect to t and setting $t=0$ then yields

$$\tilde{X}_i=\sum_{j=1}^{6} H^{-1}\frac{\partial H}{\partial q_j}q_j^{R,i},$$

or

$$(\tilde{X}_i)^\vee=\sum_{j=1}^{6}\left(H^{-1}\frac{\partial H}{\partial q_j}\right)^\vee q_j^{R,i}.$$

The 6×6 matrix with columns $[H^{-1}(\partial H/\partial q_j)]^\vee$ is denoted $\mathcal{J}_R$. One then writes

$$\mathbf{q}^{R,i}=\mathcal{J}_R^{-1}(\tilde{X}_i)^\vee,$$

which is used to calculate

$$\tilde{X}_i^R f=\sum_{j=1}^{6}\frac{\partial f}{\partial q_j}q_j^{R,i}=\mathcal{J}_R^{-1}\sum_{j=1}^{6}(\tilde{X}_j)^\vee\frac{\partial f}{\partial q_j}. \tag{A2}$$

Let q_1,q_2,q_3 parametrize rotation (i.e., the Euler angles) and q_4,q_5,q_6 parametrize translation (i.e., the components of the vector $\mathbf{a}$). Then $\mathcal{J}_R$ and its inverse take the explicit forms

$$\mathcal{J}_R=\begin{pmatrix}J_R & 0_3\\ 0_3 & A^T\end{pmatrix} \quad\text{and}\quad \mathcal{J}_R^{-1}=\begin{pmatrix}J_R^{-1} & 0_3\\ 0_3 & A\end{pmatrix},$$

where 0_3 is the 3×3 with zero entries and J_R is the matrix relating rates of rotation parameters and angular velocity (in the body-fixed frame): $\boldsymbol{\omega}=J_R[\dot{q}_1,\dot{q}_2,\dot{q}_3]^T$. Substitution of these definitions into Eq. (A2) results in Eq. (28).

APPENDIX B: HELICITY REPRESENTATIONS

In this appendix we explain the term $\Delta_s(R_{\mathbf{p}}^{-1}A\,R_{A^{-1}\mathbf{p}})$ (which is often called a helicity representation) in Eq. (30). Let $H_{\hat{\mathbf{v}}}$ denote the group which leaves the point $\hat{\mathbf{v}}\in S^2$ fixed. To calculate the representations of $H_{\hat{\mathbf{v}}}$ explicitly, we first choose a particular coset representative $\hat{\mathbf{v}}=\mathbf{e}_3\in S^2\cong\mathrm{SO}(3)/\mathrm{SO}(2)$. The vector $\hat{\mathbf{v}}$ is invariant with respect to rotations from the SO(2) subgroup of SO(3), and for this particular choice of $\hat{\mathbf{v}}$ we not only have $H_{\hat{\mathbf{v}}}\cong\mathrm{SO}(2)$, but rather $H_{\hat{\mathbf{v}}}=\mathrm{SO}(2)$.

For each $\mathbf{v}\in S^2$ we may find $R_{\mathbf{v}}\in\mathrm{SO}(3)/\mathrm{SO}(2)$, such that

$$R_{\mathbf{v}}\hat{\mathbf{v}}=\mathbf{v}.$$

Explicitly, this rotation matrix is the one which has an axis pointing in the direction defined by $\hat{\mathbf{v}}\times\mathbf{v}$, and has a rotation angle whose sin is $\|\hat{\mathbf{v}}\times\mathbf{v}\|$. In general, the rotation $R(\mathbf{a},\mathbf{b})$ which transforms a unit vector $\mathbf{a}$ into the unit vector $\mathbf{b}$,

$$\mathbf{b}=R(\mathbf{a},\mathbf{b})\mathbf{a},$$

is defined by

$$R(\mathbf{a},\mathbf{b})=e^C=I+C+\frac{(1-\mathbf{a}\cdot\mathbf{b})}{\|\mathbf{a}\times\mathbf{b}\|^2}C^2, \tag{B1}$$

where $\mathbf{c}=\mathbf{a}\times\mathbf{b}$ and C is defined by $C\mathbf{x}=\mathbf{c}\times\mathbf{x}$. This follows easily from the fact that $\|\mathbf{a}\times\mathbf{b}\|=\sin\theta_{ab}$ and $\mathbf{a}\cdot\mathbf{b}=\cos\theta_{ab}$ where $0\leqslant\theta_{ab}\leqslant\pi$ is the counterclockwise measured angle from $\mathbf{a}$ to $\mathbf{b}$ as measured in the direction defined by $\mathbf{c}$. Hence, in the current context,

$$R_{\mathbf{v}}=R(\hat{\mathbf{v}},\mathbf{v})=e^{\mathrm{matr}[\hat{\mathbf{v}}\times\mathbf{v}]},$$

where $\mathrm{matr}[\mathbf{c}]$ is the skew-symmetric matrix such that $(\mathrm{matr}[\mathbf{c}])\mathbf{x}=\mathbf{c}\times\mathbf{x}$.

For any $A\in\mathrm{SO}(3)$ it follows from the definition of $R_{\mathbf{v}}$ that

$$R_{A^{-1}\mathbf{v}}\hat{\mathbf{v}}=A^{-1}\mathbf{v}.$$

Multiplying both sides by A, making the replacement $\mathbf{v}=R_{\mathbf{v}}\hat{\mathbf{v}}$ on the right-hand-side, and multiplying both sides by $R_{\mathbf{v}}^{-1}$ means

$$(R_{\mathbf{v}}^{-1}A\,R_{A^{-1}\mathbf{v}})\,\hat{\mathbf{v}}=\hat{\mathbf{v}}.$$

Therefore,

$$Q(\mathbf{v},A) \overset{\triangle}{=} (R_{\mathbf{v}}^{-1}\, A\, R_{A^{-1}\mathbf{v}}) \in H_{\hat{\mathbf{v}}}.$$

The representations of $H_{\hat{\mathbf{v}}}$ may be taken to be of the form

$$\Delta_s : \phi \rightarrow e^{is\phi}, \quad 0 \leqslant \phi \leqslant 2\pi,$$

and $s = 0, \pm 1, \pm 2, \ldots$. This is just the usual Fourier series on $S^1 \cong \mathrm{SO}(2)$.

We now derive the form of $Q(\mathbf{v},A)$ explicitly. At first sight this would appear to be a complicated function of $\mathbf{v}$ and A. We show that this is not as complicated as one might believe.

We begin by observing that

$$R_{A^{-1}\mathbf{v}} = R(\hat{\mathbf{v}}, A^{-1}\mathbf{v}) = e^{\mathrm{matr}[\hat{\mathbf{v}} \times (A^{-1}\mathbf{v})]}.$$

Using general rules for cross-products, one finds that

$$\hat{\mathbf{v}} \times (A^{-1}\mathbf{v}) = A^{-1}[(A\hat{\mathbf{v}}) \times \mathbf{v})]$$

and

$$\mathrm{matr}[A^{-1}\{(A\hat{\mathbf{v}}) \times \mathbf{v}\}] = A^{-1}\mathrm{matr}[(A\hat{\mathbf{v}}) \times \mathbf{v}]A.$$

Since conjugation commutes with the matrix exponential, it follows that

$$R_{A^{-1}\mathbf{v}} = A^{-1}R(A\hat{\mathbf{v}},\mathbf{v})A = A^{-1}e^{\mathrm{matr}[(A\hat{\mathbf{v}}) \times \mathbf{v}]}A.$$

Substitution of this into the definition of $Q(\mathbf{v},A)$, and using the fact that

$$R_{\mathbf{v}}^{-1} = \exp\{-\mathrm{matr}[(\hat{\mathbf{v}} \times \mathbf{v})]\} = \exp\{\mathrm{matr}[(\mathbf{v} \times \hat{\mathbf{v}})]\},$$

one finds

$$Q(\mathbf{v},A) = e^{\mathrm{matr}[(\mathbf{v} \times \hat{\mathbf{v}}]}e^{\mathrm{matr}[(A\hat{\mathbf{v}}) \times \mathbf{v}]}A. \tag{B2}$$

While the derivation here is for unit vectors $\mathbf{v}$, everything follows in exactly the same way for $\mathbf{p} = p\mathbf{v}$.

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