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

Gregory S. Chirikjian and Yunfeng Wang
Department of Mechanical Engineering, Johns Hopkins University, Baltimore, Maryland 21218
(Received 4 March 1999; revised manuscript received 9 February 2000)

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 Kratyky-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.

PACS number(s): 36.20.Ey, 87.16.Ac, 05.10.-a, 02.30.Jr

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., [5,6] 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 Kratyky-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 Kratyky-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 \( 3 \times 3 \) real matrices satisfying \( A^T A = I \) and \( \det(A) = 1 \)]. Translations (and positions) are described as elements of three-space: \( a \in \mathbb{R}^3 \). 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 \( g=(a, A) \in SE(3) \), where \( A \in SO(3) \) and \( a \in \mathbb{R}^3 \). The group law is written as \( g_1 g_2 = (a_1 + A_1 a_2, A_1 A_2) \) and \( g^{-1} = (-A^T a, A) \). Any element of \( SE(3) \) can be written as the product of a pure translation and pure rotation as \( (a, A) = (0, A) \).

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

\[
H(g) = \begin{pmatrix}
A & a \\
0^T & 1
\end{pmatrix},
\]

Clearly, \( H(g_1) H(g_2) = H(g_1 g_2) \) 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.

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

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

\[
A(\alpha, \beta, \gamma) = \Omega_{\alpha}[e_3, \alpha] \Omega_{\beta}[e_1, \beta] \Omega_{\gamma}[e_3, \gamma],
\]
where $\Omega_{0\phi}[e_i, \varphi]$ denotes the rotation matrix describing counterclockwise rotation by $\varphi$ about the natural basis vector $e_j$ which has elements $(e_j)_i = \delta_{ij}$.

**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

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

where $L$ is the length of the macromolecule and

$$U = \frac{1}{2} \omega^T B \omega - \beta' \omega + \beta'.$$  \hspace{1cm} (1)

Here $B = B^T \in \mathbb{R}^{3 \times 3}$ is a positive semidefinite matrix, $b \in \mathbb{R}^3$, and $\beta' \in \mathbb{R}$. $\omega$ is the "angular velocity" of a frame of reference which traverses the macromolecule, coinciding with each frame $[a(s), A(s)]$ affixed to the backbone of the molecule for each value of arc length $s$. This "angular velocity" is the dual of the skew symmetric matrix $A^T \dot{A}$, where the overdot denotes $d/ds$. That is, $\omega \times x = A^T \dot{A} x$ for all $x \in \mathbb{R}^3$. 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 $U = U(\omega) = U(A, \dot{A})$ to denote the fact that the bending energy is a function of the rotation matrix and its derivative through the definition of $\omega$.

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

The *Krasky-Porod model* [1,45]:

$$B = \begin{pmatrix} \alpha_0 & 0 & 0 \\ 0 & \alpha_0 & 0 \\ 0 & 0 & \beta_0 \end{pmatrix}, \quad b = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}, \quad \beta' = 0.$$

The *Yamakawa model* [4]:

$$B = \begin{pmatrix} \alpha_0 & 0 & 0 \\ 0 & \alpha_0 & 0 \\ 0 & 0 & \beta_0 \end{pmatrix}, \quad b = \begin{pmatrix} 0 \\ 0 \alpha_0 \theta_0 \\ 0 \beta_0 \theta_0 \end{pmatrix},$$

$$\beta' = \frac{1}{2} (\beta_0 \theta_0^2 + \alpha_0 \theta_0^2).$$

The *Marko-Siggia DNA model* [48]:

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

The revised Marko-Siggia model [49]:

$$B = \begin{pmatrix} A + B^2/C & 0 & B \\ 0 & A & 0 \\ B & 0 & C \end{pmatrix}, \quad b = \begin{pmatrix} B \omega_0 \\ 0 \\ C \omega_0 \end{pmatrix}, \quad \beta' = \frac{1}{2} C \omega_0^2.$$
\[
\left( \frac{\partial}{\partial L} - \frac{1}{2} \sum_{k,m=1}^{3} \left( B_{kk}^{-1} r_{X_k}^{R} r_{X_k}^{R} - 2B_{kk}^{-1} b_k X_k^R \right) + ik \cdot u \right) \dot{F} = 0. 
\]

(9)

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

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

\[
\left( \frac{\partial}{\partial L} - \frac{1}{2} \sum_{k,m=1}^{3} D_{kk} X_k^R \dot{X}_k^R - \sum_{\ell=1}^{3} d_{\ell} \dot{X}_{\ell}^R + u \cdot \nabla_{a} \right) F = 0,
\]

(10)

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

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

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

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

\[
\left( \frac{\partial}{\partial L} - \frac{1}{2} \sum_{k,l=1}^{3} D_{kk} X_k^R \dot{X}_l^R - \sum_{\ell=1}^{3} d_{\ell} \dot{X}_{\ell}^R \right) f = 0
\]

(11)

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

Equation (11) is a partial differential equation that governs the evolution of the function \( f \) on the rotation group \( \text{SO}(3) \). 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 \( \text{IUR’s} \) of \( \text{SO}(3) \) are given to within an arbitrary unitary transformation by [55–57]:

\[
U_{mn}^l(g(\alpha, \beta, \gamma)) = (-1)^m e^{-i \kappa_{\alpha} + \gamma} p_{mn}^l(\cos \beta)
\]

(12)

where

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

(13)

and \( p_{l-m}^{(m,n)}(\cdot) \) are the Jacobi polynomials.

The matrices \( U^l \) with entries \( U_{mn}^l \) are \((2l+1) \times (2l+1)\) dimensional, and the indices take the range of values \(-l \leq m, n \leq l\). These representation matrices possess the homomorphism and orthogonality properties.
\[ U'(A_1A_2) = U'(A_1) U'(A_2) \]  \hspace{1cm} (14)

and

\[ \int_{SO(3)} U''_{m' n'}(A) U'_{m n}(A) \, dA = \frac{\delta_{m'm} \delta_{n'n} \delta_{l'l}}{(2l+1)}. \]  \hspace{1cm} (15)

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

\[ f(A) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \sum_{n=-l}^{l} \hat{f}^l_{mn} U'_{mn}(A) \]

\[ = \sum_{l=0}^{\infty} (2l+1) \hat{f}^l \cos^l \theta, \]  \hspace{1cm} (16)

where the entries of the Fourier transform matrix \( \mathcal{F}(f) = \hat{f} \)

are defined as

\[ \hat{f}^l_{mn} = \int_{SO(3)} f(A) U'_{mn}(A^{-1}) \, dA. \]  \hspace{1cm} (17)

Here \( dA = (1/8\pi^2) \sin \theta d\theta d\phi d\psi \) 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 \( X^R_l \) transform the matrix elements \( U'_{mn}(A) \). In fact, this is well known, and can be found in [55,56] (adjusted for the differing definitions of \( U'_{mn} \)) as

\[ X^R_l U'_{mn} = \frac{1}{2} \left( c^l_{l-n} U'_{m,n-1} - c^l_{l+n} U'_{m,n+1} \right), \]  \hspace{1cm} (18)

\[ X^R_l U'_{mn} = \frac{1}{2} \left( c^l_{l-n} U'_{m,n-1} + c^l_{l+n} U'_{m,n+1} \right), \]  \hspace{1cm} (19)

\[ X^R_l U'_{mn} = -i n U'_{mn}, \]  \hspace{1cm} (20)

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

\[ \frac{d}{dt} U'_{mn}(\Omega_v(e_1,t)) \bigg|_{t=0} = \frac{1}{2} l c^l_{l-n} \delta_{m+1,n} - \frac{1}{2} l c^l_{l-n} \delta_{m-1,n}, \]  \hspace{1cm} (21)

\[ \frac{d}{dt} U'_{mn}(\Omega_v(e_2,t)) \bigg|_{t=0} = \frac{i}{2} l c^l_{l-n} \delta_{m+1,n} + \frac{i}{2} l c^l_{l-n} \delta_{m-1,n}, \]  \hspace{1cm} (22)

\[ \frac{d}{dt} U'_{mn}(\Omega_v(e_3,t)) \bigg|_{t=0} = -i n \delta_{m,n}. \]  \hspace{1cm} (23)

By repeated application of these rules one finds

\[ (X^R_l)^2 U'_{mn} = \frac{1}{4} c_{l-n} U'_{m,n-1} + \frac{1}{4} c_{l-n} U'_{m,n+1} - \frac{1}{4} c_{l-n} U'_{m,n-1}, \]  \hspace{1cm} (24)

\[ (X^R_l)^2 U'_{mn} = - \frac{1}{4} c_{l-n} U'_{m,n-1} - \frac{1}{4} c_{l-n} U'_{m,n+1}, \]  \hspace{1cm} (25)

\[ (X^R_l)^2 U'_{mn} = - n^2 U'_{mn}, \]  \hspace{1cm} (26)

\[ X^R_1 X^R_2 U'_{mn} = i \frac{1}{2} c_{l-n} U'_{m,n-1} + \frac{i}{2} c_{l-n} U'_{m,n+1}, \]  \hspace{1cm} (27)

\[ X^R_1 X^R_2 U'_{mn} = - i \frac{1}{2} c_{l-n} U'_{m,n-1} - \frac{i}{2} c_{l-n} U'_{m,n+1}, \]  \hspace{1cm} (28)

\[ X^R_1 X^R_3 U'_{mn} = i \frac{n}{2} (c_{l-n} U'_{m,n-1} - c_{l-n} U'_{m,n+1}), \]  \hspace{1cm} (29)

\[ X^R_2 X^R_3 U'_{mn} = - \frac{n-1}{2} c_{l-n} U'_{m,n-1} + \frac{n+1}{2} c_{l-n} U'_{m,n+1}, \]  \hspace{1cm} (30)

\[ X^R_3 X^R_3 U'_{mn} = \frac{n}{2} (c_{l-n} U'_{m,n-1} + c_{l-n} U'_{m,n+1}). \]  \hspace{1cm} (31)

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

\[ X U'_{mn} = x(n) U'_{m,n+p}, \]  \hspace{1cm} (32)

then there is a corresponding operational property of the Fourier transform

\[ \mathcal{F}(X f')_{m,n} = x(m-p) f'_{m-m,n}. \]  \hspace{1cm} (33)

We use this to write

\[ \mathcal{F}(X^R_1 f')_{m,n} = \frac{1}{2} c_{l-n} U'_{m,n-1} + \frac{1}{2} c_{l-n} U'_{m,n+1}, \]  \hspace{1cm} (34)

\[ \mathcal{F}(X^R_2 f')_{m,n} = \frac{1}{2} i c_{l-n} U'_{m,n-1} + \frac{1}{2} i c_{l-n} U'_{m,n+1}, \]  \hspace{1cm} (35)

\[ \mathcal{F}(X^R_3 f')_{m,n} = - i n f'_{m,n}. \]  \hspace{1cm} (36)
\[ \mathcal{F}(X^{R}_{1} f)_{mm} = \frac{1}{4} c_{m+1} c_{m-1} \hat{J}_{m+2n} - \frac{1}{4} c_{m} c_{m-1} \hat{J}_{m-2n} \]
\[ + c_{m} c_{m-1} \hat{J}_{mn} + \frac{1}{4} c_{m+1} c_{m-1} \hat{J}_{m-2n}, \]
\[ \mathcal{F}(X^{R}_{2} f)_{mm} = -\frac{1}{4} c_{m+1} c_{m-1} \hat{J}_{m+2n} - \frac{1}{4} c_{m} c_{m-1} \hat{J}_{m-2n} \]
\[ + c_{m} c_{m-1} \hat{J}_{mn} - \frac{1}{4} c_{m+1} c_{m-1} \hat{J}_{m-2n}, \]
\[ \mathcal{F}(X^{R}_{3} f)_{mm} = -m^{2} \hat{J}_{mn}, \]
\[ \mathcal{F}(X^{R}_{1} X^{R}_{2} f)_{mn} = \frac{i}{2} c_{m+1} c_{m-1} \hat{J}_{m+2n} - \frac{i}{2} c_{m} c_{m-1} \hat{J}_{m-2n}, \]
\[ \mathcal{F}(X^{R}_{1} X^{R}_{3} f)_{mn} = -i \frac{2m+1}{2} c_{m-1} \hat{J}_{m+1n} + i \frac{2m-1}{2} c_{m-1} \hat{J}_{m-1n}, \]
\[ \mathcal{F}(X^{R}_{2} X^{R}_{3} f)_{mn} = \frac{(2m+1)}{2} c_{m-1} \hat{J}_{m+1n} + \frac{(2m-1)}{2} c_{m-1} \hat{J}_{m-1n}. \]

Collecting everything together we have
\[ \mathcal{F} \left( \frac{1}{2} \sum_{i,j=1}^{3} D_{ij} X^{R}_{i} X^{R}_{j} + \sum_{i=1}^{3} d_{i} X^{R}_{i} \right)_{mn} \]
\[ = \min(m+2) \sum_{\hat{J}_{mn}} \mathcal{A}_{m,k} \hat{J}_{mn}, \]
\[ \mathcal{A}_{m+2} = \left[ \frac{(D_{11} - D_{22})}{8} + \frac{i}{4} D_{12} \right] c_{m+1} c_{m-1}, \]
\[ \mathcal{A}_{m+1} = \left[ \frac{2m+1}{4} (D_{23} - iD_{13}) + \frac{1}{2} (-d_{1} + id_{2}) \right] c_{m-1}, \]
\[ \mathcal{A}_{m} = \left[ \frac{-(D_{11} + D_{22})}{8} (c_{m} c_{m-1} + c_{m} c_{m-1}) \right. \]
\[ \left. - \frac{D_{33} m^{2}}{2} - id_{3} m \right], \]
\[ \mathcal{A}_{m-1} = \left[ \frac{(2m-1)}{4} (D_{23} + iD_{13}) + \frac{1}{2} (-d_{1} + id_{2}) \right] c_{m+1}, \]
\[ \mathcal{A}_{m-2} = \left[ \frac{(D_{11} - D_{22})}{8} - \frac{i}{4} D_{12} \right] c_{m+1} c_{m-1} \cdot \]

Hence, application of the SO(3)-Fourier transform to Eq. (11) and corresponding initial conditions reduces (11) to a set of linear time-invariant ODE’s of the form
\[ \frac{df^{l}}{dL} = \mathcal{A}^{l} f^{l} \text{ with } f(0) = I_{2l+1}, \]

\[ (25) \]

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 \( l = 0,1,2,3; \)

\[ \mathcal{A}^{0} = \mathcal{A}^{0}_{0} = 0, \]
\[ \mathcal{A}^{1} = \left( \begin{array}{ccc} A_{1,0}^{1} & A_{1,0}^{1} & A_{1,0}^{1} \\ A_{0,1}^{1} & A_{0,1}^{1} & A_{1,0}^{1} \\ A_{1,0}^{1} & A_{0,1}^{1} & A_{1,0}^{1} \end{array} \right), \]
\[ \mathcal{A}^{2} = \left( \begin{array}{ccccccc} A_{2,0}^{2} & A_{2,0}^{2} & A_{2,0}^{2} & 0 & 0 \\ A_{1,1}^{2} & A_{1,2}^{2} & A_{2,0}^{2} & A_{2,1}^{2} & 0 \\ A_{0,2}^{2} & A_{1,1}^{2} & A_{0,2}^{2} & A_{2,1}^{2} & A_{2,2}^{2} \\ 0 & A_{1,1}^{2} & A_{1,1}^{2} & A_{1,1}^{2} & A_{2,2}^{2} \\ 0 & 0 & A_{2,0}^{2} & A_{2,1}^{2} & A_{2,2}^{2} \end{array} \right), \]
\[ \mathcal{A}^{3} = \left( \begin{array}{cccc} A_{3,0}^{3} & A_{3,0}^{3} & A_{3,0}^{3} & 0 \\ A_{2,1}^{3} & A_{2,2}^{3} & A_{3,0}^{3} & A_{3,1}^{3} \\ A_{1,2}^{3} & A_{2,2}^{3} & A_{1,2}^{3} & A_{3,1}^{3} \\ A_{0,3}^{3} & A_{1,2}^{3} & A_{2,2}^{3} & A_{3,2}^{3} \\ A_{0,3}^{3} & A_{1,2}^{3} & A_{2,2}^{3} & A_{3,2}^{3} \end{array} \right). \]
As is well known in systems theory, the solution to Eq. (25) is of the form of a matrix exponential,

$$
\hat{f}(L) = e^{tA(L)}.
$$

(26)

Since $A(l)$ 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 $LA$ by observing the symmetry

$$
A_m^n = (-1)^{m-n}A_{-n}^{-m}.
$$

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 $\lambda$, then $(-1)^n x_{-m}$ will be the components of the eigenvector corresponding to $\overline{x}$ [58].

In general, the numerically calculated values of $\hat{f}(L)$ 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 $\hat{f}(L)$ are of a simple enough form to write analytically by inspection. I.e., since $D_{11} = D_{22} = 1/a_0$, $D_{33} \rightarrow \infty$, and every other parameter in $D$ and $d$ is zero, the matrices $A(l)$ are all diagonal. This implies that the nonzero Fourier coefficients are of the form

$$
\hat{f}_{m,n}(L) = \exp(LA_{m,n}^L).
$$

However, for $m \neq 0$ the value of $D_{33}$ causes $\hat{f}_{m,n}(L)$ to be zero and what remains is a series in $l$ with $m = 0$:

$$
\begin{align*}
\hat{f}_{K,L}(A; L) &= \sum_{l=0}^{\infty} (2l+1)e^{-l/2l/2a_0} U_{0d}(A) \\
&= \sum_{l=0}^{\infty} (2l+1)e^{-l/2l/2a_0} P(\cos \beta).
\end{align*}
$$

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

$$
\begin{align*}
X^R_i &= \left( \begin{array}{cccc}
A_{3,3}^R & A_{3,2}^R & A_{3,1}^R & 0 \\
A_{3,2}^R & A_{2,2}^R & A_{2,1}^R & 0 \\
A_{3,1}^R & A_{2,1}^R & A_{1,1}^R & 0 \\
0 & A_{1,2}^R & A_{1,1}^R & 0 \\
0 & 0 & A_{1,1}^R & 0 \\
0 & 0 & 0 & A_{3,1}^R \\
0 & 0 & 0 & 0 & A_{3,1}^R
\end{array} \right).
\end{align*}
$$

(27)

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

$$
X_1 = \left( \begin{array}{cccc}
0 & 0 & 0 & 0 \\
0 & 0 & -1 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0
\end{array} \right),
\quad X_2 = \left( \begin{array}{cccc}
0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 \\
-1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0
\end{array} \right),
$$

$$
X_3 = \left( \begin{array}{cccc}
0 & -1 & 0 & 0 \\
1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0
\end{array} \right),
\quad X_4 = \left( \begin{array}{cccc}
0 & 0 & 0 & 1 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0
\end{array} \right),
$$

$$
X_5 = \left( \begin{array}{cccc}
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0
\end{array} \right),
\quad X_6 = \left( \begin{array}{cccc}
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0
\end{array} \right).
$$

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

In Appendix A we show that

$$
\begin{align*}
X^R_i &= X^R_i^L(A_{v} \hat{a}) & \text{for } i = 1, 2, 3 \\
X^R_i &= (A^T \nabla_{v})_{i-3} & \text{for } i = 4, 5, 6
\end{align*}
$$

(28)

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

$$
\left( \frac{\partial}{\partial L} - \frac{1}{2} \sum_{i=1}^{3} D_{ik} \chi_{i} \chi_{k} - \frac{3}{2} \sum_{i=1}^{3} d_{i} \chi_{i} + \chi_{6} \right) F = 0.
$$

(29)

With an appropriate concept of Fourier transform, the differential operators $\chi^R_i$ 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 \( U^\beta(\mathbf{a}, A) \) of \( \text{SE}(3) \), which act on functions \( \phi(p) \in L^2(S^2) \) with the usual inner product, are defined by [60,59]

\[
[U^\beta(\mathbf{a}, A) \phi](p) = e^{-i\mathbf{p} \cdot \Delta \mathbf{a}} R_p^{-1} A R_{-\mathbf{p}}^{-1} A^{-1} \phi(A^{-1} p),
\]

(30)

where \( A \in \text{SO}(3), R_p \) is the rotation matrix which converts (04,0) \( p \) to any \( p \in \mathbb{R}^3 \) with \( |p| = p \), and \( \Delta \mathbf{a} \) are representations of \( \text{SO}(2) \) enumerated by \( s = 0, \pm 1, \pm 2, \ldots \). (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 \( \text{SE}(3) \) to \( \text{SO}(3) \), i.e., when \( |\mathbf{a}| = 0 \). They are unitary, because \( (U^\beta(\mathbf{a}, A) \phi_1, U^\beta(\mathbf{a}, A) \phi_2) = (\phi_1, \phi_2) \). The set of all such representations is also complete.

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

\[
U^\beta(g_1 g_2,p) = U^\beta(g_1,p) \cdot U^\beta(g_2,p),
\]

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

\[
U^\beta(\mathbf{a}, A) = U^\beta(\mathbf{a}, I) \cdot U^\beta(0, A).
\]

(31)

The translation matrix elements are given by the integral

\[
[U^\beta(\mathbf{a}, I) h_{lm,s}(p)](A) = \int_0^\pi \int_0^{2\pi} Q_{lm,s}^{\beta}(\cos \theta) e^{-i(p \cdot \Delta \mathbf{a})} \sin \theta \, d \theta \, d \phi,
\]

(34)

Finally, using the group property (31), the matrix elements of the unitary representation \( U^\beta(g,p) \) (30) (for \( s = 0, \pm 1, \pm 2, \ldots \)) are expressed as

\[
U^\beta_{p,m';l;m}(\mathbf{a}, A;p) = \sum_{j=-j}^{j} [I', m' \mid p, s \mid I, j](\mathbf{a}) U^\beta_{j,m}(A).
\]

(35)

B. Fourier transform

Here we review the definition of the Fourier transform of functions \( F(\mathbf{a}, A) \in L^2(\text{SE}(3)) \). To define an invertible Fourier transform for functions on \( \text{SE}(3) \) 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 \( U^\beta(g,p) \) (30) (for \( s = 0, \pm 1, \pm 2, \ldots \)), 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 \( \text{SE}(3) \), the Fourier transform is the matrix-valued function

\[
\mathcal{F}(F) = \hat{F}(p) = \int_{\text{SE}(3)} F(g) U(g^{-1} \cdot p) \, dg,
\]

where \( g = (\mathbf{a}, A) \in \text{SE}(3), dg = dA \, d^3a \), 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

\[
\hat{F}_{p',m';l;m}(p) = \int_{\text{SE}(3)} F(\mathbf{a}, A) U^\beta_{l;m';m}(\mathbf{a}, A;p) \, dA \, d^3a,
\]

(36)

where we have used the unitary property.

The inverse Fourier transform recovers \( F(\mathbf{a}, A) \) from \( \hat{F}(p) \) as [59]

\[
F(g) = \mathcal{F}^{-1}(\hat{F}) = \frac{1}{2 \pi^2} \int_0^\infty \text{Tr} \left[ \hat{F}(p) U(g,p) \right] p^2 \, dp.
\]

(37)

In component form this is written as

\[
F(\mathbf{a}, A) = \frac{1}{2 \pi^2} \sum_{l = -\infty}^{\infty} \sum_{m = -l}^{l} \sum_{s = -l}^{l} \sum_{l' = -\infty}^{\infty} \sum_{m' = -l'}^{l'} \int_0^\infty p^2 \, dp \times \hat{F}_{lm,l,m'}(p) U^\beta_{l,m',l,m}(\mathbf{a}, A;p).
\]

(38)
We note that as a direct result of Eqs. (14), (35), and the above inversion formula,
\[
\int_{S_{O(3)}} F(a, A) dA = \frac{1}{2\pi^2} \sum_{l=0}^{\infty} \sum_{m_l=-m_l}^{m_l} \int_0^\infty p^2 dp \times F_{0l,m_l}^0(p)(l', m', [l, m, 0, 0, 0, 0]_l, a).
\]
If this distribution of end positions is then integrated over the surface of a sphere with radius \(a = |a|\), the result is the end-to-end distance distribution:
\[
\frac{a^2}{2\pi^2} \int_{S_{O(3)}} F(a, A) \sin(\theta) dA
\]
\[
= \frac{\pi}{2} \int_0^\infty p^2 dp F_{000000}^0(p)[0, 0, 0, 0, 0, 0](a).
\] (39)

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

C. Operational Properties and Solutions of PDEs

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
\[
\mathcal{F}[(\tilde{X}_i^R)^F] = \int_{\text{SE}(3)} dt \mathcal{F}[U^R(\exp(l\tilde{X}_i))]|_{l=0} = \mathcal{F}[g \mathcal{F}[\exp(l\tilde{X}_i)]]|_{l=0} = \delta(t') U^R(0, 1, p)d\theta.
\] (40)

Here \(g\) can be thought of as \(H(g)\) and \(\exp(l\tilde{X}_i)\) is an element of the subgroup of \(\text{SE}(3)\) generated by \(\tilde{X}_i\), which for small values of \(t\) is approximated as \(t + t\tilde{X}_i\). By performing the change of variables \(h = g \mathcal{F}[\exp(l\tilde{X}_i)]\) and using the homomorphism property of the representations \(U^R(\cdot)\), one finds
\[
\mathcal{F}[(\tilde{X}_i^R)^F] = \int_{\text{SE}(3)} F(h) \frac{d}{dt} [U^R(\exp(l\tilde{X}_i))]|_{l=0} dh
\]
\[
= \frac{d}{dt} [U^R(\exp(l\tilde{X}_i))]|_{l=0}
\]
\[
\times \int_{\text{SE}(3)} F(h) U^R(h^{-1}, p) dh.
\] (42)

By defining
\[
u^R(\tilde{X}_i, p) = \frac{d}{dt} [U^R(\exp(l\tilde{X}_i))]|_{l=0},
\]
we write
\[
\mathcal{F}[(\tilde{X}_i^R)^F] = \nu^R(\tilde{X}_i, p) F^R(p).
\]

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

V. NUMERICAL RESULTS

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

In practice, however, we must truncate \(B^R(p)\) 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 $[B^0(p)]_{L_B}$ for $0 \leq p \leq P_B$. In the numerical results that follow, we exponentiate $L[B^0(p)]_{L_B}$, and examine the convergence of the 00:00 element of $\exp(L[B^0(p)]_{L_B})$ 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 $\alpha_0$ 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 $\sigma$ 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:

$$\langle R^2 \rangle = c \frac{\tau_0}{2} - \frac{2 \kappa_0^2 (4 - \nu^2)}{\nu^2} + e^{-2L} \frac{2 \nu}{\nu^2}$$

$$\times \left( \frac{\tau_0}{2} + \frac{2 \kappa_0^2}{\nu^2} [(4 - \nu^2) \cos(\nu L) - 4 \nu \sin(\nu L)] \right),$$

(44)

where

$$c = \frac{4 + \tau_0}{4 + 2 \kappa_0^2 + \tau_0^2}$$

(45)

and

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

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

Here $\kappa_0$ and $\tau_0$ are the unperturbed values of curvature and torsion of the helix. In our notation, $\langle R^2 \rangle = \langle |a|^2 \rangle$.

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 Krichin-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 PDFs 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, $\kappa_0 = 3.0$ 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 compatibility of our method with the KP and helical wormlike models, our method is valid for

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

**ACKNOWLEDGMENTS**

We thank A. Krylov and R. Altendorfer for their helpful comments. This work was performed while the authors were supported by NSF Grant No. IIS 9731720.

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

In this appendix it will be helpful to associate each matrix $\tilde{X}_i^\nu$ defined in Sec. IV with a vector $(\tilde{X}_i^\nu)^\nu$ in the following way:
\[
\begin{pmatrix}
1 \\
0 \\
0
d(\hat{X}_1) = \\
0 \\
0 \\
1 
\end{pmatrix},
\begin{pmatrix}
1 \\
0 \\
0
d(\hat{X}_2) = \\
0 \\
0 \\
1 
\end{pmatrix},
\begin{pmatrix}
1 \\
0 \\
0
d(\hat{X}_3) = \\
0 \\
0 \\
1 
\end{pmatrix}
\]

\[
\begin{pmatrix}
1 \\
0 \\
0
d(\hat{X}_4) = \\
0 \\
0 \\
1 
\end{pmatrix},
\begin{pmatrix}
1 \\
0 \\
0
d(\hat{X}_5) = \\
0 \\
0 \\
1 
\end{pmatrix},
\begin{pmatrix}
1 \\
0 \\
0
d(\hat{X}_6) = \\
0 \\
0 \\
1 
\end{pmatrix}
\]

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

\[
\hat{X}_i^R f(H) = \left. \frac{d f(H \cdot (I + t \hat{X}_i))}{dt} \right|_{t=0}, \tag{A1}
\]

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

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

since

\[
d(\hat{X}_i) = \left. \frac{d}{dt}(q_j + tq^{R,i,j}) \right|_{t=0}.
\]

Differentiating with respect to \( t \) and setting \( t=0 \) then yields

\[
\begin{pmatrix}
\hat{X}_i \\
\hat{X}_j
\end{pmatrix} = \sum_{j=1}^{6} H^{-1} \frac{\partial H}{\partial q_j} \frac{d}{dt} q^{R,i,j},
\]

or

\[
(\hat{X}_i)^{\nu} = \sum_{j=1}^{6} \left( H^{-1} \frac{\partial H}{\partial q_j} \right)^{\nu} q^{R,i,j}.
\]

The \( 6 \times 6 \) matrix with columns \( [H^{-1}(\partial H/\partial q_j)]^{\nu} \) is denoted \( J_R \). One then writes

\[
q^{R,i,j} = J_R^{-1}(\hat{X}_i)^{\nu},
\]

which is used to calculate

\[
\hat{X}_i^R f = \sum_{j=1}^{6} \frac{d f}{d q_j} q^{R,i,j} = J_R^{-1} \sum_{j=1}^{6} (\hat{X}_i)^{\nu} \frac{d f}{d q_j}
\]

\[
(A2)
\]

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 \( a \)). Then \( J_R \) and its inverse take the explicit forms

\[
J_R = \begin{pmatrix} J_R^{11} & 0_3 \\ 0_3 & A \end{pmatrix}, \quad J_R^{-1} = \begin{pmatrix} J_R^{-11} & 0_3 \\ 0_3 & A^{-1} \end{pmatrix},
\]

where \( 0_3 \) is the \( 3 \times 3 \) zero matrix. Substitution of these definitions into Eq. (A2) results in Eq. (28).

**APPENDIX B: HELICITY REPRESENTATIONS**

In this appendix we explain the term \( \Delta_3(R_{12}^{-1} A R_{12}^{-1} R) \) (which is often called a helicity representation) in Eq. (30). Let \( H^\sigma \) denote the group which leaves the point \( \hat{v} \in S^2 \) fixed. To calculate the representations of \( H^\sigma \) explicitly, we first choose a particular coset representative \( \hat{v} = e_3 \in S^2 \equiv SO(3)/SO(2) \). The vector \( \hat{v} \) is invariant with respect to rotations from the SO(2) subgroup of SO(3), and for this particular choice of \( \hat{v} \) we do not only have \( H^\sigma \equiv SO(2) \), but rather \( H^\sigma = SO(2) \).

For each \( \hat{v} \in S^2 \) we may find \( R_v \in SO(3)/SO(2) \), such that

\[
R_v \hat{v} = v.
\]

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

\[
b = R(a,b) a,
\]

is defined by

\[
R(a,b) = e^C = I + C + \frac{(1-a \cdot b)}{||a \times b||^2} C^2,
\]

\[
(B1)
\]

where \( c = a \times b \) and \( C \) is defined by \( Cx = c \times x \). This follows easily from the fact that \( ||a \times b|| = \sin \theta_{ab} \) and \( a \cdot b = \cos \theta_{ab} \)

where \( 0 \leq \theta_{ab} \leq \pi \) is the counterclockwise measured angle from \( a \) to \( b \) as measured in the direction defined by \( c \). Hence, in the current context,

\[
R_v = R(\hat{v}, \hat{v}) = e^{\text{null}[\hat{v} \times \hat{v}]},
\]

where \( \text{null}[c] \) is the skew-symmetric matrix such that \( \text{null}[c]x = c \times x \).

For any \( A \in SO(3) \) it follows from the definition of \( R_v \) that

\[
R_{A^{-1}} \hat{v} = A^{-1} v.
\]

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

\[
(R_v^{-1} A R_v^{-1} \hat{v}) \hat{v} = \hat{v}.
\]

Therefore,
\[ Q(v,A) = (R_{A}^{-1}A R_{A^{-1}v}) \in H_z. \]

The representations of \( H_z \) may be taken to be of the form
\[ \Delta_{s,\phi} \rightarrow e^{i\phi}, \quad 0 \leq \phi \leq 2\pi, \]
and \( s = 0, \pm 1, \pm 2, \ldots \). This is just the usual Fourier series on \( S^1 = \text{SO}(2) \).

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

We begin by observing that
\[ R_{A^{-1}v} = R(\hat{v}, A^{-1}v) = e^{\text{matr}[\hat{v} \times (A^{-1}v)].} \]

Using general rules for cross-products, one finds that
\[ \hat{v} \times (A^{-1}v) = A^{-1}[(A\hat{v}) \times v)] \]
and
\[ \text{matr}[A^{-1}((A\hat{v}) \times v)] = A^{-1}\text{matr}[(A\hat{v}) \times v]A. \]

Since conjugation commutes with the matrix exponential, it follows that
\[ R_{A^{-1}v} = A^{-1}R(A\hat{v}, v)A = A^{-1}e^{\text{matr}(A\hat{v}) \times v}A. \]

Substitution of this into the definition of \( Q(v,A) \), and using the fact that
\[ R_{v}^{-1} = \exp\{-\text{matr}[(\hat{v} \times v)]\} = \exp\{\text{matr}[(v \times \hat{v})]\}, \]
one finds
\[ Q(v,A) = e^{\text{matr}(v \times \hat{v})\text{matr}(A\hat{v}) \times v}A. \]  

While the derivation here is for unit vectors \( v \), everything follows in exactly the same way for \( p = pv. \)


