Nonequilibrium statistics of flexible macromolecules in dilute solutions. I. Macromolecular configuration

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For a macromolecule modeled as a Rouse chain in dilute solution, we give the exact nonequilibrium expression for the joint probability density for the configuration of any number of links of the chain, expressed in terms of the connector vector coordinates. From this expression we get the probability density for a single link and the joint probability density for two links. For these two functions we give the associated diffusion equations. We also give the length-independent probability density for the orientation of a single link. Finally we illustrate the application of these results in steady shear flow.

I. INTRODUCTION

Polymer solutions and undiluted polymer melts have flow properties which are quite different from those of Newtonian liquids. These properties can cause unusual flow behavior.[1] Molecular theory serves as a source of constitutive equations that provide a connection between the unique flow properties of polymers and their chain-like molecular structure.

In most molecular theories, in order to gain an understanding of the rheological behavior, it is necessary to develop some knowledge of the distribution of the configurations of the macromolecules. For flowing polymer fluids, the calculation of macromolecular configurations requires the use of models which are simple enough to allow nonequilibrium calculations. Even with the simplest models the calculations are very complex, and only a few general results are known. For dilute solutions an important result is the expression for the distribution of configurations for an arbitrary bead-rod-spring model given by Curtiss, Bird, and Hassager[2]; however this result is restricted to steady-state, homogeneous, potential flows. Only for the Rouse model (the flexible chain of beads connected by Hookean springs) can the distribution of configurations be found in any general flow. Previous investigations which used this model took the approach of normal-modes analysis[3,4,5]; in these studies the distribution of configurations is given in terms of the normal-mode coordinates of the chain. The normal-mode coordinates are linear combinations of the connector coordinates. Although the normal modes may be interpreted as being related to vibrational or "breathing" motions of the chain, they do not give a clear picture of the stretching and orientation of segments of the macromolecule.

In this paper we will go beyond the normal-modes treatment and study the distributions of quantities pertaining to the orientation and extension certain portions of the macromolecule under general flow conditions. The macromolecular model used throughout is the Rouse freely jointed bead–spring chain. First we review the necessary details of the Rouse theory. Then we derive the joint probability density for any number of links of the chain, from which we get the probability density functions for one link and for two links. For these two functions we give the appropriate diffusion equations. We also show how the one-link probability density function can be integrated to give a length-independent probability density function for the orientation of a link. Finally we show how these functions can be calculated in steady shear flow.

II. THE ROUSE MODEL

Two avenues are available for the development of the Rouse theory for dilute polymer solutions. In one approach, the Rouse theory is found as a special case of the general phase-space kinetic theory for polymeric fluids of Curtiss, Bird, and Hassager.[2] A summary of this approach is given by Curtiss and Bird.[6] The second approach, pioneered by Kirkwood and his co-workers,[7] is based on the theory of fluctuations and stochastic processes. Its advantage is that it makes clear the connection between the Langevin formulation, which forms the basis of the non-equilibrium Brownian dynamics (NEBD) computer simulation technique,[8–10] and the diffusion equation or Fokker–Planck formulation, which plays a central part in the Rouse theory. In part II we make comparisons between the predictions of the Rouse theory and those of NEBD. Therefore we find it advantageous to discuss the second approach.

The dynamics of the Rouse chain immersed in a flowing solution can be treated by an extension of the theory of the Brownian motion of a single particle to the case of N bound particles. The abbreviated discussion that follows draws on the discussions of van Kampen,[11] Yamakawa,[12] and Hinch[13]; in addition, recently Phan-Thien and Atkinson[14] and Edwards[15] have given related discussions of the polymer chain dynamics.

In the Rouse model the mass of the macromolecule, as well as its hydrodynamic resistance, are concentrated at N

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mass points, or "beads," connected by $N-1$ Hookean "springs." The substitution of springs for sections of the macromolecule has its basis in the theory of rubber elasticity.[16–18] The chain is freely jointed: there is no restriction on the orientation of the springs. Each bead is treated as a Brownian particle of mass m with isotropic friction coefficient ζ. Its motion follows the Langevin equation:

$$m\ddot{\mathbf{r}}_\nu = -\zeta\,[\dot{\mathbf{r}}_\nu - \mathbf{v}(\mathbf{r}_\nu)] + \mathbf{F}_\nu + \mathbf{A}_\nu(t) \quad (\nu = 1,\ldots,N)\,. \tag{2.1}$$

In Eq. (2.1) $\mathbf{r}_\nu$ is the position of bead "ν"; $\mathbf{v}(\mathbf{r}_\nu)$ is the fluid velocity calculated from the macroscopic flow field at $\mathbf{r}_\nu$;$\mathbf{F}_\nu$ is the spring force acting on bead ν; and $\mathbf{A}_\nu(t)$ is the rapidly fluctuating random force, which by definition has the properties:

$$\langle \mathbf{A}_\nu(t)\rangle = 0\,, \tag{2.2}$$

$$\langle \mathbf{A}_\nu(t)\mathbf{A}_\mu(t')\rangle = \delta_{\nu\mu}\delta(t-t')\mathbf{B}\,. \tag{2.3}$$

In the above the angular brackets denote the ensemble average (that is, the average over all realizations for a given initial condition) of the enclosed quantity. The tensor $\mathbf{B}$ can be related to the friction coefficient and the temperature by $\mathbf{B} = kT\zeta\boldsymbol{\delta}$, with $\boldsymbol{\delta}$ the unit tensor.[13]

For a given set of initial positions of the beads, Eq. (2.1) can be integrated to give the time evolution of the N-bead system. In Brownian dynamics simulations, this integration over time is carried out numerically.[8–10] However we are not interested in the explicit time history of the Rouse chain but in its statistical distribution of configurations. We denote by $\Psi(r_1,\ldots,r_N,t)$ the probability density for the configuration of the chain; that is, $\Psi(r_1,\ldots r_N,t)\mathbf{d}r_1,\ldots\mathbf{d}r_N$ is the probability that the chain is found with each $\mathbf{r}_\nu$ in the range from $\mathbf{r}_\nu$ to $\mathbf{r}_\nu + \mathbf{d}\mathbf{r}_\nu$ (the $\mathbf{r}_\nu$ denote the position coordinates of the beads, whereas the r_ν are dummy variables]. It is known from the theory of stochastic processes that the Fokker–Planck equation governing Ψ is given in terms of the ensemble-averaged displacement $\langle \Delta\mathbf{r}_\nu\rangle$ and square displacement $\langle \Delta\mathbf{r}_\nu\Delta\mathbf{r}_\nu\rangle$:

$$\frac{\partial\Psi}{\partial t} = \left(-\frac{1}{\Delta t}\right)\sum_{\nu=1}^{N}\left(\frac{\partial}{\partial r_\nu}\right) \cdot\left[\langle\Delta\mathbf{r}_\nu\rangle\Psi - \left(\frac{1}{2}\right)\left(\frac{\partial}{\partial r_\nu}\right)\cdot\langle\Delta\mathbf{r}_\nu\Delta\mathbf{r}_\nu\rangle\Psi\right]. \tag{2.4}$$

In the long-time regime, where $\Delta t \gg m/\zeta$ (this condition is equivalent to the discarding of the inertial terms in the configuration-space kinetic theories), $\langle\Delta\mathbf{r}_\nu\rangle$ and $\langle\Delta\mathbf{r}_\nu\Delta\mathbf{r}_\nu\rangle$ can be found as

$$\langle\Delta\mathbf{r}_\nu\rangle = [\mathbf{v}(\mathbf{r}_\nu) + (1/\zeta)\mathbf{F}_\nu]\Delta t\,, \tag{2.5a}$$

$$\langle\Delta\mathbf{r}_\nu\Delta\mathbf{r}_\nu\rangle = (2kT/\zeta)\boldsymbol{\delta}\Delta t\,. \tag{2.5b}$$

The diffusion equation for Ψ becomes

$$\frac{\partial\Psi}{\partial t} = -\sum_{\nu=1}^{N}\left(\frac{\partial}{\partial r_\nu}\right)\cdot\left\{\left[\mathbf{v}(r_\nu) + (1/\zeta)\mathbf{F}_\nu\right]\Psi - (kT/\zeta)\frac{\partial\Psi}{\partial r_\nu}\right\}. \tag{2.6}$$

Equation (2.6) is generally taken as a starting point of configuration-space kinetic theories for polymeric fluids. Curtiss and Bird[6] have shown how it can be found in an alternative way from a general phase-space kinetic theory.[2]

III. THE PROBABILITY DENSITY FOR THE CONFIGURATION OF THE CHAIN

In this section our discussion follows that of Chap. 12 of "Dynamics of Polymeric Liquids,"[19] referred to as DPL. For a homogeneous fluid (i.e., no concentration gradients) subject to a homogeneous flow field [$\mathbf{v}(\mathbf{r}_\nu) = \boldsymbol{\kappa}\cdot\mathbf{r}_\nu$, with $\boldsymbol{\kappa}$ the transpose of the solution velocity gradient] Ψ can be factored as $n\psi$, where n is the number density of chains present in solution and ψ is the probability density for the internal configurations of the chain. The internal coordinates of the chain can be chosen as the set of $N-1$ connector coordinates $\mathbf{Q}_1,\ldots,\mathbf{Q}_{N-1}$, denoted by $(\mathbf{Q}^{N-1})$ and given by

$$\mathbf{Q}_k = \mathbf{r}_{k+1} - \mathbf{r}_k \quad (k = 1,\ldots,N-1)\,. \tag{3.1}$$

For the Rouse chain, the spring force acting through connector "k," which is the difference between the spring forces acting on beads "$k+1$" and k, is given by $H\,\mathbf{Q}_k$, with H the spring constant. This expression for the interbead force and Eq. (3.1) can be substituted into Eq. (2.6). After some manipulation [DPL Sec. 12.2], Eq. (2.6) gives a diffusion equation for $\psi(\mathbf{q}^{N-1},t)$, which is the probability density for the internal configuration of the chain [$\psi(\mathbf{q}^{N-1},t)\mathbf{d}\mathbf{q}^{N-1}$ is the probability of finding the chain with each of the $\mathbf{Q}_i$ in the range of $\mathbf{q}_i$ to $\mathbf{q}_i + \mathbf{d}\mathbf{q}_i$, where the $\mathbf{Q}_i$ represent the actual connector vectors and the $\mathbf{q}_i$ are dummy variables]:

$$\left(\frac{\partial}{\partial t}\right)\psi(\mathbf{q}^{N-1},t) = -\sum_{j=1}^{N-1}\left(\frac{\partial}{\partial\mathbf{q}_j}\right)\cdot\left\{[\boldsymbol{\kappa}\cdot\mathbf{q}_j]\psi - (1/\zeta)\sum_{k=1}^{N-1}A_{jk}\left[kT\left(\frac{\partial\psi}{\partial\mathbf{q}_k}\right) + H\mathbf{q}_k\psi\right]\right\}. \tag{3.2}$$

In the above A_{jk} is an element of the $(N-1)\times(N-1)$ Rouse matrix ($A_{jk} = 2$ if $j = k$, -1 if $j = k \pm 1$, and zero otherwise). Equation (3.2) can be simplified by the introduction of a set of $N-1$ normal coordinates $(\mathbf{Q}'^{N-1})$, related to the connector coordinates by a linear transformation:

$$\mathbf{Q}_k = \sum_{m=1}^{N-1}\Omega_{km}\mathbf{Q}'_m\,, \tag{3.3a}$$

$$\Omega_{km} = (2/N)^{1/2}\sin(km\pi/N)\,, \tag{3.3b}$$

where Ω_{km} is an element of the orthogonal matrix that diagonalizes the Rouse matric [DPL Sec. 12.2]. Separation of variables then leads to the well-known solution for ψ[3–5]:

$$\psi(\mathbf{q}^{N-1},t) = \psi(\mathbf{q}'^{N-1},t) = \prod_{j=1}^{N-1}\psi_j(\mathbf{q}'_j,t)\,, \tag{3.4a}$$

$$\psi_j(\mathbf{q}'_j,t) = [\det(2\pi\langle\mathbf{Q}'_j\mathbf{Q}'_j\rangle)]^{-1/2} \times\exp[-(1/2)\langle\mathbf{Q}'_j\,\mathbf{Q}'_j\rangle^{-1}:\mathbf{q}'_j\mathbf{q}'_j]\,, \tag{3.4b}$$

$$\langle\mathbf{Q}'_j\,\mathbf{Q}'_j\rangle = \underbrace{\int\cdots\int_{-\infty}^{\infty}}_{N-1}\mathbf{q}'_j\mathbf{q}'_j\prod_{i=1}^{N-1}\psi_i(\mathbf{q}'_i,t)\mathbf{d}\mathbf{q}'_i = (kT/H)\boldsymbol{\delta} - (1/nH)\boldsymbol{\tau}_j\,, \tag{3.4c}$$

$$\boldsymbol{\tau}_j = -(nkT/\lambda_j)\int_{-\infty}^{\infty} \exp[-(t-t')/\lambda_j]\boldsymbol{\gamma}_{[0]}(t,t')dt', \tag{3.4d}$$

$$\lambda_j = 2\lambda_H c_j\,; \quad \lambda_H = \zeta/4H\,; \quad c_j = 1/4\sin^2(j\pi/2N)\,. \tag{3.4e}$$

In the above $\mathbf{q}'^{N-1}$ denotes a set of $(N-1)$ dummy variables $\mathbf{q}_i'$ related to the $\mathbf{q}_i$ in the same way that the normal-mode coordinates $\mathbf{Q}_i'$ are related to the connector-vector coordinates $\mathbf{Q}_i$ (i.e., $\mathbf{q}_k = \Sigma_{m=1}^{N-1}\Omega_{km}\mathbf{q}_m'$);$n$ is the number density of polymer chains present in solution; $\boldsymbol{\delta}$ is the unit tensor; $\boldsymbol{\tau}_j$ is the partial stress tensor associated with normal mode j; the angular brackets denote the average of the enclosed quantity taken over the entire chain configuration space; $\boldsymbol{\gamma}_{[0]}(t,t')$ is a codeformational finite strain tensor which can be found if the flow field is known [DPL Appendix C]; and λ_j is the time constant characteristic of normal mode j, related to λ_H, the fundamental time constant, and c_j, the jth eigenvalue of the Kramers matrix $[C_{jk}]$, inverse of the Rouse matrix. The probability density for the configuration of the chain is factored as the product of $N-1$ probability density functions ψ_j for the normal modes $\mathbf{Q}_j'$. Each of the ψ_j is of normal Gaussian form. Furthermore the normal modes are all statistically independent of each other, in the sense that the moment $\langle \mathbf{Q}_i'\mathbf{Q}_j'\rangle = \delta_{ij}\langle \mathbf{Q}_i'\mathbf{Q}_i'\rangle$ (that is, $\langle \mathbf{Q}_i'\mathbf{Q}_j'\rangle = \mathbf{O}$ when i is different from j). Equations (3.3a) and (3.4c) lead to expressions for the moment $\langle \mathbf{Q}_k\mathbf{Q}_j\rangle$:

$$\langle \mathbf{Q}_k\mathbf{Q}_j\rangle = \delta_{jk}(kT/H)\boldsymbol{\delta} - (1/nH)\sum_{m=1}^{N-1}\Omega_{km}\Omega_{jm}\boldsymbol{\tau}_{jm}\,. \tag{3.5}$$

Some additional relations which will be used later concern the elements and eigenvalues of the Kramers matrix [DPL Sec. 12.1]:

$$\begin{aligned} C_{ij} &= i(N-j)/N \quad (i\leqslant j)\\ &= j(N-i)/N \quad (i\geqslant j)\,, \end{aligned} \tag{3.6}$$

$$\sum_{j=1}^{N-1} c_j = (N^2-1)/6\,, \tag{3.7}$$

$$\sum_{j=1}^{N-1} c_j^2 = (N^2-1)(2N^2+7)/180\,, \tag{3.8}$$

$$\sum_{j=1}^{N-1} c_j^3 = (N^2-1)(8N^4+29N^2+71)/[(21)(360)]\,. \tag{3.9}$$

The general expression for the probability density function for the configuration of the Rouse chain was first found by van Wiechen and Booij.[5] However they did not show the relation between the moments $\langle \mathbf{Q}_k\mathbf{Q}_j\rangle$ and the partial stress tensors $\boldsymbol{\tau}_j$ [that is, they gave Eqs. (3.4a) and (3.4b) but not Eqs. (3.4c) and (3.4d)]; they were able to find the moments explicitly only for specific flows by solving the differential equations which result from taking the second moments of the diffusion equation [Eq. (3.2)]. Their method required solving a different set of differential equations for each different flow. Lodge and Wu[3] soon thereafter pointed out the relation between the moments $\langle \mathbf{Q}_i'\mathbf{Q}_j'\rangle$ and the partial stress tensors $\boldsymbol{\tau}_j$ [Eq. (3.4c)]; furthermore they used the body tensor formalism to derive the general expression for the partial stress tensors [Eq. (3.4d)].

Recently King and James[4] used the two-sided Laplace transform technique to rederive the expression for the probability density ψ, and they demonstrated the usefulness of this technique in the calculation of mean values of configurational quantities for the chain. Although their methods are very powerful and inspired much of this work, their work does contain a few errors: Their use of the substantial derivative instead of the usual partial time derivative in the diffusion equation for ψ is inconsistent with the form of the continuity equation which results from statistical mechanics; in addition Booij[20] has shown that their expression for the energy storage is incorrect and has given the correct expression, which had been given earlier by Sarti and Marrucci.[21]

A novel use for the Rouse chain has been demonstrated by Armstrong and Jhon.[22] They used the Rouse model to study the turbulence-induced change in the conformation of polymer molecules, and, although they carried out detailed calculations only for the case of the two-bead dumbbell, they found that the effect of the stochastic velocity field on the macromolecule can be interpreted as a renormalization of the connector potential.

IV. THE JOINT PROBABILITY DENSITY FOR THE CONFIGURATION OF SEVERAL LINKS

In this section we develop a general method for finding the joint probability density for the configuration of any number of links expressed in terms of the "natural" connector vector coordinates.

The normal-mode coordinates of the chain constitute a set of independent, normal Gaussian distributed variables; furthermore the means and variances of any set of r connector vectors $(\mathbf{Q}_{\alpha_1},\ldots\mathbf{Q}_{\alpha_r})$ can all be found directly from those of the normal-mode coordinates, of which they are linear combinations:

$$\langle \mathbf{Q}_{\alpha_i}\rangle = \sum_{k=1}^{N-1}\Omega_{\alpha_i k}\langle \mathbf{Q}_k'\rangle = 0\,, \tag{4.1a}$$

$$\langle \mathbf{Q}_{\alpha_i}\mathbf{Q}_{\alpha_j}\rangle = \delta_{\alpha_i\alpha_j}(kT/H)\boldsymbol{\delta} - (1/nH)\sum_{k=1}^{N-1}\Omega_{\alpha_j k}\Omega_{\alpha_i k}\boldsymbol{\tau}_k\,. \tag{4.1b}$$

We denote by $f_{\alpha_1,\ldots,\alpha_r}(\mathbf{q}_1,\ldots,\mathbf{q}_r,t)$ the joint probability density for finding the r connector vectors $(\mathbf{Q}_{\alpha_1},\ldots,\mathbf{Q}_{\alpha_r})$ with $\mathbf{Q}_{\alpha_1} = \mathbf{q}_1, \mathbf{Q}_{\alpha_2} = \mathbf{q}_2\ldots, \mathbf{Q}_{\alpha_r} = \mathbf{q}_r$ (the $\mathbf{Q}_{\alpha_i}$ represent the connector vector coordinates while the $\mathbf{q}_i$ are dummy variables); r is not greater than the total number of links $(N-1)$ and the α_i denote a set of r distinct indices between 1 and $N-1$. This joint probability density function can be expressed as a contraction of the function ψ for the configuration of the entire chain:

$$\begin{aligned} &f_{\alpha_1,\ldots,\alpha_r}(\mathbf{q}_1,\ldots,\mathbf{q}_r,t)\\ &\quad = \left[\underbrace{\int\cdots\int_{-\infty}^{\infty}}_{N-1-r}\psi(\boldsymbol{q}^{N-1},t) = \prod_{j\neq\alpha_i}\mathbf{d}\boldsymbol{q}_j\right]\Bigg|_{\boldsymbol{q}_{\alpha_i}=\mathbf{q}_i}\\ &\qquad\qquad\qquad\qquad (i=1,\ldots,r)\\ &\quad = \underbrace{\int\cdots\int_{-\infty}^{\infty}}_{N-1}\psi(\boldsymbol{q}^{N-1},t)\left[\prod_{i=1}^{r}\delta(\boldsymbol{q}_{\alpha_i}-\mathbf{q}_i)\right]\left[\prod_{j=1}^{N-1}d\boldsymbol{q}_j\right]. \end{aligned} \tag{4.2}$$

The above integration is performed with the variables $\mathbf{q}_{\alpha_i}$ set equal to the $\mathbf{q}_i$, for the index i ranging between 1 and r. Using standard arguments of probability theory,[23] we can infer directly that $f_{\alpha_1,\ldots,\alpha_r}$ is of normal Gaussian form and is given by

$$f_{\alpha_1,\ldots,\alpha_r}(\mathbf{q}_1,\ldots,\mathbf{q}_r,t) = [\det(2\pi\boldsymbol{\sigma}^r)]^{-1/2} \times\exp\left[-(1/2)\sum_{i=1}^{r}\sum_{j=1}^{r}(\boldsymbol{\Sigma}^r)_{ij}:\mathbf{q}_i\,\mathbf{q}_j\right]. \tag{4.3}$$

In the above σ^r is the $r\times r$ tensor matrix whose elements $(\boldsymbol{\sigma}^r)_{ij}$ are the moments $\langle\mathbf{Q}_{\alpha_i}\mathbf{Q}_{\alpha_j}\rangle$, and $\boldsymbol{\Sigma}^r$ is the inverse of $\boldsymbol{\sigma}^r$.

The method of finding $f_{\alpha_1,\ldots,\alpha_r}$ which we have just presented is similar to the method of finding multivariate Gaussian distributions at equilibrium first formulated by Wang and Uhlenbeck[24] in one dimension and extended to the three-dimensional case by Fixman.[25]

To complete the derivation of $f_{\alpha_1,\ldots,\alpha_r}$ we need to give general expressions for $\boldsymbol{\Sigma}^r$ and $\det(\boldsymbol{\sigma}^r)$ for any number of connector vectors r. To do so we follow Aguirre[26] and decompose $\boldsymbol{\sigma}^r$ as the product of two matrices of tensors:

$$\boldsymbol{\sigma}^r = (\mathbf{L}^r)^{-1}\cdot\mathbf{U}^r. \tag{4.4}$$

The tensor matrix $\mathbf{U}^r$ is upper diagonal and its elements are given by

$$(\mathbf{U}^r)_{ij} = 0 \quad (i>j)$$
$$= {}_{(i-1)}\boldsymbol{\sigma}^r_{ij} \quad (i\leqslant j). \tag{4.5}$$

The tensors ${}_k\boldsymbol{\sigma}^r_{ij}$ are determined by the recurrence relation given by Aguirre:

$${}_k\boldsymbol{\sigma}^r_{ij} = {}_{(k-1)}\boldsymbol{\sigma}^r_{ij} - {}_{(k-1)}\boldsymbol{\sigma}^r_{ik}\cdot[{}_{(k-1)}\boldsymbol{\sigma}^r_{kk}]^{-1}\cdot{}_{(k-1)}\boldsymbol{\sigma}^r_{kj}, \tag{4.6a}$$

$${}_0\boldsymbol{\sigma}^r_{ij} = (\boldsymbol{\sigma}^r)_{ij} = \langle\mathbf{Q}_{\alpha_i}\mathbf{Q}_{\alpha_j}\rangle. \tag{4.6b}$$

Aguirre also shows that the tensor matrix $\mathbf{L}^r$ is lower diagonal, with all its diagonal elements given by the 3×3 identity tensor, and the last two elements of row r given by

$$\mathbf{L}^r_{r,(r-1)} = {}_{(r-2)}\boldsymbol{\sigma}^r_{r,(r-1)}\cdot[{}_{(r-2)}\boldsymbol{\sigma}^r_{(r-1),(r-1)}]^{-1},$$
$$L^r_{rr} = \boldsymbol{\delta}. \tag{4.7}$$

Aguirre shows that two of the elements of $\boldsymbol{\Sigma}^r$ can be determined immediately:

$$\boldsymbol{\Sigma}^r_{rr} = [{}_{(r-2)}\boldsymbol{\sigma}^r_{(r-1),(r-1)}]^{-1}, \tag{4.8}$$

$$\boldsymbol{\Sigma}^r_{r,(r-1)} = [{}_{(r-1)}\boldsymbol{\sigma}^r_{rr}]^{-1}\cdot[{}_{(r-2)}\boldsymbol{\sigma}^r_{(r-1),(r-1)}]^{-1}. \tag{4.9}$$

All of the remaining diagonal elements $\boldsymbol{\Sigma}^r_{ii}$ can be found by interchanging the indices i and r in Eq. (4.8). The off-diagonal elements $\boldsymbol{\Sigma}^r_{ij}$ can be found by interchanging the indices i with r and j with $r-1$ in Eq. (4.9). In addition we can use Eq. (4.4) and the properties of the lower and upper diagonal matrices $\mathbf{L}^r$ and $\mathbf{U}^r$ to show the following identity[28]:

$$\det(\boldsymbol{\sigma}^r) = \prod_{i=1}^{r}\det[{}_{(i-1)}\boldsymbol{\sigma}^r_{ii}]. \tag{4.10}$$

With this we have completely specified all of the terms which appear in Eq. (4.3) for the r-connector joint probability density $f_{\alpha_1,\ldots,\alpha_r}$. Furthermore the properties of the matrix $[\Omega_{ij}]$ can be used to show that Eq. (4.3) reduces exactly to the probability density for the entire chain when r is taken as $N-1$.

V. ONE AND TWO-LINK PROBABILITY DENSITY FUNCTIONS

Two cases of $f_{\alpha_1,\ldots,\alpha_r}$ which are of particular interest are the one-link probability density f_i and the two-link probability density f_{ij}. The one-link function f_i results from $f_{\alpha_1,\ldots,\alpha_r}$ when r is taken as 1 and α_1 is set equal to i, and the two-link function f_{ij} results when r is taken as 2 with $\alpha_1=i$ and $\alpha_2=j$. For f_i we find:

$$f_i(\mathbf{q},t) = \left[\underbrace{\int\cdots\int_{-\infty}^{\infty}}_{N-2}\psi(q^{N-1},t)\prod_{k\neq i}\mathbf{d}q_k\right]\Bigg|_{q_i=\mathbf{q}} = \underbrace{\int\cdots\int_{-\infty}^{\infty}}_{N-1}\psi(q^{N-1},t)\delta(q_i-\mathbf{q})\prod_{k=1}^{N-1}\mathbf{d}q_k = [\det(2\pi\langle\mathbf{Q}_i\,\mathbf{Q}_i\rangle)]^{-1/2} \times\exp[-(1/2)\langle\mathbf{Q}_i\mathbf{Q}_i\rangle^{-1}:\mathbf{q}\mathbf{q}]. \tag{5.1}$$

The above integration is performed with $\mathbf{q}_i$ set equal to $\mathbf{q}$. For f_{ij} the result is

$$f_{ij}(\mathbf{q}_1,\mathbf{q}_2,t) = \left[\underbrace{\int\cdots\int_{-\infty}^{\infty}}_{N-3}\psi(q^{N-1},t)\prod_{\substack{k\neq i\\ k\neq j}}\mathbf{d}q_k\right]\Bigg|_{q_i=\mathbf{q}_1,\,q_j=\mathbf{q}_2} = \underbrace{\int\cdots\int_{-\infty}^{\infty}}_{N-1}\psi(q^{N-1},t)\delta(q_i-\mathbf{q}_1)\delta(q_j-\mathbf{q}_2)\prod_{k=1}^{N-1}\mathbf{d}q_k$$
$$= (2\pi)^{-3}[\det(\boldsymbol{\sigma}_{ij})\det(\boldsymbol{\sigma}_{ii}\cdot\boldsymbol{\sigma}_{ij}^{-1}\cdot\boldsymbol{\sigma}_{jj}-\boldsymbol{\sigma}_{ij})]^{-1/2}\times\exp[-(1/2)(\boldsymbol{\sigma}_{ii}-\boldsymbol{\sigma}_{ij}\cdot\boldsymbol{\sigma}_{jj}^{-1}\cdot\boldsymbol{\sigma}_{ij})^{-1}:\mathbf{q}_1\mathbf{q}_1]$$
$$\times\exp[-(1/2)(\boldsymbol{\sigma}_{jj}-\boldsymbol{\sigma}_{ij}\cdot\boldsymbol{\sigma}_{ii}^{-1}\cdot\boldsymbol{\sigma}_{ij})^{-1}:\mathbf{q}_2\mathbf{q}_2]\times\exp[-(1/2)(\mathbf{q}_{jj}\cdot\boldsymbol{\sigma}_{ij}^{-1}\cdot\boldsymbol{\sigma}_{ii}-\boldsymbol{\sigma}_{ij})^{-1}:\mathbf{q}_2\mathbf{q}_1]$$
$$\times\exp[-(1/2)(\boldsymbol{\sigma}_{ii}\cdot\boldsymbol{\sigma}_{ij}^{-1}\cdot\boldsymbol{\sigma}_{jj}-\boldsymbol{\sigma}_{ij})^{-1}:\mathbf{q}_1\mathbf{q}_2]. \tag{5.2}$$

In the above we have introduced the convention $\boldsymbol{\sigma}_{ij} = \langle\mathbf{Q}_i\,\mathbf{Q}_j\rangle$. Proof of Eq. (5.2) requires the identities:

$$\boldsymbol{\sigma}_{ii}^{-1}\cdot\boldsymbol{\sigma}_{ij}\cdot(\boldsymbol{\sigma}_{jj}-\boldsymbol{\sigma}_{ij}\cdot\boldsymbol{\sigma}_{ii}^{-1}\cdot\boldsymbol{\sigma}_{ij})^{-1} = (\boldsymbol{\sigma}_{jj}\cdot\boldsymbol{\sigma}_{ij}^{-1}\cdot\boldsymbol{\sigma}_{ii}-\boldsymbol{\sigma}_{ij})^{-1}, \tag{5.3}$$

$$(\boldsymbol{\sigma}_{jj}-\boldsymbol{\sigma}_{ij}\cdot\boldsymbol{\sigma}_{ii}^{-1}\cdot\boldsymbol{\sigma}_{ij})^{-1}\cdot\boldsymbol{\sigma}_{ij}\cdot\boldsymbol{\sigma}_{ii}^{-1} = (\boldsymbol{\sigma}_{ii}\cdot\boldsymbol{\sigma}_{ij}^{-1}\cdot\boldsymbol{\sigma}_{jj}-\boldsymbol{\sigma}_{ij})^{-1}, \tag{5.4}$$

$$\boldsymbol{\sigma}_{ii}^{-1}+\boldsymbol{\sigma}_{ii}^{-1}\cdot\boldsymbol{\sigma}_{ij}\cdot(\boldsymbol{\sigma}_{jj}-\boldsymbol{\sigma}_{ij}\cdot\boldsymbol{\sigma}_{ii}^{-1}\cdot\boldsymbol{\sigma}_{ij})^{-1}\cdot\boldsymbol{\sigma}_{ij}\cdot\boldsymbol{\sigma}_{ii}^{-1} = (\boldsymbol{\sigma}_{ii}-\boldsymbol{\sigma}_{ij}\cdot\boldsymbol{\sigma}_{jj}^{-1}\cdot\boldsymbol{\sigma}_{ij})^{-1}, \tag{5.5}$$

$$\det(\boldsymbol{\sigma}_{ii})\det(\boldsymbol{\sigma}_{jj} - \boldsymbol{\sigma}_{ij}\cdot\boldsymbol{\sigma}_{ii}^{-1}\cdot\boldsymbol{\sigma}_{ij}) = \det(\boldsymbol{\sigma}_{ij})\det(\boldsymbol{\sigma}_{ii}\cdot\boldsymbol{\sigma}_{ij}^{-1}\cdot\boldsymbol{\sigma}_{jj} - \boldsymbol{\sigma}_{ij})\,. \qquad (5.6)$$

In the form given Eq. (5.2) satisfies the symmetry condition $f_{ij}(\mathbf{q}_1,\mathbf{q}_2,t) = f_{ji}(\mathbf{q}_2,\mathbf{q}_1,t)$.

VI. CHARACTERISTIC FUNCTIONS

Previous investigators have found transform and characteristic function methods to be very useful in the treatment of Rouse chains.[4,5,27] There is a relatively simple relation between the characteristic functions of the one-link probability density f_i and the r-link probability density $f_{\alpha_1,\ldots,\alpha_r}$. Define the r-connector characteristic function $\bar{f}_{\alpha_1,\ldots,\alpha_r}$ as

$$\bar{f}_{\alpha_1,\ldots,\alpha_r}(\mathbf{p}_1,\ldots,\mathbf{p}_r,t) = \underbrace{\int\cdots\int_{-\infty}^{\infty}}_{r} f_{\alpha_1,\ldots,\alpha_r}(\mathbf{q}_1,\ldots,\mathbf{q}_r,t) \prod_{i=1}^{r} \exp[-\mathbf{p}_i\cdot\mathbf{q}_i]\,d\mathbf{q}_i\,. \qquad (6.1)$$

Use of the two-sided Laplace transform rather than the Fourier transform makes it possible to avoid imaginary arguments. The reader interested in the two-sided Laplace transform is referred to the comprehensive treatise by van der Pol and Bremmer.[29] Equation (6.1) leads to

$$\bar{f}_{\alpha_1,\ldots,\alpha_r}(\mathbf{p}_1,\ldots,\mathbf{p}_r,t) = \exp\left[(1/2)\sum_{i=1}^{r}\sum_{j=1}^{r}\langle\mathbf{Q}_{\alpha_i}\,\mathbf{Q}_{\alpha_j}\rangle:\mathbf{p}_i\,\mathbf{p}_j\right]. \qquad (6.2)$$

The one-link characteristic function can be found as

$$\bar{f}_{\alpha_i}(\mathbf{p},t) = \int_{-\infty}^{\infty} f_{\alpha_i}(\mathbf{q},t)\exp[-\mathbf{p}\cdot\mathbf{q}]\,d\mathbf{q} = \exp[(1/2)\langle\mathbf{Q}_{\alpha_i}\,\mathbf{Q}_{\alpha_i}\rangle:\mathbf{pp}]\,. \qquad (6.3)$$

Therefore the r-connector characteristic function can be factored as

$$\bar{f}_{\alpha_1,\ldots,\alpha_r}(\mathbf{p}_1,\ldots\mathbf{p}_r,t) = \left[\prod \bar{f}_{\alpha_i}(\mathbf{p}_i,t)\right]\left[\prod_{i=1}^{r}\prod_{j=1}^{i-1}\bar{F}_{\alpha_i\alpha_j}(\mathbf{p}_i,\mathbf{p}_j,t)\right], \qquad (6.4a)$$

$$\bar{F}_{\alpha_i\alpha_j}(\mathbf{p}_i,\mathbf{p}_j,t) = \exp[\langle\mathbf{Q}_{\alpha_i}\,\mathbf{Q}_{\alpha_j}\rangle:\mathbf{p}_i\,\mathbf{p}_j]\,. \qquad (6.4b)$$

The r-connector characteristic functions is the product of the r corresponding one-link characteristic functions times $r\times(r-1)$ coupling terms $\bar{F}_{\alpha_i\alpha_j}$. For the two-connector characteristic function $\bar{f}_{ij}(\mathbf{p}_1,\mathbf{p}_2,t)$:

$$\bar{f}_{ij}(\mathbf{p}_1,\mathbf{p}_2,t) = \int\int_{-\infty}^{\infty} f_{ij}(\mathbf{q}_1,\mathbf{q}_2,t)\exp[-\mathbf{p}_1\cdot\mathbf{q}_1] \times\exp[-\mathbf{p}_2\cdot\mathbf{q}_2]\,d\mathbf{q}_1\,d\mathbf{q}_2 = \bar{f}_i(\mathbf{p}_1,t)\,\bar{f}_j(\mathbf{p}_2,t)\,\bar{F}_{ij}(\mathbf{p}_1,\mathbf{p}_2,t)\,, \qquad (6.5a)$$

$$\bar{F}_{ij}(\mathbf{p}_1,\mathbf{p}_2,t) = \exp[\langle\mathbf{Q}_i\,\mathbf{Q}_j\rangle:\mathbf{p}_i\,\mathbf{p}_j]\,. \qquad (6.5b)$$

VII. ONE- AND TWO-LINK DIFFUSION EQUATIONS

The diffusion equation for the entire chain, Eq. (3.2) can be contracted to give the diffusion equations which govern f_i and f_{ij}. For f_i both sides of the equation are multiplied by $\delta(\mathbf{q}_i - \mathbf{q})$ and integrated over all connector coordinates. The resulting diffusion equation is

$$\left(\frac{\partial}{\partial t}\right)f_i(\mathbf{q},t) = -\left(\frac{\partial}{\partial\mathbf{q}}\right)\cdot\left\{[\boldsymbol{\kappa}\cdot\mathbf{q}]f_i - (1/\zeta)\times\sum_{k=1}^{N-1}A_{ki}\left[kT\delta_{ki}\left(\frac{\partial f_i}{\partial\mathbf{q}}\right) + H\langle\mathbf{Q}_k|\mathbf{Q}_i = \mathbf{q}\rangle\right]\right\} \qquad (7.1a)$$

$$\langle\mathbf{Q}_k|\mathbf{Q}_i = \mathbf{q}\rangle = \langle\mathbf{Q}_k\delta(\mathbf{Q}_i - \mathbf{q})\rangle = \left[\underbrace{\int\cdots\int_{-\infty}^{\infty}}_{N-1}\psi(q^{N-1},t)q_k\delta(q_i - \mathbf{q})\prod_{j=1}^{N-1}dq_j\right] \qquad (7.1b)$$

The conditional average $\langle\mathbf{Q}_k|\mathbf{Q}_i = \mathbf{q}\rangle$ denotes the average of $\mathbf{Q}_k$ with $\mathbf{Q}_i$ set equal to $\mathbf{q}$, and results from the average of the product of $\mathbf{Q}_k$ with the delta function as shown in Eq. (7.1b). To calculate the conditional average $\langle\mathbf{Q}_k|\mathbf{Q}_i = \mathbf{q}\rangle$ we need the identity:

$$\langle\mathbf{Q}_k B(\mathbf{Q}^{N-1})\rangle = \sum_{n=1}^{N-1}\langle\mathbf{Q}_k\,\mathbf{Q}_n\rangle\cdot\left\langle\frac{\partial B}{\partial\mathbf{Q}_n}\right\rangle, \qquad (7.2)$$

where $B(\mathbf{Q}^{N-1})$ is a function of the set of connector vector coordinates. With $\delta(\mathbf{Q}_i - \mathbf{q})$ substituted for $B(\mathbf{Q}^{N-1})$ in Eq. (7.2), an explicit expression is obtained for the conditional average $\langle\mathbf{Q}_k|\mathbf{Q}_i = \mathbf{q}\rangle$:

$$\langle\mathbf{Q}_k|\mathbf{Q}_i = \mathbf{q}\rangle = \langle\mathbf{Q}_k\,\mathbf{Q}_i\rangle\cdot\frac{\partial f_i}{\partial\mathbf{q}} \qquad (7.3)$$

and Eq. (7.1) becomes

$$\left(\frac{\partial}{\partial t}\right)f_i(\mathbf{q},t) = -\left(\frac{\partial}{\partial\mathbf{q}}\right)\cdot\left\{[\boldsymbol{\kappa}\cdot\mathbf{q}]f_i - (1/\zeta)\times\sum_{k=1}^{N-1}A_{ki}[kT\delta_{ki}\boldsymbol{\delta} - H\langle\mathbf{Q}_k\,\mathbf{Q}_i\rangle]\cdot\left(\frac{\partial f_i}{\partial\mathbf{q}}\right)\right\} = D_i(\mathbf{q})f_i\,. \qquad (7.4)$$

In the above the notation $D_i(\mathbf{q})$ is introduced for convenience.

In a previous treatment of flexible chain models, Kovac and Fixman[30] used a "Gaussian correlation" closure approximation for calculating the conditional average $\langle\mathbf{Q}_k|\mathbf{Q}_i = \mathbf{q}\rangle$. On the basis of linear response theory, they *assumed*:

$$\langle\mathbf{Q}_k|\mathbf{Q}_i = \mathbf{q}\rangle = [\delta_{ki}\boldsymbol{\delta} + 2(1-\delta_{ki})c_{ki}\boldsymbol{\kappa}]\cdot\mathbf{q}f_i\,, \qquad (7.5).$$

where δ_{ki} is the Kronecker delta and the c_{ki} are "coupling factors." This *assumption* leads to an *approximate* diffusion equation of the form:

$$\left(\frac{\partial}{\partial t}\right)f_i(\mathbf{q},t) = -\left(\frac{\partial}{\partial\mathbf{q}}\right)\cdot\left\{[(1-\alpha_i)\boldsymbol{\kappa}\cdot\mathbf{q}]f_i - (1/\zeta)\mathrm{A}_{ii}\left[kT\left(\frac{\partial f_i}{\partial\mathbf{q}}\right) + H\mathbf{q}f_i\right]\right\}, \qquad (7.6)$$

where the α_i are coefficients found from $\alpha_i = \Sigma_{k=1}^{N-1}A_{ki}c_{ik}$. Kovac and Fixman then used this approximate diffusion equation (with appropriate constraining forces substituted for the Hookean force expression) as a basis for calculating linear viscoelastic functions for a freely rotating chain of rigid rods (their Gaussian correlated chain). However comparison of Eq. (7.6) with the exact Eq. (7.4) shows that the Gaussian correlation closure approximation of Kovac and Fixman may result in an unwarranted coupling between the hydrodynamics and the connector forces. This coupling is not to be confused with the usual preaveraged Oseen hydrodynamic interaction, which would require simply that the Rouse matrix $[A_{jk}]$ and the Kramers matrix $[C_{jk}]$ be replaced by modified matrices $[\tilde{A}_{jk}]$ and $[\tilde{C}_{jk}]$ that contain information about the hydrodynamic interaction [DPL Sec. 12.4]. Rather it appears as a modification of the macroscopic velocity field by a factor $(1-\alpha_i)$. Aside from this modification, the approximate Kovac–Fixman diffusion equation is identical in form to the diffusion equation for a dumbbell [see DPL Chap. 10]. However the exact diffusion equation for a single link [Eq. (7.4)] is different in form from the dumbbell equation, with the coupling between hydrodynamics and connector forces entering through the moment terms $\langle \mathbf{Q}_k\, \mathbf{Q}_i \rangle$.

Kovac and Fixman also gave a formal version of an exact diffusion equation for two links. For the sake of completeness, we here give the exact diffusion equation for f_{ij}; Eq. (3.2) multiplied by the product $\delta(\mathbf{q}_i-\mathbf{q}_1)\times\delta(\mathbf{q}_j-\mathbf{q}_2)$ and integrated over all the coordinates. The result is

$$\left(\frac{\partial}{\partial t}\right) f_{ij}(\mathbf{q}_1,\mathbf{q}_2,t) = D_i(\mathbf{q}_1) f_{ij} + D_j(\mathbf{q}_2) f_{ij} + D_{ij}(\mathbf{q}_1,\mathbf{q}_2) f_{ij}\,, \tag{7.7a}$$

$$\begin{aligned} D_{ij}(\mathbf{q}_1,\mathbf{q}_2) &= (1/\zeta)\left[2A_{ij}\, kT\boldsymbol{\delta} - H\sum_{k=1}^{N-1} (A_{ik}\langle \mathbf{Q}_k \mathbf{Q}_j\rangle \right. \\ &\quad \left. + A_{jk}\langle \mathbf{Q}_k\, \mathbf{Q}_i\rangle)\right] : \left(\frac{\partial}{\partial \mathbf{q}_1}\right)\left(\frac{\partial}{\partial \mathbf{q}_2}\right) \end{aligned} \tag{7.7b}$$

The two-link diffusion equation for links i and j includes both corresponding one-link operators D_i and D_j defined as in Eq. (8.4), which arise from the independent behavior of the two links. In addition it includes the pair operator D_{ij}, which reflects the interactions between the two links.

It can be verified that our expressions for f_i and f_{ij} do satisfy the diffusion equations given in this section.

VIII. LENGTH INDEPENDENT ONE-LINK ORIENTATION PROBABILITY DENSITY

The one-link probability density $f_i(\mathbf{q},t)$ can be integrated over the length of the link to give a function which depends only on the orientation of the link and not on its length. We define

$$\begin{aligned} g_i(\mathbf{u},t) &= \int_0^\infty f_i(\mathbf{q},t) q^2\, dq \\ &= (1/4\pi)[\det\langle \mathbf{Q}_i\, \mathbf{Q}_i\rangle]^{-1/2}[\langle \mathbf{Q}_i\, \mathbf{Q}_i\rangle^{-1}{:}\mathbf{uu}]^{-3/2}\,. \end{aligned} \tag{8.1}$$

In the above $\mathbf{u}$ is a unit vector whose rectangular Cartesian components are $(\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$. The function $g_i(\mathbf{u},t)$ is the dilute solution analog of the single-link probability density used in the melt theories of Doi and Edwards[31] and Curtiss and Bird,[32] and used by Lawrey, Prud'homme, and Koberstein[33] for the calculation of polymer chain orientation during stress relaxation.

IX. STEADY SHEAR FLOW

The expressions for the probability density functions which we have given in the foregoing sections can be used to calculate functions in any flow. We will illustrate how this can be done for steady shear flow. In a steady shear flow with the components of the velocity $\mathbf{v}$ given as $(\dot\gamma y,0,0)$, where $\dot\gamma$ is the shear rate, the partial stress tensors $\boldsymbol{\tau}_i$ can be found as

$$\boldsymbol{\tau}_i = -2nkT\lambda_H\dot\gamma \begin{pmatrix} 4\lambda_H\dot\gamma\, c_j & c_j & 0 \\ c_j & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \tag{9.1}$$

The moment tensors $\langle \mathbf{Q}_i\, \mathbf{Q}_j\rangle$ can be found from Eq. (3.5):

$$\langle \mathbf{Q}_i\, \mathbf{Q}_j\rangle = (kT/H)\begin{pmatrix} 8\lambda_H{}^2\dot\gamma^2(C^2)_{ij}+\delta_{ij} & 2\lambda_H\dot\gamma\, C_{ij} & 0 \\ 2\lambda_H\dot\gamma\, C_{ij} & \delta_{ij} & 0 \\ 0 & 0 & \delta_{ij} \end{pmatrix}, \tag{9.2}$$

$$\langle \mathbf{Q}_i\, \mathbf{Q}_i\rangle^{-1} = [(kT/H)^2/\det\langle \mathbf{Q}_i\, \mathbf{Q}_i\rangle]\begin{pmatrix} 1 & -2\lambda_H\dot\gamma C_{ii} & 0 \\ -2\lambda_H\dot\gamma C_{ii} & 1+8\lambda_H{}^2\dot\gamma^2(C^2)_{ii} & 0 \\ 0 & 0 & 1+4\lambda_H{}^2\dot\gamma^2[2(C^2)_{ii}-(C_{ii})^2] \end{pmatrix}, \tag{9.3}$$

$$\det\langle \mathbf{Q}_i\, \mathbf{Q}_i\rangle = (kT/H)^3\{1+4\lambda_H{}^2\dot\gamma^2[2(C^2)_{ii}-(C_{ii})^2]\}\,. \tag{9.4}$$

In the above $(C^2)_{ij}$ denotes the ijth element of the square of the Kramers matrix and can be found as

$$\begin{aligned} (C^2)_{ij} &= [i(N-j)/6N][j(2N-j)-(i^2-1)] \quad (i\leqslant j) \\ &= [j(N-i)/6N] \\ &\quad \times[i(2N-i)-(j^2-1)] \quad (i\geqslant j)\,. \end{aligned} \tag{9.5}$$

With these expressions it is possible to get explicit expressions for the functions we have given. For example, the complete expression for $g_i(\mathbf{u},t)$ is

$$\begin{aligned} g_i(\mathbf{u},t) &= (1/4\pi)[1+4\lambda_H{}^2\dot\gamma^2[2(C^2)_{ii}-(C_{ii})^2] \\ &\quad \times[1+8\lambda_H{}^2\dot\gamma^2(C^2)_{ii}u_z^2+4\lambda_H{}^2\dot\gamma^2 \\ &\quad \times[2(C^2)_{ii}-(C_{ii})^2]u_y^2-4\lambda_H\dot\gamma C_{ii}u_x u_z]\,, \end{aligned} \tag{9.6}$$

where u_x, u_y, and u_z are the x,y, and z components of the vector **u**. Similar expressions can be developed for either f_i or f_{ij}.

X. CONCLUSION

Our principal result is the exact expression for the joint probability density for any number of links, Eq. (4.3), which we used for finding the probability density for a single link, Eq. (5.1), and the joint probability density for two links, Eq. (5.2). For these two functions we gave the exact Fokker–Planck–Smoluchowski diffusion equations, Eqs. (7.4) and (7.7). We also gave the length-independent orientation probability density for one link, Eq. (8.1), and an exact expression for the characteristic function of the multilink joint probability density, Eq. (6.4). Our work is not restricted to any particular kinematics or flow field; by way of example we have shown, in Sec. VIII, how our results may be applied in steady shear flow.

Our results are based on, and constitute an extension of, previous studies of the Rouse chain by Lodge and Wu,[3] van Wiechen and Booij,[5] and King and James.[4] Our exact results for the diffusion equations can be compared with the previous approximate work of Kovac and Fixman.[30]

For simplicity we have used the free-draining Rouse chain; however our results can be extended to include the effect of equilibrium-averaged hydrodynamic interaction. To do so, we replace the Rouse matrix $[A_{jk}]$ and the Kramers matrix $[C_{jk}]$ and the eigenvalues c_j by modified matrices $[\tilde{A}_{jk}]$ and $[\tilde{C}_{jk}]$ and eigenvalues $\underset{\sim}{c}_j$ that contain information about the hydrodynamic interaction [DPL Sec. 12.4]. Aside from these replacements the entire development remains the same.

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