

FIRST CUMULANT FOR CHAINS WITH CONSTRAINTS

A.Z AKCASU^a, B HAMMOUDA^b, W.H STOCKMAYER^c AND G. TANAKA^d
 (a)Dept. of Nuclear Engin., U. of Michigan, Ann Arbor, MI 48109
 (b)Research Reactor and Dept. of Physics, U. of Missouri, Columbia, MO 65211
 (c)Dept. of Chemistry, Dartmouth College, Hanover, NH 03755
 (d)The Clayton Foundation Labs., The Salk Inst., La Jolla, CA 92037

ABSTRACT

The Fixman-Kovac formulation of chain dynamics with constraints is used to calculate the first cumulant $\Omega(q)$ of the dynamic scattering function. This general formalism is applied to the case of freely jointed chains. It is shown that the large q limit (q being the scattering wavenumber) of $\Omega(q)$ for a chain of N bonds in the absence of hydrodynamic interaction is proportional to the ratio $(2N+3)/3(N+1)$ representing the fraction of unconstrained degrees of freedom of the chain. The inclusion of hydrodynamic interaction seems to enhance the apparent segmental diffusion. The use of constrained chain dynamics has no appreciable effects, however, on the behavior of $\Omega(q)$ in the small and intermediate q regions for long enough chains. This formalism can be used to interpret neutron (spin echo) scattering experiments from semiflexible polymers in solution.

INTRODUCTION

The first cumulant of the dynamic scattering function can be expressed as[1]:

$$\Omega(q) = \langle \rho^*(q) L \rho(q) \rangle / \langle \rho^*(q) \rho(q) \rangle \quad (1)$$

where $\langle \dots \rangle$ represents an equilibrium average,

$$\rho(q) = \sum_v \exp(i\vec{q} \cdot \vec{R}_v)$$

is the density of the $N+1$ beads of a polymer chain in the Fourier space, and L is the Kirkwood-Riseman diffusion operator in the full $3N$ configuration space. $\Omega(q)$ has been extensively studied for flexible (Gaussian) chains. For instance, the high q limit yields the segmental diffusion $q^2 D$, regardless of chain length. When applied to freely jointed chains, special care must be taken. Constrained degrees of freedom (bond lengths in this case) must be excluded before performing the equilibrium average. This was pointed out by Stockmayer and

Burchard[2] who considered the example of a Fraenkel dumbbell.

A generalized dynamical operator L is obtained using the Fixman-Kovacs[3] formalism of chain dynamics with constraints and then used in Eq. (1) to derive the first cumulant for freely jointed chains. Other approaches such as the Titulaer-Deutsch[4] formalism could also be followed.

DIFFUSION EQUATION WITH CONSTRAINTS

Following Fixman and Kovacs[3], a set of constraining forces \vec{P}_j ($j=1, \dots, N$) are introduced in the Langevin equation of motion of each bead:

$$d\vec{R}_v/dt = H_{v\lambda}(\vec{S}_\lambda + C_{\lambda j}\vec{P}_j + \vec{F}_\lambda) \quad (2)$$

In this notation, Greek indices run over beads while Latin ones run over bond lengths, $H_{v\lambda}$ is the diffusion matrix (case of preaveraged hydrodynamic interaction), \vec{F}_λ are the random Brownian forces acting on the beads, \vec{S}_λ are "soft" coupling forces between different bonds and

$$C_{\lambda j} = \delta_{\lambda, j} - \delta_{\lambda, j-1}$$

is a constant matrix introduced for notation convenience. A better suited coordinate system corresponds to the center of friction \vec{B}_0 and bond lengths \vec{B}_j . The constraining forces can be eliminated by using the fact that they are in the direction of the bond vectors whose magnitudes are constant. Langevin equations for \vec{B}_0 and \vec{B}_j can be derived:

$$\begin{aligned} d\vec{B}_0/dt &= v_0 \vec{f}_0 \\ d\vec{B}_j/dt &= \vec{h}_{jk} \cdot (\vec{g}_k + \vec{f}_k) \end{aligned} \quad (3)$$

where $\{\vec{f}_0, \vec{f}_k\}$ and \vec{g}_k are redefined Brownian and soft forces respectively, v_0 is the lowest Zimm eigenvalue and

$$\vec{h} = (\underline{I} - \underline{C}^T \underline{H} \underline{C}) \underline{C}^T \underline{H} \underline{C}$$

with

$$\begin{aligned} \vec{h}_{km} &= \vec{B}_k \cdot \vec{B}_m (R^{-1})_{km} \\ \vec{r}_{km} &= \vec{B}_k \cdot \vec{B}_m B_{km} \end{aligned}$$

$$\underline{B} = \underline{C}^T \underline{H} \underline{C}$$

The vectorial notation used contains arrows to represent cartesian components and underlining to identify the different beads in the polymer chain. Using the fluctuation-dissipation theorem, a Smoluchowski equation $N+1$ for the probability distribution for bead positions $\vec{R}^{N+1} = \{\vec{R}_0, \dots, \vec{R}_N\}$ can be obtained:

$$d\psi(\vec{R}^{N+1}, t)/dt = D(\vec{R}^{N+1}) \psi(\vec{R}^{N+1}, t) \quad (4)$$

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where $D(\mathbb{R}^{N+1})$ is the diffusion dynamical operator which is related to a generalized Kirkwood-Riseman operator through

$$D(\mathbb{R}^{N+1})[\rho(q)\Psi_{eq}(\mathbb{R}^{N+1})] = -\Psi_{eq}(\mathbb{R}^{N+1})L(\mathbb{R}^{N+1})\rho(q).$$

with

$$L(\mathbb{R}^{N+1}) = k_B T [\partial \ln(\Psi_{eq}) / \partial \mathbb{R}_\nu + \partial / \partial \mathbb{R}_\nu] \cdot \bar{\mathbb{K}}_{\nu\lambda} \cdot \partial / \partial \mathbb{R}_\lambda \quad (5)$$

and

$$\bar{\mathbb{K}} = [\mathbb{I} - \underline{\underline{HC}} \underline{\underline{MC}}^T] \underline{\underline{H}}$$

where $\Psi_{eq}(\mathbb{R}^{N+1})$ is the equilibrium distribution function. The second Ψ_{eq} term in the bracket represents contributions due to the constrained (sometimes called "hard") coordinates.

FIRST CUMULANT OF THE DYNAMIC SCATTERING FUNCTION

Using the following identity:

$$\langle \rho^*(q) L \rho(q) \rangle = k_B T \int \langle (\partial \rho^*(q) / \partial \mathbb{R}_\nu) \cdot \bar{\mathbb{K}}_{\nu\lambda} \cdot (\partial \rho(q) / \partial \mathbb{R}_\lambda) \rangle$$

the first cumulant for freely jointed chains can be obtained as:

$$\begin{aligned} \Omega(q) &= k_B T \int \langle \exp(i\vec{q} \cdot \mathbb{R}_{\nu\lambda}) H_{\nu\lambda} \rangle / \int \langle \exp(i\vec{q} \cdot \mathbb{R}_{\nu\lambda}) \rangle \\ &- k_B T \int \langle \exp(i\vec{q} \cdot \mathbb{R}_{\nu\lambda}) [\underline{\underline{HC}} \hat{\underline{\underline{q}}} \cdot \underline{\underline{M}} \cdot \hat{\underline{\underline{q}}}^T \underline{\underline{H}}]_{\nu\lambda} \rangle / \int \langle \exp(i\vec{q} \cdot \mathbb{R}_{\nu\lambda}) \rangle \end{aligned} \quad (6)$$

$\hat{\underline{\underline{q}}}$ is a unit vector along the \vec{q} direction. The first term in eq. (6) was calculated by Akcasu and Higgins[6] and yields the segmental diffusion (characterized by a diffusion coefficient D_m) at high q . The second term comprises contributions from the constrained degrees of freedom and therefore tends to decrease this high q limit to:

$$\lim_{q \rightarrow 0} [\Omega(q)/q^2] = [(2N+3)/3(N+1)] D_m \quad (7)$$

when hydrodynamic interactions are neglected. The ratio $(2N+3)/3(N+1)$ represents the fraction of unconstrained degrees of freedom. The inclusion of preaveraged hydrodynamic interactions tends to enhance the apparent segmental diffusion[5]. The use of constrained chain dynamics, however, has no appreciable effects on the behavior of $\Omega(q)$ in the small and intermediate q regions whereby the whole chain or large chain portions are probed.

CONCLUSIONS

Eq. (6) represents the main result of this work. Evaluation of the ensemble average in the second term is not possible analytically. An approximation which consists in replacing \bar{R} by its ensemble average $\langle R \rangle$ brings some simplifications[5]. In the free draining limit, for instance, eq. (6) simplifies further to become:

$$\begin{aligned} \alpha(q) = & [q^2 D_m / \langle \rho^*(q) \rho(q) \rangle] \{ (2N+3)/3 \\ & + N [j_0(qb) - (2/qb) j_1(qb)] \} \end{aligned} \quad (8)$$

where $j_n(qb)$ is the spherical Bessel function of order n and b is the bond length.

The formalism presented here is well suited to interpret neutron spin echo scattering data from dilute semiflexible polymer solutions provided a concentration dependence scheme (not discussed here) is used. Akcasu and Higgins[6] used the first term in eq. (6) to interpret such experiments on polytetrahydrofuran in carbon disulfide and polystyrene in the same solvent performed by Allen and Coworkers[7]. Nicholson, Higgins and Hayter[8] were able to interpret their spin echo experiments with only partial quantitative success using a Gaussian chain model. The corrections discussed here (second term in eq. (6)) may improve the interpretation of such data.

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