First cumulant for chains with constraints

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The first cumulant $\Omega(q)$ of the dynamic structure factor is calculated for freely jointed chains by applying the Fixman–Kovac formulation of chain dynamics with constraints. It is shown that the large q limit of $\Omega(q)$ for a chain of N bonds is proportional to a factor $(2N+3)/3(N+1)$ representing the fraction of the unconstrained degrees of freedom of the chain. The relevance of this result to spin-echo neutron scattering experiments is pointed out. As an alternative approach, an expression for $\Omega(q)$ is obtained with a formalism due to Titulaer and Deutch.

I. INTRODUCTION

The first cumulant $\Omega(q)$ for a freely jointed chain was earlier calculated[1] for all values of the momentum transfer wave number q by using the Kirkwood–Riseman diffusion operator $\mathscr{L}$ in the general expression[2]

$$\Omega(q)=\frac{\langle \rho^* \mathscr{L} \rho\rangle}{\langle \rho^* \rho\rangle}, \tag{1}$$

where $\rho(q)$ is the density of $N+1$ beads in the Fourier space

$$\rho(q)=\sum_{\mu=0}^{N}\exp(i\mathbf{q}\cdot\mathbf{R}_\mu)\,. \tag{2}$$

The positions of the beads are denoted by $\mathbf{R}_0,\mathbf{R}_1,\ldots,\mathbf{R}_N$. The angular brackets $\langle\cdots\rangle$ denote the thermal average over the equilibrium distribution $\psi_{\rm eq}(\mathbf{R}^N)$ where $\mathbf{R}^N$ denotes collectively $\{\mathbf{R}_0,\ldots,\mathbf{R}_n\}$. For a rigid dumbbell for which $N=1$, the general expression for $\Omega(q)$ reported earlier[1] reduces to[3]

$$\Omega(q)=q^2D_m\{1+(3\pi/4)^{1/2}h^*\times[j_0(K)-K^{-1}j_1(K)]\}[1+j_0(K)]^{-1}, \tag{3}$$

where $D_m=k_BT/\xi$, $K=qb$, $j_k(x)$ is the spherical Bessel function of order k, and $h^*=\xi/\eta b\pi(12\pi)^{1/2}$. In these definitions b is the fixed bond length, ξ the friction coefficient per statistical segment, k_BT the thermal energy, η the viscosity of the solvent, D_m the diffusion coefficient of an isolated monomer, and h^* the draining parameter.

The large q limit of $\Omega(q)/q^2$ is D_m according to Eq. (3). This limit was also found[1,2] for a freely jointed chain of arbitrary length, as well as for a Gaussian chain.[2,3] It is independent of whether or not the hydrodynamic interaction h^* is taken into account. These observations are intuitively plausible, because large values of q imply small distances at which one would experimentally observe only the diffusion of individual monomers, independent of the rest of the chain. Implicit in the last statement however is the assumption that the interaction of a given monomer with the rest of the chain becomes negligible for vanishingly small displacements of that monomer. This is strictly true only for soft interaction potentials. In the case of a freely jointed chain with fixed bond lengths, the above result corresponds to treating the bond length constraint as the limit of a peaked soft potential in the calculation of $\Omega(q)$ from Eq. (1). In this procedure, the above limit is taken *after* the first cumulant is obtained as the short-time limit of $d\ln S(q,t)/dt$, where $S(q,t)$ is the dynamic scattering function.

It was pointed out by Stockmayer and Burchard[4] that the inclusion of the bond length constraint in the dynamics of the chain at the outset leads to a different value for $\Omega(q)$ in the large q limit. Indeed, if one adopts a description of the rigid rod as used by Pecora[5] to calculate the dynamic structure factor in the absence of hydrodynamic interaction, the appropriate operator for a rigid dumbbell is[3]

$$\mathscr{L}=-(D_m/2)\left[\nabla^2_{\mathbf{R}_c}-(\tfrac{1}{2}b^2)\,\hat{I}^2(\boldsymbol{\Omega})\right], \tag{4}$$

where $\hat{I}^2(\boldsymbol{\Omega})$ is the usual total angular momentum operator operating on $\boldsymbol{\Omega}$, the unit vector characterizing the orientation of the rod, and $\nabla^2_{\mathbf{R}_c}$ is the Laplacian operator operating on the position $\mathbf{R}_c$ of the center of mass. Substitution of Eq. (4) into Eq. (1) yields

$$\Omega(q)=q^2D_m\left[\tfrac{5}{6}+\tfrac{1}{2}j_0(K)-K^{-1}j_1(K)\right][1+j_0(K)]^{-1} \tag{5}$$

which incorporates the bond length constraints from the very beginning. A comparison of Eqs. (5) and (3) with $h^*=0$ shows that both yield for $\Omega(q)/q^2$ in the limit of $q=0$ the same value $D_m/2$, which is the translational diffusion coefficient of the rigid dumbbell. In the large q limit, however, Eq. (5) yields $(\frac{5}{6})D_m$ for $\Omega(q)/q^2$, whereas Eq. (3) gives D_m. It was this discrepancy which was first pointed out by Stockmayer and Burchard.[4] Mathematically it arises

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from the interchange of the short-time limit in the definition of the first cumulant with the limit of the peaked potential to introduce the bond length constraint. Since that time, the calculation of the first cumulant for freely jointed chains of arbitrary length, including the bond length constraint in the dynamics, has remained an unfinished problem. It is the purpose of this paper to attempt such a calculation.

This problem is not only of theoretical interest. The interpretation of neutron scattering experiments with the spin-echo technique, in which the dynamic structure factor $S(q,t)$ is measured directly[6,7] in the q region where $qb \sim 1$, requires theoretical values of $\Omega(q)$ for large values of q. It is precisely in this region where the inclusion of the constraints in the dynamics at the outset, or at the end as the limit of an appropriate hard potential makes a difference. Nicholson, Higgins, and Hayter[7] were able to interpret their spin-echo experiments by using the expression for $\Omega(q)$ for Gaussian chains with only partial quantitative success, although the general trends of the data were understood in terms of existing theories. It is hoped that the refinement reported in this paper for the calculation of the first cumulant in the high-q region may improve the quantitative agreement between the spin-echo experiments and the theory.

The foundations of the dynamics of stiff polymer chains were laid by Fixman and Kovac[8] in 1974, Titulaer and Deutch[9] in 1975, and Fixman[10] in 1978. Other relevant literature on chain dynamics with constraints includes work by Helfand,[11] who considered the motion of a simple system with two degrees of freedom, one constrained and one unconstrained, and a recent paper by Perchak, Skolnick, and Yaris,[12] who investigated numerically the effect of the Fixman potential on the chain dynamics, and presented a survey of the literature on chain dynamics with constraints.

The derivations in this paper follow the formalism developed by Fixman and Kovac.[8,10] Their notation is adopted as much as possible in order to facilitate comparison. Section II is devoted to the derivation of the diffusion equation for the distribution function of the monomer positions of a softly jointed[8] chain including the constraints, and to the identification of the dynamical operator $\mathscr{L}$ to be used in Eq. (1). This section may be considered as an extension of the Akcasu–Gürol[2] formalism to chains with bond length constraints. In the first part of Sec. III the application of this formalism to the calculation of the first cumulant in the free-draining limit is demonstrated. The second part is devoted to the calculation of $\Omega(q)$ in the presence of hydrodynamic interactions and to the development of useful approximations. In Sec. IV we present our conclusions and some discussion. In the Appendix an alternative approach to the calculation of the first cumulant, based on the expansion method of Titulaer and Deutch[9] is introduced.

II. DIFFUSION EQUATION WITH CONSTRAINTS

The acceleration-free Langevin equations for the instantaneous positions of $N+1$ beads of a chain in the presence of hydrodynamic interaction and bond length constraints can be written[8] as

$$\dot{\mathbf{R}}_\mu = \mathbf{H}_{\mu\nu} \cdot (\mathbf{S}_\nu + C_{\nu j}\mathbf{p}_j + \mathbf{F}_\nu), \quad \mu = 0,1,...,N, \tag{6}$$

where $\mathbf{F}_0,...,\mathbf{F}_N$ denote the usual random Langevin forces acting on the beads; $\mathbf{p}_1,...,\mathbf{p}_N$ are the constraining forces; and $\mathbf{C}$ is a $(N+1)\times N$ matrix defined by

$$C_{\mu j} = \delta_{\mu j} - \delta_{\mu, j-1}, \tag{7}$$

where $\mu = 0,1,...,N$ and $j = 1,...,N$. The possibility of coupling among different rigid bonds is allowed through a soft potential $U(\mathbf{b}_1,...,\mathbf{b}_N)$ and the corresponding forces $\mathbf{S}$ in Eq. (6):

$$\mathbf{S}_\nu = -\nabla_\nu U. \tag{8}$$

Fixman and Kovac[8] refer to such a chain as "softly jointed." It reduces to the freely jointed chain when $U = 0$. The hydrodynamic interactions among the beads are represented by the usual tensor $\mathbf{H}_{\mu\nu}$:

$$\mathbf{H}_{\mu\nu} = \xi^{-1}\delta_{\mu\nu}\mathbf{I} + (1-\delta_{\mu\nu})\mathbf{T}_{\mu\nu}, \tag{9}$$

where $\mathbf{T}_{\mu\nu}$ is the Oseen tensor, ξ is the friction coefficient of a bead, and $\mathbf{I}$ is a 3×3 unit matrix operating on the Cartesian components of vector quantities. Repeated Greek and Latin indices will always imply summation from 0 to N, and from 1 to N, respectively, except when explicitly stated. Although it is possible to proceed otherwise, we prefer for simplicity to use the preaveraged hydrodynamic interaction from the beginning, and to replace $\mathbf{H}_{\mu\nu}$ by $H_{\mu\nu}\mathbf{I}$ where

$$H_{\mu\nu} = \xi^{-1}(\delta_{\mu\nu} + \tau_{\mu\nu})$$

and

$$\tau_{\mu\nu} = (\xi/6\pi\eta)\langle 1/R_{\mu\nu}\rangle_{\text{eq}}(1-\delta_{\mu\nu}). \tag{10a}$$

The indicated average is taken over the equilibrium distribution ψ_{eq} for a softly jointed chain. For example, for Gaussian chains[13]

$$H_{\mu\nu} = \xi^{-1}[\delta_{\mu\nu} + (1-\delta_{\mu\nu})\tau(6/\pi)^{1/2}|\mu-\nu|^{-1/2}] \tag{10b}$$

and for freely jointed chains[1]:

$$H_{\mu\nu} = \xi^{-1}\left[\delta_{\mu\nu} + (1-\delta_{\mu\nu})\tau(2/\pi)\int_0^\infty dx\, j_0(x)^{|\mu-\nu|}\right], \tag{10c}$$

where $j_0(x) = \sin x/x$ and $\tau = \xi/6\pi\eta b$, which is equal to H_{12}. The Langevin equations (6) then become

$$\dot{\mathbf{R}}_\mu = H_{\mu\nu}(\mathbf{S}_\nu + C_{\nu j}\mathbf{p}_j + \mathbf{F}_\nu). \tag{11}$$

In order to eliminate the constraining forces $\mathbf{p}_j$, and to determine the relevant statistical properties of the Langevin forces, we have first to obtain the Langevin equations for the bond vectors

$$\mathbf{b}_j = C^T_{j\mu}\mathbf{R}_\mu. \tag{12}$$

The center of friction $\mathbf{b}_0$ is defined by

$$\mathbf{b}_0 = \beta^{(1)}_\mu \mathbf{R}_\mu. \tag{13}$$

The eigenvector $\beta^{(1)}_\mu$ is determined from[13]

$$\beta^{(1)}_\mu H_{\mu\nu} = \nu_0 \alpha^{(1)}_\nu, \tag{14}$$

where the $N+1$ components of the eigenvector $\alpha^{(1)}_\nu$ are all unity,[13] and ν_0 is the lowest Zimm eigenvalue, which is calculated from

$$\nu_0 = (\alpha_\mu [\mathbf{H}^{-1}]_{\mu\nu} \alpha_\nu)^{-1} . \tag{15}$$

Here and subsequently the superscripts on $\beta_\mu^{(1)}$ and $\alpha_\mu^{(1)}$ have been supressed. The eigenvectors are normalized as[13]

$$\beta_\mu \alpha_\mu = 1 . \tag{16}$$

The reason for separating the center of friction rather than the center of mass or any other translational coordinate is that the motion of the former is decoupled from the internal motions (in the preaveraged approximation). Multiplying both sides of Eq. (11) by β_μ and summing, we obtain

$$\dot{\mathbf{b}}_0 = \nu_0 \mathbf{f}_0 , \tag{17}$$

where

$$\mathbf{f}_0 = \alpha_\mu \mathbf{F}_\mu \tag{18}$$

which denotes the total Langevin force on the chain. The covariance matrix of $\mathbf{f}_0$ is necessarily

$$\langle \mathbf{f}_0(t) \mathbf{f}_0^T(t') \rangle = 2(k_B T/\nu_0) \mathbf{I} \delta(t-t') \tag{19}$$

so that the usual expression $D = k_B T \nu_0$ for the translational diffusion coefficient of the center of friction, defined by $\langle |\Delta \mathbf{b}_0|^2 \rangle = 6Dt$, is recovered.

The Langevin equations for the bond vectors are obtained by use of Eq. (12) as

$$\dot{\mathbf{b}}_j = B_{jk}(\mathbf{s}_k + \mathbf{p}_k) + C_{j\mu}^T H_{\mu\nu} \mathbf{F}_\nu , \tag{20}$$

where the $N \times N$ matrix $\mathbf{B}$ is defined by

$$\mathbf{B} = \mathbf{C}^T \mathbf{H} \mathbf{C} \tag{21}$$

and

$$\mathbf{s}_k = -\nabla_{\mathbf{b}_k} U(\mathbf{b}^N) . \tag{22}$$

In expressing $\mathbf{S}_\mu$ in terms of $\mathbf{s}_k$ we have used the fact that the soft potential $U(\mathbf{b}^N)$ is independent of $\mathbf{b}_0$. We can express the Langevin forces $\mathbf{F}_\mu$ as a linear combination of $\mathbf{f}_0$ and a set of forces $\mathbf{f}_1,\ldots,\mathbf{f}_N$ as

$$\mathbf{F}_\mu = C_{\mu j} \mathbf{f}_j + [\mathbf{H}^{-1}]_{\mu\nu} \alpha_\nu \nu_0 \mathbf{f}_0 . \tag{23}$$

The reason for this decomposition is that the $\mathbf{f}_j$ with $j \geqslant 1$ enter the Langevin equations for the bond vectors. They are obtained uniquely from $\mathbf{F}_\mu$ as

$$\mathbf{f}_j = [\mathbf{B}^{-1}]_{jk} [\mathbf{C}^T \mathbf{H}]_{k\mu} \mathbf{F}_\mu \quad (j = 1,\ldots,N) . \tag{24}$$

Substitution of Eq. (23) into Eq. (20) yields

$$\dot{\mathbf{b}}_j = B_{jk}(\mathbf{s}_k + \mathbf{f}_k + \mathbf{p}_k) . \tag{25}$$

Fixman and Kovac[8] eliminated the constraining forces by using the fact that they are in the direction of the bond vectors and by determining the N unknown proportionality constants from the bond length constraints $d|\mathbf{b}_j|^2/dt = 0$:

$$\mathbf{p}_k = -\mathbf{M}_{km} B_{mn} \cdot (\mathbf{s}_n + \mathbf{f}_n) . \tag{26}$$

The matrix $\mathbf{M}_{km}$ is defined through a sequence of other matrices:

$$\begin{aligned} R_{km} &= \mathbf{b}_k \cdot \mathbf{b}_m B_{km} \\ \mathbf{M}_{km} &= \mathbf{b}_k \mathbf{b}_m [\mathbf{R}^{-1}]_{km} \end{aligned} \quad \text{(no summation on } k,m) . \tag{27}$$

Eliminating $\mathbf{p}_k$ in Eq. (25) from Eq. (26), we obtain the Langevin equations for the bond vectors with constraints:

$$\dot{\mathbf{b}}_j = \mathbf{h}_{jk} \cdot (\mathbf{s}_k + \mathbf{f}_k) , \tag{28}$$

where

$$\mathbf{h} \equiv (\mathbf{I} - \mathbf{BM})\mathbf{B} . \tag{29}$$

The following projection property of $\mathbf{h}_{jk}$ is essential for the subsequent derivations:

$$\sum_{t=1}^{3} h_{jk}^{st} b_k^t = 0 \quad \text{(no summation on } k) , \tag{30}$$

where the superscripts refer to the Cartesian components of vectors and dyadics.

The diffusion equation for the bond vector distribution function $\psi(\mathbf{b}^N,t)$ can be obtained from Eq. (28) in terms of the covariance matrix γ_{ij} defined by

$$\langle \mathbf{f}_i(t) \mathbf{f}_j^T(t') \rangle = 2\gamma_{ij} \delta(t-t') \tag{31}$$

by following the procedure developed by Lax[14] as

$$\frac{\partial \psi}{\partial t} = \frac{\partial}{\partial b_j^s} \left\{ h_{jk}^{st} \left[\psi \frac{\partial U}{\partial b_k^t} + \frac{\partial}{\partial b_m^r} (h_{mn}^{rz} \gamma_{kn}^{tz} \psi) \right] \right\} . \tag{32}$$

The covariance matrix γ_{ij}^{tz} is determined by requiring that Eq. (32) is satisfied by the equilibrium distribution $\psi_{\text{eq}}(\mathbf{b}^N)$ appropriate to the chain model under consideration. In the case of the softly jointed chain model:

$$\psi_{\text{eq}}(\mathbf{b}^N) = (1/Z)\exp(-\beta U)\varphi_0(\mathbf{b}^N) \quad (\beta^{-1} = k_B T) , \tag{33a}$$

where

$$\varphi_0(\mathbf{b}^N) = \prod_{j=1}^{N} \left[\left(\frac{1}{4\pi b^2} \right) \delta(b - |\mathbf{b}_j|) \right] \tag{33b}$$

which incorporates the bond length constraints. It is now asserted that if γ_{ij}^{tz} is chosen to satisfy

$$h_{mn}^{rz} \gamma_{kn}^{tz} = k_B T \delta^{rt} \delta_{mk} \tag{34}$$

then ψ_{eq} also satisfies the steady state diffusion equation (32). Indeed, the substitution of Eqs. (33) and (34) into Eq. (32) leads to

$$\frac{\partial}{\partial b_j^s} \left(\psi_{\text{eq}} h_{jk}^{st} \frac{\partial \ln \varphi_0}{\partial b_k^t} \right) = 0 \tag{35}$$

and since

$$\frac{\partial \ln \varphi_0}{\partial b_k^t} = -b_k^t \frac{\partial}{\partial b} [b^{-1} \delta(b - |\mathbf{b}_k|)] \tag{36}$$

the use of Eq. (30) in Eq. (35) proves the equality. It also follows from Eq. (36) that

$$h_{jk}^{st} \frac{\partial U}{\partial b_k^t} = -k_B T h_{jk}^{st} \frac{\partial \ln \psi_{\text{eq}}}{\partial b_k^t} . \tag{37}$$

Using this identity and Eq. (34) in Eq. (32), we arrive at the desired diffusion equation for $\psi(\mathbf{b}^N,t)$:

$$\frac{\partial \psi}{\partial t} = -k_B T \frac{\partial}{\partial \mathbf{b}} \cdot \mathbf{h} \cdot \left[\psi \frac{\partial \ln \psi_{\text{eq}}}{\partial \mathbf{b}} - \frac{\partial \psi}{\partial \mathbf{b}} \right] . \tag{38}$$

The diffusion equation for the center of friction follows from Eqs. (17) and (18) as

$$\frac{\partial\psi(\mathbf{b}_0,t)}{\partial t}=k_BT\nu_0\nabla^2_{\mathbf{b}_0}\psi(\mathbf{b}_0,t)\,. \tag{39}$$

Defining $\psi(\mathbf{b}_0,\mathbf{b}^N,t)$ as the distribution function of the entire chain and including all the degrees of freedom we finally write

$$\frac{\psi(\mathbf{b}_0,\mathbf{b}^N,t)}{\partial t}=k_BT\left\{\nu_0\nabla^2_{\mathbf{b}_0}\psi-\frac{\partial}{\partial\mathbf{b}_j}\cdot\mathbf{h}_{jk}\cdot\left[\psi\frac{\partial\ln\psi_{eq}}{\partial\mathbf{b}_k}-\frac{\partial\psi}{\partial\mathbf{b}_k}\right]\right\}. \tag{40}$$

The dynamics of a softly jointed chain, including both internal and external motions, is completely described by this equation. Except for the inclusion of the center of friction coordinate, this equation is the same as that obtained by Fixman and Kovac.[8,10] Although it is possible to calculate the first cumulant in Eq. (1) with Eq. (40), it is still desirable to obtain a more compact diffusion equation in coordinate space for $\psi(\mathbf{R}^{N+1},t)$. This can be done by simply transforming from $(\mathbf{b}_0,\mathbf{b}^N)$ to $\mathbf{R}^{N+1}$ using

$$\frac{\partial}{\partial\mathbf{R}_\mu}=\beta_\mu\frac{\partial}{\partial\mathbf{b}_0}+C_{\mu j}\frac{\partial}{\partial\mathbf{b}_j}\,.$$

After some algebra we find

$$\frac{\partial\psi(\mathbf{R}^{N+1},t)}{\partial t}=-k_BT\frac{\partial}{\partial\mathbf{R}_\mu}\cdot\mathbf{K}_{\mu\nu}\cdot\left[\psi\frac{\partial\ln\psi_{eq}}{\partial\mathbf{R}_\nu}-\frac{\partial\psi}{\partial\mathbf{R}_\nu}\right]\equiv\mathscr{D}\psi(\mathbf{R}^{N+1},t)\,, \tag{41}$$

where

$$\mathbf{K}=(\mathbf{I}-\mathbf{HCMC}^T)\mathbf{H} \tag{42}$$

which is related to $\mathbf{h}$ by

$$\mathbf{h}=\mathbf{C}^T\mathbf{KC}\,.$$

The adjoint $\mathscr{L}$ of the diffusion operator is introduced as usual through

$$\mathscr{D}(\psi_{eq}Q)=-\psi_{eq}\mathscr{L}Q\,,$$

where Q is an arbitrary dynamical variable depending on R^{N+1}. After a few steps one finds

$$\mathscr{L}=-k_BT\left[\frac{\partial\ln\psi_{eq}}{\partial\mathbf{R}_\mu}+\frac{\partial}{\partial\mathbf{R}_\mu}\right]\cdot\mathbf{K}_{\mu\nu}\cdot\frac{\partial}{\partial\mathbf{R}_\nu}\,. \tag{43}$$

It can be shown that $\mathscr{L}$ is self-adjoint when the scalar product is defined as the equilibrium average, and that its matrix element between two arbitrary dynamical variables P and Q satisfies

$$\langle P\mathscr{L}Q\rangle=k_BT\left\langle\frac{\partial P}{\partial\mathbf{R}_\mu}\cdot\mathbf{K}_{\mu\nu}\cdot\frac{\partial Q}{\partial\mathbf{R}_\nu}\right\rangle. \tag{44}$$

The equilibrium average $\langle[\cdots]\rangle$ is to be performed with the distribution function ψ_{eq} given in Eq. (33) for a softly jointed chain. There is no restriction on the form of the soft potential $U(\mathbf{b}^N)$.

In the subsequent sections we present applications of the above general formalism.

III. CALCULATION OF THE FIRST CUMULANT

Choosing P and Q in Eq. (44) as $\rho^*(\mathbf{q})$ and $\rho(\mathbf{q})$, and defining a q dependent mobility $\mu(q)$ through

$$\mu(q)=\langle\rho^*\mathscr{L}\rho\rangle/q^2k_BT \tag{45}$$

we obtain

$$\mu(q)=\langle\exp(i\mathbf{q}\cdot\mathbf{R}_{\mu\nu})\hat{\mathbf{q}}\cdot\mathbf{K}_{\mu\nu}\cdot\hat{\mathbf{q}}\rangle\,, \tag{46}$$

where the unit vector $\hat{\mathbf{q}}$ indicates the direction of $\mathbf{q}$, and the summation rule on the repeated indices μ,ν from 0 to N is still being used. The first cumulant $\Omega(q)$ defined in Eq. (1) is then

$$\Omega(q)=q^2k_BT\mu(q)/\langle\rho^*\rho\rangle\,. \tag{47}$$

The static structure factor $\langle\rho^*\rho\rangle$ in this equation is to be calculated with ψ_{eq} for a softly jointed chain.

A. Free-draining limit

In the absence of hydrodynamic interactions $H_{\mu\nu}=\delta_{\mu\nu}/\xi$, and $\mathbf{K}_{\mu\nu}$ reduces to

$$\mathbf{K}_{\mu\nu}=\xi^{-1}[\delta_{\mu\nu}\mathbf{I}-\xi^{-1}(\mathbf{CMC}^T)_{\mu\nu}] \tag{48}$$

with

$$\mathbf{M}_{ij}=\mathbf{b}_i[\mathbf{R}^{-1}]_{ij}\mathbf{b}_j, \tag{49a}$$

$$R_{ij}=\xi^{-1}\mathbf{b}_i\cdot\mathbf{b}_j[\mathbf{C}^T\mathbf{C}]_{ij}\,, \tag{49b}$$

where $\xi^{-1}\mathbf{C}^T\mathbf{C}$ corresponds to $\mathbf{B}$ in Eq. (21) in the free-draining limit. Substituting Eq. (48) into Eq. (46) we express the mobility as

$$\mu(q)=\mu_1(q)-\mu_2(q)\,,$$

where $\mu_1(q)=(N+1)/\xi$ denotes the mobility of a flexible chain in the absence of hydrodynamic interaction, and

$$\mu_2(q)=\xi^{-2}C_{\mu j}\langle\exp(i\mathbf{q}\cdot\mathbf{R}_{\mu\nu})\hat{\mathbf{q}}\cdot\mathbf{M}_{jk}\cdot\hat{\mathbf{q}}\rangle C^T_{k\nu}\,. \tag{50}$$

The latter is the correction that arises from the inclusion of the bond length constraint in the dynamic operator. We concentrate below on the contribution of this term as function of q and N in various limits.

1. Small q limit

Since $\alpha_\mu C_{\mu j}=0$, μ_2 vanishes in the limit of $q\to0$, and the first cumulant reduces to $q^2D_m/(N+1)$ showing that, as expected the short-time diffusion coefficient is not affected by the inclusion of bond length constraints.

2. Large q limit

In this limit only the diagonal terms in Eq. (50), for which $\mu=\nu$, contribute to $\mu_2(q)$, and Eq. (50) reduces to

$$\mu_2(q\to\infty)=\xi^{-2}\,\mathrm{Tr}(\mathbf{C}\langle\hat{\mathbf{q}}\cdot\mathbf{M}\cdot\hat{\mathbf{q}}\rangle\,\mathbf{C}^T)\,. \tag{51}$$

Since $\mu_2(q)$ can depend only on the magnitude of $\mathbf{q}$, we may average the right-hand side of Eq. (51) with respect to the direction of $\mathbf{q}$, and thus obtain

$$\mu_2(q\to\infty)=(1/3\xi^2)\mathrm{Tr}\langle\mathbf{CMC}^T\rangle\,, \tag{52}$$

where

$$M_{jk}=\mathbf{b}_j\cdot\mathbf{b}_k[\mathbf{R}^{-1}]_{jk}\,. \tag{53}$$

Using the cyclic invariance of a trace and Eq. (49b) we find $\mu_2(q\to\infty)=N/3\xi$. Hence, the large q limit of the first cumulant in the absence of hydrodynamic interaction is obtained as

$$\Omega(q\to\infty)=q^2D_m(2N+3)/3(N+1) \tag{54}$$

which is one of the main results of this paper.

For a rigid dumbbell $N=1$, and Eq. (54) yields $(\frac{8}{9})q^2D_m$, i.e., the result found by Stockmayer and Burchard.[4] In the long chain limit we find $(\frac{4}{3})q^2D_m$, which is significantly different from q^2D_m for a flexible chain. It is noted that these results are valid for any softly jointed free-draining chain, and are independent of the specific form of the soft potential $U(\mathbf{b}^N)$ as long as it is soft. We also note that the factor $(2N+3)/(3N+3)$ is simply the fraction of the unconstrained degrees of freedom.

3. Rigid dumbbell

The full expression of $\Omega(q)$ for all values of q can be obtained exactly in this case by substituting $\mathbf{C}^T=[-1,1]$, $\mathbf{C}^T\mathbf{C}=2$, $\mathbf{R}=\xi^{-1}2b^2\mathbf{I}$, and $\mathbf{M}=(\xi/2b^2)\mathbf{bb}$ in Eq. (50). The result is identical to Eq. (5) which is obtained directly from Pecora's equation.

4. Once-broken rod ($N=2$)

In the previous special cases we did not have to specify the soft potential to proceed in a general way. In the present case we have to set $U=0$ in order to be able to perform equilibrium averages. This choice restricts the subsequent analysis to freely jointed chains.

When $N=2$ the matrix $\mathbf{R}^{-1}$ becomes

$$\mathbf{R}^{-1}=[1/b^2(4-\mu^2)]\begin{bmatrix}2 & \mu\\ \mu & 2\end{bmatrix},$$

where μ is the cosine of the bond angle. Substitution of $\mathbf{R}^{-1}$ into Eqs. (49) and (50) yields after lengthy manipulations

$$\Omega(q)=\frac{q^2D_m}{\langle\rho^*\rho\rangle}\left[\frac{7}{3}+(2\ln 3)j_0(K)+4(1-2\ln 3)j_1(K)/K-4(1-\ln 3)j_2(K)+\int_{-1}^{+1}d\mu\,\frac{\mu P(\mu)}{4-\mu^2}\right], \tag{55a}$$

where $K=qb$ and

$$P(\mu)=(\mu/x)j_1(x)-[(1+\mu)/2]j_2(x) \tag{55b}$$

with $x^2\equiv 2(1+\mu)K$.

Using $\langle\rho^*\rho\rangle\to 3$, we find the large q limit as $\Omega(q\to\infty)=(7/9)q^2D_m$, which also follows from the general result in Eq. (54) with $N=2$. In the large q limit the form of the soft potential does not play any role as pointed out earlier.

5. An approximate expression for $\Omega(q)$

In the general case of a freely jointed chain with an arbitrary number N of bonds, we resort to an approximation reminiscent of replacing the Oseen tensor by its preaveraged form: *we replace the matrix* $\mathbf{R}$ *introduced in Eq. (49b) by its equilibrium average* $2b^2\mathbf{I}$. This simplification leads to

$$\mathbf{M}_{jk}=(\xi/2b^2)\delta_{jk}\mathbf{bb} \tag{56}$$

in Eq. (50). Performing the summation on μ and ν, and using

$$(1/2b^2)\langle|1-\exp(-i\mathbf{q}\cdot\mathbf{b})|^2(\mathbf{q}\cdot\mathbf{b})^2\rangle = q^2[(1/3)-j_0(K)+(2/K)j_1(K)]$$

one obtains

$$\Omega(q)\cong\frac{q^2D_m}{\langle\rho^*\rho\rangle}\left\{\frac{2N+3}{3}+N\left[j_0(K)-\frac{2}{K}j_1(K)\right]\right\}. \tag{57}$$

This approximation coincides with the exact results presented above in the small and large q limits for any N, and with the dumbbell result for any q. In Fig. 1 it is compared with the exact result for $N=2$ given in Eq. (55) to test its validity. In the intermediate q region where $K\ll 1$ but $qR_G\gg 1$, it yields $\Omega(q)=(D_m/12)b^2q^4$ which is the same as that obtained by including the bond length constraints at the end.[2,3] The variation of $\Omega(q)$ as function of K calculated from Eq. (57) is compared with the flexible chain result[2,3]

$$\Omega(q)=q^2D_m(N+1)/\langle\rho^*\rho\rangle \tag{58}$$

in Fig. 2. The static structure factor in the case of a freely jointed chain is to be calculated from $\langle\rho^*\rho\rangle=(N+1)[1+2G_N(K)]$ where $G_N(K)$ is given by[1,3,15]

$$G_N=\frac{N}{N+1}\frac{j_0}{1-j_0}\left(1-\frac{j_0}{1-j_0}\frac{1-j_0^N}{N}\right). \tag{59}$$

B. Non-free-draining case

In this case also, the generalized mobility introduced in Eq. (46) can be expressed as

$$\mu(q)=\mu_1(q)-\mu_2(q), \tag{60}$$

where

$$\mu_1(q)=\langle\exp(i\mathbf{q}\cdot\mathbf{R}_{\mu\nu})\rangle H_{\mu\nu} \tag{61}$$

and

$$\mu_2(q)=\langle\exp(i\mathbf{q}\cdot\mathbf{R}_{\mu\nu})(\mathbf{HC}\hat{\mathbf{q}}\cdot\mathbf{M}\cdot\hat{\mathbf{q}}\mathbf{C}^T\mathbf{H})_{\mu\nu}\rangle. \tag{62}$$

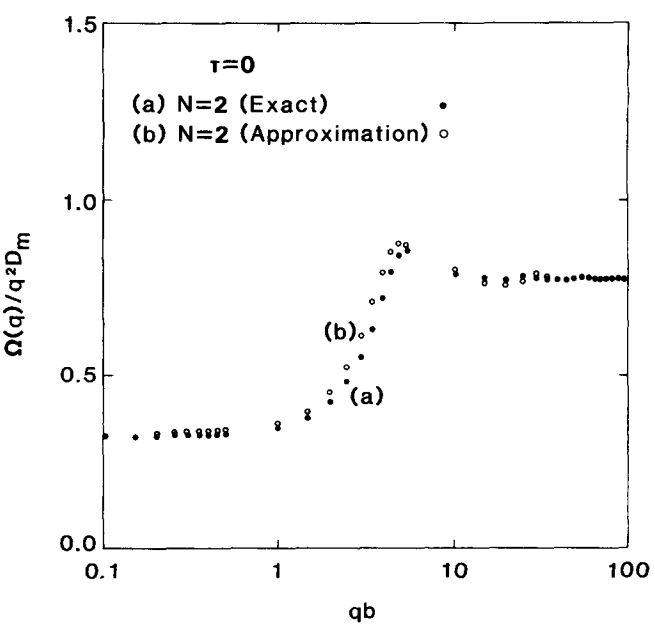

FIG. 1. Comparison of the exact [Eq. (55)] and approximate [Eq. (57)] calculations of $\Omega(q)/q^2D_m$ vs qb for the free-draining ($\tau=0$) once-broken rod.

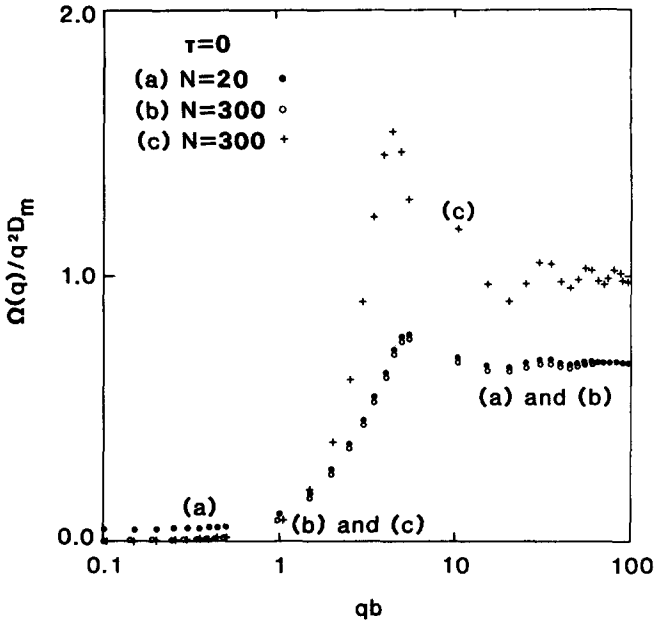

FIG. 2. $\Omega(q)/q^2D_m$ vs qb using the approximate expression in Eq. (57) for (a) $N=20$ and (b) $N=300$, and (c) using Eq. (58) for $N=300$, which does not include constraints in the dynamics.

As before, $\mu_1(q)$ denotes the mobility in the presence of preaveraged hydrodynamic interaction when the constraints are included as the limit of a hard potential through the equilibrium distribution. The first cumulant associated with $\mu_1(q)$ was earlier calculated *without* preaveraging the Oseen tensor for all values of q using

$$\Omega_1(q) = (k_BT/\langle\rho^*\rho\rangle)\langle\exp(i\mathbf{q}\cdot\mathbf{R}_{\mu\nu})\mathbf{q}\cdot\mathbf{H}_{\mu\nu}\cdot\mathbf{q}\rangle \quad (63)$$

by Akcasu and Gürol[2] for flexible Gaussian chains, and by Akcasu and Higgins[1] for freely jointed chains. It is also possible to express[16] $\Omega_1(q)$ using Eq. (63) as a functional of the static structure factor $S(q) = (N+1)^{-1}\langle\rho^*\rho\rangle$. Since these results are well documented in the literature we do not reproduce them here. It is of course possible to calculate $\mu_1(q)$ and $\Omega_1(q)$ directly without resorting to these general results in the present context using Eq. (61), which reduces in the case of freely jointed chains to

$$\mu_1(q) = j_0(qb)^{|\mu-\nu|}H_{\mu\nu}\,. \quad (64)$$

Since our main concern in this paper is the effect of including the bond length constraints in the dynamics, we now concentrate on $\mu_2(q)$ in Eq. (62) which accounts for this effect. We first consider a rigid dumbbell for which exact analytical results are easily obtained.

1. Rigid dumbbell ($N=1$)

Substitution of $H_{\mu\nu}$ from Eq. (10) into Eq. (64) yields

$$\mu_1(q) = (2/\xi)[1+\tau j_0(K)]\,, \quad (65)$$

where $\tau = (\xi/6\pi\eta b)$. To calculate $\mu_2(q)$ we first show

$$\hat{\mathbf{q}}\cdot\mathbf{M}\cdot\hat{\mathbf{q}} = \xi(\hat{\mathbf{q}}\cdot\mathbf{b})^2/2(1-\tau)b^2$$

and the use $\langle(\hat{\mathbf{q}}\cdot\mathbf{b})^2\rangle = b^2/3$ and

$$\langle(\hat{\mathbf{q}}\cdot\mathbf{b})^2\exp(i\mathbf{q}\cdot\mathbf{b})\rangle = b^2[j_0(K) - (2/K)j_1(K)]$$

to obtain

$$\mu_2(q) = \xi^{-1}(1-\tau)[(1/3) - j_0(K) + (2/K)j_1(K)]\,. \quad (66)$$

Since $\langle\rho^*\rho\rangle = 2[1+j_0(K)]$ for a rigid dumbbell we obtain the first cumulant as

$$\Omega(q) = q^2D_m[1+j_0(K)]^{-1}\{(5/6) + j_0(K)/2 - j_1(K)/K + \tau[(1/6) + j_0(K)/2 + j_1(K)/K]\}\,. \quad (67)$$

In the absence of hydrodynamic interaction ($\tau=0$) this result reduces to Eq. (5), which was obtained directly from Pecora's equation (4). It differs from Eq. (3), which we reproduce here in the present notation for comparison

$$\Omega(q) = q^2D_m[1+j_0(K)]^{-1} \times\{1 + (3/2)\tau[j_0(K) - j_1(K)/K]\}\,. \quad (68)$$

The difference is due to the inclusion of the bond length constraints in the dynamics in Eq. (67). They both yield the same translational diffusion coefficient:

$$D_0 = D_m(1+\tau)/2\,. \quad (69)$$

Their asymptotic values as $q\to\infty$ however are different: $\Omega(q\to\infty) = q^2D_m$ according to Eq. (68) and

$$\Omega(q\to\infty) = (5/6)q^2D_m(1+\tau/5) \quad (70)$$

according to Eq. (67). We note that the effect of the hydrodynamic interaction persists even in the large q limit, and further modifies the Rouse value $(\frac{5}{6})q^2D_m$ by a factor $(1+\tau/5)$. We also note that Eq. (67) is not restricted to the preaveraged hydrodynamic interaction because there is no distinction between preaveraged and fluctuating hydrodynamic interactions in the case of a rigid dumbbell.

2. Diffusion coefficient for arbitrary N

The complete expression for the short-time translational diffusion coefficient of a freely jointed chain follows from Eqs. (46) and (47) as

$$D_0 = [k_BT/(N+1)^2][\boldsymbol{\alpha}^T\mathbf{H}\boldsymbol{\alpha} - (1/3)\mathbf{L}^T\langle\mathbf{M}\rangle\mathbf{L}]\,, \quad (71)$$

where $\boldsymbol{\alpha} = \mathrm{col}[1,1,\ldots,1]$ with $N+1$ components, M_{ij} is defined in Eq. (53), and $\mathbf{L} = \mathbf{C}^T\mathbf{H}\boldsymbol{\alpha}$. With Eqs. (7) and (10c) the latter can be written as

$$L_k = (2\tau/\pi\xi)\int_0^\infty dx[j_0(x)^k - j_0(x)^{N-k+1}]\,. \quad (72)$$

The first term in Eq. (71) was calculated before[1,3,15] for a freely jointed chain. We reproduce its expression here for completeness,

$$D_0^{(1)} = D_m(N+1)^{-1}\left[1 + (4\tau/\pi)\int_0^\infty dx\, G_N(x)\right], \quad (73)$$

where $G_N(x)$ was defined in Eq. (59). To calculate the second term, representing the correction due to the inclusion of the constraints at the outset, we again approximate R_{ij} in Eq. (27) by $\langle R_{ij}\rangle = 2b^2(1-\tau)\delta_{ij}/\xi$, and use $M_{ij} = \delta_{ij}\xi/2(1-\tau)$ in Eq. (71). After some steps one finds

$$D_0^{(2)} = D_m[4\tau^2/3\pi^2(1-\tau)]I_N(x,y)\,, \quad (74a)$$

where

$$I_N(x,y) = \frac{1}{(N+1)^2}\int_0^\infty dx \int_0^\infty dy \times AB\left(\frac{1-A^N B^N}{1-AB} - \frac{A^N - B^N}{A-B}\right), \quad (74b)$$

where $A \equiv j_0(x)$ and $B \equiv j_0(y)$. We first note that in the case of a dumbbell Eqs. (73) and (74) yield, respectively, $D_0^{(1)} = (D_m/2)(1+\tau)$ and $D_0^{(2)} = 0$, in accordance with the previous exact calculations. In the case of the once-broken rod ($N=2$), one again finds from Eq. (74) $D_0^{(2)} = 0$, so that

$$D_0 = (D_m/3)(1+2\tau)\,. \quad (75)$$

The correction term is nonzero for $N \geqslant 3$. Indeed, we find from Eqs. (74) for $N=3$, $D_0^{(2)} = D_m\tau^2/192(1-\tau)$. Obtaining $D_0^{(1)}$ from Eq. (73) in $D_0 = D_0^{(1)} - D_0^{(2)}$ we find in this case

$$D_0 = D_m\left[(\tfrac{1}{4})(1+23\tau/8) - \tau^2/192(1-\tau)\right].$$

The long chain limit of D_0 also follows from Eqs. (73) and (74) after some algebra as

$$D_0 = D_m\left[N^{-1} + N^{-1/2}8\tau(\tfrac{2}{3}\pi)^{1/2} - 2\tau^2 \ln N/N^2(1-\tau)\pi\right]. \quad (76)$$

Hence, the inclusion of bond length constraints in the dynamics does not affect the short time diffusion coefficient when $N\to\infty$. The logarithmic N dependence in Eq. (76) can be verified by first finding the large-N limit of dI_N/dN with change of variables $x^2 = 6u^2/N$ and $y^2 = 6v^2/6$.

3. Large q limit of Ω(q)

The large q limit of $\mu_1(q)$ is easily obtained as $\mu_1(q\to\infty) = \mathrm{Tr}\,\mathbf{H} = (N+1)/\xi$. We use the approximation $M_{ij} = \xi\delta_{ij}/2(1-\tau)$ to investigate the large q limit of $\mu_2(q)$ in

$$\mu_2(q\to\infty) = (1/3\xi)\{N + \mathrm{Tr}[\tau\mathbf{C}\mathbf{M}\mathbf{C}^T\mathbf{H}]\} \quad (77)$$

which follows from Eq. (62) by retaining the diagonal terms only, and averaging $\hat{\mathbf{q}}\cdot\mathbf{M}\cdot\hat{\mathbf{q}}$ over $\hat{\mathbf{q}}$. After some steps one finds

$$\mu_2(q\to\infty) = (N/3\xi)[1 - \tau + \mathscr{T}_N\tau^2/(1-\tau)]\,, \quad (78)$$

where

$$\mathscr{T}_N = \frac{4}{\pi^2}\int_0^\infty dx\int_0^\infty dy(1-A)(1-B) \times \frac{AB}{1-AB}\left[1 - \frac{1-A^NB^N}{N(1-AB)}\right] \quad (79)$$

with $A \equiv j_0(x)$ and $B \equiv j_0(y)$. The first term in Eq. (79) is evaluated numerically as approximately 0.082. The second term vanishes as $1/N$ for large N, and is significant only for very short chains. For $N=1$ and $N=2$, $\mathscr{T}_N = 0$. Hence, except for very short chains, the large q limit of the first cumulant is obtained from Eq. (47) with the above results as

$$\Omega(q\to\infty) = q^2D_m\frac{2N+3}{3(N+1)} \times\left[1 + \frac{N\tau}{2N+3}\left(1 - \frac{0.082\tau}{1-\tau}\right)\right]. \quad (80)$$

In the case of a rigid dumbbell and once-broken chain $\Omega(q\to\infty)$ is obtained, respectively, as $q^2D_m(5/6)(1+\tau/5)$ and $q^2D_m(7/9)(1+2\tau/7)$. It is observed in Eq. (80) that the effect of the hydrodynamic interaction persists in the large q limit of $\Omega(q)$ even in the long chain limit. However, this is numerically a small effect, for example, for $\tau = 0.2$[17,18] corresponding to $\xi/\eta b = 3.77$. The major effect of the constraints is still the factor $(2N+3)/3(N+1)$. Figure 3 depicts the large q behavior of $\Omega(q)/q^2D_m$ as function of N with $\tau = 0.5$. The latter value is chosen to magnify the effect of hydrodynamic interaction at large q.

4. Finite q values

The calculation of $\mu_2(q)$ and hence $\Omega(q)$ for finite values of q becomes cumbersome even with the approximation of replacing R_{ij} by its equilibrium average at the outset:

$$\mu_2(q) = \frac{\xi}{2b^2(1-\tau)}[\mathbf{HC}]_{\mu j} \times\langle\exp(i\mathbf{q}\cdot\mathbf{R}_{\mu\nu})(\hat{\mathbf{q}}\cdot\mathbf{b}_j)^2\rangle[\mathbf{C}^T\mathbf{H}]_{j\nu}\,, \quad (81)$$

where summation over $\mu,\nu = 0,1,\ldots,N$ and $j = 1,\ldots,N$ is implied, and where

$$\langle\exp(i\mathbf{q}\cdot\mathbf{R}_{\mu\nu})(\hat{\mathbf{q}}\cdot\mathbf{b}_j)^2\rangle = (b^2/3)\,j_0(K)^{|\mu-\nu|}$$

if $\mathbf{R}_{\mu\nu}$ does not contain $\mathbf{b}_j$ or $-\mathbf{b}_j$, and

$$= b^2 j_0(K)^{(|\mu-\nu|-1)}[\,j_0(K) - 2j_1(K)/K\,]$$

otherwise. The expression of $H_{\mu\nu}$ is given in Eq. (10c) for freely jointed chains. We computed $\mu_2(q)$ from Eq. (81), and $\mu_1(q)$ from Eq. (64) numerically and plotted, in Figs. 4 and 5, $\Omega(q)/q^2D_m$ as function of q for various values of N and with and without hydrodynamic interaction.

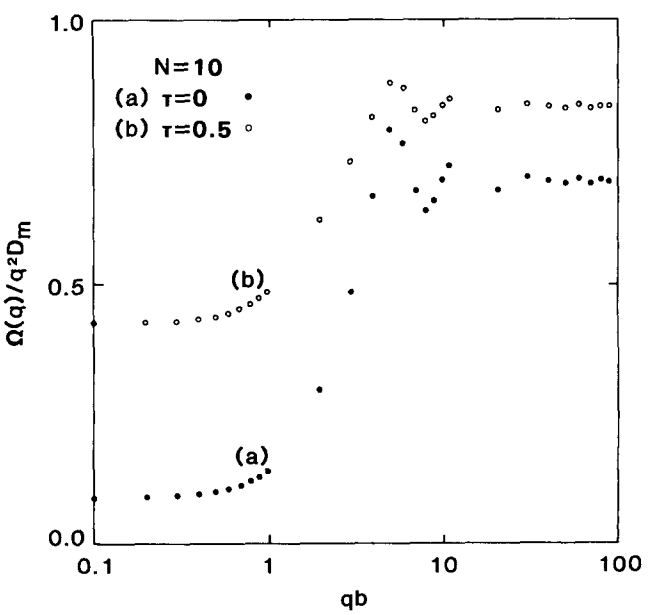

FIG. 3. Comparison of $\Omega(q)/q^2D_m$ vs qb for $N=10$ with ($\tau=0.5$) and without ($\tau=0$) hydrodynamic interaction, using Eqs. (64) and (81).

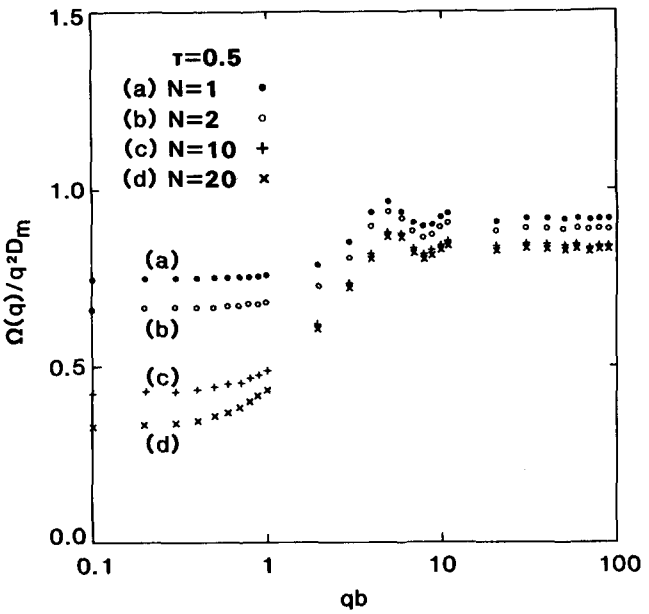

FIG. 4. $\Omega(q)/q^2D_m$ vs qb with hydrodynamic interaction for various values of N using Eqs. (64) and (81).

IV. CONCLUSIONS AND DISCUSSIONS

In the preceding sections we have calculated the first cumulant of the dynamic structure factor at all values of q for a freely jointed chain by taking into account bond length constraints in the dynamics of the chain through the general formalism developed by Fixman and Kovac.[8] The main conclusion of the paper from an experimental point of view is that in the absence of hydrodynamic interaction the large q limit of the first cumulant $\Omega(q)$ is $(2/3)\,q^2D_m$ for long chains. For flexible chains this limit is always q^2D_m with or without hydrodynamic interaction and irrespective of chain length. Hence, the inclusion of bond length constraints reduces the segmental diffusion coefficient D_m to a factor $(2/3)D_m$. The physical origin of this factor is that a given bead in the freely jointed chain model is rigidly connected to the rest of the chain so that its number of degrees of freedom is reduced from 3 to 2. For finite chains, the center of mass of the rest of the chain is also diffusing, so that the apparent diffusion coefficient of a bead acquires an N dependence, and becomes $[(2N+3)/3(N+1)]D_m$. The latter is the fraction of the unconstrained degrees of freedom of the entire chain. The inclusion of the hydrodynamic interaction seems to enhance the apparent segmental diffusion coefficient somewhat, even in the long chain limit, but this effect may be due to an approximation introduced in the calculations of the first cumulant with hydrodynamic interaction. The use of constrained chain dynamics has no appreciable effect on the behavior of $\Omega(q)$ in the small and intermediate q regions for long chains.

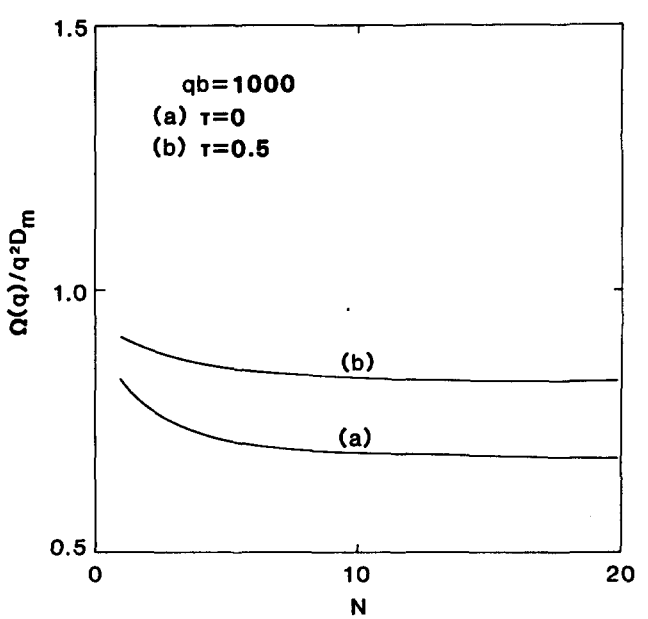

FIG. 5. The large q behavior of $\Omega(q)/q^2D_m$ as function of N without and with hydrodynamic interaction, using Eqs. (64) and (81).

The importance of the change in the large q behavior of the first cumulant when constraints are included lies in the fact that spin-echo neutron scattering experiments explore $S(q,t)$ and its first cumulant precisely in the transition region from intermediate to high q values where $qb \sim 1$. Since the upper plateau of $\Omega(q)/q^2$ is about 2/3 of that obtained in the case of flexible chains, as used until now in the interpretation of these experiments,[7] one may expect appreciable improvement in the agreement between theory and experiment with the new results, and in the values of bond lengths and friction coefficients extracted from comparison of data and theory in this q region.

The use of the first cumulant in the interpretation of dynamic light and neutron scattering experiments requires some caution, as pointed out by Schmidt and Stockmayer[19] previously. When the dynamics of polymer solutions is described by the full Liouville operator L, including both solvent and polymer coordinates, the first cumulant vanishes as a consequence of time reversibility. Since the relaxation times of fluid modes are smaller than the internal molecular relaxation times, it is permissible to describe the dynamics of polymer molecules through the Smoluchowski equation for time scales of scattering experiments designed to study only the internal and translational motions of the macromolecule. In this case, the first cumulant calculated with the diffusion operator is nonvanishing, and provides a good understanding of the initial relaxation of $S(q,t)$ in various q regions. The present calculations emphasize that the utility of the first cumulant for analysis of scattering experiments depends on the correct choice of the dynamical operator in the experimental time interval. As the rigidity of a polymer molecule increases, the relaxation times associated with the stiff coordinates grow shorter and shorter, and eventually become widely separated from the relaxation times of the other slower internal modes. If the experimental time scales are chosen to study only these slow modes, then the first cumulant must be calculated with a modified diffusion operator in which appropriate constraints are imposed at the outset. It is this procedure that has been followed in the previous sections of this paper. If, however, one is still interested in the relaxation of $S(q,t)$ on time scales short compared to the relaxation times of the stiff coordinates, then the observable first cumulant should be calculated with the full diffusion

operator. A continuous transition from flexible to constrained coordinates can be implemented, as demonstrated by Titulaer and Deutch[9] by introducing a hard potential that contains a parameter κ such that in the limit $\kappa \to \infty$ the constraints on the stiff coordinates are recovered. However, the order of this limit and the short-time limit inherent in the definition of the first cumulant:

$$\Omega(q) = -\lim_{t\to 0} d \ln S(q,t)/dt$$

becomes important, and two different results for $\Omega(q)$ are obtained depending on their order, as pointed out by Stockmayer and Burchard.[4] In order to clarify this point further we consider the following equation obtained by the projection operator technique[2]:

$$\frac{dS(q,t)}{dt} = -\Omega(q)S(q,t) + \int_0^t du\, K(q,u)S(q,t-u)\,, \tag{82}$$

where $K(q,t)$ is the memory function. The initial relaxation of $S(q,t)$ is always determined by $\Omega(q)$ for any finite value of κ, for the second term vanishes as $t \to 0$. However, if the $\kappa \to \infty$ limit is taken first, the memory function approaches a delta function $K_0(q)\delta(t)$, so that the initial relaxation of $S(q,t)$ is determined in this limit by $\Omega(q) - K_0(q)$. The first cumulant calculated with the modified diffusion operator including the constraints directly yields $\Omega(q) - K_0(q)$. The application of the Titulaer and Deutch expansion method is presented in an Appendix.

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APPENDIX: CALCULATION OF THE FIRST CUMULANT BY THE TITULAER–DEUTCH METHOD

Here we follow the Titulaer–Deutch method,[9] developed by them for calculating the intrinsic viscosity, as an alternative approach to the first cumulant for chains with constraints.

The diffusion equation in full coordinate space including all the degrees of freedom is $\dot{f} = \mathscr{D} f$ where

$$\mathscr{D} f = \sum_{i,j} \nabla_i \cdot D_{ij} \cdot (\nabla_j f - f \nabla_j \ln f_e)\,. \tag{A1}$$

The dynamic scattering function is defined by

$$S(q,t) = \langle \rho^*(0)\rho(t)\rangle,$$

where

$$\rho(t) = \rho(q,t) = \sum_j \exp[i\mathbf{q}\cdot\mathbf{R}_j(t)]\,.$$

Introducing a self-adjoint operator $\mathscr{L}$ such that $\mathscr{D}(Af_e) = -f_e \mathscr{L} A$, where A is an arbitrary function of the coordinates, we obtain

$$S(q,t) = \sum_m C_m^2 \exp(-\lambda_m t)\,,$$

where λ_m are the eigenvalues associated with the eigenfunctions f_m of

$$\mathscr{L} f_m = -\lambda_m f_m \tag{A2}$$

and

$$C_m = \int (\rho f_m) f_e \, d\{R\} = (\rho, f_m) \quad \text{(scalar product)}\,. \tag{A3}$$

The potential energy U is the sum of a soft potential $U^{(s)}$ and a hard potential which is a generalization of the Frankel dumbbell model, i.e.,

$$U = U^{(s)} + \left(\frac{1}{2}\right)\kappa \sum_{a,b=1}^{h} G^{ab}\xi_a \xi_b\,,$$

where ξ_a represents a deviation of a hard coordinate "a" from its equilibrium value, and G^{ab} is a positive definite matrix, which may be a function of the configuration of the system.

In order to determine the eigenfunctions and eigenvalues in the limit $\kappa \to \infty$, the quantities $\mathscr{L}$, f_m, and λ_m are separated into sums of terms according to their order in $\kappa^{-j/2}$:

$$\mathscr{L} = \mathscr{L}^{(-2)} + \mathscr{L}^{(-1)} + \mathscr{L}^{(0)} + \cdots,$$
$$f = f^{(0)} + f^{(1)} + f^{(2)} + \cdots,$$
$$\lambda = \lambda^{(-2)} + \lambda^{(-1)} + \lambda^{(0)} + \cdots.$$

The leading eigenvalue equation is

$$\mathscr{L}^{(-2)} f_m^{(0)} = -\lambda_m^{(-2)} f_m^{(0)}\,, \tag{A4a}$$

with

$$\mathscr{L}^{(-2)} = \sum_{a,b=1}^{h} {}^0D_{ab} \frac{\partial}{\partial \xi_a}\frac{\partial}{\partial \xi_b} - \beta\kappa \sum_{a,b,c}^{h} {}^0G^{ab} D_{bc}\, \xi_a \frac{\partial}{\partial \xi_c}$$

and

$${}^0D_{ab} = [D_{ab}]_{\{\xi\}=0}\,.$$

Titulaer and Deutch solved Eq. (A4), obtaining

$$\lambda^{(-2)}(n_1,n_2,\ldots,n_h) = -\beta\kappa \sum_{k=1}^{h} n_k \mu_{(k)}\,, \tag{A4b}$$

$$f^{(0)}(n_1,n_2,\ldots,n_h) = C(n_1,\ldots,n_h)\prod_k H_{n_k}[(\beta\kappa\mu_{(k)})^{1/2} P^a_{(k)}\xi_a]\,, \tag{A5}$$

where $P^a_{(k)}$ is a right eigenvector of the nonsymmetric matrix $\Sigma_b\, {}^0G^{ab}\, {}^0D_{bc}$:

$$\sum_{b,c} {}^0G^{ab}\, {}^0D_{bc} P^c_{(k)} = \mu_{(k)} P^a_{(k)}\,,$$

$$\sum_{a,b} P^a_{(k)}\, {}^0D_{ab} P^b_{(m)} = \delta_{km}\,.$$

In order to estimate C_m, ρ is expanded around $\{\xi\} = 0$ as

$$\rho = {}^0\rho + \kappa^{-1/2} \sum_a (\beta\mu_{(k)})^{1/2}\, {}^0\left(\frac{\partial \rho}{\partial \xi_a}\right) + \left(\frac{1}{2}\right)\kappa^{-1} \sum_{k,m} (\beta\mu_{(k)})^{-1}\left[H_{n_k=1}\, H_{n_m=1}(1-\delta_{km}) + H_{n_k=2}\,\delta_{km}\right]{}^0\left(\frac{\partial^2 \rho}{\partial \xi_k\, \partial \xi_m}\right) + \cdots . \tag{A6}$$

Substitution of Eqs. (A5) and (A6) into Eq. (A3), yields

$$C_m = \int d\{\mathbf{q}\}\, {}^0\rho\, f_m^{(0)} \left(\sum n_k = 0\right) {}^0 f_e\, {}^0 J + O(\kappa^{-1/2}) ,$$

$$= O(\kappa^{-n/2})$$

with $n = \Sigma_k\, n_k$. Thus for $n \geqslant 1$,

$$C_m^2 \exp(-\lambda_m t) \to 0 \quad \text{as} \quad \kappa \to \infty .$$

In other words, only the $n = 0$ set contributes to $S(q,t)$ as $\kappa \to \infty$. From Eq. (A5), the eigenfunctions for this case, designated by g_m, involve soft coordinates only. Titulaer and Deutch's analysis shows that the eigenvalue equation for g_m is

$$\zeta g_m^{(0)} = \left[{}^0 J^{-1} \sum_{i,j=1}^{3N} \left(\frac{\partial}{\partial q_i}\right) {}^0 J\, \bar{D}_{ij} \left(\frac{\partial}{\partial q_j}\right) - \beta \sum_{i,j=1}^{3N} {}^0\left(\frac{\partial U^{(s)}}{\partial q_i}\right) \bar{D}_{ij} \left(\frac{\partial}{\partial q_j}\right)\right] g_m^{(0)} = -\lambda_m^{(0)}\, g_m^{(0)} , \tag{A7}$$

where

$$\bar{D}_{ij} = {}^0 D_{ij} - \sum_{a,b=1}^{h} {}^0 D_{ia} ({}^0 D_h^{-1})^{ab}\, {}^0 D_{bj}$$

with D_h denoting the restriction of $\mathbf{D}$ to the hard subspace. It should be noted that Eq. (A7) is written in the full configuration space, as is Eq. (A2). Thus,

$$S(q,t) = \left[\sum_m C_m^2 \exp(-\lambda_m t)\right]_{n=0}$$

$$= \sum_m ({}^0\rho, g_m^{(0)})^2 \exp(-\lambda_m^{(0)} t) ,$$

$$= \sum_m ({}^0\rho, g_m^{(0)})^2 - \left[\sum_m ({}^0\rho, g_m^{(0)})^2 \lambda_m^{(0)}\right] t + \cdots . \tag{A8}$$

The linear term in t is obtained by the use of a projection operator ${}^0\mathscr{P}$:

$${}^0\mathscr{P} A = {}^0\rho ({}^0\rho^*, {}^0\rho)^{-1} ({}^0\rho^*, A) .$$

Multiplying Eq. (A7) with $({}^0\rho^*, g_m^{(0)})$ and summing over m we get

$$\zeta\, {}^0\rho = -\sum_m \lambda_m^{(0)} ({}^0\rho^*, g_m^{(0)})\, g_m^{(0)} . \tag{A9}$$

Next operating with $\mathscr{P}$, multiplying by ${}^0\rho^*$, and taking the equilibrium average we obtain

$$({}^0\rho^*, \mathscr{P}\zeta\, {}^0\rho) = -\sum_m \lambda_m^{(0)} ({}^0\rho^*, g_m^{(0)}) ({}^0\rho^*, {}^0\rho) ({}^0\rho^*, {}^0\rho)^{-1} ({}^0\rho^*, g_m^{(0)})$$

$$= -\sum_m \lambda_m^{(0)} ({}^0\rho^*, g_m^{(0)})^2 ,$$

$$= ({}^0\rho^*, \zeta\, {}^0\rho) . \tag{A10}$$

The third equality is obtained by multiplying Eq. (A9) by ${}^0\rho^*$ and taking the equilibrium average. Similarly, from Eqs. (A1) and (A2) we can obtain

$$(\rho^*, \mathscr{L}\rho) = -\sum_m \lambda_m C_m^2 .$$

This is the result for the first cumulant of $S(q,t)$ that is obtained by first calculating the initial slope and then taking the limit $\kappa \to \infty$. In the present method the order of these two limits is reversed, and the right-hand side is obtained as

$$(\rho^*, \mathscr{L}\rho) = -\left(\sum_m \lambda_m C_m^2\right)_{n=0} - \left(\sum_m \lambda_m C_m^2\right)_{n=1'} \quad \kappa \to \infty .$$

The first term is just the one we have calculated in Eq. (A10). The second term is the correction term due to the inclusion of the constraints in the dynamics.

Finally, as shown by Titulaer and Deutch, ζ is the same operator used by Fixman and Kovac, written in Cartesian coordinates.

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