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Comments on the Diffusion Coefficient and First Cumulant

A. Ziya Akcasu[†]

Department of Nuclear Engineering, The University of Michigan, Ann Arbor, Michigan 48109. *Received January 27, 1982*

ABSTRACT: An equation for the time-dependent distribution function of the center of mass of a flexible chain is obtained by using the projection operator technique and Kirkwood–Riseman theory. Mean-square displacement of the center of mass is calculated and expressed as $6D(t)t$ to define a time-dependent translational diffusion coefficient $D(t)$. It is shown that the general expression of $D(t)$ reduces to the known results when calculated for a Gaussian chain with preaveraged Oseen tensor. An alternative derivation of the short- and long-time limits of $D(t)$ directly from the Langevin equation of the scattering function $S(q,t)$ is also presented, and their connection with the first cumulant of $S(q,t)$ is discussed.

Introduction

When hydrodynamic interaction is represented by the preaveraged Oseen tensor in Kirkwood's theory, the translational diffusion coefficient D of a linear Gaussian chain is known to be[1,2]

$$D = D_{\mathrm{m}}/\mathbf{E}^{\mathrm{T}}\bar{\mathbf{H}}^{-1}\mathbf{E} \tag{1}$$

where $D_{\mathrm{m}} = k_{\mathrm{B}}T/\xi$ is the diffusion constant for a monomer, $\mathbf{E} = \mathrm{col}\ [1, ..., 1]$ is an $(N + 1) \times 1$ column vector, and

$$\bar{H}_{ij} = \delta_{ij} + h^*(1 - \delta_{ij})(|i - j|)^{-1/2} \qquad i, j = 0, 1, ..., N \tag{2}$$

The strength of hydrodynamic interaction is measured by the draining parameter $h^* = \xi/\eta_0 b\pi(6\pi)^{1/2}$. The chain consists of $N + 1$ identical beads and N segments of root-mean-square length b. The other symbols have their conventional meaning.

Kirkwood's approximate formula[2,3] for the diffusion coefficient can be expressed as

$$D_0 = D_{\mathrm{m}}(N + 1)^{-2}\mathbf{E}^{\mathrm{T}}\bar{\mathbf{H}}\mathbf{E} \tag{3}$$

Calculating the mean-square displacement of the center of mass of the chain, Dubois-Violette and de Gennes[4] showed in the appendix of their 1967 paper that D_0 and D correspond to the diffusion coefficients for short and long times, respectively, and the distinction between them is due to the deformation of the chain during diffusion. More recently, Mansfield[5] reproduced these results in a different manner starting from the dynamic structure factor $S(q,t)$ and investigated the time dependence of the diffusion coefficient $D(t)$ in more detail. Similar calculations have also been presented by Schurr.[6]

It is known that[2,7] for large N, $D_0 = (8/3)h^*/N^{1/2}$ and $D = 2\pi h^*\Gamma(5/4)/\Gamma(1/2)\Gamma(3/4)N^{1/2}$, where Γ is the gamma function. Hence the relative error $D_1/D_0 = (D_0 - D)/D_0$ in the Kirkwood equation is 1.686% and independent of h^* for large N. In Figure 1 we plotted D_1/D_0 for finite chains containing 3–250 monomers and for three values of h^*. The value $h^* = 0.38$ corresponds to Flory's estimate[8] of h^*. It is interesting to note that the asymptotic value of 1.686% is slowly reached from below for $h^* = 0.1$ and from above for $h^* = 0.5$. We calculated D by solving for $\mathbf{x}$ in $\bar{\mathbf{H}}\mathbf{x} = \mathbf{E}$ and forming $\mathbf{E}^{\mathrm{T}}\mathbf{x}$. These observations may be of significance in computer simulations of polymer motion with finite N.

A crude estimate of D_1/D_0 in the long-chain limit was given as 0.014 by Horta and Fixman[9] using a Rouse mode representation. More recently, Fixman[10] obtained D_1, without preaveraging the Oseen tensor, as

$$D_1 = (1/3)\int_0^\infty \mathrm{d}t\ \langle \mathbf{A}(0)\cdot\mathbf{A}(t)\rangle \tag{4}$$

where

$$\mathbf{A} = D_{\mathrm{m}}\frac{\beta}{N + 1}\sum_{i,j=0}^{N} \mathbf{H}_{ij}\cdot\frac{\partial}{\partial \mathbf{R}_j}U(\mathbf{R}_0, ..., \mathbf{R}_N) \tag{5}$$

In eq 5, $U(\mathbf{R}^N)$ is the intermonomer interaction potential and $\mathbf{H}_{ij} = \mathbf{H}_{ij}(\mathbf{R}_{ij})$ is defined by

$$\mathbf{H}_{ij}(\mathbf{R}) = \mathbf{I}\delta_{ij} + h^*(6\pi)^{1/2}(1 - \delta_{ij})(b/8R)\left[\mathbf{I} + \frac{\mathbf{R}\mathbf{R}}{R^2}\right] \tag{6}$$

where $\mathbf{I}$ is the 3×3 unit matrix. In the case of preaveraged tensor, $\mathbf{H}_{ij}$ is replaced by $\langle \mathbf{H}_{ij}\rangle = \mathbf{I}\bar{H}_{ij}$, and eq 4 reduces to

$$D_1 = D_{\mathrm{m}}(N + 1)^{-2}\mathbf{E}^{\mathrm{T}}\bar{\mathbf{H}}\mathbf{m}^{\mathrm{T}}\mathbf{S}^{-1}\mathbf{m}\bar{\mathbf{H}}\mathbf{E} \tag{7}$$

where

$$\mathbf{S} \equiv \mathbf{m}\bar{\mathbf{H}}\mathbf{m}^{\mathrm{T}} \tag{8}$$

and $\mathbf{m}$ is an $N \times (N + 1)$ matrix with elements

$$m_{ij} = \delta_{ij} - \delta_{i-1,j} \qquad i = 1, 2, ..., N; \qquad j = 0, 1, ..., N \tag{9}$$

Fixman[9] calculated D_1/D_0 for large N using eq 7 and 3 as $1 - [3\pi/8(2^{1/2})]\Gamma(1/2)[\Gamma(3/4)]^{-2}$, which is identical with the large-N limit of D_1/D_0 calculated with eq 1 and 3. One of the aims of this paper is to prove, with matrix algebra, the identity

$$(N + 1)^{-2}\mathbf{E}^{\mathrm{T}}\bar{\mathbf{H}}\mathbf{m}^{\mathrm{T}}\mathbf{S}^{-1}\mathbf{m}\bar{\mathbf{H}}\mathbf{E} \equiv (N + 1)^{-2}\mathbf{E}^{\mathrm{T}}\bar{\mathbf{H}}\mathbf{E} - (\mathbf{E}^{\mathrm{T}}\bar{\mathbf{H}}^{-1}\mathbf{E})^{-1} \tag{10}$$

and hence to show that the two expressions of D_1 are identical not only for large N but for all N.

We also show that the time-dependent diffusion coefficient $D(t)$ defined by $\langle|\Delta\mathbf{R}_{\mathrm{c}}(t)|^2\rangle \equiv 6D(t)t$, where $\Delta\mathbf{R}_{\mathrm{c}}(t) = \mathbf{R}_{\mathrm{c}}(t) - \mathbf{R}_{\mathrm{c}}(0)$ is the displacement of the center of mass of the chain, can be expressed quite generally as

$$D(t) = D_0 - (1/3)\int_0^t \mathrm{d}u\ (1 - u/t)\langle \mathbf{A}(0)\cdot\mathbf{A}(u)\rangle \tag{11}$$

which reduces to the results obtained by Dubois-Violette and de Gennes[4] and others[5,6] for Gaussian chains with preaveraged Oseen tensor and reproduces Fixman's[10] general expression for large t.

Finally, we obtain D_1 directly from the Langevin equation[11] for $S(q,t)$ in the Markov limit in which $q \to 0$, $t \to \infty$ with q^2t fixed, without resorting to any specific form of $S(q,t)$.

The method of approach presented here may be useful in other contexts, besides providing extension of the existing calculations of the translational diffusion coefficient.

Distribution Function of the Center of Mass

We start with the monomer distribution function $\psi(\mathbf{R}^N,t)$, where $\mathbf{R}^N \equiv \{\mathbf{R}_0, \mathbf{R}_1, ..., \mathbf{R}_N\}$ denotes the positions

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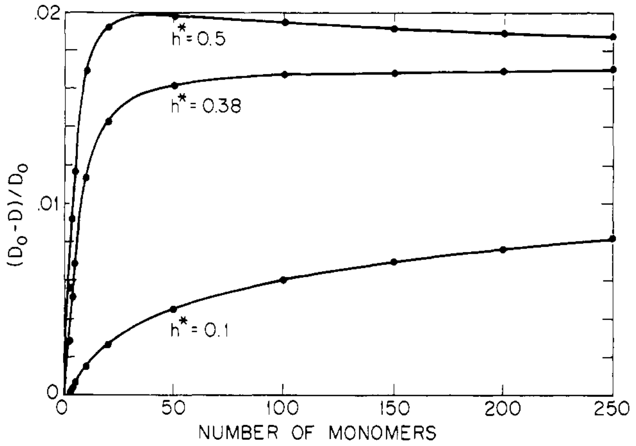

Figure 1. Variation of D_1/D_0 with chain length for various values of the draining parameter h^*.

of the monomers, and separate the equilibrium distribution function $\psi_{\mathrm{eq}}(\mathbf{R}^N)$ as $\psi = \psi_{\mathrm{eq}}f$. It is known[12,13] that $f(\mathbf{R}^N,t)$ satisfies

$$\partial f/\partial t = -\mathcal{L}f \qquad (12)$$

where, with summation convention,

$$\mathcal{L} \equiv -D_{\mathrm{m}}[\nabla_i + \nabla_i \ln \psi_{\mathrm{eq}}]\cdot\mathbf{H}_{ij}\cdot\nabla_j \qquad i, j = 0, ..., N \qquad (13)$$

We transform position coordinates $\mathbf{R}_0, ..., \mathbf{R}_N$ to bond vector coordinates $\mathbf{b} \equiv \{\mathbf{b}_1, ..., \mathbf{b}_N\}$, defined by

$$\begin{aligned}\mathbf{b}_i &= \mathbf{R}_i - \mathbf{R}_{i-1} \\ &= m_{ij}\mathbf{R}_j \qquad i = 1, ..., N; \qquad j = 0, ..., N\end{aligned}$$

and to center-of-mass coordinates

$$\begin{aligned}\mathbf{R}_{\mathrm{c}} &= (N+1)^{-1}\sum_{j=0}^{N}\mathbf{R}_j \\ &= (N+1)^{-1}E_j\mathbf{R}_j \qquad j = 0, ..., N\end{aligned}$$

The details of this transformation can be found elsewhere.[14] In these coordinates, the operator $\mathcal{L}$ reads

$$\mathcal{L} \equiv -D_{\mathrm{m}}[\nabla_{\mathrm{c}}\cdot\mathbf{h}_0\cdot\nabla_{\mathrm{c}} + 2\nabla_{\mathrm{c}}\cdot\mathbf{h}_j\cdot\nabla_j] - \mathbf{A}\cdot\nabla_{\mathrm{c}} + \mathcal{L}_{\mathrm{I}} \qquad (14)$$

where $\nabla_{\mathrm{c}} \equiv \partial/\partial\mathbf{R}_{\mathrm{c}}$, $\nabla_j \equiv \partial/\partial\mathbf{b}_j$, and

$$\mathbf{h}_0 \equiv (N+1)^{-2}E_i\mathbf{H}_{ij}E_j \qquad (15a)$$

$$\mathbf{h}_j \equiv (N+1)^{-1}E_i[\mathbf{Hm}^{\mathrm{T}}]_{ij} \qquad j = 1, 2, ..., N \qquad (15b)$$

$$\mathbf{A} \equiv D_{\mathrm{m}}\mathbf{h}_j\cdot\nabla_j \ln \psi_0 \qquad (15c)$$

$$\mathcal{L}_{\mathrm{I}} \equiv -D_{\mathrm{m}}[\nabla_i + \nabla_i \ln \psi_0]\cdot\mathbf{S}_{ij}\cdot\nabla_j \qquad (15d)$$

The symmetric $N \times N$ matrix $\mathbf{S}_{ij}$ is defined by

$$\begin{aligned}\mathbf{S}_{ij} &\equiv [\mathbf{mHm}^{\mathrm{T}}]_{ij} \\ &\equiv \mathbf{H}_{ij} + \mathbf{H}_{i-1,j-1} - \mathbf{H}_{i-1,j} - \mathbf{H}_{i,j-1} \qquad (16) \\ &\qquad i, j = 1, ..., N\end{aligned}$$

which was introduced by Lodge and Wu.[15] In obtaining eq 14, one uses the identity

$$\sum_{j=1}^{N}(\partial/\partial\mathbf{b}_j)\cdot\mathbf{h}_j = 0 \qquad (17)$$

which follows from $(\partial/\partial\mathbf{R}_i)\cdot\mathbf{H}_{ik} = 0$ (no summation on i). The matrices $\mathbf{h}_0$, $\mathbf{h}_j$, and $\mathbf{S}_{ij}$ and the vector $\mathbf{A}$ depend only on bond vector coordinates $\mathbf{b}$. This is also true for the equilibrium distribution $\psi_{\mathrm{eq}} = V^{-1}\psi_0(b)$, where V is the volume of the system.

The distribution function of the center of mass is calculated as

$$g(\mathbf{R}_{\mathrm{c}},t) = \int \mathrm{d}\mathbf{b}\ \psi_0(\mathbf{b})f(\mathbf{R}_{\mathrm{c}},\mathbf{b},t) \equiv \langle f\rangle_0 \qquad (18)$$

where we introduce $\langle\cdots\rangle_0$ to denote equilibrium average over bond vector coordinates. In order to obtain a closed equation for g, we define a projection operator P, operating only on the internal variables $\mathbf{b}$, by

$$PG = \langle G\rangle_0 \qquad (19)$$

Then, $g = Pf$. We follow Zwanzig's[16] original projection operator formalism to derive a master equation. Although not essential, it is convenient to work with Fourier transforms of $\tilde{g}(\mathbf{q},t)$ and $\tilde{f}(\mathbf{q},\mathbf{b},t)$ with respect to $\mathbf{R}_{\mathrm{c}}$. One finds

$$\partial\tilde{g}/\partial t = -P\mathcal{L}(\mathbf{q})\tilde{g} + \int_0^t \mathrm{d}u\ \tilde{M}(\mathbf{q}, t-u)\tilde{g}(\mathbf{q},u) \qquad (20)$$

where the memory function has its usual form:

$$\tilde{M}(\mathbf{q},t) = \langle\mathcal{L}(\mathbf{q})\exp[-t(1-P)\mathcal{L}(\mathbf{q})](1-P)\mathcal{L}(\mathbf{q})\rangle_0 \qquad (21)$$

The operator $\mathcal{L}(\mathbf{q})$ is obtained from eq 14 as

$$\mathcal{L}(\mathbf{q}) = D_{\mathrm{m}}[\mathbf{q}\cdot\mathbf{h}_0\cdot\mathbf{q} - 2i\mathbf{q}\cdot\mathbf{h}_j\cdot\nabla_j] - i\mathbf{q}\cdot\mathbf{A} + \mathcal{L}_{\mathrm{I}} \qquad (22)$$

The following identities are needed:

$$\mathcal{L}(q)G(\mathbf{q}) \equiv [D_{\mathrm{m}}\mathbf{q}\cdot\mathbf{h}_0\cdot\mathbf{q} - i\mathbf{q}\cdot\mathbf{A}]G(\mathbf{q})$$

$$P\mathcal{L}(q)G(\mathbf{q}) \equiv q^2D_0G(\mathbf{q})$$

$$(1-P)\mathcal{L}(q)G(\mathbf{q}) \equiv [D_{\mathrm{m}}\mathbf{q}\cdot\delta\mathbf{h}_0\cdot\mathbf{q} - i\mathbf{q}\cdot\mathbf{A}]G(\mathbf{q})$$

$$\langle\mathcal{L}(q)G(\mathbf{b},\mathbf{q},t)\rangle_0 \equiv \langle[D_{\mathrm{m}}\mathbf{q}\cdot\mathbf{h}_0\cdot\mathbf{q} + i\mathbf{q}\cdot\mathbf{A}]G\rangle_0$$

where $G(\mathbf{q})$ and $G(\mathbf{b},\mathbf{q},t)$ are arbitrary functions, $D_{\mathrm{m}}\delta\mathbf{h}_0 = D_{\mathrm{m}}\mathbf{h}_0 - D_0\mathbf{I}$, and D_0 is defined by $D_{\mathrm{m}}\langle\mathbf{h}_0\rangle_0 = \mathbf{I}D_0$ or

$$D_0 = (1/3)D_{\mathrm{m}}(N+1)^{-2}\sum_{i,j=1}^{N}\mathrm{Tr}\ \langle\mathbf{H}_{ij}\rangle_0 \qquad (23)$$

In the Stokes–Oseen approximation for hydrodynamic interaction and the Gaussian chain model, D_0 reduces to Kirkwood's formula given in eq 3.

Taking the Laplace transforms of eq 20 and making use of the above identities, we obtain the first significant equation of this work:

$$\tilde{g}(\mathbf{q},s) = \{s + q^2[D_0 - \mathcal{D}_1(q,s)]\}^{-1}\tilde{g}(\mathbf{q}, t=0) \qquad (24)$$

where

$$\mathcal{D}_1(q,s) \equiv q^{-2}\left\langle[D_{\mathrm{m}}\mathbf{q}\cdot\mathbf{h}_0\cdot\mathbf{q} + i\mathbf{q}\cdot\mathbf{A}]\frac{1}{s + (1-P)\mathcal{L}(q)}[D_{\mathrm{m}}\mathbf{q}\cdot\delta\mathbf{h}_0\cdot\mathbf{q} - i\mathbf{q}\cdot\mathbf{A}]\right\rangle_0 \qquad (25)$$

In order to calculate the mean-square displacement $\langle|\Delta\mathbf{R}_{\mathrm{c}}(t)|^2\rangle$ of the center of mass as a function of time, we choose the initial distribution $g(\mathbf{R}_{\mathrm{c}}, t=0)$ as $\delta(\mathbf{R}_{\mathrm{c}})$, which implies $\tilde{g}(\mathbf{q}, t=0) = 1$ in eq 24. With this choice, $g(\mathbf{R}_{\mathrm{c}},t)$ becomes the probability of finding the center of mass at $\mathbf{R}_{\mathrm{c}}$ at time t when it is at the origin at $t = 0$. Using

$$\begin{aligned}\langle|\Delta\mathbf{R}_{\mathrm{c}}(t)|^2\rangle &= \int \mathrm{d}\mathbf{R}_{\mathrm{c}}\ |\mathbf{R}_{\mathrm{c}}|^2g(\mathbf{R}_{\mathrm{c}},t) \\ &\equiv -\lim_{q\to0}\nabla_q{}^2\tilde{g}(\mathbf{q},t) \qquad (26)\end{aligned}$$

we can easily obtain the mean-square displacement of the center of mass from eq 24. We present the result in terms of a time-dependent diffusion coefficient defined by

$$\langle|\Delta\mathbf{R}_{\mathrm{c}}(t)|^2\rangle \equiv 6D(t)t \qquad (27)$$

as

$$D(t) = D_0 - \int_0^t \mathrm{d}u\ (1 - u/t)C_{\mathrm{A}}(u) \qquad (28)$$

where $\tilde{C}_A(s) = \lim \mathcal{D}_1(q,s)$ as $q \to 0$, or explicitly

$$C_A(t) = (1/3)\langle \mathbf{A}\cdot\exp(-t\mathcal{L}_I)\mathbf{A}\rangle_0 \tag{29}$$

which is the time correlation function of the vector $\mathbf{A}$. Note that the time evolution of $\mathbf{A}(t)$ is given by $\dot{\mathbf{A}} = -\mathcal{L}_I\mathbf{A}$. Equation 28 is the general expression for the time-dependent diffusion coefficient. It is valid for any chain statistics $\psi_0(\mathbf{b})$ and hydrodynamic interaction model $\mathbf{H}_{ij}$, provided $\nabla_j\cdot\mathbf{H}_{jk} = 0$. Clearly, $D(0) = D_0$ and $D(\infty) = D_0 - D_1$, with

$$D_1 = (1/3)\int_0^\infty \mathrm{d}u\ \langle \mathbf{A}\cdot\exp(-t\mathcal{L}_I)\mathbf{A}\rangle_0 \tag{30}$$

which was first given by Fixman[10] apart from changes in units.

The above definition of $D(t)$ is a matter of choice. One can also define it as

$$\langle|\Delta\mathbf{R}_c|^2\rangle = \int_0^t \mathrm{d}u\ D(u)$$

with a result

$$D(t) = D_0 - \int_0^t \mathrm{d}u\ C_A(u)$$

with the same short- and long-time limits.

Calculation of $D(t)$ for a Gaussian Chain with Preaveraged Oseen Tensor

The purpose of this section is to demonstrate how the general expression of $D(t)$ in eq 28 reduces to that originally given by Dubois-Violette and de Gennes[4] in this particular case. For a Gaussian chain, $\nabla_j \ln \psi_0 = -(3/b^2)\mathbf{b}_j$. When the Oseen tensor is preaveraged, $\mathbf{h}_j = \mathbf{I}h_j$, where $h_j = (N+1)^{-1}E_i(\bar{\mathbf{H}}\mathbf{m}^T)_{ij}$. It is convenient to work with $N \times N$ matrices and introduce, following Fixman,[10] $\mathbf{h} = \mathbf{m}\bar{\mathbf{H}}\mathbf{E}/(N+1)$. Then $\mathbf{A}$ in eq 15c becomes

$$\mathbf{A} = -\sigma\mathbf{h}^T\mathbf{b} \tag{31}$$

where $\mathbf{b} = \mathrm{col}\ [\mathbf{b}_1, ..., \mathbf{b}_N]$ and $\sigma \equiv (3/b^2)D_m$. The time evolution of $\mathbf{b}(t)$ follows from $\dot{\mathbf{b}} = -\mathcal{L}_I\mathbf{b}$, where $\mathcal{L}_I$ is given by eq 15d as

$$\mathbf{b}(t) = \exp(-t\sigma\mathbf{S})\mathbf{b}(0) \tag{32}$$

where $\mathbf{S}$ is an $N \times N$ symmetric matrix and is defined as $\mathbf{S} = \mathbf{m}\bar{\mathbf{H}}\mathbf{m}^T$. The correlation function $C_A(t)$ defined in eq 29 follows with $\langle\mathbf{b}_j\cdot\mathbf{b}_k\rangle_0 = \delta_{jk}b^2$ as

$$C_A(t) = (b^2/3)\sigma^2\mathbf{h}^T \exp(-t\sigma\mathbf{S})\mathbf{h} \tag{33}$$

Lodge and Wu[15] and later Fong and Peterlin[17] showed that the nonzero eigenvalues of $\mathbf{HA}$, where $\mathbf{A} = \mathbf{m}^T\mathbf{m}$ is the nearest-neighbor interaction matrix, and $\mathbf{S}$ are identical, and the eigenvectors of $\mathbf{S}\mathbf{y}_j = \nu_j\mathbf{y}_j$ are related to those of $\mathbf{HA}\alpha_j = \nu_j\alpha_j$ by $\mathbf{y}_j = \mathbf{m}\alpha_j$ for $j = 1, 2, ..., N$. The eigenvectors $\mathbf{y}_j$ are orthogonal and normalized as $\mathbf{y}_j^T\mathbf{y}_k = \delta_{jk}$. The latter implies a normalization of the nonorthogonal vectors α_j as $\alpha_j^T\mathbf{A}\alpha_j = 1$ for $j = 1, 2, ..., N$. Hence

$$\exp(-t\sigma\mathbf{S}) = \sum_{j=1}^N \exp(-t\sigma\nu_j)\mathbf{y}_j\mathbf{y}_j^T \tag{34}$$

and after some algebra

$$C_A(t) = \frac{b^2}{3}\frac{\sigma^2}{N+1}\sum_{j=1}^N \frac{[\alpha_0^T\alpha_j]^2}{\alpha_j^T\mathbf{A}\alpha_j}\nu_j^2 e^{-\sigma\nu_j t} \tag{35}$$

where $\mathbf{h}^T\mathbf{y}_j = \mathbf{E}^T\bar{\mathbf{H}}\mathbf{m}^T\mathbf{m}\alpha_j/(N+1) = \mathbf{E}^T\alpha_j\nu_j/(N+1)$ and $\alpha_0 = \mathbf{E}/(N+1)^{1/2}$ have been used. The inclusion of $\alpha_j^T\mathbf{A}\alpha_j$ in the denominator makes the result independent of normalization of α_j. Substitution of $C_A(t)$ into eq 28 yields

$$tD(t) = Dt + (b^2/3)\frac{1}{N+1}\sum_{j=1}^N \frac{[\alpha_0^T\alpha_j]^2}{\alpha_j^T\mathbf{A}\alpha_j}(1 - e^{-\sigma\nu_j t}) \tag{36}$$

where $D = D(\infty) = D_0 - D_1$ with

$$D_1 = D_m\frac{1}{N+1}\sum_{j=1}^N \frac{[\alpha_0^T\alpha_j]^2}{\alpha_j^T\mathbf{A}\alpha_j}\nu_j \tag{37}$$

The above result is identical with that obtained in ref 4. Fixman's expression[10] for D_1 in eq 7 is obtained from eq 30 directly using

$$\mathbf{S}^{-1} = \sigma\int_0^\infty \mathrm{d}t\ \exp(-t\sigma\mathbf{S}) \tag{38}$$

as

$$\begin{aligned} D_1 &= D_m\mathbf{h}^T\mathbf{S}^{-1}\mathbf{h} \\ &= D_m(N+1)^{-2}\mathbf{E}^T\bar{\mathbf{H}}\mathbf{m}^T\mathbf{S}^{-1}\mathbf{m}\bar{\mathbf{H}}\mathbf{E} \end{aligned} \tag{39}$$

It is almost trivial to demonstrate the identity in eq 10 at this point, starting from eq 37 and rewriting it as

$$D_1 = D_m(N+1)^{-1}[\sum_{j=0}^N [\alpha_0^T\alpha_j]^2\nu_j - (\alpha_0^T\alpha_0)^2\nu_0] \tag{40}$$

where we use normalized eigenvectors α_j. Remembering[2] that $\mathbf{Q}^{-1}\bar{\mathbf{H}}(\mathbf{Q}^T)^{-1} = \mathrm{diag}\ [\nu_0, \nu_1, ..., \nu_N]$, where $\mathbf{Q} = \mathrm{col}\ [\alpha_0, \alpha_1, ..., \alpha_N]$, one verifies $\bar{\mathbf{H}} = \sum_{k=0}^N \nu_k\alpha_k\alpha_k^T$ or

$$(N+1)^{-1}\mathbf{E}^T\bar{\mathbf{H}}\mathbf{E} = \sum_{k=0}^N \nu_k[\alpha_0^T\alpha_k]^2$$

The last term in eq 40 $(\alpha_0^T\alpha_0)^2\nu_0 = (\alpha_0^T\alpha_0)^2[\alpha_0^T\bar{\mathbf{H}}^{-1}\alpha_0]^{-1}$ as follows from $\mathbf{Q}^T\bar{\mathbf{H}}^{-1}\mathbf{Q} = \mathrm{diag}\ [\nu_0^{-1}, ..., \nu_N^{-1}]$. This leads with $\alpha_0^T\alpha_0 = 1$ to

$$D_1 = D_m[(N+1)^{-2}\mathbf{E}^T\bar{\mathbf{H}}\mathbf{E} - (\mathbf{E}^T\bar{\mathbf{H}}^{-1}\mathbf{E})^{-1}] \tag{41}$$

As pointed out by others before,[4-6] D_1 vanishes in the Rouse limit, where $\bar{\mathbf{H}} = \mathbf{I}$, and in the case of ring polymers. In the latter, $\bar{\mathbf{H}}$ and $\mathbf{A}$ are both cyclic and the eigenvectors are orthogonal; viz., $\alpha_0^T\alpha_j = 0$ in eq 37.

Connection with Light Scattering

In dynamic light scattering experiments, one measures the intermediate scattering function $S(\mathbf{q},t)$. It satisfies[11,18]

$$\frac{\partial S(q,t)}{\partial t} = -\Omega(q)S + \int_0^t \mathrm{d}u\ \phi(q,u)S(q, t-u) \tag{42}$$

where $\Omega(q)$ is the first cumulant

$$\Omega(q) = \langle\rho^*\mathcal{L}\rho\rangle\langle\rho^*\rho\rangle^{-1}$$

and the memory function is defined by

$$\phi(q,t) = \langle Q\mathcal{L}\rho^* \exp(-tQ\mathcal{L})Q\mathcal{L}\rho\rangle\langle\rho^*\rho\rangle^{-1} \tag{43}$$

The operator $\mathcal{L}$ is given in eq 13. The monomer density is

$$\rho(\mathbf{q}) = \sum_{j=0}^N \exp(i\mathbf{q}\cdot\mathbf{R}_j)$$

The operator Q denotes $1 - P$, where P is the projection operator defined by $PG(\mathbf{R}^N) \equiv \langle G\rho^*\rangle\langle\rho\rho^*\rangle^{-1}\rho$. The angled brackets imply equilibrium averages over $\psi_{eq}(\mathbf{R}^N)$.

It was shown before[11,18] that the small-q limit of the first cumulant is equal to the short-time diffusion coefficient D_0; viz.

$$\lim_{q\to 0} q^{-2}\Omega(q) = \frac{D_m}{3(N+1)^2}\sum_{i,j=0}^N \mathrm{Tr}\ \langle\mathbf{H}_{ij}\rangle \tag{44}$$

(see eq 23). To attain maximum accuracy, the normalized

$S(q,t)$ is measured in time intervals in which it decays appreciably and yet remains above the noise level. Since its decay is predominantly determined by $\Omega(q)t$, experiments are performed in time intervals ranging from $\Omega t \approx 0.05$ to $\Omega t \approx 3$. In the small-q region this implies $q^2D_0t \approx 0.05$–3. The translational diffusion coefficient is measured as the decay constant of $S(q,t)$ in the limit of $q \rightarrow 0$ and $t \rightarrow \infty$ such that q^2tD_0 is fixed, which is the usual Markov limit in statistical mechanics. In this limit eq 42 reduces to

$$\frac{\partial S(q,t)}{\partial t} = -q^2[D_0 - D_1]S(q,t)$$

where

$$D_1 = \lim_{q \to 0} q^{-2} \int_0^\infty \mathrm{d}t\, \phi(q,t) \tag{45}$$

which is yet another general expression for Fixman's correction.

The equivalence of this form to eq 30 can be shown as follows: First we note that $\rho \rightarrow N\rho_c(\mathbf{R}_c) \equiv N \exp(i\mathbf{q}\cdot\mathbf{R}_c)$ when $qR_G \ll 1$, where R_G is the radius of gyration of the chain (N now denotes the number of monomers). In this limit $\langle \rho^*\rho \rangle \rightarrow N^2$ and $S(q,t) \rightarrow \langle \rho_c^*(0)\rho_c(t) \rangle$ as expected. Secondly, we observe

$$N^{-1}\mathcal{L}\rho = [D_m q^2 - i\mathbf{q}\cdot\mathbf{A}]\rho_c \rightarrow -i\mathbf{q}\cdot\mathbf{A}\rho_c$$

and

$$N^{-1}P\mathcal{L}\rho = N^{-1}\Omega(q)\rho \rightarrow D_0 q^2 \rho_c$$

so that

$$q^{-2}\phi(q,t) \rightarrow (1/3)\langle \mathbf{A}\rho_c^* \cdot \exp(-t\mathcal{L})\mathbf{A}\rho_c \rangle \tag{46}$$

where $Q\mathcal{L}$ is replaced by $\mathcal{L}$ because $P\mathcal{L}G(\mathbf{R}^N)$ for any $G(\mathbf{R}^N)$ is proportional to q and hence disappears as $q \rightarrow 0$. Finally, $\mathcal{L}$ is replaced by $\mathcal{L}_I$ because the remaining terms in $\mathcal{L}$ contain ∇_c that gives rise to terms also proportional to q when they operate on $\mathbf{A}\rho_c$. The resulting operator $\exp(-t\mathcal{L}_I)$ does not operate on $\mathbf{R}_c$; hence the product $\rho_c^*\rho_c$ in eq 46 is replaced by unity. The equilibrium average reduces to $\langle \cdots \rangle_0$ that involves only bond vector coordinates $\mathbf{b}$, and eq 30 is recaptured.

The advantage of this approach is that it established the connection between the short-time diffusion coefficient and the first cumulant of $S(q,t)$ without resorting to any chain model.

Discussion

In this paper we have developed a closed equation for the time-dependent distribution function $g(\mathbf{R}_c,t)$ of the center of mass of a flexible chain using the projection operator technique. This equation has been used to calculate the mean-square displacement $\langle |\Delta\mathbf{R}_c|^2 \rangle$ of the center of mass as a function of time. We have introduced a time-dependent diffusion coefficient through $D(t) = (1/6t)\langle |\Delta\mathbf{R}_c|^2 \rangle$. However, one may also define $D(t)$ as $(1/6)d\langle |\Delta\mathbf{R}_c|^2 \rangle/\mathrm{d}t$, which has a different behavior for finite times although it possesses the same short- and long-time limits. In fact, one could have considered the mean-square displacement of the center of resistance,[2] instead, to introduce a time-dependent diffusion coefficient. In any case, the asymptotic behavior of the mean-square displacement for large times uniquely defines the translational diffusion coefficient of a deformable macromolecule. On the other hand, the time dependence of the mean-square displacement for short times and the time-dependent diffusion coefficient $D(t)$ extracted from it according to a particular prescription depend on the reference point chosen to define translation of the molecule. For example, the mean-square displacement of the center of resistance is equal to $6Dt$ at all times for a Gaussian chain with preaveraged Oseen tensor, so that $D(t) = D$ and there is no distinction between short- and long-time diffusion coefficients. These points may be significant in the interpretation of diffusion experiments attempting to observe the variation of $D(t)$ with time.

It is interesting to note that the initial decay of the scattering function $S(q,t)$ is determined by the first cumulant $\Omega(q)$, which in the small-q limit is proportional to the short-time diffusion coefficient associated with the center of mass. For large times, it decays exponentially with a decay constant q^2D for any value of q. In finite time intervals accessible experimentally, the mode of decay of $S(q,t)$ is controlled by both the translational motion and internal modes, with varying relative importance as a function of q.

No attempt has been made in this paper to estimate the magnitude of the correction term $D_1 = D_0 - D$ in the case of nonpreaveraged Oseen tensor. Recent computer simulations of Zimm[19] predict an error of 15%, whereas Fixman's[10] simulations give errors of the order of a few percent. An analytical evaluation of D_1 without preaveraging hydrodynamic interaction does not seem to be possible at present.

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