Transport Coefficients of Weakly Bending Rods. Effects of the Preaveraging Approximation†

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ABSTRACT: Effects of the preaveraging approximation on the mean translational diffusion coefficient D_t and intrinsic viscosity $[\eta]$ of weakly bending rods are examined on the basis of an arc rod model. A lower bound to D_t and an upper bound to $[\eta]$ are obtained by exactly evaluating them for a rigid-body ensemble following the Oseen–Burgers procedure without the preaveraging, i.e., D_t taking exact account of the translational and rotational coupling and $[\eta]$ without the assumption of the constant angular velocity equal to one-half of the unperturbed rate of shear. The preaveraged D_t is an upper bound, while a lower bound to $[\eta]$ is determined from Fixman's formula. With these bounds, it is concluded that the preaveraged D_t and $[\eta]$ are very good approximations for long, weakly bending rods.

I. Introduction

Since the recent work of Zimm[1] on chain molecule hydrodynamics, there has been some renewal of activity in the study of the effects of the preaveraging of hydrodynamic interaction on steady-state transport coefficients,[2–5] giving attention to his rigid-body ensemble approximation for Gaussian chains. The object of the present paper is to examine, along a similar line, the effects on the mean translational diffusion coefficient (or sedimentation coefficient) and intrinsic viscosity of weakly bending rods.

In a previous paper,[6] we have examined various possible sources of the disagreement between the diameters estimated from various transport coefficients for certain stiff chains by the use of the Yamakawa–Fujii equations[7] for wormlike cylinder models and arrived at the conclusion that the most probable source seems to be the replacement of a rough surface of a real macromolecular chain by the smooth cylinder surface. However, we have also noted that another possibility may be the preaveraging of the hydrodynamic interaction but that its effects will be rather small near the rod limit. Thus the present paper is also supplementary to the previous one.[6]

Now, it is very difficult even near the rod limit to carry out present necessary calculations analytically on the basis of the wormlike cylinder model. We therefore adopt, as a model for a weakly bending rod, an arc rod, where for the present purpose, it is not necessary to give explicitly the distribution of its radius of curvature. Then, following the Oseen–Burgers (OB) procedure with the nonpreaveraged Oseen tensor, we evaluate *exactly* the mean translational diffusion coefficient D_t and intrinsic viscosity $[\eta]$ for a rigid-body ensemble of such long arc rods, i.e., D_t taking exact account of the coupling between translational and rotational motions and $[\eta]$ without the assumption of the uniform rotation with the angular velocity equal to one-half of the unperturbed rate of shear. Recall that the OB procedure with the nonpreaveraged Oseen tensor is exactly valid for long rods.[6] As easily demonstrated from Fixman's general formula, eq 3.13 of ref 4, for variational bounds, the result thus obtained for D_t gives a lower bound to its correct value for the bending arc rod, while the result for $[\eta]$ gives an upper bound. We also evaluate D_t and $[\eta]$ with the preaveraged Oseen tensor, a lower bound to $[\eta]$ from Fixman's formula,[4] and the Zimm bounds.[1] Note that the preaveraged D_t is an upper bound. All these quantities serve to examine the effects of the preaveraging near the rod limit.

The plan of the present paper is as follows. In section II, we define the ensemble of arc rods and make some comments on its equilibrium configuration in comparison with the wormlike chain. In section III, we formulate the diffusion equation for the rigid arc rod in terms of fundamental diffusion tensors. It is required since we avoid the assumption of the uniform rotation in a shear flow. We evaluate, in section IV, D_t from the fundamental diffusion tensors, and in section V, $[\eta]$ with the flux from the solution of the diffusion equation. In section VI, we evaluate the Zimm and Fixman bounds. Section VII is devoted to a discussion of the effects of the preaveraging.

II. Model

We consider an arc rod of contour length L and diameter d. Let its contour be an arc of circle of radius ρ and introduce an angle $\chi = L/\rho$. Its end-to-end distance R is given by

$$R = (2L/\chi)\sin(\chi/2) \qquad (1)$$

We assume that χ is so small that terms higher than the quadratic may be neglected in any expansion in powers of χ. Further, we assume that $p \equiv L/d \gg 1$. We consider an equilibrium ensemble of such arc rods with different χ but with the same L and assume for the equilibrium ensemble average $\langle\chi^2\rangle$

$$\langle\chi^2\rangle = C\lambda L \qquad (2)$$

where λ^{-1} is the Kuhn segment length of the wormlike chain and C is a constant independent of λL. Then we have for the mean-square end-to-end distance

$$\begin{aligned}\langle R^2\rangle &= L^2\left(1 - \frac{1}{12}\langle\chi^2\rangle + ...\right)\\ &= L^2\left(1 - \frac{C}{12}\lambda L + ...\right)\end{aligned} \qquad (3)$$

If we force this $\langle R^2\rangle$ to agree with that for the wormlike chain near the rod limit, i.e., the WKB rod,[8] we have $C = 8$. Similar correspondence between the arc and the wormlike chain has been introduced by Verdier[9] in his evaluation of the scattering function. However, such a correspondence is of no great significance, or even incorrect, as shown below. Let $R(s)$ be the distance between two contour points of the arc separated by a contour distance s ($<L$). We then have

$$\begin{aligned}\langle R^2(s)\rangle &= s^2\left[1 - \frac{1}{12}\left(\frac{s}{L}\right)^2\langle\chi^2\rangle + ...\right]\\ &= s^2\left[1 - \frac{C}{12}\left(\frac{s}{L}\right)\lambda s + ...\right]\end{aligned} \qquad (4)$$

† This paper is dedicated to Professor Walter H. Stockmayer on his 70th birthday.

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where $\langle \chi^2 \rangle$ is given by eq 2, and we note that $\langle \chi^2(s) \rangle = (s/L)C\lambda s$. This is inconsistent with eq 3 (but is rather the definition of our ensemble). In other words, our ensemble never represents that of Markov chains, i.e., precisely that of wormlike chains. Thus we should merely regard it as a model or replacement for an ensemble of weakly bending rods and do not assign any particular value to C. The assignment of $C = 8$ never reproduces the previous results for the transport coefficients.[7]

Now we introduce external ($\mathbf{e}_x$, $\mathbf{e}_y$, $\mathbf{e}_z$) and molecular ($\mathbf{e}_1$, $\mathbf{e}_2$, $\mathbf{e}_3$) Cartesian coordinate systems, choosing as the origin of the latter the center of mass, the point 0. Let $\mathbf{R}_0 = (x_0, y_0, z_0)$ be the position vector of the point 0 in the external system, and let $\Theta = (\theta, \phi, \psi)$ be the Euler angles defining the orientation of the molecular system with respect to the external system. For convenience, we choose the molecular coordinate system so that $\mathbf{e}_1$ is in the direction of the curvature vector at the middle point M of the arc (M $\rightarrow$ 0), $\mathbf{e}_3$ is parallel to the tangent vector at M, and $\mathbf{e}_2$ completes the right-handed system.

III. Diffusion Equation

The diffusion equation satisfied by the time t-dependent distribution function $P(\mathbf{R}_0,\Theta;t)$ for the rigid arc rod in an unperturbed solvent flow field $\mathbf{v}^0$ may readily be written down by a slight modification of that for a spheroid cylinder[10] as follows:

$$\left(\frac{\partial}{\partial t} - \mathcal{L}\right)P = \mathcal{L}_v P \tag{5}$$

with

$$\mathcal{L} = \nabla_{R_0}{}^{\mathrm{T}}\cdot\mathbf{A}^{\mathrm{T}}\cdot\mathbf{D}_{0,\mathrm{t}}\cdot\mathbf{A}\cdot\nabla_{R_0} + \nabla_{R_0}{}^{\mathrm{T}}\cdot\mathbf{A}^{\mathrm{T}}\cdot\mathbf{D}_{0,\mathrm{c}}{}^{\mathrm{T}}\cdot\mathbf{L} + \mathbf{L}^{\mathrm{T}}\cdot\mathbf{D}_{0,\mathrm{c}}\cdot\mathbf{A}\cdot\nabla_{R_0} + \mathbf{L}^{\mathrm{T}}\cdot\mathbf{D}_{\mathrm{r}}\cdot\mathbf{L} \tag{6}$$

$$\mathcal{L}_v = (k_{\mathrm{B}}T)^{-1}[(\nabla_{R_0}{}^{\mathrm{T}}\cdot\mathbf{A}^{\mathrm{T}}\cdot\mathbf{D}_{0,\mathrm{t}} + \mathbf{L}^{\mathrm{T}}\cdot\mathbf{D}_{0,\mathrm{c}})\cdot\mathbf{F}_v + (\nabla_{R_0}{}^{\mathrm{T}}\cdot\mathbf{A}^{\mathrm{T}}\cdot\mathbf{D}_{0,\mathrm{c}}{}^{\mathrm{T}} + \mathbf{L}^{\mathrm{T}}\cdot\mathbf{D}_{\mathrm{r}})\cdot\mathbf{T}_{0,v}] \tag{7}$$

where $\nabla_{R_0}{}^{\mathrm{T}} = (\partial/\partial x_0, \partial/\partial y_0, \partial/\partial z_0)$, with the superscript T indicating the transpose, $\mathbf{L}$ is the angular momentum operator, $\mathbf{A}$ is the orthogonal matrix of transformation from the external to the molecular coordinate system, k_{B} is the Boltzmann constant, and T is the absolute temperature. ($\mathbf{L}$ and $\mathbf{A}$ are given by eq 3 and 15 of ref 10, respectively, with θ, ϕ, and ψ in place of α, β, and γ.) $\mathbf{D}_{0,\mathrm{t}}$, $\mathbf{D}_{0,\mathrm{c}}$, and $\mathbf{D}_{\mathrm{r}}$ are the translational, coupling, and rotatory diffusion tensors, respectively, and $\mathbf{F}_v$ and $\mathbf{T}_{0,v}$ are the frictional force and torque arising from $\mathbf{v}^0$, respectively, all of them being expressed in the molecular coordinate system. The subscript 0 on the vectors and tensors indicates that they depend on the location of the point 0 if it is an arbitrary point affixed to the body. (In the present paper, it is taken to be the center of mass.) We evaluate $\mathbf{D}_{0,\mathrm{t}}$, $\mathbf{D}_{0,\mathrm{c}}$, and $\mathbf{D}_{\mathrm{r}}$ in section IV and consider $\mathbf{F}_v$ and $\mathbf{T}_{0,v}$ in section V.

With the solution P of the diffusion eq 5, the instantaneous translational velocity $\mathbf{U}_0$ of the point 0 and the instantaneous angular velocity $\boldsymbol{\Omega}$ of the arc expressed in the molecular coordinate system are given by

$$\begin{bmatrix} \mathbf{U}_0 \\ \boldsymbol{\Omega} \end{bmatrix} = -P^{-1}\begin{bmatrix} \mathbf{D}_{0,\mathrm{t}} & \mathbf{D}_{0,\mathrm{c}}{}^{\mathrm{T}} \\ \mathbf{D}_{0,\mathrm{c}} & \mathbf{D}_{\mathrm{r}} \end{bmatrix} \cdot \left[\begin{bmatrix} \mathbf{A}\cdot\nabla_{R_0} \\ \mathbf{L} \end{bmatrix} + (k_{\mathrm{B}}T)^{-1}\begin{bmatrix} \mathbf{F}_v \\ \mathbf{T}_{0,v} \end{bmatrix}\right] P \tag{8}$$

Note that eq 5–8 are formally valid for any rigid body.

IV. Translational Diffusion Coefficient

The diffusion tensors introduced in the preceding section may be written in terms of the translational, coupling, and rotatory friction tensors, which we designate by $\boldsymbol{\Xi}_{\mathrm{t}}$, $\boldsymbol{\Xi}_{0,\mathrm{c}}$, and $\boldsymbol{\Xi}_{0,\mathrm{r}}$, respectively, as follows:[11]

$$\mathbf{D}_{0,\mathrm{t}} = k_{\mathrm{B}}T(\boldsymbol{\Xi}_{\mathrm{t}} - \boldsymbol{\Xi}_{0,\mathrm{c}}{}^{\mathrm{T}}\cdot\boldsymbol{\Xi}_{0,\mathrm{r}}{}^{-1}\cdot\boldsymbol{\Xi}_{0,\mathrm{c}})^{-1}$$

$$\mathbf{D}_{0,\mathrm{c}} = -\boldsymbol{\Xi}_{0,\mathrm{r}}{}^{-1}\cdot\boldsymbol{\Xi}_{0,\mathrm{c}}\cdot\mathbf{D}_{0,\mathrm{t}} = -\mathbf{D}_{\mathrm{r}}\cdot\boldsymbol{\Xi}_{0,\mathrm{c}}\cdot\boldsymbol{\Xi}_{\mathrm{t}}{}^{-1}$$

$$\mathbf{D}_{\mathrm{r}} = k_{\mathrm{B}}T(\boldsymbol{\Xi}_{0,\mathrm{r}} - \boldsymbol{\Xi}_{0,\mathrm{c}}\cdot\boldsymbol{\Xi}_{\mathrm{t}}{}^{-1}\cdot\boldsymbol{\Xi}_{0,\mathrm{c}}{}^{\mathrm{T}})^{-1} \tag{9}$$

We evaluate these friction tensors following the OB procedure. Then they are given by eq 37 of ref 12; i.e.

$$\boldsymbol{\Xi}_{\mathrm{t}} = 8\pi\eta_0 \int_{-1}^{1} \boldsymbol{\Psi}_1(x)\,\mathrm{d}x$$

$$\boldsymbol{\Xi}_{0,\mathrm{c}} = 4\pi\eta_0 L \int_{-1}^{1} \mathbf{H}_0(x)^{\mathrm{T}}\cdot\boldsymbol{\Psi}_1(x)\,\mathrm{d}x$$

$$\boldsymbol{\Xi}_{0,\mathrm{r}} = 2\pi\eta_0 L^2 \int_{-1}^{1} \mathbf{H}_0(x)^{\mathrm{T}}\cdot\boldsymbol{\Psi}_2(x)\,\mathrm{d}x \tag{10}$$

where η_0 is the solvent viscosity and we have introduced the reduced contour distance $x = (2s/L) - 1$, with s the contour distance of the contour point x from one end ($-1 \le x \le 1$; $0 \le s \le L$). The tensor $\mathbf{H}_0$ is given by

$$\mathbf{H}_0 = \frac{2}{L}\begin{bmatrix} 0 & r_{0,3} & -r_{0,2} \\ -r_{0,3} & 0 & r_{0,1} \\ r_{0,2} & -r_{0,1} & 0 \end{bmatrix} \tag{11}$$

where $\mathbf{r}_0(x)^{\mathrm{T}} \equiv (r_{0,1}, r_{0,2}, r_{0,3})$ is the position vector of the contour point x from the center of mass expressed in the molecular coordinate system and is given by

$$\mathbf{r}_0 = \rho\begin{bmatrix} 2\chi^{-1}\sin\frac{\chi}{2} - \cos\frac{\chi x}{2} \\ 0 \\ \sin\frac{\chi x}{2} \end{bmatrix} \tag{12}$$

The tensors $\boldsymbol{\Psi}_1$ and $\boldsymbol{\Psi}_2$ in eq 10 are the solutions of the integral equations

$$\int_{-1}^{1} \mathbf{K}(x,y)\cdot\boldsymbol{\Psi}_1(y)\,\mathrm{d}y = \mathbf{I}$$

$$\int_{-1}^{1} \mathbf{K}(x,y)\cdot\boldsymbol{\Psi}_2(y)\,\mathrm{d}y = \mathbf{H}_0(x) \tag{13}$$

with $\mathbf{I}$ the unit tensor and with $\mathbf{K}(x,y)$ the nonpreaveraged OB kernel. It may be evaluated from the Oseen tensor with the use of the geometry of the arc rod, as in the case of the regular helix.[12] The result is

$$\mathbf{K}(x,y) = f_{10}(|x-y|)\mathbf{I} + \sum_{i=0}^{2} f_{3i}(|x-y|)\mathbf{M}_i(x,y) \tag{14}$$

where $f_{ij}(x)$ is defined by

$$f_{ij}(x) = \frac{2(-1)^j}{\pi[a(x)+b(x)]^{i/2}} \times \int_0^{\pi/2} \left[1 - \frac{2b(x)}{a(x)+b(x)}\sin^2\alpha\right]^{-i/2} \cos^j 2\alpha\,\mathrm{d}\alpha \tag{15}$$

with

$$a(x) = 4\rho^2\sin^2\frac{\chi x}{4} + \frac{d^2}{4}$$

$$b(x) = 2\rho d\sin^2\frac{\chi x}{4} \tag{16}$$

and the nonzero elements $M_{i,kl}$ of the 3×3 matrices

$\mathbf{M}_i(x,y)$ (i = 0, 1, 2) are given by

$$M_{0,11} = \rho^2\left(\cos\frac{\chi x}{2} - \cos\frac{\chi y}{2}\right)^2$$
$$M_{0,22} = d^2/4$$
$$M_{0,33} = \rho^2\left(\sin\frac{\chi x}{2} - \sin\frac{\chi y}{2}\right)^2$$
$$M_{0,13} = M_{0,31} = -\rho^2\left(\sin\frac{\chi x}{2} - \sin\frac{\chi y}{2}\right)\left(\cos\frac{\chi x}{2} - \cos\frac{\chi y}{2}\right)$$
$$M_{1,11} = -\rho d\cos\frac{\chi x}{2}\left(\cos\frac{\chi x}{2} - \cos\frac{\chi y}{2}\right)$$
$$M_{1,33} = -\rho d\sin\frac{\chi x}{2}\left(\sin\frac{\chi x}{2} - \sin\frac{\chi y}{2}\right)$$
$$M_{1,13} = M_{1,31} = \frac{\rho d}{2}\left[\sin\frac{\chi x}{2}\left(\cos\frac{\chi x}{2} - \cos\frac{\chi y}{2}\right) + \cos\frac{\chi x}{2}\left(\sin\frac{\chi x}{2} - \sin\frac{\chi y}{2}\right)\right]$$
$$M_{2,11} = \frac{d^2}{4}\cos^2\frac{\chi x}{2}$$
$$M_{2,22} = -d^2/4$$
$$M_{2,33} = \frac{d^2}{4}\sin^2\frac{\chi x}{2}$$
$$M_{2,13} = M_{2,31} = -\frac{d^2}{4}\sin\frac{\chi x}{2}\cos\frac{\chi x}{2} \qquad (17)$$

As seen from eq 14–17, the kernel $\mathbf{K}(x,y)$ is not symmetric with respect to x and y; i.e., $\mathbf{K}(x,y) \neq \mathbf{K}(y,x)$. This arises from the use of the OB approximation and leads to a violation of the condition that the 6 × 6 diffusion and friction tensors be symmetric, as mentioned previously.[12] However, in the present case, for which only the asymptotic solutions for $p = L/d \gg 1$ are considered, this condition is asymptotically fulfilled. Further, we note that the rigid arc rod is a body symmetric with respect to the 12 and 13 planes, so that both Ξ_t and $\Xi_{0,r}$ are diagonal, and among the components of $\Xi_{0,c}$, only the 23 and 32 components are nonzero.[11] This is also the case with $\mathbf{D}_{0,t}$, $\mathbf{D}_{0,c}$, and $\mathbf{D}_r$.

Now, according to Wegener,[13] the mean translational diffusion coefficient D_t (of a rigid body) is equal to one-third of the trace of $\mathbf{D}_{0,t}$, with the center of diffusion chosen as the point 0. In the present case, for which the center of mass is chosen as the point 0, D_t may be written as

$$D_t = \tfrac{1}{3}\,\mathrm{Tr}\,\mathbf{D}_{0,t} - \tfrac{1}{3}(D_{r,22} + D_{r,33})^{-1}(D_{0,c,23} - D_{0,c,32})^2 \qquad (18)$$

where Tr indicates the trace and we have used a relation between $\mathbf{D}_{0,t}$ with the centers of mass and diffusion chosen as the point 0[11,13] along with the properties of $\mathbf{D}_{0,c}$ and $\mathbf{D}_r$ noted above for the arc rod. We note that a term corresponding to the second on the right-hand side of eq 18 is missing in eq 46 of ref 12, but the final result obtained there for the long regular helix need not be changed.

The asymptotic solutions for the components $D_{0,t,ij}$, $D_{0,c,ij}$, and $D_{r,ij}$ of the diffusion tensors for $p \gg 1$ (and $\chi \ll 1$) may be obtained by a Legendre polynomial expansion method.[7] The results for the nonzero components are given in the Appendix. With these, we have, from eq 18

$$D_t = \frac{k_BT}{3\pi\eta_0 L}\left[\ln p + 2\ln 2 - 1 - \frac{\langle\chi^2\rangle}{96}\left(\ln p + 2\ln 2 - \frac{23}{6}\right)\right] \qquad (19)$$

where we have taken the equilibrium rigid-body ensemble average by replacing χ^2 by $\langle\chi^2\rangle$. It is seen that D_t given by eq 19 for the bending arc rod is smaller than that of the rigid straight rod (χ = 0). The latter, of course, agrees with the corresponding exact result previously obtained.[6] We note that the contribution of the second term of eq 18 to D_t is $-(k_BT/432\pi\eta_0 L)\langle\chi^2\rangle$, it making no contribution to the ln p term.

Finally, for comparison, we evaluate D_t with the preaveraged kernel in the Kirkwood–Riseman approximation[14] to a solution of the integral equation. We designate it by D_t^P. It is equivalent to D_t from the Kirkwood formula,[15] and this procedure has been adopted previously for the evaluation of D_t of the wormlike cylinder.[7] Then, the preaveraged kernel $\langle\mathbf{K}(x,y)\rangle$ is given by

$$\langle\mathbf{K}(x,y)\rangle = \tfrac{4}{3}\langle f_{10}(|x-y|)\rangle\mathbf{I} \qquad (20)$$

where the angular brackets on the right-hand side denote the average over only χ. Thus we have

$$D_t^P = \frac{k_BT}{3\pi\eta_0}\int_0^1(1-x')\langle f_{10}(2x')\rangle\,dx' = \frac{k_BT}{3\pi\eta_0 L}\left(\ln p + 2\ln 2 - 1 + \frac{\langle\chi^2\rangle}{144}\right) \qquad (21)$$

Note that D_t^P differs from D_t with the nonpreaveraged kernel only in the $\langle\chi^2\rangle$ term, it being positive in the former and negative in the latter. The result with χ = 0 agrees with the corresponding one previously obtained for the straight rod.[7]

V. Intrinsic Viscosity

Suppose that the unperturbed solvent flow $\mathbf{v}^{0(e)}$ at the point of position vector $\mathbf{R}$ (not to be confused with the end-to-end distance) in the external coordinate system is given by

$$\mathbf{v}^{0(e)} = g\mathbf{e}_x\mathbf{e}_y\cdot\mathbf{R} \qquad (22)$$

with g the time-independent rate of shear. The unperturbed flow $\mathbf{v}^0(x)$ at the contour point x in the molecular coordinate system may then be expressed as

$$\mathbf{v}^0(x) = g[\mathbf{v}_0^{\,0} + \boldsymbol{\Omega}^0 \times \mathbf{r}_0(x) + \tfrac{1}{2}\mathbf{m}\cdot\mathbf{r}_0(x)] \qquad (23)$$

where

$$\mathbf{v}_0^{\,0} = \mathbf{A}\cdot\mathbf{e}_x\mathbf{e}_y\cdot\mathbf{R}_0 \qquad (24)$$
$$\boldsymbol{\Omega}^0 = -\tfrac{1}{2}\mathbf{A}\cdot\mathbf{e}_z \qquad (25)$$
$$\mathbf{m} = \mathbf{A}\cdot(\mathbf{e}_x\mathbf{e}_y + \mathbf{e}_y\mathbf{e}_x)\cdot\mathbf{A}^T \qquad (26)$$

For this shear flow, the frictional force and torque $\mathbf{F}_\upsilon$ and $\mathbf{T}_{0,\upsilon}$ may be obtained from equations in the OB approximation corresponding to eq 30 and 31 of ref 10. The results are

$$\mathbf{F}_\upsilon = g(-\Xi_t\cdot\mathbf{v}_0^{\,0} - \Xi_{0,c}{}^T\cdot\boldsymbol{\Omega}^0 + \tfrac{1}{2}\boldsymbol{\Gamma}_{0,F}:\mathbf{m})$$
$$\mathbf{T}_{0,\upsilon} = g(-\Xi_{0,c}\cdot\mathbf{v}_0^{\,0} - \Xi_{0,r}\cdot\boldsymbol{\Omega}^0 + \tfrac{1}{2}\boldsymbol{\Gamma}_{0,T}:\mathbf{m}) \qquad (27)$$

where $\boldsymbol{\Gamma}_{0,F}$ and $\boldsymbol{\Gamma}_{0,T}$ are the shear force and shear torque triadics, respectively, defined by

$$\mathbf{\Gamma}_{0,\mathrm{F}} = -4\pi\eta_0 L \int_{-1}^{1} \mathbf{\Psi}_1(x)\mathbf{r}_0(x)\,\mathrm{d}x$$

$$\mathbf{\Gamma}_{0,\mathrm{T}} = -2\pi\eta_0 L^2 \int_{-1}^{1} \mathbf{\Psi}_2(x)^{\mathrm{T}}\mathbf{r}_0(x)\,\mathrm{d}x \tag{28}$$

with $\mathbf{\Psi}_1$ and $\mathbf{\Psi}_2$ the solutions of the integral eq 13. Since the matrix $\mathbf{m}$ is symmetric, it is convenient to use, instead of $\mathbf{\Gamma}_{0,\mathrm{F}}$, a triadic $\mathbf{\Gamma}'_{0,\mathrm{F}}$ defined by

$$\mathbf{\Gamma}'_{0,\mathrm{F}} = \tfrac{1}{2}(\mathbf{\Gamma}_{0,\mathrm{F}} + \mathbf{\Gamma}_{0,\mathrm{F}}{}^{\dagger}) \tag{29}$$

and similarly $\mathbf{\Gamma}'_{0,\mathrm{T}}$, where the superscript dagger indicates the post transpose. In what follows, we omit the prime. Then, for the rigid arc rod, the nonzero components of $\mathbf{\Gamma}_{0,\mathrm{F}}$ and $\mathbf{\Gamma}_{0,\mathrm{T}}$ are $\Gamma_{0,\mathrm{F},ijk}$ with ijk = 111, 122, 212, 221, 313, and 331 and $\Gamma_{0,\mathrm{T},ijk}$ with ijk = 123, 132, 231, 213, 312, and 321.[16] The asymptotic solutions for these components are given in the Appendix. If we actually carry out calculations, we find that $\Gamma_{0,\mathrm{F},122} = 0$ and $\Gamma_{0,\mathrm{F},133} \neq 0$. However, we have put $\Gamma_{0,\mathrm{F},133} = 0$ (so that $\Gamma_{0,\mathrm{F},122} \neq 0$) by the use of the indeterminacy principle.[16]

Now, if we recall that for the present case, the required solution for the distribution function P is a steady-state one $P(\Theta)$ independent of $\mathbf{R}_0$ and t and if we substitute eq 28 into eq 7, then eq 5 reduces to

$$\mathbf{L}^{\mathrm{T}}\cdot\mathbf{D}_{\mathrm{r}}\cdot\mathbf{L}P(\Theta) = -\mathcal{L}_{v}P(\Theta) \tag{30}$$

with

$$\mathcal{L}_{v} = g[-\mathbf{L}^{\mathrm{T}}\cdot\mathbf{\Omega}^0 + (2k_{\mathrm{B}}T)^{-1}\mathbf{L}^{\mathrm{T}}\cdot(\mathbf{D}_{0,\mathrm{c}}\cdot\mathbf{\Gamma}_{0,\mathrm{F}} + \mathbf{D}_{\mathrm{r}}\cdot\mathbf{\Gamma}_{0,\mathrm{T}}):\mathbf{m}] \tag{31}$$

where we have used eq 9 for $\mathbf{D}_{0,\mathrm{c}}{}^{\mathrm{T}}$. Note that $\mathbf{v}_0{}^0$ does not appear in eq 30.

Following the procedure used previously,[10] we find the solution of eq 30, retaining terms of $\mathcal{O}(g)$,

$$8\pi^2 P(\Theta) = 1 + (2/5)^{1/2} i\pi g\{a_0[\mathcal{D}_2{}^{20}(\Theta) - \mathcal{D}_2{}^{(-2)0}(\Theta)] + a_2[\mathcal{D}_2{}^{22}(\Theta) - \mathcal{D}_2{}^{(-2)2}(\Theta) + \mathcal{D}_2{}^{2(-2)}(\Theta) - \mathcal{D}_2{}^{(-2)(-2)}(\Theta)]\} \tag{32}$$

where i is the imaginary unit, $\mathcal{D}_l{}^{mj}(\Theta)$ are the normalized Wigner functions as defined by eq 15 of ref 17, and a_0 and a_2 are defined by

$$a_0 = (b_2c_1 - 2b_3c_2)/(b_1b_2 - 2b_3{}^2)$$

$$a_2 = (b_1c_2 - b_3c_1)/(b_1b_2 - 2b_3{}^2) \tag{33}$$

with

$$b_1 = 3(D_{\mathrm{r},11} + D_{\mathrm{r},22})$$

$$b_2 = D_{\mathrm{r},11} + D_{\mathrm{r},22} + 4D_{\mathrm{r},33}$$

$$b_3 = \frac{6^{1/2}}{2}(D_{\mathrm{r},11} - D_{\mathrm{r},22}) \tag{34}$$

and

$$c_1 = -6^{1/2}(k_{\mathrm{B}}T)^{-1}(D_{\mathrm{r},11}\Gamma_{0,\mathrm{T},123} - D_{\mathrm{r},22}\Gamma_{0,\mathrm{T},213} - D_{0,\mathrm{c},23}\Gamma_{0,\mathrm{F},313})$$

$$c_2 = -(k_{\mathrm{B}}T)^{-1}(D_{\mathrm{r},11}\Gamma_{0,\mathrm{T},123} + D_{\mathrm{r},22}\Gamma_{0,\mathrm{T},213} - 2D_{\mathrm{r},33}\Gamma_{0,\mathrm{T},312} + D_{0,\mathrm{c},23}\Gamma_{0,\mathrm{F},313} - 2D_{0,\mathrm{c},32}\Gamma_{0,\mathrm{F},212}) \tag{35}$$

Then substitution of eq 27 and 32 into eq 8 leads to

$$\mathbf{U}_0 = g(\mathbf{v}_0{}^0 + \mathbf{v}_0{}^1)$$

$$\mathbf{\Omega} = g(\mathbf{\Omega}^0 + \mathbf{\Omega}^1) \tag{36}$$

where

$$\mathbf{v}_0{}^{1\mathrm{T}} = (v_1m_{11} + v_2m_{22}, v_3m_{12}, v_4m_{13}) \tag{37}$$

$$\mathbf{\Omega}^{1\mathrm{T}} = \omega(m_{23}, m_{13}, m_{12}) \tag{38}$$

with m_{ij} (i, j = 1, 2, 3) the ij element of the matrix $\mathbf{m}$ defined by eq 26 and with

$$v_1 = -(2k_{\mathrm{B}}T)^{-1}D_{0,\mathrm{t},11}\Gamma_{0,\mathrm{F},111}$$

$$v_2 = -(2k_{\mathrm{B}}T)^{-1}D_{0,\mathrm{t},11}\Gamma_{0,\mathrm{F},122}$$

$$v_3 = -(k_{\mathrm{B}}T)^{-1}(D_{0,\mathrm{t},22}\Gamma_{0,\mathrm{F},232} + D_{0,\mathrm{c},32}\Gamma_{0,\mathrm{T},312}) + 2a_2D_{0,\mathrm{c},32}$$

$$v_4 = -(k_{\mathrm{B}}T)^{-1}(D_{0,\mathrm{t},33}\Gamma_{0,\mathrm{F},313} + D_{0,\mathrm{c},23}\Gamma_{0,\mathrm{T},213}) + \left(\frac{6^{1/2}}{2}a_0 - a_2\right)D_{0,\mathrm{c},23} \tag{39}$$

and

$$\omega = -(k_{\mathrm{B}}T)^{-1}D_{\mathrm{r},11}\Gamma_{0,\mathrm{T},123} - \left(\frac{6^{1/2}}{2}a_0 + a_2\right)D_{\mathrm{r},11} \tag{40}$$

m_{ij} may be expanded in terms of $\mathcal{D}_l{}^{mj}$ as before,[10] but we do not give the results.

If we evaluate $\mathbf{v}_0{}^1$ and $\mathbf{\Omega}^1$ with the asymptotic solutions given in the Appendix, we find that both do not vanish. In other words, the center of mass of the arc rod does not acquire an instantaneous translational velocity equal to the local unperturbed solvent velocity $g\mathbf{v}_0{}^0$ nor does it rotate uniformly about the z axis with the angular velocity $-g/2$. For the skew body in a shear flow, in general, the instantaneous translational velocity of the center of mass in the external coordinate system depends on its orientation, and the assumption of its uniform rotation around the center of mass or registance[18] is not valid. (Note that $\mathbf{\Omega}$ is independent of the location of the point 0.) Then there arises the question: Is there a point 0 such that $\mathbf{v}_0{}^1$ vanishes? We leave this problem unsolved in the present paper.

Now the intrinsic viscosity $[\eta]$ of the rigid arc rod may be written in the form

$$[\eta] = -\frac{N_{\mathrm{A}}L}{2M\eta_0 g}\int_{-1}^{1}\mathbf{e}_x\cdot\langle\mathbf{A}^{\mathrm{T}}\cdot\mathbf{r}_0(x)\mathbf{f}(x)\cdot\mathbf{A}\rangle\cdot\mathbf{e}_y\,\mathrm{d}x \tag{41}$$

where the angular brackets denote the orientational average, N_{A} is the Avogadro number, M is the molecular weight, and $\mathbf{f}(x)$ is the frictional force per unit contour length exerted on the solvent at the contour point x and is the solution of the integral equation

$$\frac{L}{16\pi\eta_0}\int_{-1}^{1}\mathbf{K}(x,y)\cdot\mathbf{f}(y)\,\mathrm{d}y = \mathbf{U}_0 + \mathbf{\Omega}\times\mathbf{r}_0(x) - \mathbf{v}^0(x) \tag{42}$$

with $\mathbf{U}_0$ and $\mathbf{\Omega}$ being given by eq 36. Note that $\mathbf{f}$ and $[\eta]$ are independent of the location of the point 0.

If the average in eq 41 is first taken, it reduces to

$$[\eta] = \frac{2\pi N_{\mathrm{A}}L^3}{45M}(F_0 + F_1) \tag{43}$$

with

$$F_0 = \frac{9}{2L}\int_{-1}^{1}[\tfrac{1}{3}(2r_{0,3}\psi_{31} - r_{0,2}\psi_{21} - r_{0,1}\psi_{11}) + r_{0,3}\psi_{22} + r_{0,2}\psi_{32} + r_{0,3}\psi_{13} + r_{0,1}\psi_{33} + r_{0,2}\psi_{14} + r_{0,1}\psi_{24} + r_{0,1}\psi_{15} - r_{0,2}\psi_{25}]\,\mathrm{d}x$$

$$F_1 = -\frac{9}{L}\int_{-1}^{1}[(v_1 - v_2)\psi_{15} - \tfrac{1}{3}(v_1 + v_2)\psi_{11} + v_3\psi_{24} + v_4\psi_{33} + \omega(r_{0,2}\psi_{32} - r_{0,3}\psi_{22} + r_{0,3}\psi_{13} - r_{0,1}\psi_{33} + r_{0,1}\psi_{24} - r_{0,2}\psi_{14})]\,\mathrm{d}x \tag{44}$$

where $\psi_{ij}(x)$ (i = 1, 2, 3; j = 1, 2, ..., 5) is the ij element of the 3 × 5 matrix $\psi(x)$, which is the solution of the integral equation

$$\int_{-1}^{1} \mathbf{K}(x,y)\cdot\psi(y)\,dy = 2L^{-2}\mathbf{M}(x) \quad (45)$$

with $\mathbf{M}(x)$ the 3 × 5 matrix defined by

$$\mathbf{M} = \begin{bmatrix} -r_{0,1} & 0 & r_{0,3} & r_{0,2} & r_{0,1} \\ -r_{0,2} & r_{0,3} & 0 & r_{0,1} & -r_{0,2} \\ 2r_{0,3} & r_{0,2} & r_{0,1} & 0 & 0 \end{bmatrix} \quad (46)$$

We note that F_0 is the contribution from only the Ω^0 part of Ω, i.e., the uniform rotation around the center of mass with the angular velocity $-g/2$, and F_1 is the correction to it arising from $\mathbf{v}_0^1$ and Ω^1, the $\mathbf{v}_0^0$ part of $\mathbf{U}_0$ making no contribution.

We evaluate v_i and ω with the asymptotic solutions given in the Appendix and solve the integral eq 45 by the Legendre polynomial expansion method to find the asymptotic forms of F_0 and F_1

$$F_0 = (\ln p)^{-1} - \left(2\ln 2 - \frac{25}{12}\right)(\ln p)^{-2} - \frac{13\chi^2}{480}\left[(\ln p)^{-1} - \left(2\ln 2 - \frac{127}{65}\right)(\ln p)^{-2}\right]$$

$$F_1 = -\frac{5\chi^2}{192}\left[(\ln p)^{-1} - \left(2\ln 2 + \frac{1}{2}\right)(\ln p)^{-2}\right] \quad (47)$$

Thus we obtain for $[\eta]$ of the bending arc rod

$$[\eta] = \frac{2\pi N_A L^3}{45M}\left[\ln p + 2\ln 2 - \frac{25}{12} + \frac{17\langle\chi^2\rangle}{320}\left(\ln p + 2\ln 2 - \frac{871}{255}\right)\right]^{-1} \quad (48)$$

where we have taken the equilibrium rigid-body ensemble average by replacing χ^2 in eq 47 by $\langle\chi^2\rangle$. Naturally the result with $\chi = 0$ agrees with the corresponding exact one previously obtained for the straight rod.[6,19] We note that Ω^1 does not contribute to the asymptotic solution for $[\eta]$ given by eq 48.

Finally, for comparison, we evaluate $[\eta]$ with the preaveraged kernel in the Kirkwood–Riseman approximation, which we designate by $[\eta]^P$. It is given, as in ref 12, by

$$[\eta]^P = \frac{N_A L}{M}\int_{-1}^{1} \psi(x)^T\cdot\mathbf{r}_0(x)\,dx \quad (49)$$

where $\psi(x)$ is the solution of the integral equation

$$\int_{-1}^{1} \langle f_{10}(|x-y|)\rangle \psi(y)\,dy = \pi L^{-1}\mathbf{r}_0(x) \quad (50)$$

Application of the Legendre polynomial expansion method leads to the asymptotic solution

$$[\eta]^P = \frac{\pi N_A L^3}{24M}\left[\ln p + 2\ln 2 - \frac{7}{3} + \frac{\langle\chi^2\rangle}{30}\left(\ln p + 2\ln 2 - \frac{97}{80}\right)\right]^{-1} \quad (51)$$

The result with $\chi = 0$ agrees with the corresponding one previously obtained for the straight rod.[7,19]

VI. Bounds

Recently, Fixman[4] has derived general expressions for upper and lower variational bounds for the polymer transport coefficients on the basis of bead models. From them, it can readily be verified that D_t given by eq 19 and 21 are a lower bound and an upper bound, respectively, to the exact D_t of the bending arc rod, which we designate by D_t^L and D_t^U ($\equiv D_t^P$), respectively, while $[\eta]$ given by eq 48 is an upper bound, which we designate by $[\eta]^U$, if the arc rod is replaced by an equivalent discrete chain as done previously[20] and if it is then noted that $\langle \mathbf{V}^a\cdot\mathbf{H}^{-1}\cdot(\mathbf{U}-\mathbf{V}^a)\rangle_e = 0$ in eq 3.13 of ref 4, corresponding to Wilemski and Tanaka's eq 2.21 of ref 2. In this section, we evaluate a lower bound $[\eta]^L$ to $[\eta]$ from Fixman's formula and also D_t and $[\eta]$ in the Zimm version.[1] According to Fixman,[4] this D_t is another lower bound and this $[\eta]$ is another upper bound. We designate them by $D_t^{L(Z)}$ and $[\eta]^{U(Z)}$, respectively.

A. Lower Bound $[\eta]^L$. The lower bound $[\eta]^L$ for the bending arc rod may be evaluated from eq 5.9 of ref 4 with $(8\pi\eta_0)^{-1}\mathbf{K}(x,y)$ and $(8\pi\eta_0)^{-1}\langle\mathbf{K}(x,y)\rangle$ in place of $\mathbf{H}$ and $\mathbf{H}^a$, respectively, and with replacement of the sums by integrals; i.e.

$$[\eta]^L = 2[\eta]^P - \frac{9N_A L^2}{8\pi M}\int_{-1}^{1}dx\int_{-1}^{1}dy\ \langle\psi(x)^T\cdot\mathbf{m}^T\cdot\mathbf{K}(x,y)\cdot\mathbf{m}\cdot\psi(y)\rangle \quad (52)$$

where $[\eta]^P$ is given by eq 51 and $\psi(x)$ is the solution of the integral eq 50. Application of the Legendre polynomial expansion method leads to

$$[\eta]^L = \frac{19\pi N_A L^3}{480M}\left[\ln p + 2\ln 2 - \frac{275}{114} + \frac{29\langle\chi^2\rangle}{1140}\left(\ln p + 2\ln 2 - \frac{5261}{2755}\right)\right]^{-1} \quad (53)$$

B. Zimm Bounds $D_t^{L(Z)}$ and $[\eta]^{U(Z)}$. Let $\mathbf{F}^{(e)}$ and $\mathbf{T}_0^{(e)}$ be the frictional force and torque for the rigid arc rod in the external coordinate system, respectively, and let $\mathbf{U}_0^{(e)}$ and $\Omega^{(e)}$ be the instantaneous translational and angular velocities in the same system, respectively. $\mathbf{U}_0^{(e)}$ and $\Omega^{(e)}$ are related to $\mathbf{F}^{(e)}$ and $\mathbf{T}_0^{(e)}$ by the equations

$$\mathbf{U}_0^{(e)} = (k_BT)^{-1}(\mathbf{A}^T\cdot\mathbf{D}_{0,t}\cdot\mathbf{A}\cdot\mathbf{F}^{(e)} + \mathbf{A}^T\cdot\mathbf{D}_{0,c}^T\cdot\mathbf{A}\cdot\mathbf{T}_0^{(e)})$$

$$\Omega^{(e)} = (k_BT)^{-1}(\mathbf{A}^T\cdot\mathbf{D}_{0,c}\cdot\mathbf{A}\cdot\mathbf{F}^{(e)} + \mathbf{A}^T\cdot\mathbf{D}_r\cdot\mathbf{A}\cdot\mathbf{T}_0^{(e)}) \quad (54)$$

In Zimm's algorithm for D_t or the sedimentation coefficient, we have

$$\mathbf{F}^{(e)T} = (0, 0, F_z)$$

$$\mathbf{T}_0^{(e)T} = (T_{0,x}, T_{0,y}, 0)$$

$$\mathbf{U}_0^{(e)T} = (U_{0,x}, U_{0,y}, U_{0,z})$$

$$\Omega^{(e)T} = (0, 0, \Omega_z) \quad (55)$$

Now, regarding eq 54 with eq 55 as equations for $T_{0,x}$, $T_{0,y}$, $\mathbf{U}_0^{(e)}$, and Ω_z with F_z being known, we solve them to find

$$\langle U_{0,z}\rangle = (k_BT)^{-1}D_t^{L(Z)}F_z \quad (56)$$

with

$$D_t^{L(Z)} = \tfrac{1}{3}k_BT\langle \mathrm{Tr}\ \Xi_t^{-1}\rangle + \langle(\mathbf{A}^T\cdot\mathbf{D}_r^{-1}\cdot\mathbf{D}_{0,c}\cdot\mathbf{A})_{zz}^2/(\mathbf{A}^T\cdot\mathbf{D}_r^{-1}\cdot\mathbf{A})_{zz}\rangle \quad (57)$$

The first term on the right-hand side of eq 57 is equal to D_t with neglect of the coupling between translational and rotational motions, and the second term is the correction to it arising from the consideration of the rotation only about the z axis. With the asymptotic solutions given in the Appendix, we have, from eq 57

$$D_t^{L(Z)} = \frac{k_B T}{3\pi\eta_0 L}\left[\ln p + 2\ln 2 - 1 - \frac{\langle\chi^2\rangle}{48}(\ln p + 2\ln 2 - 4)\right] \quad (58)$$

In Zimm's algorithm for $[\eta]$, the center of mass of the rigid arc rod acquires a translational velocity equal to $\mathbf{U}_0 = g(\mathbf{v}_0^0 + \mathbf{v}_0')$, where $\mathbf{v}_0'$ is determined from the condition that the total frictional force $\mathbf{F}$ vanishes, and it rotates about the z axis with the angular velocity $-g/2$. $\mathbf{v}_0'$ is easily found to be

$$\mathbf{v}_0' = -\tfrac{1}{2}\Xi_t^{-1}\cdot\boldsymbol{\Gamma}_{0,F}:\mathbf{m} \quad (59)$$

With the asymptotic solutions given in the Appendix, we have $\mathbf{v}_0' = \mathbf{v}_0^1$. Thus $[\eta]^{U(Z)}$ is identical with $[\eta]$ given by eq 48.

VII. Discussion

With the asymptotic solutions obtained for $p \gg 1$ and $\chi \ll 1$ in the preceding sections, we have $D_t^{L(Z)} < D_t^L < D_t^P = D_t^U$ and $[\eta]^L < [\eta]^P < [\eta]^U = [\eta]^{U(Z)}$, where D_t^L and $[\eta]^U$ are given by eq 19 and 48, respectively. Let D_t and $[\eta]$ be the exact mean translational diffusion coefficient and intrinsic viscosity of the bending arc rod. Then it follows that

$$\frac{D_t^P - D_t}{D_t} < \frac{D_t^P - D_t^L}{D_t^L} = \frac{\langle\chi^2\rangle}{96}\left[1 - \frac{13}{6}(\ln p)^{-1}\right] \quad (60)$$

$$\frac{|[\eta]^P - [\eta]|}{[\eta]} < \frac{[\eta]^U - [\eta]^L}{[\eta]^L} = \frac{7}{57}\left\{1 - \frac{400}{133}(\ln p)^{-1} - \frac{101\langle\chi^2\rangle}{399}\left[1 - \frac{96353}{28785}(\ln p)^{-1}\right]\right\} \quad (61)$$

For the rigid straight rod, we have $D_t^P = D_t$ and $[\eta]^U = [\eta]$, so that

$$\frac{[\eta] - [\eta]^P}{[\eta]} = \frac{1}{16}\left[1 - \frac{15}{4}(\ln p)^{-1}\right] \quad \text{(straight rod)} \quad (62)$$

Now it is well-known that for the long straight rod, the Kirkwood formula for D_t^P gives the correct result. As seen from eq 60, D_t^P is a good approximation also for the long, weakly bending rod since $\langle\chi^2\rangle$ is small. It is also well-known that for the straight rod, $[\eta]^P/[\eta] = {}^{15}/_{16}$ in the limit $p \to \infty$, and ${}^{15}/_{16} < [\eta]^P/[\eta] \simeq 1$ over a range of finite p.[10] Equation 61 indicates that the relative difference between $[\eta]^P$ and $[\eta]$ is smaller for the weakly bending rod than for the straight rod. Thus it may be concluded that the effects of the preaveraging are rather small near the rod limit, as was expected. The present analysis may be considered to guarantee the validity of our equations for the transport coefficients for wormlike (or helical wormlike) cylinder models that have been derived with the preaveraged Oseen tensor and constructed to well extrapolate to the exact expressions for straight rods (or spheroid cylinders),[10,21] as far as the flexibility is not very large. For chains with intermediate or large flexibility, the effects are, of course, not negligible and are still difficult to examine completely.

Appendix

The asymptotic solutions for the nonzero components of the diffusion tensors $\mathbf{D}_{0,t}$, $\mathbf{D}_{0,c}$, and $\mathbf{D}_r$ are given by

$$D_{0,t,11} = \frac{k_B T}{4\pi\eta_0 L}\left[\ln 4p - \frac{1}{2} + \frac{\chi^2}{24}\left(\ln 4p - \frac{10}{3}\right)\right]$$

$$D_{0,t,22} = \frac{k_B T}{4\pi\eta_0 L}\left(\ln 4p - \frac{1}{2} + \frac{\chi^2}{144}\right)$$

$$D_{0,t,33} = \frac{k_B T}{2\pi\eta_0 L}\left[\ln 4p - \frac{3}{2} - \frac{\chi^2}{24}\left(\ln 4p - \frac{23}{6}\right)\right]$$

$$D_{0,c,23} = \frac{k_B T\chi}{4\pi\eta_0 L^2}\left(\ln 4p - \frac{17}{6}\right)$$

$$D_{0,c,32} = -\frac{5k_B T}{2\pi\eta_0 L^2\chi}\left(1 - \frac{853\chi^2}{8400}\right)$$

$$D_{r,11} = \frac{3k_B T}{\pi\eta_0 L^3}\left[\ln 4p - \frac{11}{6} + \frac{\chi^2}{20}\left(\ln 4p - \frac{103}{60}\right)\right]$$

$$D_{r,22} = \frac{3k_B T}{\pi\eta_0 L^3}\left[\ln 4p - \frac{11}{6} + \frac{\chi^2}{8}\left(\ln 4p - \frac{251}{75}\right)\right]$$

$$D_{r,33} = \frac{180k_B T}{\pi\eta_0 L^3\chi^2}\left(\ln 4p - \frac{71}{30}\right) \quad (A1)$$

The asymptotic solutions for the nonzero components of the shear force triadic $\boldsymbol{\Gamma}_{0,F}$ and the shear torque triadic $\boldsymbol{\Gamma}_{0,T}$ are given by

$$\Gamma_{0,F,111} = -\frac{1}{6}\pi\eta_0 L^2\chi\left[(\ln p)^{-1} - \left(2\ln 2 - \frac{2}{3}\right)(\ln p)^{-2}\right]$$

$$\Gamma_{0,F,122} = -\frac{1}{6}\pi\eta_0 L^2\chi\left[(\ln p)^{-1} - \left(2\ln 2 - \frac{1}{3}\right)(\ln p)^{-2}\right]$$

$$\Gamma_{0,F,212} = \Gamma_{0,F,221} = -\frac{1}{36}\pi\eta_0 L^2\chi(\ln p)^{-2}$$

$$\Gamma_{0,F,331} = \Gamma_{0,F,313} = \frac{1}{12}\pi\eta_0 L^2\chi\left[(\ln p)^{-1} - \left(2\ln 2 - \frac{1}{6}\right)(\ln p)^{-2}\right]$$

$$\Gamma_{0,T,123} = \Gamma_{0,T,132} = \frac{1}{6}\pi\eta_0 L^3\left\{(\ln p)^{-1} - \left(2\ln 2 - \frac{11}{6}\right)\times (\ln p)^{-2} - \frac{\chi^2}{20}\left[(\ln p)^{-1} - \left(2\ln 2 - \frac{39}{20}\right)(\ln p)^{-2}\right]\right\}$$

$$\Gamma_{0,T,231} = \Gamma_{0,T,213} = -\frac{1}{6}\pi\eta_0 L^3\left\{(\ln p)^{-1} - \left(2\ln 2 - \frac{11}{6}\right)\times (\ln p)^{-2} - \frac{2\chi^2}{15}\left[(\ln p)^{-1} - \left(2\ln 2 - \frac{121}{96}\right)(\ln p)^{-2}\right]\right\}$$

$$\Gamma_{0,T,312} = \Gamma_{0,T,321} = -\frac{1}{360}\pi\eta_0 L^3\chi^2\left[(\ln p)^{-1} - \left(2\ln 2 - \frac{71}{30}\right)(\ln p)^{-2}\right] \quad (A2)$$

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Translational Diffusion of Polymer Chains in Dilute Solution†

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ABSTRACT: The equations describing the diffusive motion of polymer chains in the rigid-body approximation have been examined in detail, and the situation in which the molecule has zero angular velocity is considered. It is treated in the Oseen approximation with strong and weak hydrodynamic interactions between chain segments and using the preaveraged Oseen tensor, which is unambiguously defined. The case of weak hydrodynamic interactions, independent of preaveraging, relates to the treatment of Kirkwood and Riseman and results in the Kirkwood equation. Thus, three cases are considered, the Oseen, the Kirkwood–Riseman (K–R) (weak interactions), and the preaveraged Oseen, and are used to interpret experimental diffusion coefficients of short polymethylene chains. The interpretation is in terms of ζ/f, where ζ is the segmental friction coefficient and f is the molecular friction coefficient, and uses the equation $\zeta/f = \langle {}^1/_3 \,\mathrm{Tr}\,(\mathbf{K}^{-1})\rangle_{\mathrm{conf}}$. $\mathbf{K}^{-1}$ is a tensor related to the Oseen tensor $\mathbf{T}_{ij}$ for all pairs of segments i and j. $\langle ... \rangle_{\mathrm{conf}}$ denotes configurational average, which was found by evaluating $\mathbf{K}^{-1}$ for samples of chain configurations generated for the longer chains by Monte Carlo methods using Metropolis sampling and for the shorter chains by using all possible configurations. The chain model used was the rotational-isomeric-state model due to Flory and co-workers. All three cases can be used to interpret the experimental data if ζ is allowed to vary approximately in proportion to the effective bond length of the chain. Approximate extrapolation of the differences between the K–R and Oseen values of ζ/f to infinite chain length indicates that the former underestimates f by 6–8% for the unperturbed PM chain in benzene at 25 °C. The underestimation is in broad agreement with previous correlations of experimental data on unperturbed poly(methyl methacrylate) and polystyrene chains of high molar mass and with calculations of Garcia de la Torre and Freire using related polymethylene chain models.

1. Introduction

The translational diffusion coefficient (D) of a solute molecule in dilute solution is a measure of the differential thermal motion of the center of mass of the molecule relative to that of the surrounding solvent molecules. For a macromolecular solute, where there are many centers of interaction with solvent, the only tractable method of predicting D is to assume that the solvent is a continuum characterized by its viscosity η_0. The centers of interaction or friction centers are then taken as segments of the polymer chain based on skeletal atoms or groups of skeletal atoms and are conventionally assumed to be spherical. The establishment of a relationship between D and the segment distribution of the molecule is a dynamical problem, with D characterizing the lowest normal mode of the molecule. Thus, D could be calculated from a molecular dynamics simulation incorporation hydrodynamic interactions between friction centers. In practice, this is not possible at present, as solving the equations of motion for a macromolecule requires a prohibitive amount of computer time.

Alternative approaches to the problem assume that the molecule diffuses as an instantaneously rigid body and compute D for an ensemble of such rigid bodies. Implicit here is the assumption that center-of-mass motion, as measured in classical boundary-spreading experiments, is separable from the internal modes of the molecule.[1] It is also assumed that the equilibrium segment distribution of the molecule is not perturbed by the solvent flow. Thus the mechanisms by which configurations interconvert,[1] which are important for the higher dynamical modes of macromolecule, are not considered, but the result of the interconversions (the ensemble of configurations) is employed. Historically, this was the approach used by Kirkwood and Riseman[2] and Kirkwood,[3] resulting in the well-known equation[3] for the diffusion coefficient of a polymer molecule of x segments

$$D = \frac{kT}{x\zeta} + \frac{kT}{6\pi\eta_0}\frac{[R^{-1}]}{x^2} \qquad (1)$$

where ζ is the segmental friction coefficient, η_0 is the viscosity of the solvent, and $[R^{-1}] = \sum_i\sum_j\langle r_{ij}^{-1}\rangle$, $i \neq j$, with $\langle r_{ij}^{-1}\rangle$ denoting the average reciprocal separation of segments i and j. At high molar mass, there is little flow of solvent through the molecular domain, and the first term in eq 1 (the free-draining term) can be neglected. However, at low molar mass, correlations of measured diffusion coefficients for several polymer chains in a variety of

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