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Efforts toward an Exact Kirkwood–Riseman Theory of the Intrinsic Viscosity

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ABSTRACT: A new, formally exact formula is derived for the steady-flow Newtonian intrinsic viscosity of a polymer chain. The result is expressed as a sum of two terms: One is an upper bound for the exact intrinsic viscosity and requires the evaluation of only two kinds of equilibrium moments of the friction tensor. The other involves the velocities of the chain segments and vanishes only if the molecule rotates as a whole around its center of mass with the rotational component of the solvent flow. The upper bound formula is found to give the known exact results for the rigid rod, polygon, and dumbbell models and to be a very good approximation for nearly rigid dumbbells. By explicit calculation for the stiff dumbbell model it is also shown that the coupling between chain flexibility and hydrodynamic interactions causes segment motions to deviate from the rotational component of the solvent flow.

1. Introduction

In their pioneering theory of the steady-flow intrinsic viscosity, Kirkwood and Riseman[1] made two important simplifications. First, ignoring the Brownian motion of the polymer chain, they set the velocities of the chain segments (or beads) equal to the rotational component of the solvent flow field. Second, they preaveraged the Oseen hydrodynamic interaction tensor over all conformations of the molecule. It is now known from the work of Gotlib and Svetlov[2] that these two approximations are not independent. Rigid-body rotation in steady laminar flow at low shear rates follows from the solution to the polymer diffusion equation, regardless of the chain model considered, when the diffusion tensor is preaveraged. However, when preaveraging is avoided, segment velocities generally can deviate from the rotational part of the solvent flow. This will be explicitly demonstrated in section 3 for the stiff elastic dumbbell model. It is also implicit in the earlier work of Pyun and Fixman[3] on flexible coils.

The work reported here was motivated by the desire to develop an exact Kirkwood–Riseman theory for the steady-flow Newtonian intrinsic viscosity. Our goal was to avoid the two above approximations and obtain a formula involving only equilibrium averages of quantities

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independent of specific solutions to the polymer diffusion equation. All such model-dependent information would instead be contained in the potential of mean force that determines the equilibrium distribution function used in the averaging. Such a model-free formulation might be valuable, for example, in Monte Carlo calculations for complex models not conducive to analytical treatment.

We have been only partly successful in our efforts. The formula we present is a sum of two types of terms. One class depends on the segment velocities, which, at present, must still be obtained by solving a model-specific polymer diffusion equation. In a recent calculation, Zimm[4] assumed that rigid-body motion is a sufficiently accurate description of the chain dynamics in low shear rate flow. However, as noted above and illustrated in section 3, flexible molecules with nonpreaveraged hydrodynamic interactions do not strictly conform to rigid-body rotation, even at low shear rate. The remaining class of terms in our formula involves only certain equilibrium moments of the chain friction tensor and, therefore, do satisfy our goal. These terms, in fact, are exact for certain rigid bodies of revolution, as will be shown in Appendix A. Our general conclusions are similar to those reached by Iwata.[5]

In the next section, we derive a general expression for the intrinsic viscosity in terms of the chain friction tensor. In section 3, the stiff elastic dumbbell model is examined in detail for small deviations from rigidity. Deviations from the rigid-body solution for both the relative bead velocity and the intrinsic viscosity are explicitly calculated. Finally, in two appendices, the solution for rigid bodies of revolution is presented, and analytical implementations of the "exact" rigid-body formula are illustrated for the rigid polygon and rigid rod models.

2. Derivation

We begin with a familiar prescription[6] for the intrinsic viscosity $[\eta]$:

$$[\eta] = -\frac{N_A}{M\eta_0 g^2}\sum_j \langle \mathbf{F}_j \cdot \mathbf{v}_j{}^0 \rangle \qquad (2.1)$$

Here N_A is Avogadro's number, M is the polymer molecular weight, η_0 is the solvent viscosity, g is the shear rate, $\mathbf{v}_j{}^0$ is the externally imposed solvent flow, and $\mathbf{F}_j$ is the frictional force exerted on the fluid by segment j. The angle brackets denote an average taken with respect to the nonequilibrium chain configuration distribution function f. Many of our subsequent equations, including our principal result, will involve only averages with the equilibrium distribution function f_e; these will be indicated by the subscript e: $\langle\ \rangle_e$.

The force $\mathbf{F}_j$ arises from the motion of the segment relative to the surrounding solvent

$$\mathbf{F}_j = \zeta_j(\mathbf{u}_j - \mathbf{v}_j) \qquad (2.2)$$

Here $\mathbf{u}_j$ and $\mathbf{v}_j$ are the velocities of the jth segment and the solvent at the segment's position $\mathbf{r}_j$ $[=(x_j,y_j,z_j)]$ and ζ_j is the friction coefficient. The velocity field $\mathbf{v}_j$ differs from the value $\mathbf{v}_j{}^0$ it would have in the absence of the polymer molecule because of hydrodynamic interactions between chain segments. The difference is a sum of extra velocity fields produced by the forces exerted on the solvent by all other segments and is given by

$$\mathbf{v}_j - \mathbf{v}_j{}^0 = \sum_{k\neq j} \mathbf{T}_{jk}\cdot\mathbf{F}_k \qquad (2.3)$$

Here $\mathbf{T}_{jk}$ is a hydrodynamic interaction tensor to be determined from the Navier–Stokes equation. A particular formula for $\mathbf{T}_{jk}$ is not required at present. On combining eq 2.2 and 2.3, we can eliminate the actual velocity field from $\mathbf{F}_j$:[7]

$$\mathbf{F}_j = \sum_k \zeta_{jk}\cdot(\mathbf{u}_k - \mathbf{v}_k{}^0) \qquad (2.4)$$

Here the friction tensor, ζ_{jk}, is related to the diffusion tensor $\mathbf{D}_{jk}$ by the equations

$$\zeta_{jk} = k_B T(\mathbf{D}^{-1})_{jk} \qquad (2.5a)$$

$$\mathbf{D}_{jk} = k_B T(\zeta_j{}^{-1}\delta_{jk}\boldsymbol{I} + \mathbf{T}_{jk}) \qquad (2.5b)$$

where k_B is Boltzmann's constant and T is the absolute temperature.

To simplify the remaining presentation in this section, we adopt a matrix notation: every vector is to be understood as a column vector whose elements are 3-vectors referring to individual segments of the polymer, and $\mathbf{D}$ and ζ are square matrices whose elements are $\mathbf{D}_{ij}$ and ζ_{ij}, respectively.

Equation 2.4 can now be written as

$$\mathbf{F} = \zeta\cdot(\mathbf{u} - \mathbf{v}^0) \qquad (2.6)$$

An alternative equation for $\mathbf{F}$ can be found by balancing the frictional, entropic, and intramolecular forces acting on the chain elements:

$$\mathbf{F} = -k_B T\vec{\nabla}\ln\rho \qquad (2.7)$$

where

$$\rho = f/f_e \qquad (2.8)$$

With the continuity equation, eq 2.6 and 2.7 determine the Smoluchowski equation that describes the chain Brownian motion in configuration space. For steady flow, this can be written compactly as

$$\vec{\nabla}^T\cdot\mathbf{D}\cdot f_e\vec{\nabla}\rho = \vec{\nabla}^T\cdot(\mathbf{v}^0\rho f_e) \qquad (2.9)$$

where superscript T denotes the transpose of a matrix.

Now we consider a simple shear flow, $\mathbf{v}^0$, which is decomposed[6] into irrotational and rotational components, $\mathbf{v}^i$ and $\mathbf{v}^r$,

$$\mathbf{v}^0 = \mathbf{v}^i + \mathbf{v}^r \qquad (2.10)$$

with the elements

$$\mathbf{v}_j{}^0 = gy_j\mathbf{e}_x \qquad (2.11a)$$

$$\mathbf{v}_j{}^i = (g/2)(y_j\mathbf{e}_x + x_j\mathbf{e}_y) \qquad (2.11b)$$

$$\mathbf{v}_j{}^r = (g/2)(y_j\mathbf{e}_x - x_j\mathbf{e}_y) \qquad (2.11c)$$

Here $\mathbf{e}_x$ and $\mathbf{e}_y$ are unit vectors in the laboratory-fixed Cartesian Frame. Using eq 2.10, we rewrite eq 2.1 as

$$[\eta] = -N_A(M\eta_0 g^2)^{-1}[\langle\mathbf{F}^T\cdot\mathbf{v}^i\rangle + \langle\mathbf{F}^T\cdot\mathbf{v}^r\rangle] \qquad (2.12)$$

Next, we examine the second term more closely. With the aid of eq 2.7 and 2.11c and following an integration by parts, we find

$$g^{-1}\langle\mathbf{F}^T\cdot\mathbf{v}^r\rangle = \langle k_B T g^{-1}(\vec{\nabla}^T\ln f_e)\cdot\mathbf{v}^r\rangle$$

The quantity being averaged on the right-hand side of this equation is just the z component of the torque induced by intramolecular forces among chain elements, and it must vanish for any chain conformation. Hence we have

$$\langle\mathbf{F}^T\cdot\mathbf{v}^r\rangle = 0 \qquad (2.13)$$

With eq 2.6 we may now rewrite eq 2.12 as

$$[\eta] = N_A(M\eta_0 g^2)^{-1}[\langle(\mathbf{v}^i)^T\cdot\zeta\cdot\mathbf{v}^i\rangle - \langle(\mathbf{v}^i)^T\cdot\zeta\cdot\mathbf{v}'\rangle] \qquad (2.14)$$

where

$$\mathbf{v}' = \mathbf{u} - \mathbf{v}^{\mathrm{r}} \tag{2.15}$$

The second term of eq 2.14 may be expressed in a symmetric form in the limit of $g \to 0$. To show this, we first multiply eq 2.9 by ρ and integrate over all chain coordinates in order to find the relation

$$\langle(\vec{\nabla}^{\mathrm{T}}\rho)\cdot\mathbf{D}\cdot\vec{\nabla}\rho\rangle_{\mathrm{e}} = \langle(\mathbf{v}^0)^{\mathrm{T}}\cdot\vec{\nabla}\rho\rangle \tag{2.16}$$

Next, combining eq 2.6 and 2.7, we obtain

$$\mathbf{D}\cdot\vec{\nabla}\rho = -(\mathbf{u} - \mathbf{v}^0)\rho \tag{2.17}$$

so that eq 2.16 now becomes

$$\langle(\vec{\nabla}^{\mathrm{T}}\rho)\cdot(\mathbf{v}^0 - \mathbf{u})\rangle = \langle(\vec{\nabla}^{\mathrm{T}}\rho)\cdot\mathbf{v}^0\rangle \tag{2.18}$$

With the aid of eq 2.7, eq 2.18 implies that

$$\langle(\vec{\nabla}^{\mathrm{T}}\rho)\cdot\mathbf{u}\rangle = \langle\rho\mathbf{F}^{\mathrm{T}}\cdot\mathbf{u}\rangle = 0 \tag{2.19}$$

Next, for small g we expand ρ as

$$\rho = 1 + gf_1 + \mathcal{O}(g^2) \tag{2.20}$$

It is now apparent from eq 2.6, 2.7, 2.11, and 2.20 that both $\mathbf{F}$ and $\mathbf{u}$ are proportional to g in lowest order. Equation 2.19 can now be seen to have the limiting property

$$\lim_{g\to 0} g^{-2}\langle\rho\mathbf{F}^{\mathrm{T}}\cdot\mathbf{u}\rangle = \lim_{g\to 0} g^{-2}\langle\mathbf{F}^{\mathrm{T}}\cdot\mathbf{u}\rangle_{\mathrm{e}} = 0$$

and because, to lowest order in g, $g^{-2}\langle\mathbf{F}^{\mathrm{T}}\cdot\mathbf{u}\rangle_{\mathrm{e}}$ is independent of g, we may conclude that

$$\langle\mathbf{F}^{\mathrm{T}}\cdot\mathbf{u}\rangle_{\mathrm{e}} = 0 \tag{2.21}$$

for small g.

Restricting our attention to the small g limit, we next subtract eq 2.13 from eq 2.21 and use eq 2.6 and 2.15 to find

$$\langle\mathbf{F}^{\mathrm{T}}\cdot\mathbf{v}'\rangle_{\mathrm{e}} = \langle(\mathbf{v}' - \mathbf{v}^{\mathrm{i}})^{\mathrm{T}}\cdot\boldsymbol{\zeta}\cdot\mathbf{v}'\rangle_{\mathrm{e}} = 0 \tag{2.22}$$

Hence, we see that

$$\langle(\mathbf{v}^{\mathrm{i}})^{\mathrm{T}}\cdot\boldsymbol{\zeta}\cdot\mathbf{v}'\rangle_{\mathrm{e}} = \langle(\mathbf{v}')^{\mathrm{T}}\cdot\boldsymbol{\zeta}\cdot\mathbf{v}'\rangle_{\mathrm{e}} \tag{2.23}$$

Use of eq 2.23 enables us to write eq 2.14 in the symmetric form

$$[\eta] = N_{\mathrm{A}}(M\eta_0 g^2)^{-1}[\langle(\mathbf{v}^{\mathrm{i}})^{\mathrm{T}}\cdot\boldsymbol{\zeta}\cdot\mathbf{v}^{\mathrm{i}}\rangle_{\mathrm{e}} - \langle(\mathbf{v}')^{\mathrm{T}}\cdot\boldsymbol{\zeta}\cdot\mathbf{v}'\rangle_{\mathrm{e}}] \tag{2.24}$$

for the zero shear rate intrinsic viscosity. Only equilibrium averages are required here becuase both $\mathbf{v}^{\mathrm{i}}$ and $\mathbf{v}'$ are proportional to g in lowest order. Furthermore, from eq 2.15, 2.17, and 2.20 we find, for small g, that $\mathbf{v}'$ depends only on $\mathbf{v}^{\mathrm{i}}$ and f_1

$$\mathbf{v}' = \mathbf{u} - \mathbf{v}^{\mathrm{r}} = \mathbf{v}^{\mathrm{i}} - g\mathbf{D}\cdot\vec{\nabla}f_1$$

and from eq 2.9 and 2.20 that f_1, in turn, is fully determined by just $\mathbf{v}^{\mathrm{i}}$

$$g\vec{\nabla}^{\mathrm{T}}\cdot\mathbf{D}\cdot f_{\mathrm{e}}\vec{\nabla}f_1 = \mathbf{v}^{\mathrm{i}}\cdot\vec{\nabla}f_{\mathrm{e}}$$

Thus, the zero shear rate intrinsic viscosity is independent of whether simple shear flow or irrotational flow is chosen, a point exploited long ago by Kramers.[8]

The favorable feature of eq 2.24 is its clean separation into two symmetric terms. Because of this symmetry we can derive an upper bound to the exact intrinsic viscosity for any model. The second term of eq 2.24 is quadratic in $\mathbf{v}'$ and can be transformed into diagonal form by an orthogonal matrix, $\mathbf{O}$. The *correct* friction tensor must have positive eigenvalues λ_i; otherwise its inverse, the diffusion tensor, would contain singularities. Therefore, the second sum is nonnegative

$$\langle\mathbf{v}'\cdot\boldsymbol{\zeta}\cdot\mathbf{v}'\rangle = \sum_i\langle\lambda_i\mathbf{V}_i^2\rangle \geq 0 \tag{2.25}$$

where

$$\mathbf{V}_i = \sum_j \mathbf{O}_{ij}{}^{\mathrm{T}}\mathbf{v}_j' \tag{2.26}$$

The equality in eq 2.25 holds if and only if $\mathbf{V}_i = \mathbf{0} = \mathbf{v}_j'$ for all i and j, i.e., if

$$\mathbf{u} = \mathbf{v}^{\mathrm{r}} \tag{2.27}$$

In this case the first term in eq 2.24 remains as an upper bound:

$$[\eta] = \frac{N_{\mathrm{A}}}{2M\eta_0}\sum_{j,k}[\langle y_j\zeta_{jk}{}^{xx}y_k\rangle_{\mathrm{e}} + \langle y_j\zeta_{jk}{}^{xy}x_k\rangle_{\mathrm{e}}] \tag{2.28}$$

This result is clearly model free in the sense mentioned in the Introduction. Under preaveraging of the hydrodynamic interactions, eq 2.27 is not only exact, but the off-diagonal components of the friction tensor, ζ^{xy}, are absent, and eq 2.28 simplifies to a previously known result.[2,9,10] However, it should be noted that the preaveraged result is not always an upper bound to the exact one. For complete neglect of the hydrodynamic interactions, the friction tensor is diagonal in j and k, $\zeta_{jk} = \zeta_j\delta_{jk}\mathbf{I}$, and eq 2.28 reduces further to a slightly more general form of the early result of Kramers[8] and Debye.[11]

In Appendix A, using Kirkwood's approximate expressions for the diffusion tensor and segment velocities, we show that eq 2.27 and 2.28 are valid for all rigid bodies of revolution whose translational and rotational motions are not coupled. Further, in Appendix B, avoiding Kirkwood's approximations, we demonstrate that eq 2.28 gives exact results for the rigid polygon and rigid rod models. In the next section, we show that eq 2.28 is also exact for the rigid dumbbell model.

3. Stiff Elastic Dumbbell

The simplicity of the dumbbell model has long made it a favorite candidate for analysis.[12-16] Here, an exact perturbative analysis in terms of the reciprocal force constant of the stiff elastic dumbbell model (Fraenkel[12] dumbbell) will enable us to assess the importance of the segment velocity dependent term in our prescription for $[\eta]$.

In terms of the position vector $\mathbf{r}$ for the relative separation of the two beads with identical friction constants, the dumbbell diffusion equation for steady flow reads

$$\vec{\nabla}\cdot\mathbf{D}_{\mathrm{r}}\cdot[\vec{\nabla}f + (k_{\mathrm{B}}T)^{-1}(\vec{\nabla}U)f] = \vec{\nabla}\cdot\mathbf{v}^0 f \tag{3.1}$$

where $\mathbf{v}^0 = \mathbf{v}_1{}^0 - \mathbf{v}_2{}^0$ and U is the dumbbell potential energy. With the modified Oseen tensor,[17] the diffusion tensor $\mathbf{D}_{\mathrm{r}}$ can be expressed as

$$\mathbf{D}_{\mathrm{r}} = D[\mathbf{I} - (h/r)(\mathbf{I} + \mathbf{e}_{\mathrm{r}}\mathbf{e}_{\mathrm{r}}) - (2/3)(ha^2/r^3)(\mathbf{I} - 3\mathbf{e}_{\mathrm{r}}\mathbf{e}_{\mathrm{r}})] \tag{3.2}$$

where $\mathbf{e}_{\mathrm{r}}$ is the radial unit vector, a is the bead radius,

$$h = k_{\mathrm{B}}T/(4\pi\eta_0 D)$$

and

$$D = 2k_{\mathrm{B}}T/\zeta$$

After specializing to shear flow, $\mathbf{v}^0 = y\mathbf{e}_x$, substituting for f the expansion

$$f = f_{\mathrm{e}}(1 + gf_1 + ...)$$

and converting to spherical coordinates, we find that the angular dependence of eq 3.1 may be satisfied by writing

$$f_1 = \chi(r)\sin^2\theta\sin 2\phi \tag{3.3}$$

To lowest order in g, $\chi(r)$ satisfies the following equation, which is still valid for any dumbbell model:

$$D\left\{\left[\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}r^2-(k_\mathrm{B}T)^{-1}\frac{\mathrm{d}U}{\mathrm{d}r}\right]p(r)\frac{\mathrm{d}}{\mathrm{d}r}-\frac{6q(r)}{r^2}\right\}\chi(r)=-\frac{r}{2k_\mathrm{B}T}\frac{\mathrm{d}U}{\mathrm{d}r}\quad(3.4)$$

where

$$p(r)=1-\frac{2h}{r}+\frac{4ha^2}{3r^3}$$

and

$$q(r)=1-\frac{h}{r}-\frac{2ha^2}{3r^3}$$

The potential energy for the stiff elastic dumbbell is given by

$$U={}^1\!/_2\kappa(r-b)^2\equiv{}^1\!/_2k_\mathrm{B}T\xi^2$$

where κ is the force constant and b is the dumbbell equilibrium length. For very large κ, the dumbbell will execute low-amplitude oscillations about its equilibrium length b, and inverse powers of r may be expanded in terms of the deviation $r - b$

$$r-b=\nu\xi$$

where ν is the stiffness parameter

$$\nu^2=k_\mathrm{B}T/\kappa b^2$$

Equation 3.4 can then be solved perturbatively in terms of the Hermite polynomials $H_n(\xi)$. The solution is

$$\chi=(b^2/4D)\{c_{00}+\nu c_{11}H_1(\xi)+\nu^2(c_{20}+c_{22}H_2(\xi))+\nu^3(c_{31}H_1(\xi)+c_{33}H_3(\xi))+\ldots\}\quad(3.5)$$

where

$$H_1(\xi)=\xi\qquad H_2(\xi)=\xi^2-1\qquad H_3(\xi)=\xi^3-3\xi$$

$$c_{00}=1/(1-\lambda-\alpha)$$

$$c_{11}=2/(1-2\lambda+2\alpha)$$

$$c_{20}=c_{00}[1+(\lambda+6\alpha)c_{00}-(\lambda+3\alpha)c_{11}]$$

$$2c_{22}=c_{11}[1-(\lambda-3\alpha)c_{11}]$$

$$c_{31}=3c_{33}-3c_{11}[(\lambda+3\alpha)c_{00}+(\lambda-3\alpha)c_{11}]$$

$$3c_{33}={c_{11}}^2[(\lambda-3\alpha)^2c_{11}-3\alpha]$$

and finally

$$\lambda=\frac{h}{b}\qquad\alpha=\frac{2\lambda}{3}\left(\frac{a}{b}\right)^2\quad(3.6)$$

Next, the relative bead velocity **u** may be calculated from the equation

$$\mathbf{u}=\mathbf{v}^0-g\mathbf{D}_\mathrm{r}\cdot\vec{\nabla}f_1\quad(3.7)$$

After decomposing $\mathbf{v}^0$ into rotational and irrotational flows, we obtain from eq 3.2, 3.3, and 3.7

$$\mathbf{u}-\mathbf{v}^\mathrm{r}=g\mu_r\sin^2\theta\sin2\phi\mathbf{e}_r+g\mu_\theta(\sin2\theta\sin2\phi\mathbf{e}_\theta+2\sin\theta\cos2\phi\mathbf{e}_\phi)\quad(3.8)$$

where

$$\mu_r=\frac{r}{2}-Dp(r)\frac{\mathrm{d}\chi}{\mathrm{d}r}\quad(3.9)$$

$$\mu_\theta=\frac{r}{4}-Dq(r)\frac{\chi}{r}\quad(3.10)$$

Using eq 3.5 with eq 3.9 and 3.10, we find to order ν^2 that

$$\mu_r=3\nu^2\Lambda b\quad(3.11)$$

and

$$8\mu_\theta/b=-4\nu\Lambda H_1(\xi)+\nu^2\{4\Lambda+[2(2\lambda+9\alpha)c_{00}+(\lambda-15\alpha)c_{11}+(\lambda-3\alpha)^2{c_{11}}^2]H_2(\xi)\}\quad(3.12)$$

where

$$2\Lambda=(\lambda+3\alpha)c_{00}+(\lambda-3\alpha)c_{11}$$

From these equations it is easy to see that the nonzero velocity deviation, $\mathbf{u}-\mathbf{v}^\mathrm{r}$, arises from the coupling between the dumbbell's flexibility and the hydrodynamic interactions. Clearly, in either the free-draining limit (λ, $\alpha = 0$) or the rigid limit (ν, $\xi = 0$), the deviation vanishes and the dumbbell just follows the rotational part of the solvent flow. If the velocity deviation (to order ν) is transformed back to the laboratory Cartesian system, we find the expression

$$\mathbf{u}-\mathbf{v}^\mathrm{r}=-2\Lambda(r-b)r^{-3}[(yr^2-2x^2y)\mathbf{e}_x+(xr^2-2xy^2)\mathbf{e}_y-2xyz\mathbf{e}_z]$$

The existence of x and y components is perhaps not surprising, but the presence of a small z component to the dumbbell velocity is interesting. A loose interpretation of this is that the dumbbell "wobbles" slightly in the z direction as it tumbles in the x–y plane.

To finish the calculation of $[\eta]$, we note that $\mathbf{D}_\mathrm{r}$ is diagonal in the spherical coordinate system, so its inverse is easily computed. After averaging over the angular dependence, eq 2.24 and 3.8 give

$$[\eta]=\frac{N_\mathrm{A}kT}{15M\eta_0D}\left[\langle r^2/p(r)\rangle_r+\frac{3}{2}\langle r^2/q(r)\rangle_r-4\langle{\mu_r}^2/p(r)\rangle_r-24\langle{\mu_\theta}^2/q(r)\rangle_r\right]\quad(3.13)$$

and only equilibrium averages with respect to r remain.

Aside from the specific representation used for $\mathbf{D}_\mathrm{r}$, this equation is a general result valid for all dumbbell models. A particular model dependence enters through the functions μ_r and μ_θ, defined in eq 3.9 and 3.10, and through the equilibrium distribution function f_e.

With χ given exactly by eq 3.5 to order ν^3, $[\eta]$ can be calculated exactly to order ν^4 from eq 3.13. Rather than perform the tedious expansions and averages needed to explicitly display $[\eta]$ through terms of order ν^4, we chose to calculate $[\eta]$ by numerically evaluating the required averages. By so doing, some higher order terms arising from r^{-1} and r^{-3} are retained, but these should contribute negligibly for the small values of ν used.

In Figures 1 and 2, $[\eta]$ is plotted as a function of the dimensionless hydrodynamic interaction strength parameter λ for three values of the stiffness parameter ν. Also shown are the results for the rigid rotation approximation $[\eta]^\mathrm{R}$, given by the first two terms of eq 3.13, and for preaveraged hydrodynamic interaction, $[\eta]^\mathrm{P}$:

$$[\eta]^\mathrm{P}=\frac{N_\mathrm{A}k_\mathrm{B}T}{6M\eta_0D}\frac{\langle r^2\rangle_\mathrm{e}}{1-(4h/3)\langle1/r\rangle_\mathrm{e}}\quad(3.14)$$

Both $[\eta]^\mathrm{P}$ and $[\eta]^\mathrm{R}$ were calculated numerically and are exact to all orders in ν. Figure 1 contains the results for the usual Oseen tensor, and Figure 2 those for the modified Oseen tensor. In the calculations, Stokes' law for the no-slip boundary condition was used to evaluate the bead friction coefficient. The dimensionless hydrodynamic interaction strength parameter λ can then be expressed as

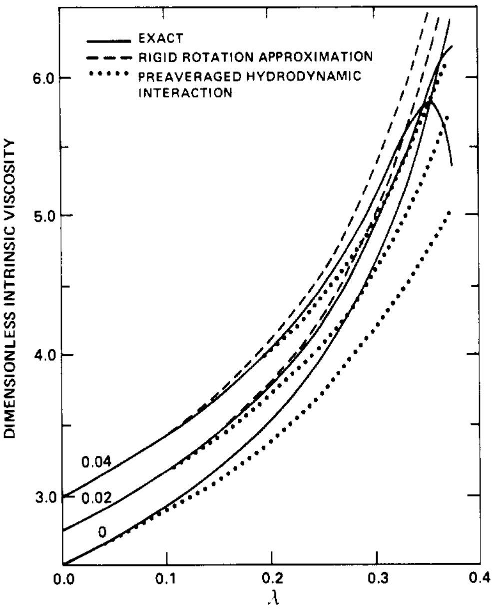

Figure 1. Intrinsic viscosity of the stiff dumbbell for the Oseen tensor plotted vs. hydrodynamic interaction parameter λ. The dimensionless quantity $15M\eta_0 D[\eta]/(N_A b^2 k_B T)$ is shown for three values of the stiffness parameter: $\nu^2 = 0$, 0.02, and 0.04.

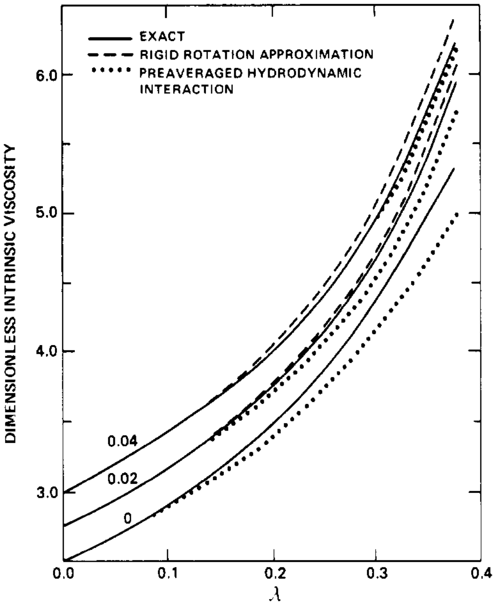

Figure 2. Intrinsic viscosity of the stiff dumbbell for the modified Oseen tensor plotted vs. hydrodynamic interaction parameter λ. The dimensionless quantity $15M\eta_0 D[\eta]/(N_A b^2 k_B T)$ is shown for three values of the stiffness parameter: $\nu^2 = 0$, 0.02, and 0.04.

$\lambda = (3/4)(a/b)$. The plots are carried out to $\lambda = 3/8$ which corresponds to the touched-bead limit.

As can be seen from eq 3.11, 3.12, and 3.13, $[\eta]^{\mathrm{R}}$ is an exact result for $\nu = 0$, i.e., in the rigid dumbbell limit. For nonzero values of ν, $[\eta]^{\mathrm{R}}$ clearly serves as a good approximation for the exact intrinsic viscosity. Some other features of the results can be noted. First, the calculations of $[\eta]$ and $[\eta]^{\mathrm{R}}$ using the modified Oseen tensor lie much closer to $[\eta]^{\mathrm{P}}$ than do the results based on the Oseen tensor. Second, the character of the rigid-rotation approximation as an upper bound is evident. Finally, the exact curve for $\nu^2 = 0.04$ displays a maximum near the touched-bead limit when the Oseen tensor is used. For larger values of ν (results not shown), $[\eta]$ actually becomes negative near the touched-bead limit. The problem is probably due to a combination of poor convergence of the series expansion of χ and inadequate treatment of hydrodynamics at small bead separations. This latter difficulty is ameliorated somewhat by the use of the modified Oseen tensor, but even in this case for large enough values of ν the abnormal behavior appears.

4. Summary

We have presented a new formally exact formula, eq 2.24, for the steady-flow Newtonian intrinsic viscosity. This result requires the evaluation of several equilibrium averages involving the chain friction tensor and, in general, the velocities of the chain segments. If the molecule rotates rigidly with the rotational component of the solvent flow, the velocity dependence disappears and the formula reduces to eq 2.28, which is an upper bound to the exact intrinsic viscosity for any polymer model. This latter result is couched solely in terms of certain equilibrium moments of the chain friction tensor. The only dynamical information needed for its implementation is the specific coordinate dependence of the chain friction tensor, which is also a prerequisite for other methods of calculating the intrinsic viscosity. This model-free character makes eq 2.28 a desirable candidate for use in Monte Carlo calculations that avoid preaveraging the hydrodynamic interactions. In addition, eq 2.28 is exact for all rigid bodies of revolution, if Kirkwood's approximate formula for the chain diffusion tensor is assumed. Independent of this latter approximation, eq 2.28 was also shown to give exact results for the rigid dumbbell, rigid polygon, and rigid rod models.

Our calculations for the stiff elastic dumbbell model showed that eq 2.28 is a very good approximation for the exact intrinsic viscosity near the rigid dumbbell limit. They also explicitly demonstrated that the motion of a flexible dumbbell in the presence of hydrodynamic interaction does not strictly conform to the rotational component of the shear flow. This deviation is caused by the coupling between the dumbbell's flexibility and the hydrodynamic interacitons. In general, this type of behavior is to be expected for any flexible molecule when hydrodynamic interactions are not preaveraged.

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Appendix A. Solution for Rigid Bodies of Revolution

This analysis is most readily carried out by using the general Riemann tensor formalism of Kirkwood.[6,18,19] For molecules with cylindrically symmetric distributions of chain segments, Hearst[20] has calculated the components of the covariant and contravariant metric tensors, $g_{\alpha\beta}$ and $g^{\alpha\beta}$, and the diffusion tensor $D^{\alpha\beta}$. His results may be adopted with only minor modifications. We replace his notation (l_k, m_k, n_k) for the molecular coordinates of the kth chain segment with (X_k, Y_k, Z_k); his quantities α and β will be designated A and B, where

$$A = \sum_l X_l^2 = \sum_l Y_l^2 \tag{A.1}$$

$$B = \sum_l Z_l^2 \tag{A.2}$$

and averages appearing in his equations for α, β, and $D^{\alpha\beta}$ are no longer necessary because the chain segments are rigidly distributed. The molecular coordinates are related to the laboratory-fixed reference system with unit vectors $\mathbf{e}_x$, $\mathbf{e}_y$, and $\mathbf{e}_z$ by means of the Euler angles θ, ϕ, ψ as defined by Hirschfelder, Curtiss, and Bird.[21] With this choice, θ and ϕ can be identified as the usual polar and azimuthal angles, respectively, in a spherical coordinate system. Hearst used another definition, but this does not affect the formal expressions for $g_{\alpha\beta}$, $g^{\alpha\beta}$, and $D^{\alpha\beta}$.

For steady, shear flow prescribed by eq 2.10a, the generalized diffusion equation with no external or "soft" internal forces can be obtained from eq 32.25 of Yamakawa:[6]

$$Lf = -Qf \tag{A.3}$$

where

$$L = D^{\theta\theta}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \left(\frac{1}{\sin\theta}\frac{\partial}{\partial\phi} - \cot\theta\frac{\partial}{\partial\psi}\right)^2\right] + D_\perp\frac{\partial^2}{\partial\psi^2} \tag{A.4}$$

$$Q = (g\delta/4)\left[6\sin^2\theta\sin 2\phi - \sin 2\theta\sin 2\phi\frac{\partial}{\partial\theta} - 2(\cos 2\phi - \delta^{-1})\frac{\partial}{\partial\phi} + 2\cos\theta\cos 2\phi\frac{\partial}{\partial\psi}\right] \tag{A.5}$$

$$\delta = (B - A)/(B + A) \tag{A.6}$$

and

$$D_\perp = D^{\psi\psi} - \cot^2\theta D^{\theta\theta} \tag{A.7}$$

The next step is to evaluate the velocities of the chain segments $\mathbf{u}_l$ with the formula[6]

$$\mathbf{u}_l = \sum_\alpha u^\alpha\frac{\partial\boldsymbol{R}_l}{\partial q^\alpha} = \sum_\alpha\left(v^{0\alpha} - \sum_\beta D^{\alpha\beta}\frac{\partial\ln f}{\partial q^\beta}\right)\frac{\partial\boldsymbol{R}_l}{\partial q^\alpha} \tag{A.8}$$

The contravariant components w^α of a vector $\mathbf{w}_l$ are readily evaluated with the two defining equations

$$w^\alpha = \sum_\beta g^{\alpha\beta}w_\beta \tag{A.9}$$

$$w_\beta = \sum_l \mathbf{w}_l\cdot\frac{\partial\boldsymbol{R}_l}{\partial q^\beta} \tag{A.10}$$

The position vector $\mathbf{R}_l$ can be written in terms of the molecular coordinates and the laboratory-fixed unit vectors as

$$\mathbf{R}_l = (X_l, Y_l, Z_l)\mathbf{E}\begin{pmatrix}\mathbf{e}_x\\ \mathbf{e}_y\\ \mathbf{e}_z\end{pmatrix} \tag{A.11}$$

where the Euler matrix $\mathbf{E}$ is given by

$$\mathbf{E} = \begin{pmatrix}\cos\theta\cos\phi\cos\psi - \sin\phi\sin\psi & \cos\theta\sin\phi\cos\psi - \cos\phi\sin\psi & -\sin\theta\cos\psi\\ -\cos\theta\cos\phi\sin\psi - \sin\phi\cos\psi & -\cos\theta\sin\phi\sin\psi + \cos\phi\cos\psi & \sin\theta\sin\psi\\ \sin\theta\cos\phi & \sin\theta\sin\phi & \cos\theta\end{pmatrix} \tag{A.12}$$

From eq 2.11a and A.10 to A.12, we then find the relationship

$$v_\beta{}^0 = g\left[A\left(E_{12}\frac{\partial E_{11}}{\partial q^\beta} + E_{22}\frac{\partial E_{21}}{\partial q^\beta}\right) + B\left(E_{32}\frac{\partial E_{31}}{\partial q^\beta}\right)\right] \tag{A.13}$$

After further algebra we obtain the results

$$\begin{aligned} v^{0\theta} &= (g\delta/4)\sin 2\theta\sin 2\phi\\ v^{0\phi} &= (g/2)(\delta\cos 2\phi - 1)\\ v^{0\psi} &= -(g\delta/2)\cos\theta\cos 2\phi \end{aligned} \tag{A.14}$$

To lowest order in g, the solution to eq A.3 does not depend on ψ and is given by

$$4\pi f = 1 + (3g\delta\tau/2)\sin^2\theta\sin 2\phi + \mathcal{O}(g^2) \tag{A.15}$$

where

$$\tau^{-1} = 6D^{\theta\theta} \tag{A.16}$$

A straightforward computation of u^α then produces the results

$$\begin{aligned} u^\theta &= 0\\ u^\phi &= -g/2\\ u^\psi &= 0 \end{aligned} \tag{A.17}$$

To interpret these results, we use eq 2.11c and A.10 to A.13 to express $v_\beta{}^{\mathrm{r}}$ as

$$v_\beta{}^{\mathrm{r}} = \frac{1}{2}v_\beta{}^0 - \frac{g}{2}\left[A\left(E_{11}\frac{\partial E_{12}}{\partial q^\beta} + E_{21}\frac{\partial E_{22}}{\partial q^\beta}\right) + B\left(E_{31}\frac{\partial E_{32}}{\partial q^\beta}\right)\right]$$

and with eq A.9 we find

$$v^{\mathrm{r}\theta} = 0$$

$$v^{\mathrm{r}\phi} = -g/2$$

$$v^{\mathrm{r}\psi} = 0$$

Equality of the contravariant components u^α and $v^{\mathrm{r}\alpha}$ confirms the expected result

$$\mathbf{u}_l = \mathbf{v}_l{}^{\mathrm{r}} \tag{A.18}$$

Thus the rigid body of revolution strictly follows the rotational stream lines of the shear flow, and the second term of eq 2.24 vanishes, leaving us with the exact result, eq 2.28.

A possible limitation on the results of this section may arise because the theory is based on approximate expressions for the velocity components u^α (shown in parentheses in eq A.8) and for $D^{\alpha\beta}$:

$$D^{\alpha\beta} = k_{\mathrm{B}}T(g^{\alpha\beta}/\zeta + T^{\alpha\beta}) \tag{A.19}$$

where $T^{\alpha\beta}$ is a contravariant component of the Oseen tensor. Both equations were orginally thought by Kirkwood to be exact but were subsequently shown to be approximate.[19,22]

The consequences of these approximations have never been systematically explored, but the few calculations that have been done with Kirkwood's theory give results that are either exact (at least asymptotically for large N) or very close to exact when compared with results obtained with other methods. For example, for the rigid rod the Kirkwood theory yields the right answers for the translational[23,24] and rotational diffusion[24,25] constants. On the other hand, the correct translational diffusion coefficient for a rigid polygon calculated by Zwanzig[26] and by Paul and Mazo[27] is smaller by the factor 11/12 than the value obtained with the Kirkwood approximation. Paul and Mazo[27] have studied the rigid polygon model in detail, avoiding the use of Kirkwood's tensor formalism. Their work is thus a valuable reference point for assessing further consequences of Kirkwood's approximations. Comparing with their results, it can be seen that the diffusion equations are identical and that the formal relationships derivable from eq A.19

$$\cot^2\theta D^{\theta\theta} = \cos^2\theta D^{\phi\phi} = -\cos\theta D^{\phi\psi} = D^{\psi\psi} - D_\perp \qquad \text{(A.20)}$$

are also correct. Furthermore, $D^{\theta\theta}$ agrees asymptotically with its counterpart $D_{\|\mathrm{R}}$ in the Paul–Mazo work, but the component $D_\perp$ differs from the Paul–Mazo value for $D_{\perp\mathrm{R}}$ by the factor 3/4:

$$D_\perp = {}^3\!/_4 D_{\perp\mathrm{R}} \qquad (N \gg 1)$$

Thus, although the Kirkwood approximation preserves the form of the diffusion equation and gives the correct relationships among the $D^{\alpha\beta}$, eq A.20, the expression for $D^{\psi\psi}$ is incorrect since it depends on $D_\perp$.

The latter discrepancy does not affect the Newtonian intrinsic viscosity. To lowest order in g, f does not depend on ψ, so $[\eta]$ depends at most on $D^{\theta\theta}$ or τ (eq A.16). In fact, it is only the frequency dependence of $[\eta]$ that is determined by $D^{\theta\theta}$; the steady-flow Newtonian intrinsic viscosity is not. For example, to compute $[\eta]$ one may use the method of Kirkwood and Auer,[28] which, in essence, is the calculation of $\mathbf{u}_l$ using the approximate eq A.8. This calculation actually depends only on the form of f and on the relationships expressed in eq A.20 but not on the specific value of $D^{\theta\theta}$, which eventually cancels out at zero frequency.

In summary, it is the form of f (eq A.15) and of the relationships in eq A.20 that guarantee the validity of eq A.18 when the velocities $\mathbf{u}_l$ are calculated with the approximate eq A.8. The particular values of any of the nonzero $D^{\alpha\beta}$ play no role in achieving this result. In the present treatment, then, the correctness of eq 2.28 for rigid bodies of revolution depends on the adequacy of eq A.8 for this class of models. We have not made any further mathematical analysis of this point.

A final note of caution concerning eq A.18 is warranted. Although this result is intuitively pleasing in that one expects fully symmetric rigid bodies to follow the rotational component of the shear flow, the present theory takes no account of possible coupling between translational and rotational motion. Because of this, the conclusions expressed here are likely to hold only for rigid bodies of revolution that are also symmetric with respect to a plane, perpendicular to the axis of revolution, that bisects the molecule. For a less symmetric body, e.g., a funnel or cone, hydrodynamic interactions undoubtedly produce translation–rotation coupling[29] which results in motions more complicated than those described by eq A.18.

Appendix B. Rigid Polygon and Rigid Rod

Analytical methods of implementing eq 2.28 are illustrated here for the rigid plane polygon and the rigid rod. These methods do not involve the use of Kirkwood's approximate formula for the chain diffusion tensor.

(i) Rigid Plane Polygon. The N beads of radius a and friction constant ζ are arranged in a regular plane polygon with sides of length b and radius $R = b(2\sin\phi/2)^{-1}$, where $\phi = 2\pi/N$. The analysis is easier to perform using molecular coordinates $\mathbf{R}_l$ with components X_l, Y_l, and Z_l. The x unit vector $\boldsymbol{\delta}_1$ of the molecular coordinate system points at bead N; the z unit vector $\boldsymbol{\delta}_3$ is orthogonal to the plane of the polygon, and the y unit vector $\boldsymbol{\delta}_2$ lies in the plane and completes the right-handed orthonormal set. The Euler matrix $\mathbf{E}$ relates the molecular frame unit vectors to those of the laboratory frame: $\boldsymbol{\delta} = \mathbf{E}\mathbf{e}$. We thus transform eq 2.28 to read

$$[\eta] = N_\mathrm{A}(2M\eta_0)^{-1}\Omega \qquad \text{(B.1)}$$

where

$$\Omega = \sum_{l,s=1}^{N}\sum_{\alpha,\beta=1}^{3}\langle(X_lE_{13} + Y_lE_{23})E_{\alpha2}\zeta_{ls}{}^{\alpha\beta}[E_{\beta2}(X_sE_{13} + Y_sE_{23}) + E_{\beta3}(X_sE_{12} + Y_sE_{22})]\rangle_\mathrm{e} \qquad \text{(B.2)}$$

The key to this calculation is the exact inversion of $\mathbf{D}$ using the method of Paul and Mazo (PM)[27] as modified slightly by Yamakawa and Yamaki (YY).[30] We also slightly extend the PM result for $[\eta]$ by employing for $\mathbf{D}_{ij}$ the positive definite form of Rotne and Prager[17a] and Yamakawa.[17b]

To proceed we perform the Euler angle averages in eq B.2, substitute for X_l $(=R\cos l\phi)$ and Y_l $(=R\sin l\phi)$, and express ζ_{ls} as

$$\zeta_{ls} = \mathbf{W}^{-1}\mathbf{B}(l)\zeta_{ls}''\mathbf{B}(s)\mathbf{W}$$

where

$$\zeta_{ls}'' = \zeta(\mathbf{I} + \zeta\mathbf{T}')_{ls}{}^{-1}$$

$\mathbf{W}$ and $\mathbf{B}$ are defined by YY and $\mathbf{T}_{ls}'$ is displayed in eq 14 of YY. Upon introducing the Fourier expansion of ζ_{ls}''

$$\zeta_{ls}'' = N\sum_k \exp[ik(l-s)\phi]\hat{\zeta}(k)$$

and after performing lengthy algebra, one can express eq B.2 as

$$\Omega = (NR^2/60)\{6[\hat{\zeta}_{11}(-2) + \hat{\zeta}_{22}(2)] + 3[\hat{\zeta}_{33}(-1) + \hat{\zeta}_{33}(1)] + \hat{\zeta}_{11}(0) + \hat{\zeta}_{22}(0) + \hat{\zeta}_{12}(0) + \hat{\zeta}_{21}(0)\} \qquad \text{(B.3)}$$

The nonzero elements of $\hat{\zeta}(k)$ are found to be

$$\hat{\zeta}_{11} = D_k{}^{-1}[1 + (3\lambda/2)(S_{k+1} - (\sigma^2/18)T_{k+1})]$$

$$\hat{\zeta}_{22} = D_k{}^{-1}[1 + (3\lambda/2)(S_{k-1} - (\sigma^2/18)T_{k-1})]$$

$$\hat{\zeta}_{33} = [1 + \lambda(S_k + (\sigma^2/6)T_k)]^{-1}$$

$$\hat{\zeta}_{12} = \hat{\zeta}_{21} = D_k{}^{-1}(\lambda/2)(S_k - (\sigma^2/2)T_k)$$

where D_k can easily be calculated from the equation

$$D_k{}^{-1} = \hat{\zeta}_{11}\hat{\zeta}_{22} - \hat{\zeta}_{12}\hat{\zeta}_{21}$$

and

$$\lambda = \zeta/(8\pi\eta_0 b) \qquad \text{(B.4)}$$

and

$$\sigma = 2a/b$$

The sums S_k and T_k have been defined and evaluated by YY. Noting that $S_k = S_{-k}$ and $T_k = T_{-k}$, we combine eq B.1 and B.3 to yield

$$[\eta] = N_\mathrm{A}N\zeta R^2(60M\eta_0)^{-1}(\xi_\mathrm{A} + 6\xi_\mathrm{B} + 3\xi_\mathrm{C}) \qquad \text{(B.5)}$$

where

$$\xi_\mathrm{A} = \{1 + (\lambda/2)[3S_1 - S_0 - (\sigma^2/18)(T_1 - 9T_0)]\}^{-1}$$

$$\xi_\mathrm{B} = \{1 + (3\lambda/2)[S_1 - (\sigma^2/18)T_1]\}D_2{}^{-1}$$

$$\xi_\mathrm{C} = \{1 + \lambda[S_1 + (\sigma^2/6)T_1]\}^{-1}$$

Note that for $\sigma = 0$, eq B.5 reduces to the earlier result of Paul and Mazo.[27] (There is an obvious misprint in their expression for ξ_B. However, the asymptotic value of $[\eta]$ for large N is unaffected by this difference.)

It is worthwhile to compare the above result with other exact and approximate results for the same and a related model. First we present the expression that occurs when

D is preaveraged. The necessary analysis is easily performed by the method just outlined. We find (superscript P stands for preaveraged **D**):

$$[\eta]^{\mathrm{P}} = \frac{N_{\mathrm{A}} N \zeta R^2}{6M\eta_0} \frac{1}{1 + (4\lambda/3)S_1}$$

For large N, we obtain

$$[\eta]^{\mathrm{P}} = \frac{N_{\mathrm{A}} L^3}{8\pi M \ln N}\left\{1 + \frac{1}{\ln N}\left[\ln\left(\frac{\pi}{2}\right) - \gamma_{\mathrm{E}} + 2 - \frac{3}{8\lambda}\right] + \ldots\right\} \tag{B.6}$$

where

$$L = Nb = 2\pi R$$

and γ_{E} is the Euler constant (=0.5772...). When eq B.5 is also expanded for large N, we obtain

$$[\eta] = \frac{17 N_{\mathrm{A}} L^3}{120\pi M \ln N}\left\{1 + \frac{1}{\ln N}\left[\ln\left(\frac{\pi}{2}\right) - \gamma_{\mathrm{E}} + \frac{453}{170} - \frac{31}{68\lambda} - K\sigma^2\right] + \ldots\right\} \tag{B.7}$$

where

$$K = (11/102)\zeta_{\mathrm{R}}(3) = 0.1296$$

and ζ_{R} is the Riemann zeta function. Comparing only the asymptotic limits of eq B.6 and B.7, we have

$$[\eta]/[\eta]^{\mathrm{P}} = 17/15$$

or about a 13.3% enhancement because of the avoidance of preaveraging. It can also be seen that because $S_k \sim 2 \ln N$ and $T_k \sim$ constant for large N, use of the modified diffusion tensor does not affect the asymptotic value of $[\eta]$. This result is not surprising in view of the shorter range, R_{ij}^{-3}, of the additional term of the modified tensor compared to the original Oseen tensor, which goes as R_{ij}^{-1}. Equations B.6 and B.7 also agree asymptotically with the results of Fujii and Yamakawa,[31] who calculated $[\eta]$ for the wormlike ring model using the Oseen–Burgers method with and without preaveraging the hydrodynamic interaction.

Because of the fundamental difference of the two models, the PM result (eq B.5 with $\sigma = 0$) and the Fujii–Yamakawa result differ in higher order beyond the asymptotic limit. Even in the touched-bead limit ($\sigma = 1$), significant disagreement still remains in higher order. Similar behavior has been found for the broken-rod model.[32]

(ii) Rigid Rod. The rod molecular weight is $M = (2N + 1)M_0$, and the length is $L = 2Nb$. We use eq 2.5b for **D** and conveniently expand eq 2.5a as

$$\zeta_{ij} = \zeta(\mathbf{I}\delta_{ij} - \zeta\mathbf{T}_{ij} + \zeta^2 \sum_{k \neq i,j} \mathbf{T}_{ik} \cdot \mathbf{T}_{kj} - \ldots)$$

In a spherical coordinate system with origin at the center of mass and unit vector $\mathbf{e}_r$ along the rod axis, the Oseen tensor has the form

$$\zeta\mathbf{T}_{ij} = \lambda(\mathbf{I} + \mathbf{e}_r\mathbf{e}_r)|i - j|^{-1}$$

where λ is defined in eq B.4, and the averages required for eq 2.28 can easily be done term by term. The two resulting infinite series can then be rearranged to read

$$\begin{aligned}[\eta] = N_{\mathrm{A}}\zeta b^2(30M\eta_0)^{-1}\sum_i \{2i[i - 2\lambda\sum_{j\neq i} j|i - j|^{-1} + \\ 4\lambda^2 \sum_{k\neq i}\sum_{j\neq k} j|i - k|^{-1}|k - j|^{-1} + \ldots] + \\ 3i[i - \lambda\sum_{j\neq i} j|i - j|^{-1} + \lambda^2 \sum_{k\neq i}\sum_{j\neq k} j|i - k|^{-1}|k - j|^{-1} + \ldots]\}\end{aligned} \tag{B.8}$$

Each of the sums in square brackets can be recognized as the infinitely iterated solution to the equation

$$\psi_i(\lambda) = i - \lambda\sum_{j\neq i}\psi_j(\lambda)|i - j|^{-1}$$

By defining

$$F(\lambda,L) = [3/(2N^3)]\sum_{i=-N}^{N} i\psi_i(\lambda)$$

we can put eq B.8 into the form of Kirkwood and Auer:[28]

$$[\eta] = \frac{N_{\mathrm{A}}\zeta L^2}{180 M_0 \eta_0}[F(2\lambda,L) + (3/2)F(\lambda,L)]$$

The remaining analysis can be done following Ullman.[33]

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