

Approximate Methods for Calculating Hydrodynamic Properties of Macromolecules in Dilute Solution. Theory and Application to Rigid Structures

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ABSTRACT: In this work we examine several approximate methods that can be used to calculate hydrodynamic properties of macromolecules in solution. We consider some well-known approximations such as the preaveraging approximation and the double-sum formula of Kirkwood for translation. We also consider newer methods such as the diagonal approximation and other double-sum formulas for rotation and viscosity. The obvious advantage of the approximate methods is that they require much less computational effort than the rigorous treatments. We first describe the nature of the approximations used in the various methods. Then we calculate translational and rotational coefficients and intrinsic viscosities of rigid rods and rings and other polygonal or polyhedral structures, using both the rigorous theory and the approximate methods. This enables us to determine the errors of the methods in terms of the geometry and size of the structures. The relative performance of the methods is discussed. A remarkable finding is the large effect from preaveraging the interaction tensor on the rotational coefficients and intrinsic viscosities. This effect is generally larger than that caused by the approximations used to derive the double-sum formulas.

Introduction

In the rigorous form of the Kirkwood-Riseman theory^{1,2} of the hydrodynamic properties of macromolecules, the frictional forces are the solutions of a set of $3N$ linear equations describing the hydrodynamic interactions between the N frictional units. In order to facilitate the handling of those equations and to allow a convenient connection with chain statistics, Kirkwood and Riseman² introduced the approximation of preaveraging the interaction tensor. Also, Kirkwood³ made an assumption about the $3N$ -dimensional diffusion tensor that was later realized to be incorrect⁴⁻⁶ but can be anyhow regarded as an additional simplifying assumption.

For many years, the Kirkwood-Riseman type of calculation of hydrodynamic properties was influenced by these approximations. More recently, however, the increasing power of modern computers prompted the utilization of the rigorous version of the theory by numerically solving the interaction equations without any simplification. This approach has been particularly useful in the field of rigid molecules, as can be appreciated in a recent review.⁷ For flexible chains, Zimm⁸ proposed to evaluate the hydrodynamic properties by averaging over Monte Carlo generated chain conformations that are regarded as instantaneously rigid particles, and his steps have been followed in subsequent works.^{9,10} In those cases the only approximation was to neglect the coupling between chain flexibility and hydrodynamic interactions,^{11,12} whose effects are hopefully small.⁹

The numerical solution of the Kirkwood-Riseman interaction equations is in practice restricted, owing to computer limitations, to macromolecular models with $N = 50$ –100. For rigid macromolecules of biological significance, this is in conflict with the necessity of a large N to model the intricate details of their shape.⁷ Also, in the case of flexible chains, computer limitations do not permit the calculations for large Monte Carlo samples as well as

for the higher N 's needed to learn about the long-chain behavior.

These considerations illustrate the interest of reconsidering approximate versions of the theory that require much less computational effort. The approximations will obviously introduce some errors but, fortunately, they can now be estimated and the results can be corrected accordingly. Thus, for a given macromolecular model, the dependence of the errors with N can be studied up to the maximum N allowed by the rigorous treatment and then extrapolated to higher or even infinite N .⁸

The purpose of this paper is to carry out the error analysis for a variety of approximate methods and rigid models. Here we discuss the nature of some well-known approximations, propose others, and obtain expressions for the translational and rotational tensors and coefficients, intrinsic viscosities and hydrodynamic centers. Application is made to rigid macromolecules that can be modeled as rods, rings, and polygonal or polyhedral structures. A forthcoming paper¹³ is dedicated to studying the performance of the same approximations in the case of flexible-chain macromolecules.

Theory

The rigorous form of the Kirkwood-Riseman theory used to calculate the results denoted as "exact" in this paper has been described in detail elsewhere.^{7,14} A brief summary of the fundamental equations has been given in our previous article,⁹ whose equation numbers will be indicated hereafter as I.x. Now we will present the various approximate methods.

Diagonal Approximation (DA). First proposed by Garcia de la Torre and Bloomfield,¹⁵ the diagonal approximation neglects the off-diagonal terms of the hydrodynamic interaction tensors, T_{ij} . Although it was primarily intended for the study of rigid macromolecules, Zimm⁸ has shown that it gives excellent results for flexible

chains. The basis of the DA is that while the diagonal components of \mathbf{T}_{ij} are of the order of R_{ij}^{-1} , R_{ij} being the distance between chain elements i and j , the off-diagonal terms fall off with distance as R_{ij}^{-3} .

In the DA, the components of the modified interaction tensors are

$$T_{ij}^{\alpha\alpha} = (8\pi\eta_0 R_{ij}^{-1}) \{1 + (R_{ij}^\alpha/R_{ij})^2 + (2\sigma/R_{ij}^2) \times [\frac{1}{3} - (R_{ij}^\alpha/R_{ij})^2]\}, \quad \alpha = x, y, z \quad (1)$$

and $T_{ij}^{\alpha\beta} = 0$ for $\alpha \neq \beta$. In eq 1, η_0 is the solvent viscosity, R_{ij}^α is the α component of \mathbf{R}_{ij} , and σ is the Stokes-law radius assigned to the chain elements. By substitution of eq 1 in eq I.5–I.7, one finds that the three components of the frictional forces are uncoupled and can be written as

$$F_i^\alpha = \sum_{j=1}^N \zeta_j S_{ij}^{\alpha\alpha} (u_j^\alpha - v_j^{0\alpha}), \quad i = 1, 2, \dots, N \quad (2)$$

where \mathbf{u}_i and \mathbf{v}_i^0 are, respectively, the velocity of the i th element and the unperturbed velocity of the solvent at its center and $\zeta_i = 6\pi\eta_0\sigma$ is the frictional coefficient of the element. (To avoid losing generality, the subscript i is attached to ζ . However, we consider in this paper models composed of identical elements, and therefore ζ can be factored out of the summations.)

$S_{ij}^{\alpha\alpha}$ is the ij component of the $N \times N$ matrix $\mathbf{S}^{\alpha\alpha}$, defined as

$$\mathbf{S}^{\alpha\alpha} = (\mathbf{Q}^{\alpha\alpha})^{-1} \quad (3)$$

where

$$Q_{ij}^{\alpha\alpha} = \delta_{ij} + (1 - \delta_{ij}) \zeta_i T_{ij}^{\alpha\alpha} \quad (4)$$

δ_{ij} in eq 4 is Kronecker's delta. The computational advantage of the DA is that one has to invert three $N \times N$ matrices instead of inverting a $3N \times 3N$ matrix as required in the exact method.

After some manipulation, we arrive at the following results:

Translational friction tensor:

$$\Xi_t^{\alpha\alpha} = \sum_i \sum_j \zeta_j S_{ij}^{\alpha\alpha} \quad (5)$$

$$\Xi_t^{\alpha\beta} = 0, \quad \alpha \neq \beta \quad (6)$$

Rotational friction tensor at some arbitrary origin O:

$$\Xi_{O,r}^{\alpha\alpha} = \sum_i \sum_j \zeta_j (S_{ij}^{\beta\beta} R_i^\gamma R_j^\gamma + S_{ij}^{\gamma\gamma} R_i^\beta R_j^\beta) \quad (7)$$

$$\Xi_{O,r}^{\alpha\beta} = -\sum_i \sum_j \zeta_j S_{ij}^{\nu\nu} R_i^\alpha R_j^\beta, \quad \alpha \neq \beta \quad (8)$$

Frictional coupling tensor at O:

$$\Xi_{O,r} = \sum_i \sum_j \zeta_j \begin{pmatrix} 0 & -S_{ij}^{\gamma\gamma} R_i^z & S_{ij}^{\gamma\gamma} R_i^y \\ S_{ij}^{\gamma\gamma} R_i^z & 0 & -S_{ij}^{\gamma\gamma} R_i^x \\ -S_{ij}^{\gamma\gamma} R_i^y & S_{ij}^{\gamma\gamma} R_i^x & 0 \end{pmatrix} \quad (9)$$

In eq 7–9, \mathbf{R}_i is the vector joining O and the center of element i . The ordered set (α, β, γ) in eq 7 and 9 must be a cyclic permutation of (x, y, z) , and ν in eq 8 is the coordinate different from α and β .

Once the frictional tensors have been calculated, one obtains the three diffusion tensors at O using eq I.11–I.13. Next, the coordinates of the center of diffusion, \mathbf{D} , are computed as

$$r_{OD}^\alpha = (D_{O,c}^{\beta\gamma} - D_{O,c}^{\gamma\beta}) / (D_r^{\beta\beta} + D_r^{\gamma\gamma}) \quad (10)$$

which is a particular form of eq I.14 valid when \mathbf{D}_r is diagonal. Finally, the translational diffusion coefficient,

D_t , and the translational friction coefficient, f_t , are given by

$$D_t = \frac{1}{3} \text{Tr} (\mathbf{D}_{D,t}) = k_B T / f_t \quad (11)$$

where $k_B T$ is Boltzmann's factor.

For the intrinsic viscosity we have from eq I.19

$$[\eta] = \frac{N_A}{M\eta_0} \sum_i \sum_j \zeta_j \left[\frac{1}{15} \sum_\alpha (R_i^\alpha - r_{OV}^\alpha) S_{ij}^{\alpha\alpha} (R_j^\alpha - r_{OV}^\alpha) + \frac{1}{20} \sum_{\alpha \neq \beta} (R_i^\alpha - r_{OV}^\alpha) S_{ij}^{\beta\beta} (R_i^\alpha - r_{OV}^\alpha) \right] \quad (12)$$

where \mathbf{r}_{OV} is the position vector of the viscosity center,^{7,14} which is calculated as

$$r_{OV}^\alpha = \frac{\sum_i \sum_j \zeta_j (R_i^\alpha + R_j^\alpha) (4S_{ij}^{\alpha\alpha} + 3S_{ij}^{\beta\beta} + 3S_{ij}^{\gamma\gamma})}{\sum_i \sum_j \zeta_j (8S_{ij}^{\alpha\alpha} + 6S_{ij}^{\beta\beta} + 6S_{ij}^{\gamma\gamma})} \quad (13)$$

Orientalional-Preaverage Approximation (OPA).

This approximation has been customarily used to date in most studies on polymer hydrodynamics. In the OPA, one substitutes the interaction tensor by its isotropic orientational preaverage

$$\mathbf{T}_{ij} = (6\pi\eta_0 R_{ij})^{-1} \mathbf{I} \quad (14)$$

It should be remarked that the term of the modified interaction tensor that corrects for the finite size of the element vanishes upon preaveraging.

The \mathbf{S}_{ij} tensors are also diagonal and isotropic and can be calculated as

$$\mathbf{S}_{ij} = (\mathbf{H}^{-1})_{ij} \mathbf{I} \quad (15)$$

where \mathbf{H} is an $N \times N$ matrix given by

$$H_{ij} = \zeta_i (6\pi\eta_0 R_{ij})^{-1} \quad \text{if } i \neq j \quad (16)$$

$$H_{ij} = 1 \quad \text{if } i = j \quad (17)$$

One straightforwardly obtains for the translational friction tensor

$$\Xi_t = [\sum_i \sum_j \zeta_j (\mathbf{H}^{-1})_{ij}] \mathbf{I} \quad (18)$$

The rotational friction tensor at the origin, $\Xi_{O,r}$, is calculated according to eq I.10, which in the OPA reduces to

$$\Xi_{O,r} = -\sum_i \sum_j \zeta_j (\mathbf{H}^{-1})_{ij} \mathbf{R}_i \times \mathbf{I} \times \mathbf{R}_j \quad (19)$$

where

$$(\mathbf{R}_i \times \mathbf{I} \times \mathbf{R}_j)^{\alpha\alpha} = -R_i^\beta R_j^\beta - R_i^\gamma R_j^\gamma \quad (20a)$$

and

$$(\mathbf{R}_i \times \mathbf{I} \times \mathbf{R}_j)^{\alpha\beta} = R_i^\alpha R_j^\beta, \quad \alpha \neq \beta \quad (20b)$$

We note that the rotational friction tensor in the OPA is neither isotropic nor diagonal.

The coupling tensor at the origin, $\Xi_{O,c}$, is calculated from eq I.9, the result being

$$\Xi_{O,c}^{\alpha\alpha} = 0 \quad (21)$$

and

$$\Xi_{O,c}^{\alpha\beta} = -\sum_i \sum_j \zeta_j (\mathbf{H}^{-1})_{ij} R_i^\nu, \quad \alpha \neq \beta \quad (22)$$

In eq 22, ν is the coordinate different from α and β . Next, we calculate the center of resistance, \mathbf{R} . Its position vector referred to the origin can be obtained from eq 9 of ref 14. Owing to the simplicity of Ξ_t and $\Xi_{O,c}$, we arrive at the following result for the position of \mathbf{R} with respect to O:

$$r_{OR}^{\alpha} = \frac{\sum_i \sum_j \zeta_j (\mathbf{H}^{-1})_{ij} R_i^{\alpha}}{\sum_i \sum_j \zeta_j (\mathbf{H}^{-1})_{ij}} \quad (23)$$

Then it is easily seen that at R , $\mathbf{Z}_{R,c} = 0$. Therefore R is a center of hydrodynamic stress and coincides with the center of diffusion; i.e., $R \equiv D$.¹⁶⁻¹⁸ Furthermore, the diffusion coupling tensor is zero, so that the translational and rotational diffusion tensors are

$$\mathbf{D}_{D,t} = k_B T \mathbf{Z}_t^{-1} \quad (24)$$

and

$$\mathbf{D}_r = k_B T \mathbf{Z}_{R,r}^{-1} \quad (25)$$

The translational and rotational diffusion coefficients are calculated as one-third of the traces of $\mathbf{D}_{D,t}$ and \mathbf{D}_r , respectively, and the friction coefficients are given by

$$f_t = k_B T / D_t = \sum_i \sum_j \zeta_j (\mathbf{H}^{-1})_{ij} \quad (26)$$

and

$$f_r = 3 / \text{Tr} (\mathbf{Z}_{R,r}^{-1}) \quad (27)$$

$\mathbf{Z}_{R,r}$, needed in eq 27, is computed as indicated in eq 19 and 20, using for the \mathbf{R}_i 's the position vectors of the frictional elements referred to R .

To obtain the intrinsic viscosity in the OPA, one substitutes eq 14 in eq 1.19. This gives

$$[\eta] = \frac{N_A}{6M\eta_0} \sum_i \sum_j \zeta_j (\mathbf{H}^{-1})_{ij} \mathbf{R}_i \cdot \mathbf{R}_j \quad (28)$$

The \mathbf{R}_i 's in eq 28 must be referred to the center of viscosity. By minimization of eq 28 we obtain in the OPA for V a result identical with that in eq 23. In other words, in the context of the OPA, R , D , and V are the same point, although they generally do not coincide with the center of mass.

Going back to the rotational coefficients, one can deduce a simple expression if one further makes the incorrect assumption that

$$f_r = 1/3 \text{Tr} (\mathbf{Z}_{R,r}) \quad (28a)$$

This yields

$$f_r = 2/3 \sum_i \sum_j \zeta_j (\mathbf{H}^{-1})_{ij} \mathbf{R}_i \cdot \mathbf{R}_j \quad (29)$$

and comparing with eq 28, we see that

$$f_r = (4M\eta_0/N_A)[\eta] \quad (30)$$

This result was derived a number of years ago by Kirkwood and Riseman.^{9,10}

Double-Sum Formulas. If one accepts the so-called Kirkwood approximation,¹¹ the hydrodynamic properties can be calculated from simple formulas that just embody a double sum over the frictional elements of terms depending only on interelement distances. Thus, f_t can be obtained from the well-known expression of Kirkwood^{3,20}

$$f_t = (\sum_i \zeta_i)^2 (\sum_i \sum_j \zeta_j H_{ij})^{-1} \quad (31a)$$

or

$$f_t = (\sum_i \zeta_i) [1 + (6\pi\eta_0 \sum_i \zeta_i)^{-1} \sum_i \sum_j \zeta_j H_{ij}]^{-1} \quad (31b)$$

The prime on the summation denotes omission of the term with $i = j$.

Tsuda²¹⁻²³ has obtained double-sum formulas for rotation and viscosity that are approximate in regard to the

solution of the hydrodynamic interaction equations⁷ but, on the other hand, correspond to the nonpreaveraged interaction tensor. These formulas are

$$[\eta] = \frac{N_A \pi}{M} (\sum_i \sigma_i R_i^2) \times \left\{ 1 + \frac{1}{(\sum_i \sigma_i R_i^2)} \frac{3}{4} \left[\sum_i \sum_j \sigma_i \sigma_j \left(\frac{R_i R_j \cos \alpha_{ij}}{R_{ij}} + \frac{4(R_i^2 + R_j^2) R_i R_j \cos \alpha_{ij} - R_i^2 R_j^2 (1 + 7 \cos^2 \alpha_{ij})}{10 R_{ij}^3} \right) \right] \right\}^{-1} \quad (32)$$

and

$$f_r = \left(\frac{2}{3} \sum_i \zeta_i R_i^2 \right) \times \left\{ 1 + \frac{1}{8\pi\eta_0 (\sum_i \zeta_i R_i^2)} \left[\sum_i \sum_j \zeta_i \zeta_j \left(\frac{R_i R_j \cos \alpha_{ij}}{R_{ij}} + \frac{R_i^2 R_j^2 \sin^2 \alpha_{ij}}{2 R_{ij}^3} \right) \right] \right\}^{-1} \quad (33)$$

where α_{ij} is the angle between vectors \mathbf{R}_i and \mathbf{R}_j , so that

$$R_i R_j \cos \alpha_{ij} = \mathbf{R}_i \cdot \mathbf{R}_j \quad (34)$$

In a recent note,²⁴ we have shown that when one uses the preaveraged tensor, the equation of Tsuda reduces to much simpler expressions. Instead of eq 32, the result for $[\eta]$ is

$$[\eta] = \frac{N_A}{6M\eta_0} \frac{(\sum_i \zeta_i R_i^2)^2}{\sum_i \sum_j \zeta_i \zeta_j H_{ij} \mathbf{R}_i \cdot \mathbf{R}_j} \quad (35a)$$

or

$$[\eta] = \frac{N_A}{6M\eta_0} (\sum_i \zeta_i R_i^2)^2 [\sum_i \zeta_i R_i^2 + (6\pi\eta_0)^{-1} \sum_i \sum_j \zeta_i \zeta_j R_{ij}^{-1} \mathbf{R}_i \cdot \mathbf{R}_j]^{-1} \quad (35b)$$

and for f_r the result would be the combination of eq 35 and 30.

In the numerical calculation with eq 32, 33, and 35, the R_i 's can be referred to an approximate hydrodynamic center, A , whose position with respect to the origin O is given by

$$\mathbf{r}_{OA} = \sum_i \zeta_i \mathbf{R}_i / \sum_i \zeta_i \quad (36)$$

Actually, A is the point at which the various centers (R , D , and V) would coincide if hydrodynamic interactions were neglected.

Results

In this section, results will be presented for rigid rods, rigid rings, and polygonal and polyhedral structures. The rigorous results will be given the following dimensionless forms:

$$f_t^* = f_t / 6\pi\eta_0 b \quad (37)$$

$$f_r^* = f_r / 6\pi\eta_0 b^3 \quad (38)$$

$$[\eta]^* = M[\eta] / N_A b^3 \quad (39)$$

where b is the distance between neighboring frictional

Table I
Results for Rigid Rings

N	translation				rotation					viscosity				
	f_t^*	error			f_r^*	error				$[\eta]^*$	error			
		K	DA	OPA		DA	OPA-1	OPA-2	TR		DA	OPA	FG	TV
5	0.9610	0.6	0.3	0.6	1.169	-4.4	-14.7	-27.4	8.4	7.898	3.4	11.1	11.1	3.7
10	1.4763	0.0	0.0	0.0	5.030	-4.5	-8.7	-20.8	6.6	31.27	2.4	8.4	8.4	2.8
20	2.4470	0.5	0.3	0.5	27.79	-4.4	-4.0	-15.5	7.0	162.1	1.7	6.6	6.6	1.9
30	3.3520	1.0	0.5	1.0	79.92	-4.5	-2.0	-13.3	7.4	456.7	1.8	6.5	6.5	2.2
50	5.0450	1.6	0.8	1.6	312.8	-4.5	-0.1	-11.2	5.3	1758	1.9	6.7	6.7	2.7
∞^a		8.3	4.1	8.3		-4.5	10.0	0	11		4	11.8	11.8	10

^a Theoretical result or estimated by extrapolation.

elements. For the several approximate methods, the results will be presented as percent errors with respect to the rigorous ones:

$$\text{error} = 100(\text{exact} - \text{approximate})/\text{exact} \quad (40)$$

The following code is used for the various approximate methods: DA, diagonal approximation; OPA, orientational preaveraging approximation (when necessary, the two possibilities for f_r in the OPA, namely, eq 27 and 28a, will be denoted as OPA-1 and OPA-2, respectively); K, eq 31 for f_t ; TV, eq 32 for $[\eta]$; TR, eq 33 for f_r ; FG, eq 35 for $[\eta]$.

Rings. Rigid rings were modeled by placing spherical elements of radius $b/2$ at the vertices of regular polygons with side b . Numerical results for rings with varying N are presented in Table I. These results reveal some interesting circumstances. First, the errors of K and OPA for f_t and FG and OPA for $[\eta]$ are identical. This was already predicted in our previous note.²⁴ Another curious fact is that the error for DA is exactly half of that for K. This situation persists if the radius of the frictional elements is decreased (results not shown in Table I).

The behavior of the rigorous method as well as that of the approximate ones can be expressed in closed form in the limit of very large N . Regardless of the method, the hydrodynamic properties of rigid rings in such limit are given by

$$f_t = C_t \pi \eta_0 N b / \ln N \quad (41)$$

$$f_r = C_r \pi \eta_0 N b R^2 / \ln N \quad (42)$$

$$[\eta] = C_\eta \pi N_A N b R^2 / M \ln N \quad (43)$$

where R is the radius of the rings and C_t , C_r , and C_η are numerical constants.

The rigorous value of C_t is $36/11^5$ (for both the modified and the original interaction tensor), while method K gives $C_t = 3^{25-27}$ with an error of $1/12 = 8.3\%$. This limiting error has been known for a number of years⁵ and, as commented above, it holds also for method OPA. Finally, from the finding noted above, we anticipate that the limiting error of the DA should be half of that method K, i.e., $1/24 = 4.1\%$. Figure 1 displays the errors of the translational results. The data points are joined by a curve drawn by the eye, and extrapolation is made to the theoretical values of the limiting errors at $N \rightarrow \infty$.

In regard to rotation, Paul and Mazo^{25,26} and Yamakawa and Yamaki⁶ obtained for large N

$$D_r^\parallel = D_r^\perp = \frac{k_B T}{2\pi\eta_0 N b R^2} \ln N \quad (\text{rigorous, } N \rightarrow \infty) \quad (44)$$

where D_r^\parallel and D_r^\perp stand respectively for the rotational diffusion coefficients around in-plane and perpendicular axes. It can be easily seen that these asymptotic results are valid for both the modified and the original interaction

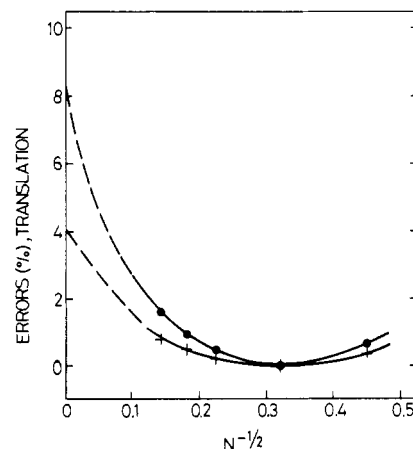


Figure 1. Percent errors of the approximate methods for f_t of rigid rings: (+) DA; (●) K and OPA. The data points, taken from Table I, are connected by a continuous line which is extrapolated to the theoretical prediction for $N \rightarrow \infty$.

tensors. It is noteworthy that the rotational diffusion (and friction) tensors of rings are isotropic for very large N . f_r is then given by eq 42 with $C_r = 2$. Being not aware of any previous analytical calculation of the rotational coefficients for the OPA, we carried it out following the procedures used in a previous paper,²⁹ arriving at the result

$$D_r^\parallel = 2D_r^\perp = 2k_B T (1 + \frac{1}{3}\lambda S_1) / N \zeta R^2 \quad (\text{OPA}) \quad (45)$$

where λ and S_1 are as defined by Yamakawa and Yamaki.^{5,27} When $N \rightarrow \infty$, $S_1(N) \simeq 2(\ln N)^{27}$ and

$$D_r^\parallel = 2D_r^\perp = \frac{2}{3} k_B T \ln N / (\pi \eta_0 N b R^2) \quad (\text{OPA, } N) \quad (46)$$

In the correct version OPA-1, $f_r = 3k_B T / \text{Tr}(\mathbf{D}_r)$ and we obtain that

$$f_r = \frac{3}{5} N \zeta R^2 (1 + \frac{1}{3}\lambda S_1)^{-1} \quad (\text{OPA-1}) \quad (47)$$

for arbitrary N , and when $N \rightarrow \infty$ eq 47 reduces to eq 42 with $C_r = 9/5$, with an error referred to the exact value of $1/10 = 10\%$. However, in the incorrect version OPA-2, the result for arbitrary N is

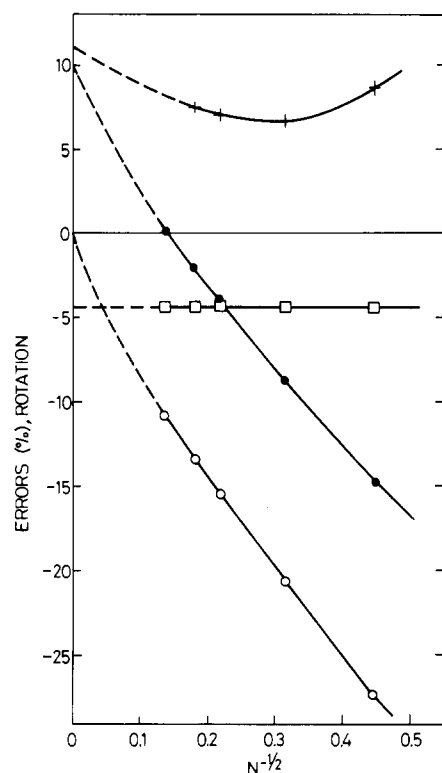
$$f_r' = (10/9) f_r \quad (48)$$

where f_r is that of eq 47, and for $N \rightarrow \infty$ this method gives $C_r = 2$, coinciding with the exact result. This shows that the OPA and the incorrect eq 28a introduce deviations of different sign that cancel out each other for finite N .

For the sake of brevity we have not carried out the asymptotic error study of methods DA and TR for rotation. Nonetheless, in the case of DA we have seen empirically that the error, -4.5% , is nearly independent of N . The errors of several approximate methods are plotted in Figure 2, from which we see that the limiting errors of DA and TR are about -4.5% and 11% , respectively.

Table II
Results for Rigid Rods

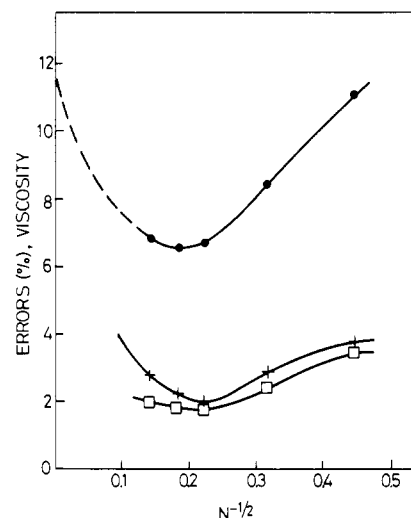
N	translation			rotation			viscosity			
	f_t^*	error		f_r^*	error		$[\eta]^*$	error		
		K	OPA		OPA	TR		OPA	FG	TV
6	1.2606	2.9	0.2	7.2460	-0.6	-0.9	23.023	0.5	5.2	6.2
10	1.7577	2.9	0.2	26.846	3.4	-1.3	81.420	0.0	5.6	7.6
20	2.8507	2.5	0.2	164.87	7.8	-1.6	477.55	0.0	5.4	8.0
30	3.8392	2.2	0.1	486.37	9.9	-1.7	1380.8	0.3	5.1	8.0
50	5.6602	1.8	0.1	1936	12.0	-1.8	5388.5	0.6	4.7	7.9
98	9.6180	1.4	0.1	12267	14.2	-2.0	33490	1.2	4.3	7.7
∞^a		0	0		25	0		6.2	6.2	10.7

^a See footnote of Table I.Figure 2. Same as in Figure 1 for f_r : (□) DA; (●) OPA-1; (○) OPA-2; (+) TR.

We next examine the results for $[\eta]$. When $N \rightarrow \infty$ the rigorous value of the constant in eq 43 is $C_\eta = 17/30$ when one uses the unmodified tensor.^{25,30,31} Recently, Wilemski and Tanaka¹¹ have shown that, as it happens for translation and rotation, the same result is obtained with the modified tensor. The latter authors have also found that method OPA gives $C_\eta = 1/2$ with an error of $2/17 = 11.8\%$. As demonstrated previously,²⁴ method FG should yield the same results.

The errors for varying N are plotted in Figure 3. The errors of OPA and FG, after showing a minimum for intermediate N , should increase to reach their limiting values. The errors of DA and TV could have a similar sharp increase for higher values of N , and this makes it difficult to forecast their limiting value. At any rate, if such increases were not too marked, 4% for DA and 10% for TV could be reasonable estimates.

Rods. Rigid rods were modeled as linear arrays of N touching spheres of radius $b/2$. Thus the length of the rod is $L = Nb$. It can be easily shown that for linear structures the DA is exact.¹⁹ A peculiarity of the rotational behavior for rodlike structures is that what one usually observes is the rotation around perpendicular axes (x, y). Many electrooptic techniques do not monitor the rotation around

Figure 3. Same as in Figure 1 for $[\eta]$: (□) DA; (●) OPA and FG; (+) TV.

the rod axis (z). Furthermore, both the rigorous and the approximate methods for touching-sphere models of rods fail in the sense that they predict $\Xi_{R,zz} = 0$. The origin of this failure has been described elsewhere.^{7,32} Consequently, we regard the component of the rotational friction tensor for perpendicular axes as the most significant rotational property and define

$$f_r \equiv \Xi_{R,r}^{xx} = \Xi_{R,r}^{yy} \quad (49)$$

Thus, the DA and OPA values of f_r for rods are directly obtained from $\Xi_{R,r}$ according to eq 49. Finally, to make the results of Tsuda's eq 33 compatible with eq 49, they must be multiplied by a factor of $3/2$.

Table II presents the results for rods with varying length. As we have shown for rings, the performance of the several methods in the limit of $N \rightarrow \infty$ can be discussed in terms of analytical expressions, which are

$$f_t = Q_t \pi \eta_0 N b / \ln N \quad (50)$$

$$f_r = Q_r \pi \eta_0 N^3 b^3 / \ln N \quad (51)$$

$$[\eta] = Q_\eta \pi N_A N^3 b^3 / M \ln N \quad (52)$$

where Q_t , Q_r , and Q_η are asymptotic constants. Both the rigorous theory³³ and approximations K^{34} and OPA² give $Q_t = 3$, so that K and OPA are correct for rods when $N \rightarrow \infty$. The numerical values of the translational errors in Table II converge well to zero.

For rotation, Yamakawa and Yamaki⁶ have found $Q_r = 1/3$ with the unmodified tensor, and it is trivial that the same result would be obtained with the modified tensor. For method TR (eq 33) Tsuda²³ obtained also $Q_r = 1/3$, with a zero limiting error. We have calculated Q_r for the OPA (details omitted here), arriving at the result $Q_r =$

Table III
Results for Polygonal and Polyhedral Structures

structure	no. ^a	translation					rotation					viscosity				
		f_t^*	error			f_r^{*b}	error				TR	$[\eta]^*$	error			
			K	DA	OPA		DA	OPA-1	OPA-2	DA			OPA	FG	TV	
dimer	21	0.6667	0.0	0.0	0.0	0.4444	0.0	-12.5		10.1	1.676	0.0	6.3	6.3	1.6	
triangle	31	0.7547	0.6	0.3	0.6	0.5161	-3.3	-16.2	-29.1	10.3	3.425	2.0	8.3	8.3	-0.3	
rod	32	0.8347	2.0	0.0	0.2	1.2427	0.0	-7.3		1.1	4.304	0.0	2.7	2.7	1.2	
square	41	0.8572	0.9	0.9	0.9	0.7997	-2.7	-16.0	-28.9	9.7	5.423	-0.5	10.4	10.4	2.2	
tetrahedron	42	0.8122	1.5	0.6	1.5	0.7619	-16.7	-31.3	-31.3	19.3	5.073	0.6	7.1	7.1	-5.9	
centered triangle	44	0.9595	4.5	0.3	0.7	1.1399	-2.5	-11.0	-23.3	-4.6	7.120	2.9	7.0	7.0	3.7	
rod	45	0.9842	2.5	0.0	0.2	2.5924	0.0	-4.4		-0.1	8.637	0.0	1.6	4.3	4.1	
pentagon	51	0.9610	0.6	0.3	0.6	1.1698	-4.3	-14.5	-27.4	8.4	7.897	3.4	11.0	11.0	3.7	
centered tetrahedron	52	1.0574	6.7	0.6	1.2	1.5701	-12.7	-22.4	-22.4	4.5	9.784	2.8	7.4	7.4	2.2	
centered square	53	1.0268	5.1	0.0	0.4	1.4210	-4.9	-12.6	-25.1	0.8	9.122	5.6	8.2	8.2	3.3	
tetragonal bipyramid	54	0.8761	2.4	0.4	1.6	0.9545	-19.4	-32.6	-36.9	15.4	6.748	3.8	8.7	11.1	-0.3	
rod	55	1.1258	2.7	0.0	0.2	4.5603	0.0	-2.2		-0.7	14.78	0.0	0.9	4.8	5.4	
hexagon	61	1.0647	0.3	0.2	0.3	1.6544	-4.6	-13.0	-25.7	7.5	11.01	3.5	11.0	11.0	4.2	
trigonal prism	62	0.9624	2.8	2.5	2.8	1.2181	-15.8	-36.4	-36.4	16.1	8.731	-3.5	9.3	10.2	-2.1	
octahedron	64	0.9256	3.3	1.8	3.3	1.1108	-21.3	-39.3	-39.3	19.0	8.071	0.9	9.7	9.7	-5.2	
rod	67	1.2606	2.9	0.0	0.2	7.2460	0.0	-0.6		-1.0	23.02	0.0	0.5	5.2	6.2	
centered hexagon	71	1.0668	4.2	0.1	4.2	1.6544	-4.6	-13.0	-25.7	7.5	11.01	3.5	11.0	11.0	4.2	
centered octahedron	72	1.1610	8.1	0.1	1.4	1.9929	-24.7	-33.8	-33.8	7.0	13.82	6.6	9.0	9.0	0.5	
cube	81	1.0816	3.9	3.9	3.9	1.6548	-14.8	-40.9	-40.9	13.8	12.38	-7.6	11.2	11.2	-1.5	

^a Notation of ref 19 and 39. See Figure 1 of ref 39 for details. ^b For the linear structures 21, 32, 45, 55, and 67, the OPA rotational result was evaluated only from eq 49, and the corresponding error is given in column OPA-1.

$1/4$, to which corresponds a limiting error of 25%.

For viscosity, the rigorous result^{35,36} is $Q_\eta = 2/45$, the same as for long straight cylinders.³⁷ The OPA value can be calculated from $Q_r = 1/4$ and by using the relationship

$$[\eta] = f_r N_A / 6M\eta_0 \quad (53)$$

which is a modified form of eq 30, correct within the context of the OPA and compatible with the definition of f_r for rods (eq 49). The result $Q_\eta = 1/24$ is the same as that predicted by method OPA for straight cylinders.³⁷ Thus the limiting error of the OPA for $[\eta]$ is 6.25%. In the case of the FG formula, substitution of the double sum in eq 35 by an integral yields the same result, $Q_\eta = 1/24$ (there is an erratum in our previous note,²⁴ where we affirmed that the limiting OPA and FG results for $[\eta]$ are not equivalent). Finally, for method TV Tsuda obtained $Q_\eta = 10/252$, with an error of 10.7%.

If one draws plots for rotation and viscosity similar to those in Figures 2 and 3, the numerical results of the errors seem to converge to limiting values that differ slightly (about 3%) from those presented above. After checking the correctness of our computer algorithms, we believe that this small discrepancy is due to round-off errors that can be noticeable for the higher N 's used in the numerical calculations. $N = 98$ was the highest N allowed by our computer installation with single-precision arithmetic, and the use of double precision would obviously restrict the range of N . At any rate, the deviation has always the same direction and is usually smaller than the differences between the errors of any two methods leading to nonidentical results for fixed N . Thus, we hope that this deviation should not change our conclusions about the behavior of the several methods for rods.

Polygonal and Polyhedral Structures. We have also obtained the errors of the approximate methods for a variety of polygonal and polyhedral structures composed of a small number of spherical elements of radius $b/2$, b being the distance between contiguous elements. In addition to their interest as models for oligomeric proteins and other macromolecular complexes,^{7,19,38,39} from the theoretical point of view these structures are useful to characterize the influence of geometrical aspects, such as symmetry and compactness, on the performance of the methods.

Table III displays the rigorous results and the errors of the approximate methods for several structures, including some rods and rings (regular polygons) with low N . It should be remarked that the values of f_t^* , f_r^* , and $[\eta]^*$ given in Table III are not intended for analysis of experimental results. Both the rigorous and the approximate values for rotation and viscosity are somehow incorrect in regard to the finite size of the frictional elements;^{7,32} in fact, better values that are more appropriate for practical uses have been already presented.³⁹ We have not included in the present calculations the modeling improvements required to account for finite size^{32,39} because here we are primarily concerned with the error analysis of the approximations, and this is more easily done with simpler models.

For translation the errors follow the order $DA < OPA \leq K$. Methods OPA and K give identical results for structures 21, 31, 41, 42, 51, 61, 62, 64, and 81. As we showed earlier,²⁴ for all these structures it holds that

$$\sum_j R_{ij} = \sum_j R_{kj}, \quad i \neq k \quad (54)$$

which is a sufficient condition for the equivalence of OPA and K. The errors of K are higher for structures 44, 52, 53, 71, and 72, whose common feature is to have a central element in contact with all the other elements of the model. Surely, the reason is that the strong hydrodynamic interaction at the central element is not well described in the K approximation. Finally, we note that the errors of methods DA and OPA are usually higher for tridimensional structures of high symmetry.

In the case of rotation, for most structures the errors increase in the order $DA < OPA-1 \leq OPA-2 < TR$, although in some instances method TR gives the least error. Methods OPA-1 and OPA-2 are equivalent for structures 42, 52, 64, 72, and 81 because they have tetrahedral, octahedral, or cubic symmetry, so that their rotational friction tensor, are isotropic, and therefore eq 27 and 28 are equivalent. For other structures, method OPA-2 yields higher results, reflecting the incorrectness of eq 28a.

For viscosity the errors increase in the order $DA < TV < OPA \leq FG$, except in the case of the most elongated structures, for which the error for TV is highest. Methods OPA and FG give identical results for the regular polygons

(rings) and polyhedrons since we stated,²⁴ in addition to eq 54 they fulfill some other symmetry requirements (for instance, all the elements are at the same distance from the particle's center).

Discussion

In the preceding paragraphs we have commented explicitly on the performance of the various approximate methods for polygonal and polyhedral structures, and for rings and rods their relative merits are clearly seen in Tables I and II and Figures 1-3. As it was expected, the DA is best for the three properties; its obvious drawback is that it requires far more computer allowances. For translation, methods OPA and K follow to DA in accuracy.

However, for the rotational coefficients we found that in some cases method TR performs nearly as well as the OPA, and in many others it does clearly better. The situation is completely similar for method TV in the case of the intrinsic viscosity. If we consider that, as commented earlier in this paper, Tsuda's methods TV and TR contain an approximation in regard to the solution of the interaction equations but do not make the approximation of preaveraging the interaction tensor, it seems reasonable to conclude that the effects of the latter approximation are more important than those of the former. This is confirmed by the fact that method FG, which includes both approximations, gives results that are either identical with or rather close to those of OPA.

The conclusions of the above error comparison of TV and TR with OPA is even more striking if we next compare their computer requirements. In the OPA one has to numerically invert an $N \times N$ matrix, which takes computer time proportional to N^3 and requires N^2 storage positions, while for methods TV and TR computer time grows as N^2 and no storage is needed.

If one accepts the OPA, method FG offers its great simplicity at the cost of an increase in the error which in most cases should be quite small. Furthermore, method FG can be useful for closed-form calculations of the intrinsic viscosity of rigid and flexible macromolecular models.

An interesting aspect of our results for rings and rods is that the errors of some methods depend strongly on N . This has two consequences. First, the relative performance of the methods may depend on the size of the macromolecule. Figure 2 provides a good illustration of such a situation. Thus, for rings method OPA-1 gives the exact f_r when $N \approx 50$, although its error is very noticeable for smaller N 's.

The second consequence is that the errors for moderate N are quite different from the limiting values for $N \rightarrow \infty$. When approximate methods have been discussed in most earlier works, the basic criterion has been the limiting error. A well-known example is Zwanzig's observation⁵ of the high error of Kirkwood's translational formula for rigid rings with large N . We note, however, that in the range of $N \leq 20$, where the model can find practical applicability, the error is smaller than 1%. In the case of rods, in the region where the model is applicable to real rodlike macromolecules (say $N < 50$), the errors for some properties are clearly different (smaller or greater) than those for infinitely long rods. In summary, we can say that the limiting errors may be misleading when used to characterize the accuracy of the approximate methods.

Concluding Remarks

It is evident that the precision of the error analysis of the approximate methods carried out in this paper depends on the actual exactness of the "exact" values obtained from

the rigorous treatment and used as reference in the calculation of errors (eq 40). A similar treatment used by Zimm for flexible chains⁸ has been found to be inexact both for sedimentation¹² and viscosity.^{11,12b} We believe that our reference values do not contain such inexactness. By the use of Brenner's coupling tensors,^{16,17} we do not place any restriction on the angular velocity of the molecules in the calculation of translational and rotational properties, and therefore neither of Fixman's symmetry criteria^{12a} are violated. Some problems could arise in the case of the intrinsic viscosity, since eq I.19 does not include possible coupling effects. Fortunately, Iwata⁴⁰ has shown that eq I.19 is exact for highly symmetric rigid bodies, and this is the case for all the models studied in this paper. A fuller discussion on this topic will be given after the presentation of results for flexible chains in a forthcoming paper.¹³

Acknowledgment. This work was supported by Grant 4073-79 from the Comisión Asesora de Investigación Científica y Técnica to J.G.T.

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