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Approximate Methods for Calculating Rotational Diffusion Constants of Rigid Macromolecules

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Received April 18, 1986

ABSTRACT: In this work we have derived a double-sum formula for the rotational diffusion coefficients of rigid particles modeled as assemblies of N beads. We also consider an alternative approach in which the hydrodynamic interactions are orientationally preaveraged. The approximate methods are applied to rigid rods, rings, and compact structures, and the performance of these methods is characterized by the percent deviations of their results from those obtained by a more rigorous procedure. The results are presented in the form of reciprocals of the rotational relaxation times, which are directly observable. The orientational-preaverage approximation, which requires the inversion of an $N \times N$ matrix, yields quite discrepant results. On the other hand, the double-sum formula, in addition to being computationally much simpler, gives deviations of a few percent only for all the cases studied here. Laterally, we have studied the influence of a 0th-order contribution to the rotational coefficients that should be included to account for the discrete size of the frictional elements.

I. Introduction

The rigorous Kirkwood–Riseman calculation of hydrodynamic properties of rigid macromolecules, modeled as a set of N spherical elements, requires the inversion of a $3N \times 3N$ matrix or the solution of systems of $3N$ linear equations with $3N$ unknowns.[1-4] The corresponding step in the computational procedure is time- and memory-consuming for the high N's needed often to describe well the intricate shapes of biological macromolecules. A similar situation arises when the hydrodynamics of flexible or semiflexible polymer chains is studied by simulation in

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terms of the rigid-body approximation,[5-9] because even for moderate N, the calculations must be repeated for a number of chain conformations to obtain statistically significant averages.

This situation has stimulated the analysis of the performance of approximate methods,[8,10,11] which require much less computational effort. Typical examples of these are the well-known preaverage and double-sum formulas. Concretely, in a previous paper[11] we presented an analysis of various approximate methods in the case of rigid bead models.

Among the various hydrodynamic properties, the rotational coefficients are particularly interesting, because they are most sensitive to the size and shape of a rigid macromolecule and can be accurately determined by techniques like fluorescence anisotropy decay or transient electric birefringence. In our previous paper[11] we studied several approximate methods for rotation, but our analysis was somewhat deficient or incomplete. Thus, a single quantity, namely the rotational friction (or diffusion) coefficient, was considered. However, a complete characterization of the rotational dynamics of a body of arbitrary shape requires up to five rotational constants (reciprocals of the relaxation times) that are combinations of the three eigenvalues of the rotational diffusion tensor.

From another point of view, it has been recently shown[12] that in a correct Kirkwood–Riseman calculation of rotational coefficients, an extra term due to the finite size of the beads has to be added to the diagonal components of the rotational friction tensor. This correction must be applied in the rigorous calculation and in the approximate methods as well.

The purpose of the present paper is to present a detailed analysis of some approximate methods for calculating rotational coefficients of rigid macromolecules. Besides considering the orientational-preaverage approximation, which still needs the inversion of an $N \times N$ matrix, we have derived a simple, double-sum formula for the rotational friction tensor, in which preaveraging can be either avoided or included. The performance of the preaveraging and double-sum approximations is then analyzed for several types of rigid structures: rods, rings, and compact, regular oligomers.

II. Theory

1. Rotational Tensors and Coefficients of a Rigid Particle. According to Wegener et al.,[13] a complete characterization of the rotational relaxation of a rigid particle requires up to five relaxation times, τ_k, whose reciprocals are combinations of the eigenvalues, D_1, D_2, and D_3, of the rotational diffusion tensor, $\mathbf{D}_r$. These relaxation times are given by

$$\begin{aligned} \tau_1^{-1} &= 6D - 2\Delta \\ \tau_2^{-1} &= 3(D + D_1) \\ \tau_3^{-1} &= 3(D + D_2) \\ \tau_4^{-1} &= 3(D + D_3) \\ \tau_5^{-1} &= 6D + 2\Delta \end{aligned} \tag{1}$$

where

$$D = \tfrac{1}{3}\,\mathrm{Tr}\,(\mathbf{D}_r) = \tfrac{1}{3}(D_1 + D_2 + D_3) \tag{2}$$

and

$$\Delta = (D_1^2 + D_2^2 + D_3^2 - D_1D_2 - D_1D_3 - D_2D_3)^{1/2} \tag{3}$$

For symmetric particles, the number of relaxation times is less than five, as will be shown in the Applications.

$\mathbf{D}_r$ is obtained from the friction tensors for translation, Ξ_t, rotation, $\Xi_{P,r}$, and translation–rotation coupling, $\Xi_{P,c}$, referred to an arbitrary point P, by means of

$$\mathbf{D}_r = k_BT(\Xi_{P,r} - \Xi_{P,c}\cdot\Xi_t^{-1}\cdot\Xi_{P,c}^{T})^{-1} \tag{4}$$

where k_BT is the Boltzmann factor. Procedures to calculate the three friction tensors have been described elsewhere (see ref 2 and 3 for reviews). We just recall that $\Xi_{P,r}$ is given by

$$\Xi_{P,r} = 6V\eta_0\mathbf{I} - \sum_i\sum_j \zeta_j\mathbf{R}_i \times \mathbf{S}_{ij} \times \mathbf{R}_j \tag{5}$$

$\mathbf{R}_i$ is the position vector of the ith bead in the macromolecular model with respect to P, and $\zeta_i = 6\pi\eta_0\sigma_i$, where σ_i is the bead radius and η_0 is the solvent viscosity. V is the volume of the model, given by

$$V = \tfrac{4}{3}\pi\sum_i \sigma_i^3 \tag{6}$$

and the first term on the right-hand side of eq 5 is the one that corrects for the finite size of the elements.[12]

In eq 5, $\mathbf{S}_{ij}$ is the 3×3 ij block of the supermatrix $\mathbf{S} = \mathbf{Q}^{-1}$, $\mathbf{Q}$ being the supermatrix whose 3×3 ij block is

$$\mathbf{Q}_{ij} = \delta_{ij}\mathbf{I} + (1 - \delta_{ij})\zeta_i\mathbf{T}_{ij} \tag{7}$$

where $\mathbf{T}_{ij}$ is the hydrodynamic interaction tensor.

2. Orientational-Preaverage Approximation (OPA). When the hydrodynamic interaction tensor is preaveraged, one finds[11]

$$\Xi_{P,r} = 6V\eta_0\mathbf{I} - \sum_i\sum_j(\mathbf{H}^{-1})_{ij}\mathbf{R}_i \times \mathbf{I} \times \mathbf{R}_j \tag{8}$$

where $\mathbf{H}$ is an $N \times N$ matrix with terms

$$H_{ij} = 1 \qquad \text{if } i = j \tag{9a}$$

$$H_{ij} = \zeta_i/6\pi\eta_0R_{ij} \qquad \text{if } i \neq j \tag{9b}$$

We have shown[11] that if P is chosen as the point whose position relative to the origin O is given by

$$\mathbf{r}_{OP}' = [\sum_i\sum_j\zeta_j(\mathbf{H}^{-1})_{ij}\mathbf{R}_i']/[\sum_i\sum_j\zeta_j(\mathbf{H}^{-1})_{ij}] \tag{10}$$

where $\mathbf{R}_i'$ is a position vector referred to O, then $\Xi_{P,c} = \mathbf{0}$ and

$$\mathbf{D}_r = k_BT\Xi_{P,r}^{-1} \tag{11}$$

3. Double-Sum Formula for $\mathbf{D}_r$. In the OPA, the size of the matrix to be inverted is $N \times N$ instead of $3N \times 3N$ as it is in the case of the rigorous procedure. Although this causes a substantial reduction in computations, the remaining necessity of matrix inversion may limit the applicability of the OPA. In addition, it is known that the OPA may give quite erroneous results for the rotational coefficients. With this situation in mind, we have derived an alternative method to calculate $\mathbf{D}_r$, using a Kirkwood–Riseman-type approximation[14] and avoiding preaveraging. This leads to a double-sum formula with far less computer requirements than the OPA.

We first replace the inversion of $\mathbf{S} = \mathbf{Q}^{-1}$ by a series expansion for $\mathbf{S}_{ij}$ which is approximately truncated at the second term:

$$\mathbf{S}_{ij} = \delta_{ij}\mathbf{I} - (1 - \delta_{ij})\zeta_i\mathbf{T}_{ij} \tag{12}$$

and from eq 5 we have

$$\Xi_{P,r} = \mathbf{A} + \mathbf{B} \tag{13}$$

where

$$\mathbf{A} = 6V\eta_0\mathbf{I} - \sum_i \zeta_i \mathbf{R}_i \times \mathbf{I} \times \mathbf{R}_i \tag{14}$$

and

$$\mathbf{B} = -\sum_{i \neq j}\sum \zeta_i\zeta_j \mathbf{R}_i \times \mathbf{T}_{ij} \times \mathbf{R}_j \tag{15}$$

The calculations are now referred to a hydrodynamic center, C, given by

$$\mathbf{r}_{\mathrm{OC}}' = \sum_i \sigma_i \mathbf{R}_i' / \sum_i \sigma_i \tag{16}$$

which is assumed to be close enough to the center of resistance[2,3] so that we can approximately take

$$\boldsymbol{\Xi}_{\mathrm{C,c}} = \mathbf{0} \tag{17}$$

and therefore

$$\mathbf{D}_{\mathrm{r}} = k_{\mathrm{B}}T\boldsymbol{\Xi}_{\mathrm{C,r}}^{-1} \tag{18}$$

The second part of the approximation consists of inverting $\boldsymbol{\Xi}_{\mathrm{C,r}}$ as if its contribution from hydrodynamic interaction, **B**, were a perturbation to the value in the absence of interaction, **A**. Thus,

$$\mathbf{D}_{\mathrm{r}} = k_{\mathrm{B}}T(\mathbf{A} - \mathbf{B})^{-1} \simeq k_{\mathrm{B}}T(\mathbf{A}^{-1} + \mathbf{A}^{-1}\cdot\mathbf{B}\cdot\mathbf{A}^{-1}) \tag{19}$$

More explicitly, **A** and **B** are given by

$$\mathbf{A} = \begin{pmatrix} 6V\eta_0 + \sum_i \zeta_i(y_i^2 + z_i^2) & -\sum_i \zeta_i x_i y_i & -\sum_i \zeta_i x_i z_i \\ 0 & 6V\eta_0 + \sum_i \zeta_i(x_i^2 + z_i^2) & -\sum_i \zeta_i y_i z_i \\ \mathbf{sym} & & 6V\eta_0 + \sum_i \zeta_i(y_i^2 + z_i^2) \end{pmatrix} \tag{20}$$

and

$$\mathbf{B} = -\sum_{i \neq j}\sum (\zeta_i\zeta_j/8\pi\eta_0 R_{ij})[p_{ij}\mathbf{R}_i \times \mathbf{I} \times \mathbf{R}_j - q_{ij}(\mathbf{R}_i \times \mathbf{R}_j) \times (\mathbf{R}_i \times \mathbf{R}_j)/R_{ij}^2] \tag{21}$$

where

$$p_{ij} = 1 + (\sigma_i^2 + \sigma_j^2)/3R_{ij}^2 \tag{22}$$

and

$$q_{ij} = 1 - (\sigma_i^2 + \sigma_j^2)/R_{ij}^2 \tag{23}$$

if the modified Oseen tensor is used in eq 14, while $p_{ij} = q_{ij} = 1$ for the Oseen tensor. Another possible choice for $\mathbf{T}_{ij}$ is the orientationally preaveraged interaction tensor. In such a case the preaveraging approximation is superposed to the Kirkwood approximation, and the only change is that **B** is then given by

$$\mathbf{B} = -\sum_{i \neq j}\sum (\zeta_i\zeta_j/6\pi\eta_0 R_{ij})\mathbf{R}_i \times \mathbf{I} \times \mathbf{R}_j \tag{24}$$

For symmetric models, like those considered in the next section, the axes of the Cartesian system of reference can be chosen so that **A** is diagonal. Then the diagonal components of $\mathbf{D}_{\mathrm{r}}$ are

$$D^{kk} = k_{\mathrm{B}}T(1 + B^{kk}/A^{kk})/A^{kk} \tag{25}$$

and the off-diagonal components are

$$D^{kl} = k_{\mathrm{B}}TB^{kl}/A^{kk}A^{ll}, \qquad k, l = x, y, z \tag{26}$$

Concretely, for the original Oseen tensor, eq 25 along with eq 20 and 21 leads to the following expression for the zz component

$$(6\pi\eta_0/k_{\mathrm{B}}T)D^{zz} = \frac{1}{\upsilon + \alpha + \beta}\left[1 + \frac{3}{4}\,\frac{1}{\upsilon + \alpha + \beta}\sum_{i \neq j}\sum \frac{\sigma_i\sigma_j}{R_{ij}}\left(x_i x_j + y_i y_j + \frac{(x_i y_j - x_j y_i)^2}{R_{ij}^2}\right)\right] \tag{27}$$

where $\alpha = \sum \sigma_i x_i^2$, $\beta = \sum \sigma_i y_i^2$, and $\upsilon = V/\pi$. Setting $\sigma_i = \sigma$ for all i and $\upsilon = 0$, eq 27 reduces to an expression derived by Hearst (eq 5 in ref 15). Thus, our double-sum method is a generalization of Hearst's procedure to the case of rotational diffusion tensor of macromolecules of arbitrary shape modeled by equal or unequal frictional elements and includes the correction for finite element size. By the way, we note that we have expressed the Kirkwood approximation in a different form[14] (eq 12 and 19). This form, when applied to translational tensors,[2] yields also the well-known Kirkwood formula for the translational diffusion coefficient.[16]

III. Applications

To indicate the several approximate methods, we use the following codes: OP, orientational preaverage, eq 8–11; DS, double sum, eq 19–23; DS-OP, double-sum formula, with eq 21 replaced by eq 24. The rigorous results, obtained as summarized in section II.1, will be denoted as EX, and taking them as reference, the errors of the approximate methods will be given as percent deviations

$$\text{error} = 100(\text{APP} - \text{EX})/\text{EX}$$

where APP stands for any of the approximate methods.

1. **Rigid Rods.** Rigid rods were modeled as straight strings of N beads of radius σ. Neighboring beads are separated by a distance b. We will restrict our calculations to the case with $\sigma = b/2$, for which hydrodynamic interaction effects are strongest. In the rigorous method, the calculation of the rotational coefficient for rotation around a perpendicular axis, $D_\perp$, requires the solution of a $3N \times 3N$ system of linear equations. An analytical result exists only in the $N \to \infty$ limit[17]

$$D_\perp = Qk_{\mathrm{B}}T \ln N/\pi\eta_0 N^3 b^3 \tag{28}$$

with $Q = 3$. This asymptotic result is obtained with or without the volume correction and for both the Oseen and the modified tensors.

On the other hand, the coefficient for rotation around the rod axis, $D_\parallel$, would be unphysically infinite if the finite size of the frictional beads were not considered. Introducing the volume correction, the result for a rod of N beads is

$$D_\parallel = k_{\mathrm{B}}T/6V\eta_0 = k_{\mathrm{B}}T/8N\pi\eta_0\sigma^3 \tag{29}$$

We anticipate that, obviously, eq 26 is also found for all the approximate methods.

In the OP approximation, $D_\perp$ is calculated from eq 8–11. The asymptotic result for $N \to \infty$, independent of the volume correction and the type of interaction tensor, has the form of eq 28 with $Q = 4$.[11]

With the DS method, eq 27 takes a simpler form

$$(6\pi\eta_0/k_{\mathrm{B}}T)D_\perp = \frac{1}{\upsilon + \alpha}\left[1 + \frac{3}{4}\,\frac{\sigma^2}{\upsilon + \alpha}\sum_{i \neq j}\sum \frac{x_i x_j}{|x_j - x_i|}\right] \tag{30}$$

with $\alpha = \sigma\sum x_i^2$ and $\upsilon = 4N\sigma^3/3$. In the $N \to \infty$ limit, the double sum in eq 30 can be replaced by an integral, and the asymptotic result is readily found to be eq 28 with Q

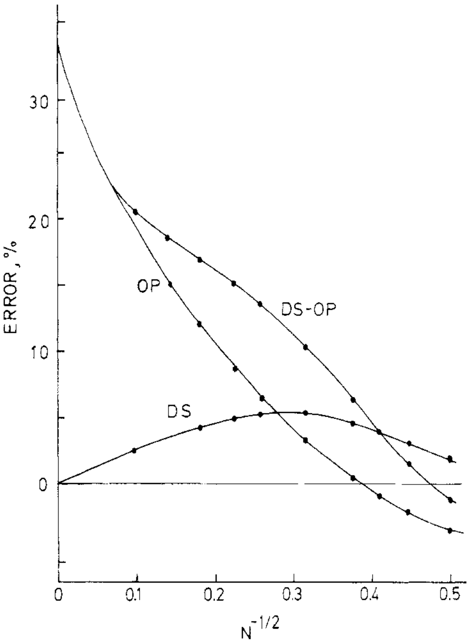

Figure 1. Percent errors in the approximate values of the reciprocal of the longest relaxation time, τ_a^{-1}, of rigid rods of varying length plotted vs. $N^{-1/2}$. OP, orientational preaverage; DS, double-sum formula; DS-OP, double-sum formula with orientational preaverage.

= 3 also. Thus, the DS approximation is exact for very high N.

In the DS-OP approximation, we again obtain eq 28 with $Q = 4$ as for the pure OP approximation. Thus the limiting error in $D_\perp$ for both OP and DS-OP is 33.3%.

It is preferable to present the rotational results in the form of relaxation times, since they are what one actually observes. For the rigid rod there will be at most three relaxation times, ordered as $\tau_a > \tau_b > \tau_c$, whose reciprocals are

$$\begin{aligned}\tau_a^{-1} &= 6D_\perp \\ \tau_b^{-1} &= 5D_\perp + D_\parallel \\ \tau_c^{-1} &= 2D_\perp + 4D_\parallel\end{aligned} \tag{31}$$

In some cases, only the longest relaxation time, τ_a, will be detected. The percent erros of the τ_a^{-1} values obtained with the three approximations are plotted in Figure 1. We see that the errors of the DS values are always smaller than 5% for $N > 2$ and tend to zero for very high N as expected. However, the errors of the preaveraging methods, OP and DS-OP, increase remarkably with increasing N. It is thus evident that for rigid rods the DS approximation is clearly better than the preaveraging methods, although it is computationally much simpler than the OP procedure.

Since both the rigorous and all the approximate methods give eq 29 for $D_\parallel$, and $D_\parallel \gg D_\perp$, the errors in the two other relaxation times must be much smaller than those for τ_a^{-1}. Thus all the errors for τ_c^{-1} are under 1% for $N > 2$.

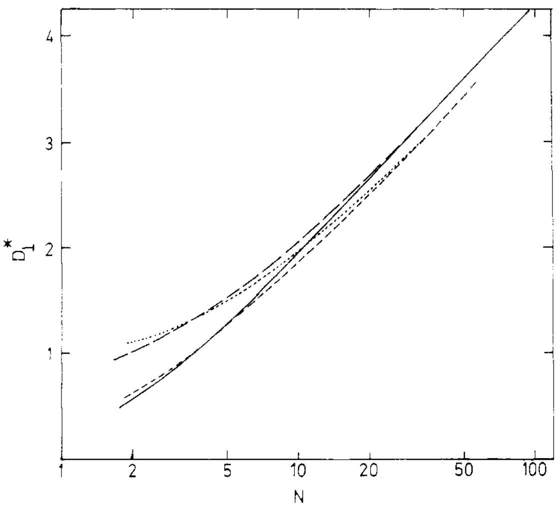

Figure 2. Rotational diffusion coefficient of rigid rods for a perpendicular axis, expressed as $D_\perp{}^* = D_\perp \pi\eta_0 N^3 b^3/3k_BT$, as a function of rod length: (—) modified tensor and volume correction; (– – –) modified tensor without volume correction; (- - -) Oseen tensor and volume correction; (···) Oseen tensor without volume correction.

Aside from the performance of the approximate methods, it is interesting to compare the various versions of the rigorous treatment. Such comparison is displayed in Figure 2, which shows that for short rods there is a strong effect due to the volume of the frictional elements, which is more important than that from the modification of the interaction tensor. This illustrates the need of including the volume correction[12] when the size of the elements is not much smaller than the dimensions of the particle. Only for high N (say $N > 20$) the volume correction is unimportant, and there is a remaining influence of the type of interaction tensor. We also recall that the volume correction is mandatory to estimate $D_\parallel$ as well as τ_b and τ_c.

Finally, we note that the results presented here for rigid rods modeled as strings of beads are intended for the analysis of various approximated methods for a typical extended, linear structure. However, in the interpretation of experimental results for rodlike polymers, the available theories for cylinders must be preferred.[18,19]

2. Rigid Rings. A rigid ring of radius R is modeled by placing N beads, with frictional coefficients $\zeta = 6\pi\eta_0\sigma$, at the vertices of a regular polygon of side b. Expressions for the rotational diffusion coefficients corresponding to rotations around a diametrical axis in the ring plane, $D_\parallel$, and around a perpendicular axis, $D_\perp$, were derived by Paul and Mazo[20] and Yamakawa and Yamaki.[17] In a previous work[11] we extended their expressions for the modified interaction tensor. Now, we have included in the treatment the volume correction, arriving at the following rigorous results:

$$D_\parallel = k_BT\{{}^1\!/\!_2 N\zeta R^2[1 + \lambda(S_1 + {}^1\!/\!_6\xi^2T_1)]^{-1} + 6V\eta_0\}^{-1} \tag{32}$$

$$D_\perp = k_BT\{N\zeta R^2[1 + \lambda({}^3\!/\!_2S_1 - {}^1\!/\!_{12}\xi^2T_1) + {}^1\!/\!_2\lambda(S_0 - {}^1\!/\!_2\xi^2T_0)]^{-1} + 6V\eta_0\}^{-1} \tag{33}$$

In eq 32 and 33

$$\lambda = \zeta/8\pi\eta_0 b = 3\sigma/4b \tag{34}$$

and

$$S_n = \sin(\phi/2)\sum_{j=1}^{N-1}\cos(nj\phi)/|\sin(j\phi/2)| \tag{35}$$

$$T_n = \sin^3(\phi/2)\sum_{j=1}^{N-1}\cos(nj\phi)/|\sin(j\phi/2)|^3 \tag{36}$$

where $\phi = 2\pi/N$ and $\xi = 2\sigma/b$ for the modified interaction tensor, or $\xi = 0$ for the Oseen tensor. If we let $\xi = 0$ and $V = 0$ eq 32 and 33 reduce to the results of Yamakawa and Yamaki.[17] When N is very large, $S_0,S_1 = 2\ln N + \mathcal{O}(N)$ and $T_0,T_1 = \mathcal{O}(N)$, so that the asymptotic results are

$$D_\parallel = D_\perp = k_BT \ln N/2\pi\eta_0 NbR^2 \quad (N \rightarrow \infty) \tag{37}$$

In this limit, the rotational diffusion tensor is isotropic.

In the previous work[11] we also derived expressions corresponding to the OP approximation. We have now

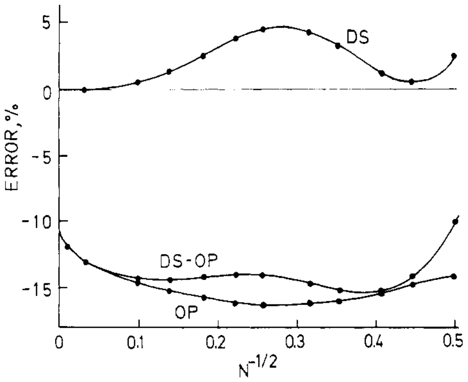

Figure 3. Same as in Figure 1 for the reciprocal of the longest relaxation time of a rigid ring.

rederived those expressions, including the volume correction, obtaining

$$D_{\parallel} = k_BT\{{}^1\!/_2N\zeta R^2[1 + {}^4\!/_3\lambda S_1]^{-1} + 6V\eta_0\}^{-1} \qquad (\text{OP}, N) \quad (38a)$$

$$D_{\perp} = k_BT\{N\zeta R^2[1 + {}^4\!/_3\lambda S_1]^{-1} + 6V\eta_0\}^{-1} \qquad (\text{OP}, N) \quad (38b)$$

which in the $N \rightarrow \infty$ limit read[11]

$$D_{\parallel} = 2D_{\perp} = 2k_BT \ln N/3\pi\eta_0 NbR^2 \qquad (\text{OP, DS-OP}, N \rightarrow \infty) \quad (39)$$

We recall that the OP result is the same for both the original and the modified tensors. A comparison of eq 38 with eq 32 and 33 shows that the OP approximation gives values for $D_{\parallel}$ and $D_{\perp}$ that differ remarkably from the rigorous ones. In the $N \rightarrow \infty$ limit, $D_{\parallel}$ and $D_{\perp}$ are 33% higher and lower, respectively, than the rigorous values.

Next, using the double-sum formalism described in section II.3, we have arrived at the following expressions for the two diffusion coefficients:

$$D_{\parallel} = k_BT[1 + {}^1\!/_2N\zeta R^2\lambda(S_1 + {}^1\!/_6\xi^2T_1)D_{\parallel}^{\circ}]D_{\parallel}^{\circ} \qquad (\text{DS}, N) \quad (40a)$$

$$D_{\perp} = k_BT[1 + N\zeta R^2\lambda({}^3\!/_2S_1 - {}^1\!/_{12}\xi^2T_1 + {}^1\!/_2S_0 - {}^1\!/_4\xi^2T_0)D_{\perp}^{\circ}]D_{\perp}^{\circ} \qquad (\text{DS}, N) \quad (40b)$$

$D_{\parallel}^{\circ}$ and $D_{\perp}^{\circ}$ are the values for the coefficients in the free-draining case

$$D_{\parallel}^{\circ} = (6V\eta_0 + {}^1\!/_2N\zeta R^2)^{-1} \quad (41a)$$

$$D_{\perp}^{\circ} = (6V\eta_0 + N\zeta R^2)^{-1} \quad (41b)$$

If we neglect the volume term (setting $V = 0$) in eq 40 and 41, they reduce to eq 32 and 33. Thus, in the absence of the volume correction, the DS approximation for rings is exact. If the volume correction is included, the DS results differ slightly from the rigorous ones (numerical results will be given later), but the difference decreases with N, and in the $N \rightarrow \infty$ limit the DS approximation is exact, giving eq 37 as the asymptotic result.

Finally, the DS-OP formulas for rings are

$$D_{\parallel} = k_BT[1 + {}^2\!/_3N\zeta R^2\lambda S_1D_{\parallel}^{\circ}]D_{\parallel}^{\circ} \qquad (\text{DS-OP}, N) \quad (42a)$$

$$D_{\perp} = k_BT[1 + {}^4\!/_3N\zeta R^2\lambda S_1D_{\perp}^{\circ}]D_{\perp}^{\circ} \qquad (\text{DS-OP}, N) \quad (42b)$$

where $D_{\parallel}^{\circ}$ and $D_{\perp}^{\circ}$ are given by eq 41. If $V = 0$ eq 42 reduce to eq 38, thus confirming the exactness of the DS treatment for rings in such a case. As expected, the $N \rightarrow \infty$ behavior of eq 42 is given by eq 39.

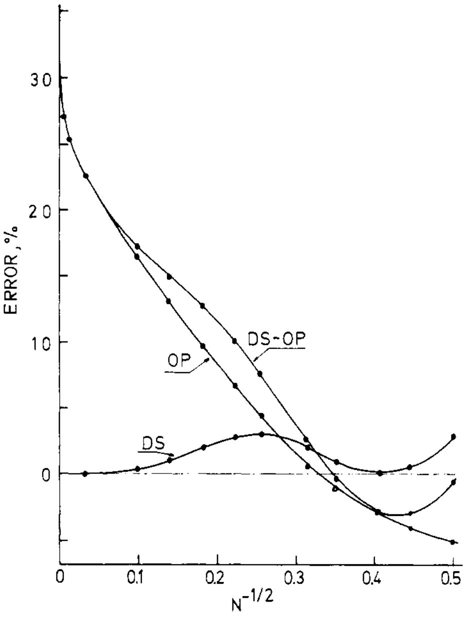

Figure 4. Same as in Figure 1 for the reciprocal of the shortest relaxation time of a rigid ring.

The rotational diffusion tensor of rings has two equal eigenvalues ($D_{\parallel}$) that are greater than the third one ($D_{\perp}$). Then from eq 1-3, there will be three relaxation times, $\tau_a > \tau_b > \tau_c$, given by

$$\tau_a^{-1} = 2D_{\parallel} + 4D_{\perp}$$
$$\tau_b^{-1} = 4D_{\parallel} + 2D_{\perp}$$
$$\tau_c^{-1} = 6D_{\parallel} \quad (43)$$

In Figures 3 and 4 we present the errors of the approximate methods in the reciprocals of the longest and shortest relaxation times, τ_a^{-1} and τ_c^{-1}. The calculations were done with the modified tensor and with the volume correction for $\sigma = b/2$ (touching beads). The errors of the OP values are appreciable, and in the $N \rightarrow \infty$ limit they reach -11.1% and 33.3% for τ_a^{-1} and τ_c^{-1}, respectively. The DS-OP results show a similar trend. On the other hand, the errors in the DS values are quite small, <5% always, and tend to zero for very long rings.

3. Compact Regular Structures. Regular (polygonal or polyhedral) structures composed of a few spherical elements are of great interest because they are presented by a variety of biopolymers, for example, oligomeric proteins.[21] Also, from a theoretical point of view, one expects that the transport properties of such structures should be strongly influenced by hydrodynamic interactions due to their very compact aspect.

The structures that we have considered are listed in Table I and displayed in Figure 1 of ref 2. In the calculations, we used the highest value of the spherical elements, i.e., $\sigma = b/2$, corresponding to touching neighbor beads. Owing to their symmetry, these structures have only two distinct eigenvalues of the rotational diffusion tensor, $D_{\parallel}$ and $D_{\perp}$, corresponding to the axis of highest symmetry and to a perpendicular axis, respectively.

Before considering the performance of the approximate methods, we comment on the influence of the volume correction in the rigorous results. Table I contains values of the two diffusion coefficients obtained with four versions of the rigorous procedure. We see that, while the influence of the modification in the interaction tensor is of a few percent, the effect from the finite size of the elements, accounted for by the volume correction, is quite strong.

Table I
Rotational Diffusion Coefficients of Regular Structures Normalized to the Diffusion Coefficient of the Spherical Elements

		$(8\pi\eta_0\sigma^3/k_BT)D_\parallel$				$(8\pi\eta_0\sigma^3/k_BT)D_\perp$[a]			
structure	no.[b]	M[c],V[d]	O[e],V	M,P[f]	O,P	M,V	O,V	M,P	O,P
tetrahedron	42	0.1166	0.130	0.2188	0.2709				
centered triangle	44	0.1017	0.1026	0.1714	0.1741	0.0692	0.0709	0.0957	0.0990
centered tetrahedron	52	0.0693	0.0712	0.1061	0.1106				
centered square	53	0.0802	0.0807	0.1341	0.1354	0.0589	0.0619	0.0836	0.0898
trigonal prism	62	0.0768	0.0828	0.1427	0.1647	0.0757	0.0809	0.1338	0.1573
octahedron	64	0.0789	0.0876	0.1500	0.1849				
centered hexagon	71	0.0629	0.0614	0.1126	0.1078	0.0500	0.0556	0.0769	0.0912
centered octahedron	72	0.0527	0.0551	0.0836	0.0980				
cube	81	0.0557	0.0603	0.1007	0.1167				

[a] Equal to $D_\parallel$ if not given. [b] Notation of ref 22. [c] Modified interaction tensor. [d] With volume correction. [e] Oseen interaction tensor. [f] Without volume correction.

Table II
Reciprocals of the Longest and Shortest Relaxation Times of Regular Structures Normalized to the Value for the Spherical Elements and the Percent Error of Each Approximate Method[a]

structure	no.	$(4\pi\eta_0\sigma^3/3k_BT)\tau_a^{-1}$-(EX)	error OP	error DS	error DS-OP	$(4\pi\eta_0\sigma^3/3k_BT)\tau_c^{-1}$-(EX)	error OP	error DS	error DS-OP
tetrahedron	42	0.1167	−14.3	4.4	−3.8				
centered triangle	44	0.0801	−9.6	1.0	−7.2	1.0169	−4.8	1.7	−2.0
centered tetrahedron	52	0.0694	−12.8	0.6	−10.0				
centered square	53	0.0661	−13.2	0.5	−12.4	0.0802	−4.2	1.2	−2.2
trigonal prism	62	0.0742	−17.5	4.2	−15.0	0.0760	−15.8	−0.7	−12.1
octahedron	64	0.0790	−17.1	0.3	−13.1				
centered hexagon	71	0.0543	−14.8	1.3	−14.8	0.0629	−3.0	0.0	−3.0
centered octahedron	72	0.0435	−17.6	0.0	−16.0				
cube	81	0.0455	−18.5	0.8	−18.0				

[a] Results corresponding to the modified tensor and including the volume correction.

This was to be expected, since the size of the elements is close to the size of the structure.

In Table II we present results for the relaxation times of these structures. Since they have a symmetry axis, they have at most three relaxation times, given by either eq 31 or eq 43. For spherically symmetric structures the three times are identical. In Table II we report only the reciprocals of the longest and shortest times, τ_a^{-1} and τ_c^{-1}. As in the preceding applications, the performance of the approximate methods is measured as the percent deviation from the rigorous results. It is clear that, as it happened for rods and rings, the DS method that avoids preaveraging, works much better than the OP approximation.

IV. Conclusions

In this paper we have derived a double-sum, approximate method for calculating rotational diffusion constants that includes the contribution from the finite size of the frictional elements. The DS method is much more efficient than the rigorous and OP methods since the number of operations is of the order of N^2 instead of N^3. Furthermore, the DS method is very accurate for the symmetric structures studied in this paper, in contrast with the poor results obtained with preaveraging procedures. Indeed, the DS is exact for infinitely long rods and rings, while for finite ones and for other compact structures as well, its errors are always under 5%.

A remaining question concerns the performance of the DS method for irregular rigid structures and flexible or semiflexible macromolecules in the rigid-body approximation. We know that the errors of double-sum formulas which avoid preaveraging, for other properties, are not much greater for instantaneous conformations of flexible chains[8] than for rigid, symmetric structure,[11] and a similar behavior is expected for the rotational DS method. In other interesting cases, namely bent, articulated, or weakly bending rods, the errors of our DS method could be close to those found here for straight rods because of their structural similarity.

Acknowledgment. This work was supported by Grant 561/84 from the Comisión Asesora de Investigación Científica y Técnica to J.G.T.

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