Monte Carlo Study of Hydrodynamic Properties of Flexible Linear Chains: Analysis of Several Approximate Methods

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ABSTRACT: Using a Monte Carlo simulation technique, we have calculated hydrodynamic properties of flexible linear chains by different methods based on the Kirkwood-Riseman theory. We first obtain the long-chain limiting values of the well-known parameters $P$ and $\Phi$, obtaining $6.0$ and $2.5 \times 10^{23}$, respectively, for completely flexible chains. We show that these results hold both for freely jointed chains of fixed bond length and for Gaussian chains. Next, we discuss the performance of several approximate methods for freely jointed chains. By distinguishing between orientational and conformational preaveraging, we note that the effect of the former is quite small, while the latter overestimates appreciably the frictional coefficient and the intrinsic viscosity. On the other hand, double-sum formulas yield values smaller than the rigorous ones. Some methods which simultaneously involve two approximations may give acceptable results owing to cancellation of errors. The approximate methods have been tested also for real poly(methylene) chains. In this case, the errors vary slowly with chain length and are generally small.

Introduction

The hydrodynamic properties of macromolecules are usually studied in terms of the Kirkwood-Riseman theory. This theory is based on obtaining the frictional forces corresponding to the $N$ frictional elements of the chain by means of a set of $3N$ linear equations. In most applications, however, and especially in the standard treatment for flexible chains, some approximations are introduced. For example, the preaverage approximation consists in using the interaction tensor in a preaveraged form. This approximation is in connection with the chain statistics since it avoids a final orientational and conformational preaveraging. Another common approximation is concerned with solving the linear equations in a noncompletely correct way and leads to the so-called “double-sum” formulas. Thus, applied to the translational properties, this approximation leads to the well-known Kirkwood formula. For viscosity, it yields the expression first proposed by Tsuda, which is further simplified by preaveraging.

On the other hand, there is the possibility of solving numerically the hydrodynamic interaction equations for a rigid chain without any simplification and, then, to have a precise test on the performance of the different approximate methods. This test is needed in order to use approximate methods in the prediction of experimental data. In a previous work we have presented an analysis of numerical results obtained with the improved and the simplified theories for totally rigid structures. The conclusions reached there may be, however, significantly altered by conformational statistics in the case of flexible chains. Moreover, the Kirkwood-Riseman theory for flexible chains, in its standard version for viscosity, contains the split into two terms of certain conformational averages of distances between units which should be also considered as an additional approximation.

In this work, we use the different versions of the Kirkwood-Riseman theory to calculate theoretical values of hydrodynamic properties for two types of linear flexible polymer models: the freely jointed chain and the real poly(methylene) chain, the latter represented by the rotational isomeric state model with excluded volume between nonneighboring units. The results have been obtained by taking averages over Monte Carlo samples constituted by chain conformations considered as instantaneously rigid. This way we calculate statistical values of the properties for chains with given values of $N$. In some cases, the long-chain behavior is investigated by adequate numerical extrapolations, in which limits obtained analytically are used as references.

This Monte Carlo method was first applied by Zimm for Gaussian chains and used by us in a previous work to calculate the properties for the same models adopted here. We have also applied recently the same procedure to study Gaussian star chains. Furthermore, Hagerman and Zimm have used the same procedure to study the rotational diffusion of wormlike macromolecules.

The present calculations are aimed at understanding the separate effects of the different approximations mentioned above and at discussing the similarities and variations found in these effects for the two molecular models and, in a more general context, between rigid and flexible chains. Since the Gaussian and the freely jointed chains are suspected to be hydrodynamically equivalent in the long-chain limit, it is also interesting to confirm this point and to compare values corresponding to both models for finite $N$.

As kindly pointed out by a reviewer of this paper, some confusion might arise from the use of the qualifier “rigorous” applied to the improved form of the Kirkwood-Riseman theory. Kirkwood and Riseman introduced some approximations such as preaveraging hydrodynamic interactions and approximating the inverse of the diffusion tensor. In what we call the rigorous version of the Kirkwood-Riseman theory, these approximations are removed, since preaveraging is avoided and the hydrodynamic interaction equations are solved numerically. Save minor differences, the procedure is equivalent to Zimm’s algorithm, as shown later. Obviously, the results are not absolutely exact; in fact, they are influenced not only by the assumption of an equilibrium statistics in the study of a hydrodynamic problem but also by the simplified treatment of hydrodynamic interactions through Oseen-type tensors. At any rate, the theoretical results will be shown...
to successfully predict experimental data, and we think that they are valid to estimate the errors introduced by the various approximations.

**Methods and Results**

Conformations of freely jointed chains were generated by joining \( N - 1 \) randomly oriented vectors of fixed length \( b \). For real poly(methylene) chains, the bond angle was fixed to be 112° and the bond status was chosen as one of the \( t \), \( g^* \), and \( g \) rotational isomers, each weighted with a probability corresponding to 25 °C and a 500 cal mol\(^{-1}\) energy difference between \( t \) and \( g \). In the simulation of poly(methylene) chains, excluded volume was represented through a hard-sphere potential with a contact distance \( d \) taken as \( d/b = 1.76 \) (\( d = 2.70 \) Å if \( b = 1.53 \) Å). These simulation procedures are essentially identical with those used in our previous work.\(^{9} \)

For each chain conformation, regarded as a rigid body, and assigning several values to the Stokes radius, \( \sigma \), of the \( N \) frictional elements, the hydrodynamic properties were calculated by different methods. The results were averaged a posteriori over the \( n \) individual values for the chains in the sample. The sample size ranged from \( n = 200 \) for \( N = 5 \) to \( n = 40 \) for \( N = 50 \). It should be remarked that the same sample was employed in the calculations for the various hydrodynamic methods.

The hydrodynamic results that we shall regard or denote as "exact" (EX) are those obtained by employing the rigorous version of the Kirkwood–Riseman theory as described previously\(^{6,8} \) (see the last paragraph in the Introduction for comments on the actual exactness of these results). The only difference with respect to our early Monte Carlo study\(^{4} \) is that provision was made for overlapping elements, which can occur in some conformations of freely jointed chains with no excluded volume. When the computer program detects overlap between two chain elements, the hydrodynamic interaction between them is evaluated via the Rotne–Prager tensor\(^{12} \) for overlapping spheres. This is an alternative to the procedure employed by Zimm,\(^{8} \) based on a cutoff distance. Nonetheless, the effect of the improvements will be shown later to be rather small.

The results from the rigorous version of the Kirkwood–Riseman theory for translation and rotation can be considered as exact for rigid bodies (keeping in mind remembering deficiencies in the description of hydrodynamic interaction\(^{13-15} \)). Thus, our EX values are only influenced by the so-called rigid-body approximation\(^{8,16} \) implicit in the Monte Carlo study of flexible-chain hydrodynamics. However, results for dumbbells\(^{16,17} \) and dynamic simulations for short chains\(^{18} \) suggest that the errors caused by such approximation are small and may be even smaller than the statistical errors of the Monte Carlo simulation.

In the rigorous calculation of the intrinsic viscosity, we have used the formula originally proposed by Garcia de la Torre and Bloomfield\(^{19} \) (eq 45 in ref 6 or eq 19 in ref 9). Later, Wilemski and Tanaka\(^{17} \) derived an expression which gives an upper bound to the intrinsic viscosity (eq 2.28 in ref 17). When the average in the Wilemski–Tanaka upper bound expression is performed over the orientations of a rigid molecule (or an instantaneously rigid conformation of a flexible chain) with respect to the velocity field, the formula of Garcia de la Torre and Bloomfield is recovered (the demonstration is straightforward and we do not present it here). It is known that such formula is strictly valid only for somewhat symmetric particles. Recently, Wegener\(^{20} \) carried out an elaborate, exact study of the intrinsic viscosity of arbitrarily shaped rigid bodies, finding that in the worst cases the error of the Garcia de la Torre–Bloomfield formula is about 1%. Therefore, the results obtained from this formula can be reasonably regarded as "exact" (EX), with the limitations described in the above paragraph, in the analysis of the performance of the other methods.

After commenting on the theoretical basis of the results used as reference in the evaluation of the performance of the approximate methods, we think that a detailed description of these methods is not necessary, for they have been described in a previous paper.\(^{7} \) We shall just mention their grounds and present some equations needed in the discussion of results.

In the diagonal approximation (DA), the only difference with respect to the rigorous procedure is that the off-diagonal elements of the interaction tensor are neglected. Another method is based in the orientational preaverage (OP) of the interaction tensor. It leads to the following expressions for the translational friction coefficient, \( f_\iota \), and the intrinsic viscosity, \( \eta \):

\[
f_\iota = \langle \sum_{i,j} \zeta_i (\mathbf{H}^{-1})_{ij} \rangle \iota \iota \quad i, j = 1, \ldots, N \tag{1}
\]

\[
\eta = \frac{N_A}{6\pi\eta_0} \langle \sum_{i,j} \zeta_i (\mathbf{H}^{-1})_{ij} \mathbf{R}_i \cdot \mathbf{R}_j \rangle \iota \iota \tag{2}
\]

where

\[
H_{ij} = \xi_i (6\pi\eta_0 R_i)^{-1} \quad \text{if } i \neq j \tag{3}
\]

\[
H_{ii} = 1 \tag{4}
\]

and

\[
\zeta_i = 6\pi\eta_0 \sigma_i \tag{5}
\]

In these equations, \( \eta_0 \) is the viscosity of the solvent, \( N_A \) is Avogadro's number, \( M \) is the molecular weight of the macromolecule, and \( \sigma_i \) is the radius of the spherical chain elements. In our calculations, all the elements are identical with radius \( \sigma \) and then \( \zeta_i \) could be factored out in eq 1–5 and the following. \( \mathbf{R}_i \) is the vector joining the viscosity center to the center of element \( i \), and \( R_{ij} \) is the distance between elements \( i \) and \( j \).

Other methods are based on double-sum formulas. Thus, \( f_\iota \) can be computed from the famous Kirkwood (K) formula\(^{2} \)

\[
f_\iota = \langle (\sum_i \zeta_i)^2 \sum_{i,j} \zeta_i H_{ij} \rangle \iota \iota \tag{6}
\]

Tsuda\(^{3} \) derived an approximation formula (T) for \( \eta \), making some approximations in the solution of the hydrodynamic interaction equations but avoiding the orientational preaverage:

\[
\eta = \frac{N_A}{6\pi\eta_0} \left( \langle \sum_i \zeta_i R_i^2 \rangle \right) \times \left[ 1 + \frac{1}{8\pi\eta_0\langle \sum_i R_i^2 \rangle} \left( \sum_{i,j} \zeta_i \left( \frac{R_i R_j \cos \alpha_{ij}}{R_{ij}} + 4(R_i^2 + R_j^2) R_{ij} \cos \alpha_{ij} - R_i^2 R_j^2/(1 + 7 \cos^2 \alpha_{ij})/10R_{ij}^3 \right) \right] \right]^{1/2} \tag{7}
\]

where

\[
\cos \alpha_{ij} = \mathbf{R}_i \cdot \mathbf{R}_j / R_{ij} \tag{8}
\]

If the tensor is orientationally preaveraged, instead of Tsuda's formula, a much simpler result is obtained\(^{6,5} \)

\[
\eta = \frac{N_A}{6\pi\eta_0} \left( \langle \sum_i \zeta_i R_i^2 \rangle^2 \langle \sum_{i,j} \zeta_i H_{ij} R_i \cdot R_j \rangle \right)^{-1} \tag{9}
\]
The approximate method for the calculation of further factorization. Equation 9 provides a good example; eq 9 takes the form

\[ f_j = \sum_{i} f_{ij} \]

This equation, approximately substituted by their conformational averaging, conforms in the Monte Carlo sample. It is important to stress this point since, as discussed below, other approaches include conformational averaging and even further factorization. Equation 9 provides a good example; the quantities that are to be summed over \( i \) and \( j \) can be approximately substituted by their conformational averages. Furthermore, introducing the additional approximation

\[ \langle H_{ij} R_i \cdot R_j \rangle_c = \langle H_{ij} \rangle_c \langle R_i \cdot R_j \rangle_c \]  

on eq 11 will be labeled as FGF.

The results for freely jointed and poly(methylene) chains with varying \( N \) and \( \sigma \) are presented in Tables I and II. The EX results are expressed in the following dimensionless form:

\[ f_\ast = f_\ast / 6 \pi \eta_0 b \]

and

\[ \eta_\ast = M/\eta_\ast N/\lambda b^5 \]  

In eq 13, \( f_\ast \) is the rotational friction coefficient obtained for each method as described in ref 7. OP-1 and OP-2 refer to the two ways of calculating \( f_\ast \) in the OP approximation. We have also calculated \( f_\ast \) from an expression similar to eq 7 (see eq 33 in ref 7); the results will be denoted as TR.

For the sake of compactness, instead of the actual values for the approximate methods, we report in Tables I and II the percent errors with reference to the EX results:

\[ \text{error} = 100(\text{exact} - \text{approximate})/\text{exact} \]

We have shown that this result is equivalent to the OP approximation for certain rigid, symmetrical structures. In eq 1, 2, 6, 7, and 9, \( \Sigma \) denotes statistical average over conformations. It should be remarked that none of the methods considered so far embodies a conformational preaveraging. As indicated previously, we obtain the average a posteriori as the mean of the property values of the chain conformations in the Monte Carlo sample. It is important to stress this point since, as discussed below, other approaches include conformational averaging and even further factorization. Equation 9 provides a good example; the quantities that are to be summed over \( i \) and \( j \) can be approximately substituted by their conformational averages. Furthermore, introducing the additional approximation

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\[ \text{error} = 100(\text{exact} - \text{approximate})/\text{exact} \]
Aside from the systematic study of the approximate methods, we have been interested also in the influence of the way of modeling completely flexible chains. Concretely, while in this work and in a previous one\(^9\) we used the way of modeling completely flexible chains, the bond length was a Gaussian, random variable, which the sample was partitioned into four subsamples (the reported values are the mean and the standard deviation of the values for each subsample); D, results for Gaussian chains with \(\sigma/b = 0.256\), from ref 10; E, new results obtained in the present work for the latter model (\(\sigma/b = 0.256\)). The A, B, and C results were all obtained for \(\sigma/b = 0.26\). The use of the Rotne–Prager tensor is implicit in results B, C, D, and E.

**Discussion**

**Comparison of the Results for Freely Jointed and Gaussian Chains.** Before entering into the discussion of the main aspect of this paper, namely, the performance of the approximate methods, it seems worthwhile to compare the various ways of obtaining the rigorous results for Gaussian and freely jointed chains reported in Table III.

First, comparing A with B and C we see that the effect of introducing the Rotne–Prager tensor in the calculations for freely jointed chains is quite small (and probably smaller than simulation uncertainties) in regard to the final values of the properties. However, it is also irrelevant from the point of view of computational time. On the other

<table>
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<th>Table II</th>
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<td>Rigorous Results and Errors of the Approximate Methods for Poly(methylene) Chains</td>
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<th>(f_2^*)</th>
<th>(\varepsilon, %)</th>
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\(P = 6\pi f_1^* (N - 1)^{1/2}\) (16)

\(\phi = N_A [\varepsilon]^2 / (N - 1)^{3/2}\) (17)

\(P = 6\pi f_1^* (N - 1)^{1/2}\) because their variation with \(N\) is rather weak.

To distinguish the different sources of the results in Table III, we have used the following labels: A, results for freely jointed chains from ref 10; B, results for freely jointed chains obtained in this work (the only difference from A is the use of a Rotne–Prager tensor for overlapping elements); C, results of an independent set of simulations in which the sample was partitioned into four subsamples (the reported values are the mean and the standard deviation of the values for each subsample); D, results for Gaussian chains with \(\sigma/b = 0.256\), from ref 10; E, new results obtained in the present work for the latter model (\(\sigma/b = 0.256\)). The A, B, and C results were all obtained for \(\sigma/b = 0.26\). The use of the Rotne–Prager tensor is implicit in results B, C, D, and E.

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First, comparing A with B and C we see that the effect of introducing the Rotne–Prager tensor in the calculations for freely jointed chains is quite small (and probably smaller than simulation uncertainties) in regard to the final values of the properties. However, it is also irrelevant from the point of view of computational time. On the other
hand, for Gaussian chains, the occurrence of overlapping may be much more noticeable since it can take place even between neighbor elements. We therefore think that although its actual influence may be quite small, it is advisable to include the Rotne–Prager tensor in the numerical algorithms.

Another point of minor relevance is the effect of small differences in the choice of $\sigma/b$. The strength of hydrodynamic interaction is usually measured through the parameter

$$h^* = \frac{\gamma/(12\pi^2)^{1/2} a b}{N}$$

which is usually set to be 0.25, so that $\sigma/b = 0.256$. From Zimm’s point of view, $\sigma$ should be chosen as the Kirkwood–Riseman value for the Stokes radius of a non-draining chain of root-mean-square $b$, which leads to $\sigma/b = 0.271$. For our study of the freely jointed chain, on which the analysis of approximate methods is based, we have taken an intermediate value, $\sigma/b = 0.26$. It is evident from Table III that the effect of such difference is not significant.

Finally, a more interesting aspect is the comparison between the two types of chains. Table III shows that for very short chains the values of $P$ and $\Phi$ of chains with fixed bonds are consistently higher than those for Gaussian bonds. The deviation, however, decreases with $N$, and for high $N$ (say $N > 20$) it is blurred by the numerical uncertainties. Thus, it seems that both models give convergent results and should have identical properties in the $N \to \infty$ limit. Further evidence of this will be presented later. We think that this indicates also that the analysis of the errors of approximate methods for long chains that we will present below does not depend on the bond’s rigidity.

Errors of the Approximate Methods for Long, Freely Jointed Chains. In a previous paper we detected that some values of $\Phi$ and $P$ (data set D in Table III) for Gaussian chains are practically independent of $N$. The calculation of new data in this work (E) confirms this finding. Thus, estimates of the limiting behavior can be obtained by just averaging the results in the right part of Table III. We obtain in this way $\Phi^{+}_{EX(G)} = 2.51 \times 10^{23}$. Also, we obtain $P_{EX(G)} = 5.99$. It is very pleasant to note that these results coincide exactly with Zimm’s. The fact that even the second decimal places coincide may be somewhat fortuitous, since the uncertainties are of the order of 2% in $P$ and 4% in $\Phi$. In any case, the agreement can be regarded as excellent.

For freely jointed chains with $\sigma/b = 0.26$, we have plotted the difference between the exact value of $P$ and
the approximate ones vs. $N^{-1/2}$ (see Figure 1). By least-squares regression we compute from the intercept the limiting values of the differences for infinite $N$. The results are $P_{\text{EX}} - P_{\text{DA}} = 0.03$, $P_{\text{EX}} - P_{\text{OP}} = 0.10$ and $P_{\text{EX}} - P_{\text{K}} = 0.95$. Now, using the known limiting value corresponding to the Kirkwood formula, $P_{\text{K}} = 5.11$, we obtain $P_{\text{EX}} = 6.06$, which differs only 1% from $P_{\text{EX(G)}} = 5.99$. Both results can be considered as identical within numerical error and are in good accordance with recent experimental data yielding $P_{\text{exp}} = 5.7 - 6.0^{21,22}$.

Similarly, we obtain $P_{\text{DA}} = 6.03$ and $P_{\text{OP}} = 5.96$. Again, the deviation with respect to the rigorous results, $P_{\text{EX}}$ or $P_{\text{EX(G)}}$, is not greater than the numerical error. This leads us to conclude that for high $N$ the DA and OP approximations are practically exact. It should be remarked that $P_{\text{OP}}$ is not equivalent to the well-known limit obtained by Kurata and Yamakawa $^{23} P_{\text{XY}} = 5.22$, because though both use the orientationally preaveraged formula for the interaction tensor, the latter limit was obtained by introducing a further conformational preaverage of distances in the definition of the matrix elements or, in other words, by using the formula

$$f_i = \sum_j \sum_j (\langle H \rangle e^{-i})_{ij}$$

(19)

where $\langle (H) e^{-i} \rangle = 1$ and

$$\langle (H) e^{-i} \rangle_{ij} = \left( \frac{\ell}{6\pi n_0} (R_i)_{ij} \right)_c, \quad i = j$$

(20)

while our results have been obtained without any previous conformational average (compare eq 1 and 19). Then it is evident that though orientational preaverage has a minor, if any, effect in the calculation of translational properties, conformational preaverage has a higher influence, yielding results as poor as those obtained with the Kirkwood double-sum approximation. As a summary, Table IV lists the limiting values of the $P$ parameter according to the various approximations.

In order to obtain limit values for $\Phi$ we need also a reference result with a role similar to that of $P_{\text{K}}$ in the analysis of translational properties. Our OP calculations from eq 2 should not reproduce the well-known Auer-Gardner limit, $\Phi_{\text{AG}} = 2.87 \times 10^{23}$ since this limit includes a previous split of the conformational preaverages so that eq 2 becomes

$$[\eta] = \frac{N_\alpha}{6M_\alpha} \sum_i \sum_j (\langle H \rangle e^{-i})_{ij} (R_i \cdot R_j)_c$$

(21)

obtaining the limiting result $\Phi_{\text{AG}} = 2.12 \times 10^{23}$. He also employed the factorized and preaveraged eq 11, reproducing the limit $\Phi_{\text{FG}} = 2.30 \times 10^{24}$. As we have, on the other hand, evaluated the FGF values for our Monte Carlo samples, the latter result can be taken as a reference.

In Figure 2 we have plotted $\Phi_{\text{EX}} - \Phi_{\text{EX(G)}}$ vs. $N^{-1/2}$ for freely jointed chains with $a/b = 0.26$ for the various approximate methods: (X) DA; (+) OP; (□) T; (●) FG; (△) FGF.

For the values of $\Phi_{\text{AG}}$ we have used a factorized version of Tsuda's non-preaveraged eq 7

$$[\eta] = \frac{N_\alpha}{6M_\alpha} (\langle \sum_i (R_i^2) \rangle_c) \times$$

$$\left\{ 1 + \frac{1}{8\pi n_0 (\sum_i (R_i^2))_c} \left[ \sum_i \sum_j (\langle R_i R_j \cos \alpha_{ij} \rangle_c / R_{ij} + [4(R_i^2 + R_j^2) R_i R_j \cos \alpha_{ij} - R_i^2 R_j^2 (1 + 7 \cos^2 \alpha_{ij})] / 10R_{ij} \right] \right\}^{-1}$$

(22)

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interaction by means of the so-called draining parameter, it is useful to gauge the influence of hydrodynamic in-
mal values is quite small. We calculated the OP values of the individual values of the approximate properties of the sample averages.
Thus, the high errors of methods OP-2 and TR are caused by the different way in which the rotational coefficient is extracted from the rotational friction tensor (this aspect has been described and discussed in ref 7). Experimental studies of rotational properties are less abundant, less precise, and more difficult to interpret or compare with theories than in the case of translational properties and intrinsic vi-
Figure 3. Percent errors of the K method for $f_1$ plotted vs. $(N^{1/2} \sigma/b)^3$. Data points correspond to $N = 10, 15, 20, 30, 40,$ and 50 and to the indicated values of $\sigma/b$.

Figure 4. Same as in Figure 3 for the FG values of $[\eta]$.
cosity. Consequently, we have intentionally evaded an in-depth analysis of the approximations for rotation.

**Dependence of the Errors on \( \sigma \) and \( N \) for Poly(methylene) Chains.** A first look at Table II reveals that, unlike in the case of freely jointed chains, the errors vary smoothly with both \( N \) and \( \sigma \). The statistical fluctuations are scarcely detectable and no anomalous values appear. The reason is that the short- and long-range interactions present in poly(methylene) chains narrow the distribution function of any distance or distance-based property. Specifically, long-range interactions exclude conformations with overlapping elements.

Another significant difference with respect to freely jointed chains is that if one draws plots of the errors vs. \( N^{-1/2}(\sigma / b)^{-1} \), the data points for various \( \sigma \) and \( N \) do not follow a single curve. As this combination of \( N \) and \( \sigma \) arises when one assumes Gaussian statistics for the interelemental distances, which is not true for finite poly(methylene) chains, the difference is well justified.

Generally speaking, the errors of the approximate methods increase with both \( \sigma \) and \( N \). However, the rate of increase with \( N \) is apparently quite slower than for freely jointed chains. Let us illustrate this situation in a significant example. In a previous paper we compared experimental data of translational diffusion and intrinsic viscosity of short \( n \)-alkanes with theoretical predictions, finding that a reasonable value of the Stokes radius of the \(-\text{CH}_2-\) groups is \( \sigma \approx 0.6 \) Å. With \( b = 1.53 \) Å, this gives \( \sigma / b \approx 0.39 \), which is one of the values used in our numerical calculations. In Figure 5 we have plotted the errors of the approximate methods for \( \sigma \) and \( \left[ \tau \right] \). The slowness in the variation of the errors with chain length is well evident. In addition, the errors for \( \left[ \tau \right] \) seem to have a minimum or a maximum for \( N \approx 15 \).

Apart from the slopes of the curves, we think that an important aspect shown by Figure 5 is that the errors are quite small. Owing to the curvature exhibited by the points, a numerical extrapolation to the limit of infinite chain length does not seem worthwhile. At any rate, by just visual inspection, one can roughly estimate upper bounds for the limiting errors: 3% for \( \text{DA(translation)} \), 5% for \( \text{OP(translation)} \), 6% for \( \text{K} \), 5% for \( \text{DA(viscosity)} \), 7% for \( \text{OP(viscosity)} \), and 8% for \( \text{FG} \). These errors are not much higher than the uncertainties of typical experimental data. We also note that the errors of the simplest methods, \( K \) and \( \text{FG} \), are clearly smaller than those found for freely jointed chains. This is surely a consequence of the more important role of extended conformations.

A topic which deserves further study is the influence of short-range (local structure) and long-range (excluded volume) interactions on the hydrodynamic behavior of real linear chains. We have seen in this paper that the approaches in which conformational preaverages are used can be misleading and therefore one should have recourse to Monte Carlo simulation. The obvious drawback of this procedure, namely, its computational expense, can be avoided by using approximate methods, whose errors, as shown in our analysis of linear poly(methylene) chains, will be small and predictable. Then the study of hydrodynamic properties of oligomers (for which short-range interactions are important) and those of perturbed long chains (with significant long-range interactions) can be greatly facilitated.

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**References and Notes**

20. Wegener, W.A. Personal communication of work to be published.