

If we use  $E_{\sigma} = 1300$  instead of  $900 \text{ cal mol}^{-1}$  (curve B, Figure 4), we obtain better agreement with the experimental data for POEG. However, then the calculated  ${}_mK$  values for POEDE (not shown here) are only in fair agreement with the experimental results.

These remaining small discrepancies should not be construed as a failure of the RIS and BAA schemes. Rather, one should bear in mind that the  ${}_mK/x$  values of POEG and POEDE are exceedingly small, being not very different from the  ${}_mK$  value of the solvent carbon tetrachloride ( $1.35 \times 10^{-12} \text{ cm}^7 \text{ SC}^{-2} \text{ mol}^{-1}$ ). Therefore, given the approximations inherent in the RIS and BAA schemes and the smallness of the  ${}_mK$  values, we think that we have accounted reasonably well for the experimental results.

### Conclusions

Our extensive data on POEG in isotropic solvents show that  ${}_mK/x$  reaches an asymptotic value, in contrast with the data of Aroney et al. which was measured in benzene. Such differences are attributed to specific solvation of the polymer with optically anisotropic benzene molecules. Our results, which were obtained in non- $\Theta$  solvent, show that  ${}_mK/x$  is independent of molecular weight and insensitive to excluded volume interactions. This makes  ${}_mK$  a particularly attractive quantity to characterize polymers, obviating the need for using  $\Theta$  solvents.

We are also able to get good agreement between the calculated and experimental values of  ${}_mK/x$  for all  $x$  for both POEG and POEDE, using energetic parameters consistent with those derived by Flory, Mark, and their co-workers from other conformationally dependent properties.

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## Monte Carlo Calculation of Hydrodynamic Properties of Freely Jointed, Freely Rotating, and Real Polymethylene Chains

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**ABSTRACT:** The hydrodynamic properties (translational and rotational coefficients and intrinsic viscosities) of freely jointed and freely rotating chains, as well as those of real polymethylene chains with excluded volume, are evaluated in this paper as functions of the chain length and the frictional radius of the repeating units. The properties are calculated as averages over samples of Monte Carlo generated chain conformations that are regarded as instantaneously rigid particles. The hydrodynamic treatment is a rigorous version of the Kirkwood-Riseman theory, which has been successfully applied earlier to rigid macromolecules. We consider also a typical approximate equation, namely, Kirkwood's formula for translational coefficients. Notwithstanding differences in model and procedure, our results for freely jointed chains are very close to those obtained in a recent paper by Zimm when the elements' frictional radius is given a well-established value. Furthermore, we analyze the effect of the chain constraints embodied in the freely rotating and polymethylene chains on the individual properties and compare the performance of Kirkwood's formula for each chain model. Some implications for long real chains are discussed.

### Introduction

Over the past 30 years, the theory of the hydrodynamic properties of macromolecules in solution proposed by Kirkwood and Riseman<sup>1,2</sup> has been extensively used.<sup>3</sup> In

its most rigorous form, such theory applies the Oseen-Burgers method to account for the hydrodynamic interactions between the frictional elements composing the macromolecular model. In practice, however, Kirkwood

and Riseman introduced some approximations whose validity remained more or less unclear. In a recent paper, Zimm<sup>4</sup> considered the effects of those approximations. Following Kramers,<sup>5</sup> he calculated the hydrodynamic properties of freely jointed chains as averages of values obtained for Monte Carlo generated conformations regarded as rigid particles. The properties were obtained without any approximation by numerical methods akin to those used previously for rigid macromolecules.<sup>6</sup> For the same Monte Carlo samples, he also made calculations with the Kirkwood–Riseman approximations in order to ascertain the errors introduced by them as functions of chain length.

In our work, we have followed Zimm's steps but with some differences in focus and procedure. In addition to freely jointed chains, we have considered freely rotating and real polymethylene chains. For these three models, the bond length is kept constant, and the radius of the frictional elements representing the repeating units is varied. Thus one can establish the influence of both chain constraints and the strength of hydrodynamic interactions. As to the procedure, we use the same computational algorithms that have been developed for rigid structures,<sup>6,7</sup> and translation–rotation coupling effects<sup>6–11</sup> are taken into account in a way that is formally different from but, we think, identical with Zimm's. The relative importance of such effects is determined by comparison with results obtained without them.

The results for polymethylene chains will be used in the following paper<sup>12</sup> to interpret literature data on translational diffusion coefficients and intrinsic viscosities of *n*-alkanes in two different solvents. In a forthcoming publication we will present a systematic error analysis of a variety of approximate hydrodynamic equations. Nonetheless, here we discuss one of them: the well-known double-sum formula of Kirkwood<sup>2</sup> for the translational coefficients. As this formula represents the most simplified result of the Kirkwood–Riseman theory,<sup>1,2</sup> one can get some feeling about the performance of the latter in terms of the type of model, chain length, and hydrodynamic interaction.

## Methods

### Monte Carlo Generation of Chain Conformations.

Freely jointed chains consisting of  $N + 1$  beads connected by  $N$  vectors of fixed length  $b$  were generated by randomly choosing the orientation of all the segments but the first one. Thus, the first bead was placed at the center of a laboratory-fixed system of Cartesian coordinates, and the second one was centered at point  $(b, 0, 0)$  on the  $x$  axis. The coordinates of the following beads are then given by

$$\begin{aligned} x_i^1 &= x_{i-1}^1 + b \sin \alpha_i \cos \beta_i \\ x_i^2 &= x_{i-1}^2 + b \sin \alpha_i \sin \beta_i \\ x_i^3 &= x_{i-1}^3 + b \cos \alpha_i \\ i &= 3, \dots, N \end{aligned} \quad (1)$$

where  $\alpha_i$  and  $\beta_i$  are the polar angles of the  $i$ th vector that were chosen at random within the intervals  $0-\pi$  and  $0-2\pi$ , respectively. The square end-to-end distance is then

$$r^2 = (x_{N+1}^1)^2 + (x_{N+1}^2)^2 + (x_{N+1}^3)^2 \quad (2)$$

and the square radius of gyration is

$$s^2 = (N + 1)^{-2} \sum_{i>j}^{N+1} \sum R_{ij}^2 \quad (3)$$

where  $R_{ij}$  is the distance between beads  $i$  and  $j$ .

Freely rotating chains with fixed bond length  $b$  and bond angle  $\theta$  were generated by randomly taking for the torsional angle  $\phi_i$  one of the three values  $0^\circ$ ,  $120^\circ$ , or  $240^\circ$ , corresponding to the *t*, *g*, and *g'* conformations. The coordinates of the beads are those obtained in the laboratory-fixed system using transformation matrices that allow calculation of the coordinates of the  $(i + 1)$ th bead from those of beads  $i - 2$ ,  $i - 1$ , and  $i$  and the torsional angle  $\phi_{i-2}$  of the bond joining bead  $i + 1$  with bead  $i$  with respect to the plane defined by beads  $i - 2$ ,  $i - 1$ , and  $i$ . In all the calculations reported here we used the bond angle of polymethylene chains,  $\theta = 112^\circ$ .

Finally, we have also considered real chains with hindered rotation and long-range (excluded volume) effects. The generation of real chains was performed with a modified version of the algorithm for freely rotating chains. The choice between the three possible values of the torsion angle was made in this case on the basis of a  $500 \text{ cal mol}^{-1}$  energy difference between the *g* or *g'* and the *t* isomers of each bond. To account for both short-range steric hindrances, corresponding to  $|i - j| > 3$ , and long-range effects, a hard-sphere potential with a contact distance of  $2.70 \text{ \AA}$  was used. More details on the generation procedure can be found in a previous paper.<sup>13</sup>

It should be noted that for the three types of chains, individual chain configurations were generated one at a time. In other works,<sup>13,14</sup> many configurations were obtained from an initial chain by changing a given rotation angle. This procedure has the obvious advantage of being faster, but one can suspect that the convergence of the calculated properties will be slower since, for instance, many  $R_{ij}$ 's in the subsequent chains will be the same as in the original one. As the computer time required to calculate the hydrodynamic properties, as described below, is usually much longer than that needed for its full generation, we have opted to generate each chain's conformation independently.

**Calculation of Hydrodynamic Properties.** For each conformation the hydrodynamic properties were obtained by using the rigid-particle formalism.<sup>6,7,15–17</sup> We will follow here the methods and notation of García de la Torre and co-workers. This formalism has been widely described in the literature, and a detailed review is available.<sup>6</sup> Therefore, we reproduce here only the fundamental equations.

From the Cartesian coordinates one computes first the modified interaction tensors as formulated by Rotne and Prager<sup>18</sup> and Yamakawa<sup>19</sup>

$$\mathbf{T}_{ij} = \frac{1}{8\pi\eta_0 R_{ij}} \left[ \mathbf{I} + \frac{\mathbf{R}_{ij}\mathbf{R}_{ij}}{R_{ij}^2} + \frac{2\sigma^2}{R_{ij}^2} \left( \frac{1}{3}\mathbf{I} - \frac{\mathbf{R}_{ij}\mathbf{R}_{ij}}{R_{ij}^2} \right) \right] \quad (4)$$

where  $\sigma$  is the radius of the beads and  $\eta_0$  is the viscosity of the solvent.  $\mathbf{I}$  is the three-dimensional unit tensor. Equation 4 is valid only for nonoverlapping beads, i.e., when  $R_{ij} > 2\sigma$ . For freely rotating chains without excluded volume restrictions, configurations will be generated in which some beads overlap. Fortunately, eq 4 can be used with little error when overlapping is not too extensive.<sup>6</sup> Once the  $\mathbf{T}_{ij}$ 's have been obtained, the frictional forces exerted on the solvent by the  $i$ th bead can be computed for any arbitrary velocity field as the solutions of the linear equations

$$\sum_{j=1}^{N+1} \mathbf{Q}_{ij} \cdot \mathbf{F}_j = \zeta(\mathbf{u}_i - \mathbf{v}_i^0) \quad i = 1, \dots, N + 1 \quad (5)$$

In eq 5  $\zeta = 6\pi\eta_0\sigma$  is the Stokes law frictional coefficient of the beads,  $\mathbf{u}_i$  and  $\mathbf{v}_i^0$  are, respectively, the velocity of bead  $i$  and the unperturbed velocity of the solvent at the

center of that bead, and the  $\mathbf{Q}_{ij}$ 's, given as

$$\mathbf{Q}_{ij} = \delta_{ij}\mathbf{I} + (1 - \delta_{ij})\zeta\mathbf{T}_{ij} \quad (6)$$

can be obtained from the coordinates via eq 4.  $\delta_{ij}$  is the Kronecker delta.

Next, a  $3(N+1) \times 3(N+1)$  supermatrix  $\mathbf{Q}$  is constructed in such a way that it contains  $(N+1) \times (N+1)$  blocks of dimension  $3 \times 3$ , which are the  $\mathbf{Q}_{ij}$ 's. Then  $\mathbf{Q}$  is inverted to get  $\mathbf{S} = \mathbf{Q}^{-1}$ , and  $\mathbf{S}$  is partitioned similarly into  $3 \times 3$  blocks,  $\mathbf{S}_{ij}$ , so that the frictional forces are given by

$$\mathbf{F}_i = \zeta \sum_{j=1}^{N+1} \mathbf{S}_{ij} \cdot (\mathbf{u}_j - \mathbf{v}_j^0) \quad (7)$$

Now, eq 7 is particularized for the bead and solvent velocities corresponding to translation, rotation, and viscosity.

For pure translation, the translational frictional tensor is obtained as<sup>15-17</sup>

$$\bar{\mathbf{Z}}_t = \zeta \sum_{i=1}^{N+1} \sum_{j=1}^{N+1} \mathbf{S}_{ij} \quad (8)$$

Owing to the obvious asymmetry of the random conformations of any of the three types of chain, they will have screwlike characteristics that will be hydrodynamically manifested as translation-rotation coupling. This can be accounted for by means of the coupling tensor.<sup>7-10</sup> In this rigid-particle version of the Kirkwood-Riseman theory, the coupling tensor referred to the origin, O, of the center of coordinates is given by<sup>7,16</sup>

$$\bar{\mathbf{Z}}_{0,c} = \zeta \sum_{i=1}^{N+1} \sum_{j=1}^{N+1} \mathbf{R}_i \times \mathbf{S}_{ij} \quad (9)$$

where  $\times$  denotes a dyadic product (as defined in Appendix B of ref 8) and  $\mathbf{R}_i$  is the vector joining O and the center of the  $i$ th bead.

Similarly, the rotational friction tensor at the origin O can be calculated from the expression<sup>7,16</sup>

$$\bar{\mathbf{Z}}_{0,r} = -\zeta \sum_{i=1}^{N+1} \sum_{j=1}^{N+1} \mathbf{R}_i \times \mathbf{S}_{ij} \times \mathbf{R}_j \quad (10)$$

From the three friction tensors, the rotational diffusion tensor, which is origin independent, is calculated as<sup>7,9</sup>

$$\mathbf{D}_r = k_B T (\bar{\mathbf{Z}}_{0,r} - \bar{\mathbf{Z}}_{0,c} \bar{\mathbf{Z}}_t^{-1} \bar{\mathbf{Z}}_{0,c}^T)^{-1} \quad (11)$$

The translational diffusion tensor, on the other hand, is origin dependent. Its value at the origin O can be obtained by the following relationship:<sup>7,9</sup>

$$\mathbf{D}_{0,t} = k_B T (\bar{\mathbf{Z}}_t - \bar{\mathbf{Z}}_{0,c}^T \bar{\mathbf{Z}}_{0,r}^{-1} \bar{\mathbf{Z}}_{0,c})^{-1} \quad (12)$$

The translational-rotational coupling in Brownian diffusion is characterized by means of an origin-dependent diffusion coupling tensor, given by<sup>7,9</sup>

$$\mathbf{D}_{0,c} = -k_B T \bar{\mathbf{Z}}_{0,r}^{-1} \bar{\mathbf{Z}}_{0,c} (\bar{\mathbf{Z}}_t - \bar{\mathbf{Z}}_{0,c}^T \bar{\mathbf{Z}}_{0,r}^{-1} \bar{\mathbf{Z}}_{0,c})^{-1} \quad (13)$$

The translational diffusion tensor is only meaningful when referred to a specific point, the center of diffusion, D, whose distance from the origin O,  $\mathbf{r}_{OD}$ , can be calculated as<sup>9,10</sup>

$$\mathbf{r}_{OD} = \begin{pmatrix} D_r^{22} + D_r^{33} & -D_r^{12} & -D_r^{13} \\ -D_r^{12} & D_r^{11} + D_r^{33} & -D_r^{23} \\ -D_r^{13} & -D_r^{23} & D_r^{11} + D_r^{22} \end{pmatrix}^{-1} \times \begin{pmatrix} D_{0,c}^{23} - D_{0,c}^{32} \\ D_{0,c}^{31} - D_{0,c}^{13} \\ D_{0,c}^{12} - D_{0,c}^{21} \end{pmatrix} \quad (14)$$

Then, the translational diffusion tensor at D is given by

$$\mathbf{D}_{D,t} = \mathbf{D}_{0,t} - \mathbf{r}_{OD} \times \mathbf{D}_r \times \mathbf{r}_{OD} + \mathbf{D}_{0,c}^T \times \mathbf{r}_{OD} - \mathbf{r}_{OD} \times \mathbf{D}_{0,c} \quad (15)$$

Finally, the translational diffusion coefficient is just the mean of the diagonal values of  $\mathbf{D}_{D,t}$ :

$$D_t = \frac{1}{3} \text{Tr} (\mathbf{D}_{D,t}) \quad (16)$$

An approximation to  $D_t$  can be obtained directly from  $\bar{\mathbf{Z}}_t$  (eq 12) by neglecting translation-rotation coupling effects, as has been implicitly assumed in most previous work on the hydrodynamics of flexible and rigid macromolecules. In this case, the expression to be used is

$$D_{t,nc} = \frac{k_B T}{3} \text{Tr} (\bar{\mathbf{Z}}_t^{-1}) \quad (17)$$

which follows immediately from eq 12-16 if one takes  $\bar{\mathbf{Z}}_{0,c} = 0$ . The subscript nc indicates that no coupling is considered. A similar approximation for rotational diffusion is not practical since the rotational coefficients must be referred to point D, whose evaluation requires the previous obtention of coupling tensors.

The sedimentation coefficient is directly proportional to the translational diffusion coefficient, as seen in Svedberg's equation. The proportionality constant embodies the molecular weight,  $M$ , and other physicochemical properties of the polymer and solvent that do not depend upon the conformation of the former. Therefore, the sedimentation coefficient will not be analyzed independently in this paper; all the conclusions for the translational diffusion coefficient hold also for it.

In regard to rotational dynamics, all the necessary information is contained in  $\mathbf{D}_r$ , and components of  $\mathbf{D}_r$  to be used will depend on the property that is actually considered. Here we will report only results for a rotational diffusion coefficient defined as

$$D_r = \frac{1}{3} \text{Tr} (\mathbf{D}_r) \quad (18)$$

We prefer to express the results in the form of translational and rotational friction coefficients,  $f_t$ ,  $f_{t,nc}$ , and  $f_r$ , which are defined according to the Stokes-Einstein relationship as  $k_B T/D_t$ ,  $k_B T/D_{t,nc}$ , and  $k_B T/D_r$ , respectively.

Finally, the intrinsic viscosity is calculated from the supermatrix  $\mathbf{S}$  by means of<sup>17</sup>

$$[\eta] = \frac{N_A \zeta}{M \eta_0} \sum_{i=1}^{N+1} \sum_{j=1}^{N+1} \left[ \frac{1}{15} \sum_{\alpha} (x_i^{\alpha} - V^{\alpha}) S_{ij}^{\alpha\alpha} (x_j^{\alpha} - V^{\alpha}) + \frac{1}{20} \sum_{\alpha \neq \beta} (x_i^{\alpha} - V_i^{\alpha}) S_{ij}^{\beta\alpha} (x_j^{\beta} - V^{\beta}) - \frac{1}{30} \sum_{\alpha \neq \beta} (x_i^{\alpha} - V^{\alpha}) S_{ij}^{\alpha\beta} (x_j^{\beta} - V^{\beta}) + \frac{1}{20} \sum_{\alpha \neq \beta} (x_i^{\alpha} - V^{\alpha}) S_{ij}^{\beta\beta} (x_j^{\alpha} - V^{\alpha}) \right] \quad (19)$$

$$\alpha, \beta = 1, 2, 3$$

$N_A$  is Avogadro's number, the  $x_i^{\alpha}$ 's are the Cartesian components of  $\mathbf{R}_i$ , and the  $V^{\alpha}$ 's are the coordinates of the center of viscosity (which do not coincide with the center of diffusion) and can be calculated as the solution of a set of three linear equations whose coefficients are simple combinations of the  $\mathbf{S}_{ij}$ 's and  $\mathbf{R}_i$ 's.<sup>17</sup> We wish to remark that eq 19 already includes the averaging over the orientations of the macromolecule, in a fixed conformation, with respect to the velocity field.

The equations we have presented so far are those we need for the evaluation of transport properties according to the rigorous form of the Kirkwood-Riseman theory. We have also calculated for each chain conformation the

Table I  
Hydrodynamic Properties of Freely Jointed Chains

| $N + 1$ | $\sigma/b$ | $n$ | $f_t^*/b$     | $f_r^*/b^3$   | $[\eta]^*/b^3$ | $P$  | $\Phi$ | $\beta$ |
|---------|------------|-----|---------------|---------------|----------------|------|--------|---------|
| 10      | 0.07       | 150 | 0.457 (0.001) | 0.438 (0.005) | 3.29 (0.06)    | 2.70 | 0.61   | 3.15    |
| 10      | 0.13       | 150 | 0.709 (0.003) | 0.833 (0.031) | 6.33 (0.12)    | 4.19 | 1.17   | 2.52    |
| 10      | 0.26       | 150 | 1.005 (0.006) | 1.60 (0.03)   | 12.5 (0.3)     | 5.94 | 2.31   | 2.22    |
| 10      | 0.39       | 150 | 1.177 (0.007) | 2.38 (0.00)   | 17.9 (0.3)     | 6.95 | 3.32   | 2.14    |
| 20      | 0.07       | 120 | 0.755 (0.011) | 1.52 (0.07)   | 11.7 (1.3)     | 3.18 | 0.79   | 2.91    |
| 20      | 0.13       | 100 | 1.094 (0.018) | 2.79 (0.06)   | 22.9 (1.9)     | 4.36 | 1.30   | 2.50    |
| 20      | 0.26       | 100 | 1.438 (0.022) | 4.80 (0.06)   | 38.5 (2.8)     | 5.72 | 2.92   | 2.27    |
| 20      | 0.39       | 120 | 1.617 (0.024) | 6.31 (0.28)   | 50.0 (3.9)     | 6.82 | 3.39   | 2.20    |
| 30      | 0.07       | 60  | 1.022 (0.003) | 3.52 (0.03)   | 25.9 (0.5)     | 3.42 | 0.87   | 2.79    |
| 30      | 0.13       | 60  | 1.414 (0.006) | 6.03 (0.03)   | 44.4 (0.8)     | 4.73 | 1.49   | 2.41    |
| 30      | 0.26       | 60  | 1.718 (0.001) | 7.70 (0.84)   | 64.5 (2.4)     | 6.01 | 2.49   | 2.25    |
| 30      | 0.39       | 60  | 1.931 (0.060) | 11.1 (0.1)    | 84.0 (4.7)     | 6.76 | 3.24   | 2.19    |
| 40      | 0.07       | 40  | 1.245 (0.016) | 6.12 (0.47)   | 45.2 (5.6)     | 3.56 | 0.95   | 2.76    |
| 40      | 0.13       | 40  | 1.678 (0.031) | 10.2 (0.9)    | 74.8 (9.2)     | 4.80 | 1.58   | 2.42    |
| 40      | 0.26       | 40  | 1.999 (0.014) | 13.5 (0.3)    | 96.9 (1.7)     | 6.26 | 2.67   | 2.22    |
| 40      | 0.39       | 40  | 2.210 (0.010) | 16.7 (0.1)    | 124 (4)        | 6.92 | 3.43   | 2.18    |

translational coefficients from the approximate, double-sum formula of Kirkwood<sup>2</sup>

$$D_{t,k} =$$

$$k_B T [(N+1)\zeta]^{-1} [1 + \zeta [6\pi\eta_0(N+1)]^{-1} \sum_{i=1}^{N+1} \sum_{j=1}^{N+1} R_{ij}^{-1}] \quad (20)$$

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

It is convenient to put the hydrodynamic properties in the following form:

$$f_t^* = k_B T / (6\pi\eta_0 D_t) \quad (21)$$

$$f_r^* = k_B T / (6\pi\eta_0 D_r) \quad (22)$$

$$[\eta]^* = [\eta] M / N_A \quad (23)$$

$f_{t,k}^*$  and  $f_{t,nc}^*$  are defined from  $D_{t,k}$  and  $D_{t,nc}$  as in eq 21. Note that  $f_t^*$  is the radius of the sphere with the same  $D_t$  as the polymer chain. Likewise,  $f_r^*$  and  $[\eta]^*$  have dimensions of a cube of a length.

We also obtain other interesting dimensionless quantities that are little sensitive to chain length. The first of these is Flory's  $P$  factor,<sup>20</sup> which we calculate as

$$P = k_B T / (6\langle s^2 \rangle^{1/2} \eta_0 D_t) = 6\pi f^* / \langle s^2 \rangle^{1/2} \quad (24)$$

We also evaluate Flory's intrinsic viscosity constant<sup>20</sup>

$$\Phi = [\eta] M / (6\langle s^2 \rangle)^{3/2} = N_A [\eta]^* / (6\langle s^2 \rangle)^{3/2} \quad (25)$$

and the Flory-Scheraga-Mandelkern parameter<sup>21,22</sup>  $\beta$  that is often used for molecular weight estimation when translational (or sedimentation) and viscosity data are available. We obtain  $\beta$  as

$$\beta = (M[\eta]/100)^{1/3} k_B T \eta_0 D_t = (N_A [\eta]^*/100)^{1/3} / (6\pi f^*) \quad (26)$$

with  $[\eta]$  in dL g<sup>-1</sup>.

## Results

For the three types of chain, the number of frictional elements,  $N + 1$ , was given one of the following values: 5, 10, 15, 20, 30, 40, or 50. Also, the elements' frictional radius was varied as 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, and 0.75. The bond length was taken as the polymethylene value,  $b = 1.53$  Å. In the generation of polymethylene chains, the temperature was set equal to 298 K.

In order to check the performance of our simulation procedures, we carried out a preliminary calculation of chain dimensions for the three models. Large samples, consisting of several thousand chains, were generated, and for each the mean-square end-to-end distance,  $\langle r^2 \rangle$ , and the mean-square radius of gyration,  $\langle s^2 \rangle$ , were obtained. The results for  $\langle r^2 \rangle$  and  $\langle s^2 \rangle$  of freely jointed chains and  $\langle r^2 \rangle$  of freely rotating chains deviate only a few percent from those predicted by exact formulas.<sup>23</sup> Similar good agreement was found between our results for  $\langle r^2 \rangle$  and  $\langle s^2 \rangle$  of polymethylene chains and those calculated in other works.<sup>14,23</sup>

The hydrodynamic properties  $f_t^*$ ,  $f_{t,k}^*$ ,  $f_{t,nc}^*$ ,  $f_r^*$ , and  $[\eta]^*$  were calculated as functions of  $N$  and  $\sigma$ . In Tables I-III results are presented for some selected values of  $N$  and  $\sigma$ . In order to make the numerical values independent of the choice of the bond length, the translational quantities are normalized to  $b$  and the rotational friction coefficient and the intrinsic viscosity are normalized to  $b^3$ . The complete tables covering all the  $N$ 's and  $\sigma$ 's are too lengthy to be reproduced here and are available upon request. The same sample was used in the calculation of the hydrodynamic properties for the various  $\sigma$ 's and fixed  $N$ . In Tables I-III  $n$  is the total number of chains comprising the sample. Each sample was actually formed by two subsamples of the same size. As a measure of the statistical error of the averages, we use half of the difference between the individual averages for each subsample. Such errors, which are given in parentheses in Tables I-III, are not statistically orthodox but give a realistic feeling of the results' precision.

Instead of  $f_{t,k}^*$  and  $f_{t,nc}^*$  we report in Table IV the percent deviations  $\delta_K$  and  $\delta_{nc}$  with respect to the exact  $f^*$ . Thus,  $\delta_K$  is given by

$$\delta_K = 100(f - f_{t,K})/f \quad (27)$$

and a similar expression holds for  $\delta_{nc}$ .

Besides the average values of the properties, their distribution functions are also of interest. The relatively small size of the samples generated in this study does not allow for a detailed analysis of these functions, but one can estimate the shape and width of the distributions by plotting frequency histograms from the values of the properties of each chain in the sample. As an example, we give such histograms for freely rotating chains with  $N + 1 = 20$  in Figure 1. For other types of chains or other values of  $N + 1$  the situation would not be much different from that seen in Figure 1. Four properties,  $r$ ,  $s$ ,  $f^*$ , and  $[\eta]^*$  (the latter two for  $\sigma = 0.60$ ), are presented in Figure 1.  $[\eta]^*$  is used instead of  $[\eta]$  since this way all the

Table II  
Hydrodynamic Properties of Freely Rotating Chains

| $N + 1$ | $\sigma/b$ | $n$ | $f_t^*/b$     | $f_r^*/b^3$   | $[\eta]^*/b^3$ | $P$  | $\Phi$ | $\beta$ |
|---------|------------|-----|---------------|---------------|----------------|------|--------|---------|
| 10      | 0.07       | 200 | 0.493 (0.001) | 0.698 (0.014) | 5.52 (0.14)    | 2.26 | 0.48   | 3.46    |
| 10      | 0.13       | 200 | 0.796 (0.002) | 1.34 (0.02)   | 10.6 (0.3)     | 3.65 | 0.92   | 2.66    |
| 10      | 0.26       | 200 | 1.157 (0.005) | 2.52 (0.03)   | 20.0 (0.5)     | 5.29 | 1.73   | 2.27    |
| 10      | 0.39       | 200 | 1.369 (0.005) | 3.60 (0.03)   | 28.7 (0.6)     | 6.26 | 2.49   | 2.16    |
| 20      | 0.07       | 100 | 0.863 (0.000) | 3.15 (0.03)   | 24.1 (0.1)     | 2.56 | 0.57   | 3.23    |
| 20      | 0.13       | 100 | 1.274 (0.024) | 5.58 (0.12)   | 42.1 (1.4)     | 3.86 | 1.05   | 2.63    |
| 20      | 0.26       | 100 | 1.747 (0.014) | 9.35 (0.31)   | 72.0 (2.2)     | 5.28 | 1.79   | 2.30    |
| 20      | 0.39       | 100 | 1.967 (0.045) | 12.0 (0.8)    | 93.5 (5.6)     | 5.99 | 2.38   | 2.23    |
| 30      | 0.07       | 60  | 1.178 (0.010) | 6.87 (0.01)   | 52.8 (4.5)     | 2.82 | 0.65   | 3.08    |
| 30      | 0.13       | 60  | 1.702 (0.020) | 12.0 (0.3)    | 91.6 (7.5)     | 4.07 | 1.13   | 2.56    |
| 30      | 0.26       | 60  | 2.163 (0.004) | 17.8 (0.2)    | 137 (3)        | 5.38 | 1.89   | 2.30    |
| 30      | 0.39       | 60  | 2.378 (0.030) | 22.7 (0.3)    | 175 (2)        | 5.91 | 2.42   | 2.27    |
| 40      | 0.07       | 40  | 1.468 (0.009) | 13.0 (0.5)    | 98.0 (1.4)     | 2.91 | 0.69   | 3.03    |
| 40      | 0.13       | 40  | 2.294 (0.014) | 22.1 (0.6)    | 164 (3)        | 4.55 | 1.15   | 2.30    |
| 40      | 0.26       | 40  | 2.604 (0.019) | 30.1 (0.6)    | 248 (11)       | 5.24 | 1.82   | 2.33    |
| 40      | 0.39       | 40  | 2.888 (0.027) | 37.7 (0.8)    | 310 (14)       | 5.81 | 2.27   | 2.26    |

Table III  
Hydrodynamic Properties of Polymethylene Chains

| $N + 1$ | $\sigma/b$ | $n$ | $f_t^*/b$     | $f_r^*/b^3$   | $[\eta]^*/b^3$ | $P$  | $\Phi$ | $\beta$ |
|---------|------------|-----|---------------|---------------|----------------|------|--------|---------|
| 10      | 0.07       | 200 | 0.506 (0.000) | 0.656 (0.008) | 8.18 (0.03)    | 1.89 | 0.38   | 3.84    |
| 10      | 0.13       | 200 | 0.829 (0.000) | 1.28 (0.01)   | 15.4 (0.0)     | 3.09 | 0.72   | 2.90    |
| 10      | 0.26       | 200 | 1.223 (0.000) | 2.47 (0.03)   | 28.2 (0.3)     | 4.56 | 1.31   | 2.40    |
| 10      | 0.39       | 200 | 1.461 (0.000) | 3.63 (0.03)   | 39.4 (0.3)     | 5.44 | 1.84   | 2.25    |
| 20      | 0.07       | 100 | 0.923 (0.001) | 4.32 (0.17)   | 46.6 (0.8)     | 1.94 | 0.39   | 3.77    |
| 20      | 0.13       | 100 | 1.436 (0.002) | 7.71 (0.17)   | 85.1 (1.1)     | 3.03 | 0.72   | 2.96    |
| 20      | 0.26       | 100 | 1.998 (0.004) | 13.3 (0.3)    | 140 (1.6)      | 4.21 | 1.18   | 2.51    |
| 20      | 0.39       | 100 | 2.297 (0.001) | 18.1 (0.1)    | 176 (1)        | 4.92 | 1.56   | 2.36    |
| 30      | 0.07       | 60  | 1.302 (0.001) | 12.8 (0.6)    | 119 (4)        | 2.07 | 0.44   | 3.67    |
| 30      | 0.13       | 60  | 1.967 (0.003) | 22.2 (1.1)    | 203 (7)        | 3.12 | 0.74   | 2.90    |
| 30      | 0.26       | 60  | 2.654 (0.020) | 34.6 (2.3)    | 343 (11)       | 4.05 | 1.10   | 2.54    |
| 30      | 0.39       | 60  | 2.946 (0.027) | 44.1 (2.8)    | 428 (14)       | 4.60 | 1.37   | 2.41    |
| 40      | 0.07       | 40  | 1.669 (0.004) | 23.8 (0.2)    | 254 (8)        | 2.05 | 0.42   | 3.66    |
| 40      | 0.13       | 40  | 2.464 (0.001) | 40.7 (0.5)    | 424 (14)       | 3.02 | 0.70   | 2.94    |
| 40      | 0.26       | 40  | 3.248 (0.004) | 67.0 (2.5)    | 627 (5)        | 4.05 | 1.10   | 2.54    |
| 40      | 0.39       | 40  | 3.647 (0.005) | 83.2 (3.1)    | 767 (5)        | 4.55 | 1.34   | 2.42    |

properties have the dimensions of a length and the widths of the distributions relative to their means are comparable.

## Discussion

As pointed out in the Introduction, there are a number of formal differences between Zimm's work<sup>4</sup> on random chains and the one reported in this paper for freely jointed chains. In regard to the model, Zimm lets the bond length to be Gaussianly distributed with a root-mean-square value equal to  $b$ , as it corresponds to the Gaussian subchains composing a flexible polymer. On the other hand, we generated freely jointed chains with fixed  $b$  in order to make the results comparable with those for freely rotating and polymethylene chains with the same bond length. In Zimm's paper, the frictional radius of the chain elements is taken as  $\sigma/b = 0.27135$ , the frictional coefficient of a Gaussian segment, while we regard  $\sigma$  as a variable parameter.

Hydrodynamic interactions are accounted for in Zimm's paper by the unmodified Oseen tensor for large  $R_{ij}$  and a special, isotropic tensor for overlapping segments. Zimm dislikes the discrete-sphere representation of hydrodynamic interaction implicit in the modified Oseen tensor<sup>18,19</sup> because it is valid only for nonoverlapping spheres, and this would restrict the study to chains with excluded volume. This problem, however, could be avoided by using the form of the modified tensor for overlapping spheres proposed by Rotne and Prager.<sup>18</sup> In our work we have used always the modified tensor for nonoverlapping spheres

Table IV  
Percent Errors of  $f_{t,K}$  and  $f_{t,nc}$

| $N + 1$ | $\sigma/b$ | $\delta_K$      |                 |                 | $\delta_{nc}$ |      |      |
|---------|------------|-----------------|-----------------|-----------------|---------------|------|------|
|         |            | FJ <sup>a</sup> | FR <sup>b</sup> | PM <sup>c</sup> | FJ            | FR   | PM   |
| 10      | 0.07       | 1.0             | 0.3             | 0.2             | -0.0          | -0.0 | -0.0 |
| 10      | 0.13       | 2.2             | 0.8             | 0.6             | -0.1          | -0.1 | -0.1 |
| 10      | 0.26       | 5.8             | 2.1             | 1.6             | -0.5          | -0.1 | -0.2 |
| 10      | 0.39       | 8.2             | 3.2             | 2.6             | -0.3          | -0.1 | -0.2 |
| 20      | 0.07       | 2.1             | 0.7             | 0.3             | -0.0          | -0.0 | -0.0 |
| 20      | 0.13       | 4.4             | 0.8             | 0.9             | -0.0          | -0.1 | -0.1 |
| 20      | 0.26       | 8.7             | 4.2             | 2.1             | -0.1          | -0.2 | -0.2 |
| 20      | 0.39       | 12.6            | 5.9             | 3.1             | -0.2          | -0.2 | -0.3 |
| 30      | 0.07       | 2.5             | 1.1             | 0.4             | -0.0          | -0.0 | -0.1 |
| 30      | 0.13       | 5.4             | 2.5             | 1.1             | -0.0          | -0.1 | -0.1 |
| 30      | 0.26       | 9.3             | 6.0             | 2.3             | -0.0          | -0.1 | -0.3 |
| 30      | 0.39       | 11.4            | 6.2             | 3.2             | -0.8          | -0.2 | -0.4 |
| 40      | 0.07       | 3.0             | 1.3             | 0.5             | -0.0          | -0.0 | -0.1 |
| 40      | 0.13       | 6.1             | 3.6             | 1.2             | -0.0          | -0.1 | -0.1 |
| 40      | 0.26       | 10.0            | 5.8             | 2.4             | -0.1          | -0.1 | -0.2 |
| 40      | 0.39       | 13.6            | 7.7             | 3.4             | -0.2          | -0.1 | -0.3 |

<sup>a</sup> Freely jointed chains. <sup>b</sup> Freely rotating chains.

<sup>c</sup> Polymethylene chains.

although there will be some overlapping in chains without excluded volume. We have done so thinking that if overlapping is not too extensive, the tensor for nonoverlapping spheres still provides a good description of hydrodynamic interaction since the values of the two forms

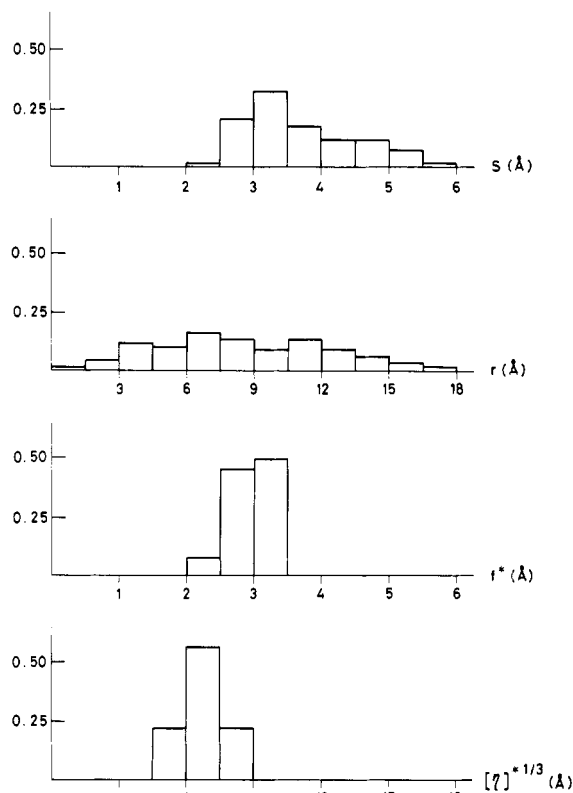


Figure 1. Frequency histograms for  $r$ ,  $s$ ,  $f^*$ , and  $[\eta]^*^{1/3}$  of freely rotating chains with  $N + 1 = 20$  and  $\sigma = 0.60$ .

of the tensor as well as those of their first derivatives coincide for touching spheres.

In addition to differences between our computational procedures used to solve the set of hydrodynamic interaction equations and Zimm's, we also differ in the way to obtain the translational quantities and the intrinsic viscosity. However, those differences are just apparent. Thus, the velocity of the macromolecule in the sedimentation direction per unit force is, after averaging over orientations, equal to  $1/f^*$  or  $D_t/k_B T$ . Our eq 19 for viscosity includes orientational averaging and was derived<sup>17</sup> from the complete expression of the laminar flow, but if one takes only the irrotational part, the result is the same (H. Nakajima, personal communication). Finally, it seems that Zimm's way of introducing translation-rotation coupling effects is equivalent to ours; he just does not write out explicitly the coupling tensors.

We are, then, made to wonder whether the many differences in the model and procedure are reflected in the final results for the hydrodynamic properties. Comparing Zimm's results with those of our work for freely jointed chains is not immediate for we have not considered the same chain lengths and mainly because we differ in the hydrodynamic representation of chain segments. At any rate, we tried to answer that question by interpolation. From the results in Table I we first drew plots of  $P$  vs.  $N + 1$  for several  $\sigma$ 's and then we interpolated for Zimm's values,  $N + 1 = 6, 11, 26$ , and  $51$ . The resulting  $P$ 's were plotted vs.  $\sigma$ , drawing a curve for each of these values of  $N + 1$ . Finally, Zimm's results for  $P$  were put in ordinates and the corresponding  $\sigma$ 's were obtained for each  $N + 1$ . The same method was applied to  $\Phi$  and the resulting values are summarized in the form of  $\sigma/b$  in Table V. It is very satisfying to see how close the values of  $\sigma/b$  are, regardless of chain length and the property where they came from. The mean value,  $\sigma/b \approx 0.25$ , is, in turn, close to Zimm's starting value for the Stokes radius of the chain elements,  $\sigma/b = 0.27$ . (The small discrepancy could arise

Table V  
Values of  $\sigma/b$  Corresponding to Zimm's Results

| $N + 1$ | $\sigma/b^a$ |             |
|---------|--------------|-------------|
|         | from $P$     | from $\Phi$ |
| 6       | 0.248        | 0.265       |
| 11      | 0.238        | 0.251       |
| 26      | 0.238        | 0.250       |
| 51      | 0.242        | 0.254       |

<sup>a</sup> Mean = 0.248.

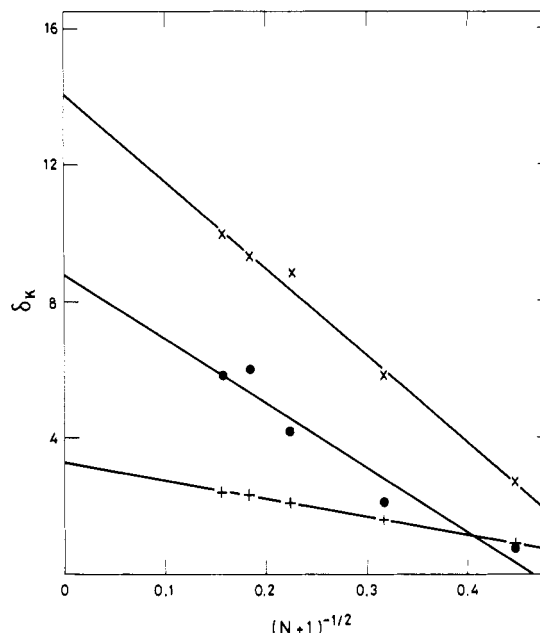


Figure 2. Plot of  $\delta_K$  vs.  $(N + 1)^{-1/2}$  for freely jointed ( $\times$ ), freely rotating ( $\bullet$ ), and polymethylene chains ( $+$ ) with  $\sigma = 0.40$  ( $\sigma/b = 0.26$ ). The limiting values for  $N \rightarrow \infty$  (intercepts at  $(N + 1)^{-1/2} = 0$ ) are about 14, 9, and 3%, respectively.

from differences in the characterization of hydrodynamic interaction.) We can conclude, putting these findings in other words, that our results for translational coefficients and intrinsic viscosities of freely jointed, or random, chains are equivalent to Zimm's when the Stokes radius of the chain elements is taken as  $0.25b$ .

Let us now discuss the results presented in Table IV. As for translation-rotation coupling effects, it is clear that they are rather small. The difference between  $f^*$  and  $f_{nc}^*$  is always less than 1%, seems to be independent of  $N$ , and increases slightly with  $\sigma$ . More interesting are the percent deviations,  $\delta_K$ , of the Kirkwood formula (eq 20). Table IV indicates that  $\delta_K$  increases markedly with  $\sigma$  for any  $N$  and for the three types of chain. This was to be expected since eq 20 is only strictly valid as a first-order correction for low  $\sigma$  to the free-draining behavior.<sup>6,24,25</sup>  $\delta_K$  also increases with  $N$  but for high  $N$  it approaches an asymptotic value that corresponds to an infinitely long chain. This limiting value can be obtained by taking advantage of the fact that  $\delta_K$  shows a fairly good linear dependence on  $(N + 1)^{-1/2}$ , as seen in Figure 2 for some typical examples. In the case of freely jointed chains with  $\sigma/b = 0.26$ ,  $\delta_K$  for  $N \rightarrow \infty$  is 14%, in agreement with Zimm's result, 13%.

When one goes from freely jointed to freely rotating chains and then to real polymethylene chains,  $\delta_K$  becomes smaller. This behavior is easily explained by noting that for fixed  $N$ ,  $b$ , and  $\sigma$ , chain constraints produce an increase in interelement distances,  $R_{ij}$ , and therefore the relative importance of hydrodynamic interactions is diminished. The remarkably small errors found for polymethylene tell us that the simple Kirkwood formula might be useful in

Monte Carlo calculations of translational properties of moderately long real polymer models. It should be recalled that most of the computational effort in this work is devoted to the rigorous calculation of hydrodynamic properties; the generation of chain conformations takes only a small fraction of the computer time and memory. Thus, it is conceivable that with the same computer allowances the region of several hundred repeating units can be easily reached with approximate hydrodynamic methods. Furthermore, the results could be corrected by using length-dependent error estimates, like those in Figure 2, obtained in a preliminary study for shorter chains.

In this sense, the only difficulty we can foresee comes from the size of the statistical samples needed to get reasonably accurate averages. As pointed out earlier by Zimm<sup>4</sup> and illustrated with detail in this paper (Figure 1), the distributions of hydrodynamic properties are substantially narrower than those of chain distances, and as a consequence the averages of the former converge with sample size faster than those of the latter. In previous works on real chains,<sup>26,30</sup> averages of powers of interelement distances were evaluated first and then used to calculate properties by more or less approximate methods. We believe that in some instances obtaining the properties directly for each generated conformation and averaging a posteriori can be more economical.

Although our above comments on the possibilities for long real chains are somewhat speculative, rigorous results for shorter chains like those obtained in this paper are directly applicable in the domain of oligomeric molecules. As an example, an analysis of translational diffusion and intrinsic viscosities of *n*-alkanes is presented in the following article.<sup>12</sup>

#### Remark

As quoted in Zimm's paper,<sup>4</sup> recent works to be published by Fixman and Wilemski and Tanaka pose some doubts as to the validity of rigid-body formulas for flexible molecules. The problems, which are associated with rotational effects, are hinted on pp 593 and 600 of ref 4. Zimm has tackled a problem of this kind in Appendix A of the same paper, finding that rotational effects on sedimentation and viscosity are rather small. At any rate, our "exact" results may not be so, and the deviation of Kirkwood's diffusion formula could consequently be somehow affected. We acknowledge the anonymous referees of this

paper for bringing to our attention these facts, which hopefully will be clarified in the near future.

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