(29) Fixman, M.; Jagannathan, S. *Macromolecules* **1980**, *16*, 685.
(30) Fulton, R. L. *J. Chem. Phys.* **1978**, *68*, 3095.
(31) Fulton, R. L. *J. Chem. Phys.* **1978**, *68*, 3089.
(32) Fulton, R. L. *J. Chem. Phys.* **1983**, *78*, 6865.
(33) Fulton, R. L. *J. Chem. Phys.* **1983**, *78*, 6877.
(34) Mysels, K. J. *J. Colloid Sci.* **1955**, *10*, 507.
(35) Princen, L. H.; Mysels, K. J. *J. Colloid Sci.* **1957**, *12*, 594.
(36) Stigter, D. J. *J. Chem. Phys.* **1960**, *64*, 842.
(37) Vrij, A.; Overbeek, J. Th. G. *J. Colloid Sci.* **1962**, *17*, 570.
(38) Le Bret, M.; Zimm, B. H. *Biopolymers* **1984**, *23*, 271.
(39) Kaji, K.; Urakawa, H.; Kanaya, T.; Kitamaru, R. *Macromolecules* **1984**, *17*, 1835.
(40) Ise, N.; Okubo, T.; Yamamoto, K.; Kawai, H.; Hashimoto, T.; Fujimura, M.; Hiragi, Y. *J. Am. Chem. Soc.* **1980**, *102*, 7901.
(41) Ise, N.; Okubo, T.; Yamamoto, K.; Matsuoka, H.; Kawai, T.; Fujimura, M. *J. Chem. Phys.* **1983**, *78*, 541.

Remarks on the Translational Diffusion Coefficient of Relatively Short Chains

A. Ziya Akcasu

Department of Nuclear Engineering, The University of Michigan, Ann Arbor, Michigan 48109

Charles M. Guttman*

National Bureau of Standards, Gaithersburg, Maryland 20899. *Received June 14, 1984*

ABSTRACT: The expansion of the hydrodynamic radius R_H in inverse powers of $N^{1/2}$ is presented for three chain models which allow only for local structure along the chain. The effect of chain stiffness is included in one of the models. Formulas are presented to interpret R_H data for relatively short chains. The approach to the Gaussian chain limit as $N \to \infty$ is discussed.

Introduction

The discrepancy between the experimental value of the translational diffusion coefficient of a polymer molecule in a dilute solution, measured by quasi-elastic light scattering, and its theoretical value obtained from Kirkwood's approximate formula has revived interest in the theoretical calculation of the diffusion coefficient of macromolecules in solution. The discrepancy, first pointed out by Schmidt and Burchard,[1] refers to the observation that the measured value of the diffusion coefficient of a polymer at the Θ point, D, is about 15% smaller than the theoretical value D_0 calculated with the Kirkwood formula[2] for Gaussian chains, i.e., $D_0 = 0.1955k_BT/bN^{1/2}$ with the usual meaning of the symbols. The magnitude of the approximation in this formula had been discussed earlier in the case of flexible chains with the preaveraged Oseen tensor. By obtaining the exact asymptotic solution of the Kirkwood–Risemann integral equation, Kurata and Yamakawa[3] calculated the diffusion coefficient as $0.192k_BT/bN^{1/2}$. Zimm[4] showed that the Kirkwood formulation represents the diffusion coefficient of the center of resistance, and obtained $k_BT\nu_0/\xi$ for the diffusion coefficient where ν_0 is the lowest Zimm eigenvalue and ξ is the friction coefficient per bead. He gave the numerical constant also as 0.192 instead of 0.1955. Horta and Fixman[5] obtained estimates for the magnitude of the correction to the Kirkwood formulas of about 1.68% of D_0, much smaller than the observed discrepancy. Recently, Zimm[6] obtained an upper bound for D_1/D, where $D_1 = D_0 - D$, in the case of the nonpreaveraged Oseen tensor as approximately 15%. Fixman[7] estimated D_1/D as about 8%, which is again not quite sufficient to explain the observed discrepancy mentioned above.

The physical nature of the approximation involved in the Kirkwood formula has been clarified essentially by Dubois-Violette and de Gennes[8] in 1968, for the case of the preaveraged Oseen tensor. They showed that D_0 is the short-time diffusion coefficient for the diffusion of the center of mass and does not take into account the coupling between the internal and translational motions. They also showed that the diffusion coefficient $D(t)$, defined in terms of the mean-square displacement of the center of mass as $\langle|\Delta R_c(t)|^2\rangle = 6D(t)t$, varies gradually from D_0 to D as $t \to \infty$, due to deformation of the molecule during diffusion (see also Mansfield[9]). Using linear response theory Akcasu[10] derived a formal expression for $D(t) = D_0 - D_1(t)$ in the case of the nonpreaveraged Oseen tensor and calculated D_1/D_0 as a function of molecular weight when the Oseen tensor is preaveraged. The asymptotic analytical form of $D_1 = D_1(\infty)$ was first obtained by Fixman[7] in the case of nonpreaveraged hydrodynamic interaction.

The remaining discrepancy, of the order of 7–8% after the D_1 correction has been made, may seem to be too small to be of any physical significance. Since the accuracy of the measurement of the diffusion coefficient by light scattering is considered to be better than about 5%, and the measured value is consistently smaller than the calculated value, the remaining discrepancy has continued intriguing the theoreticians. Guttman et al.[11] calculated D_0 for chains created by Monte Carlo simulation in which both excluded volume and nearest-neighbor interactions are included, and found that the ratio $\rho = R_G/R_H$, where R_G is the radius of gyration and R_H is the hydrodynamic radius for such chains, is closer to the experimentally obtained ρ and differs from that obtained for an analytical Gaussian chain. In this and in a recent paper,[12] they also discussed the difficulties in extrapolating $1/R_H$ to its long-chain limit from the data obtained experimentally or by computer simulation. The question of extrapolation of the Monte Carlo results for short chains to long-chain limit has also been discussed by Fixman and Mansfield[13] recently.

The molecular weights used in the measurement of the diffusion coefficient by dynamic light scattering are usually less than 10^6 to satisfy the Guinier condition. The number of statistical segments N in such molecules may not be large enough for the long-chain Gaussian chain models to be applicable to the interpretation of the diffusion experiments especially if one worries about discrepancies of the order of 10% or less. The inverse moments of the distribution function $\psi(\mathbf{R}_{ij})$ of the vector distance $\mathbf{R}_{ij}$ between two monomers, such as $\sum_{i,j}\langle 1/R_{ij}\rangle$ involved in the diffusion coefficient, attain their asymptotic limits more slowly than moments such as $\langle R_{ij}^2\rangle$ involved in computing the radius of gyration.

The purpose of this paper is to obtain the asymptotic expansion of $1/R_H$ in inverse powers of $N^{1/2}$ for various chain models and investigate analytically the manner in which the long-chain limit is approached. The analytical models considered do not include excluded volume or attractive interactions among all the segments, but one model does allow for interaction between adjacent segments of the chain in an attempt to model chain stiffness. The results enable one to assess the effect of finite chain length quantitatively on the accuracy of the calculations and to discuss the physical quantities that must be taken into account in the interpretation of experiments with relatively short chains.

Theoretical Background

The short-time diffusion coefficient of the center of mass of a flexible polymer chain in solution is given in Kirkwood–Riseman theory by[2]

$$D_0 = \frac{1}{3(N+1)^2}\sum_{j,k=0}^{N} \mathrm{tr}\,\langle \boldsymbol{D}^{jk}\rangle \tag{1}$$

where $\boldsymbol{D}^{jk} \equiv \boldsymbol{D}(\mathbf{R}_{jk})$ is the diffusion tensor, N is the number of bonds in the chain, $\mathbf{R}_{jk}$ is the vector distance between jth and kth monomers, and tr $\boldsymbol{D}^{jk}$ is the trace of the 3 × 3 Cartesian tensor $\boldsymbol{D}(\mathbf{R})$. This formula is often referred to as Kirkwood's approximation to the diffusion coefficient. By replacing $\boldsymbol{D}(\mathbf{R})$ by its Fourier representation, one can cast eq 1 into the form

$$D_0 = D_R\left\{1 + [\xi/(2\pi)^3]\int \mathrm{d}^3k\, \tilde{T}(\mathbf{k})[S(k) - 1]\right\} \tag{2}$$

where $D_R = k_BT/\xi(N + 1)$ is the diffusion coefficient in the free-draining limit, k_BT is the temperature of the solution in energy units, ξ is the friction coefficient per monomer, and $\tilde{T}(\mathbf{k})$ is the Fourier transform of $T(\mathbf{R}) = (1/3)\,\mathrm{tr}\,\boldsymbol{T}(\mathbf{R})$, where $\boldsymbol{T}(\mathbf{R})$ is the hydrodynamic interaction tensor. The $S(k)$ is the static structure factor of the chain defined by

$$S(k) = \frac{1}{N+1}\left\langle \sum_{j,l=0}^{N} \exp(i\mathbf{k}\cdot\mathbf{R}_{jl})\right\rangle \tag{3}$$

with normalization $S(0) = N + 1$. Equation 2 was first obtained by Akcasu[14] (in 1981) in a more general context to calculate the first cumulant of the dynamic structure factor as a function of momentum transfer, the concentration dependence of self-diffusion and collective diffusion coefficients, and the mobility in polyelectrolyte solutions.[15] Recently, it has been used by Burchard et al.[16] to calculate the diffusion coefficient of branched polymers with partial labeling.

An attractive and important feature of eq 2 is that it expresses D_0, which is a dynamic quantity, in terms of a static quantity $S(k)$. The nontrivial concentration and temperature dependence of D_0 is implicit in $S(k)$. Equation 2 enables one to calculate D_0 even when $S(k)$ is available only experimentally. Furthermore, the hydrodynamic tensor in eq 2 is not restricted to any particular form. One is allowed to use the usual Oseen tensor or any modified version of it that includes corrections for short separation distances and screening effects. We must however keep in mind that D_0 itself is an approximation to the true diffusion coefficient D and does not include the dynamics of the internal modes during diffusion.

In this paper, we use eq 2 to obtain a power series expansion for the hydrodynamic radius $(1/R_H)$ in powers of $N^{-1/2}$ in order to study the short-chain effects on the diffusion coefficient. We use the conventional form of the Oseen tensor in the subsequence calculations

$$\tilde{T}(\mathbf{k}) = \frac{2}{3\eta}\frac{1}{k^2} \tag{4}$$

where η is the viscosity of the solvent. Thus, eq 2 becomes

$$D_0 = D_R\left[1 + \frac{\xi}{\eta}\frac{2}{3\pi^2}\int_0^\infty \mathrm{d}k\, G_N(k)\right] \tag{5}$$

where we have introduced $G_N(k)$ through

$$S(k) = 1 + 2G_N(k) \tag{6}$$

$$G_N(k) \equiv \frac{1}{2(N+1)}{\sum_{j,l=0}^{N}}'\, \langle \exp(i\mathbf{k}\cdot\mathbf{R}_{jl})\rangle \tag{7}$$

where the prime on the summation implies the exclusion of the diagonal terms. It is often more convenient to introduce the hydrodynamic radius through the Stokes–Einstein relation $D_0 = k_BT/6\pi\eta R_H$:

$$R_H^{-1} = \left(\frac{3}{\pi}\right)^{1/2}\left(\frac{1}{N+1}\right)\frac{1}{bh^*} + \left\langle\frac{1}{R}\right\rangle \tag{8}$$

where

$$\left\langle\frac{1}{R}\right\rangle \equiv \frac{4}{\pi}\frac{1}{N+1}\int_0^\infty \mathrm{d}k\, G_N(k) \tag{9}$$

$$h^* \equiv \xi/(\eta b\pi(12\pi)^{1/2}) \tag{10}$$

In these equations b is a step length in a statistical sense that enters into the chain model used in the calculation of $S(k)$ or $G_N(k)$, and h^* is related to the conventional draining parameters $Z_H \equiv \xi/\eta b$.

In the remainder of the paper we consider two random-flight chain models and one Gaussian chain model with nearest-neighbor interaction to calculate $1/R_H$ explicitly.

Random-Flight Chains

For these chains the distributions of the bond vectors $\mathbf{b}_j = \mathbf{R}_{j+1} - \mathbf{R}_j$, $j = 1, ..., N$, are independent of each other so that $G_N(k)$ defined in eq 7 can be written as[17,18]

$$G_N(k) = \sum_{n=1}^{N}\left(1 - \frac{n}{N+1}\right)\tau^n(\mathbf{k}) \tag{11}$$

where $\tau(\mathbf{k})$ is the characteristic function of the bond vector distribution function. The geometric series involved in eq 11 can easily be summed:

$$G_N(k) = \frac{\tau}{1-\tau}\left[1 - \frac{1}{1-\tau}\left(\frac{1-\tau^{N+1}}{N+1}\right)\right] \tag{12a}$$

or

$$G_N(k) = \frac{N}{N+1}\left(\frac{\tau}{1-\tau}\right)\left[1 - \frac{\tau}{1-\tau}\left(\frac{1-\tau^{N}}{N}\right)\right] \tag{12b}$$

The reason for presenting these two identical forms is that they both have been used in the literature.[17,18] We suppressed the argument of $\tau(\mathbf{k})$ in eq 12.

The Gaussian and freely jointed chain models are characterized by the form of their $\tau(\mathbf{k})$

$$\tau(\mathbf{k}) = \exp(-k^2b^2/6) \quad \text{(Gaussian)} \tag{13a}$$

$$\tau(\mathbf{k}) = j_0(kb) \quad \text{(freely jointed)} \tag{13b}$$

where $j_0(kb) = \sin(kb)/kb$ is the spherical Bessel function

Table I

	A_0	A_1	A_2
Gaussian	3.685	4.036	−1.84
freely jointed	3.685	5.178	−0.18

of zeroth order. We note that the usual summation involved in

$$\left\langle \frac{1}{R} \right\rangle = [1/(N+1)^2] \sum_{i,j=0}^{N}{}' \langle 1/R_{ij} \rangle \tag{14}$$

has been performed exactly in this approach rather than replacing it by an integration as is usually done. Using eq 13 in eq 12 one reduces the calculation of $\langle 1/R \rangle$ to a single integral. In both chain models $bN^{1/2}\langle 1/R \rangle$ can be expressed as a power series

$$bN^{1/2}\langle 1/R \rangle = A_0 - \frac{A_1}{N^{1/2}} + \frac{A_2}{N} + O(1/N^{3/2}) \tag{15a}$$

The large-N limit, A_0, is given in both models by (see Appendix A)

$$\begin{aligned} A_0 &= \frac{4(6^{1/2})}{\pi} \int_0^\infty \mathrm{d}x \, \frac{x^2 - 1 + e^{-x^2}}{x^4} \\ &= 8(2/3\pi)^{1/2} \end{aligned} \tag{15b}$$

which is the integral of the Debye form. The coefficient A_1 has different values in Gaussian and freely jointed chain models.

$$A_1 = \frac{4(6^{1/2})}{\pi} \int_0^\infty \mathrm{d}x \left[\frac{1}{x^2} - \frac{e^{-x^2}}{1 - e^{-x^2}} \right] \quad \text{(Gaussian)} \tag{16}$$

$$A_1 = \frac{4}{\pi} \int_0^\infty \mathrm{d}x \left[\frac{6}{x^2} - \frac{j_0(x)}{1 - j_0(x)} \right] \quad \text{(freely jointed)} \tag{17}$$

The coefficient A_2 is calculable, but not important for our discussions so that we do not present its expression. Table I represents the numerical values of A_0, A_1, and A_2. We add in passing, for comparison, that $bN^{1/2}\langle 1/R \rangle = (3/2\pi)^{1/2} = 0.691$ and 0.5 for a Gaussian and rigid dumbbell ($N = 1$), respectively.

The analytical results for the freely jointed chain obtained here are implicit in the paper by Akcasu and Higgins.[18]

Gaussian Chain with Stiffness

This model assumes that the bond vector distribution $P(\mathbf{b}_1,...,\mathbf{b}_n)$ is Gaussian with an additional parameter to include the possibility of mutual dependence of adjacent bonds. A similar model was used by Jannink and Summerfield[19] to include chain stiffness in the calculation of the dynamic structure factor.

We assumed $P(\mathbf{b}_1,...,\mathbf{b}_N)$ to be of the form

$$P = A \exp\left\{ -\frac{3}{2b^2} \left[\frac{1}{1 - \bar{\mu}^2} \sum_{n=1}^{N-1} |\mathbf{b}_n - \bar{\mu}\mathbf{b}_{n+1}|^2 + |\mathbf{b}_n|^2 \right] \right\} \tag{18a}$$

where the normalization factor A is given by

$$A = (3/2\pi b^2)^{3N/2}(1 - \bar{\mu}^2)^{-3(N-1)/2}$$

This particular form is chosen because it gives

$$\langle \mathbf{b}_j \cdot \mathbf{b}_k \rangle = b^2 \bar{\mu}^{|j-k|} \tag{18b}$$

for all j, $k = 1, ..., N$ (see Appendix B for a systematic derivation of eq 18a from the requirement (18b)). Here $\bar{\mu}$ is the average of the cosine of the angle between adjacent bonds, and b is the root mean square of the bond length. Clearly $\bar{\mu} = 0$ limit reproduces the flexible Gaussian distribution. In the limit of $\bar{\mu} = 1$, the distribution reduces to

$$\begin{aligned} &P(\mathbf{b}_1,...,\mathbf{b}_N) \rightarrow \\ &\quad \delta(\mathbf{b}_1 - \mathbf{b}_2)...\delta(\mathbf{b}_{N-1} - \mathbf{b}_N)(3/2b^2\pi)^{1/2} \exp(-3b_N{}^2/2b^2) \end{aligned}$$

which represents a rod with each bond vector having the same Gaussian distribution. The advantage of the model is that it allows an exact calculation of $G_N(k)$ as

$$G_N(k) = \sum_{s=1}^{N} \left(1 - \frac{s}{N+1} \right) e^{-(k^2b^2/6)[\alpha s - \beta(1 - (\bar{\mu})^s)]} \tag{19}$$

where we have used

$$\langle |\mathbf{R}_{ij}|^2 \rangle = b^2[\alpha s - \beta(1 - (\bar{\mu})^s] \tag{20}$$

with $s = |i - j|$, and introduced

$$\alpha \equiv \frac{1 + \bar{\mu}}{1 - \bar{\mu}} \tag{21a}$$

$$\beta \equiv 2\bar{\mu}/(1 - \bar{\mu})^2 \tag{21b}$$

Equation 20 is a known result due to Kratky and Porod.[20]

The radius of gyration in this model can be calculated by using eq 20 in

$$R_G{}^2 = \frac{1}{2(N+1)^2} \sum_{i,j=0}^{N} \langle |\mathbf{R}_{ij}|^2 \rangle$$

as

$$R_G{}^2 = b^2\alpha N \left\{ \frac{1}{6}\left(\frac{N+2}{N+1} \right) - \frac{(\beta/\alpha)}{2(N+1)} \left[1 - \left(\frac{2}{N} \right) \frac{\bar{\mu}}{1 - \bar{\mu}} \left(1 - \frac{1 - \bar{\mu}^{(N+1)}}{(N+1)(1 - \bar{\mu})} \right) \right] \right\} \tag{22}$$

which behaves as $R_G = b(\alpha N/6)^{1/2}$ for large N. Since $R_G \sim b(\alpha N)^{1/2}$ in this model, we normalize $\langle 1/R \rangle$ as $b(\alpha N)^{1/2}\langle 1/R \rangle$ in finding its expansion in power of $N^{-1/2}$. After some algebra we find for $\bar{\mu} < 1$, approximately (see Appendix C)

$$b(N\alpha)^{1/2}\langle 1/R \rangle = A_0 - \frac{A_1 - B_1}{N^{1/2}} + O(1/N) \tag{23}$$

where A_1 is the slope of the Gaussian chain corresponding to $\bar{\mu} = 0$, and

$$B_1(\bar{\mu}) = 2\left\{ \frac{6}{\pi} \, \frac{\alpha^{1/2} - 1}{2} + \int_1^\infty \mathrm{d}s \left[\frac{1}{[s - \beta(1 - \bar{\mu}^s)/\alpha]^{1/2}} - \frac{1}{s^{1/2}} \right] \right\} \tag{24}$$

In the rod limit where $\bar{\mu} = 1$, $R_G{}^2 = b^2N(N + 2)/12$ so that we must normalize $\langle 1/R \rangle$ as $Nb\langle 1/R \rangle$ in its large-N expansion. The for $\bar{\mu} = 1$ we have

$$bN\langle 1/R \rangle = 2(N/(N+1))[C - 1 + \ln(N)] + O(1/N^2) \tag{25}$$

where $C = 0.57721$ is the Euler's number. The approximate formula in eq 23 is not capable of reproducing the rod limit that contains the usual logarithmic divergence. It however indicates that the slope of $b(N\alpha)^{1/2}\langle 1/R \rangle$ increases with $\bar{\mu}$ and becomes in fact positive for values of $\bar{\mu}$ larger than approximately 0.42.

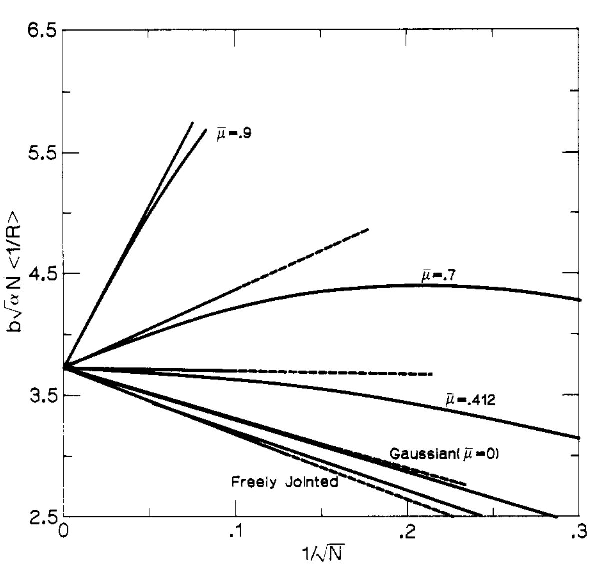

Figure 1. Variation of $\langle 1/R \rangle$ with $1/N^{1/2}$ for various chain models. The solid curves depict the exact numerical calculations for N up to 10 000. The dashed lines denote the slopes calculated analytically in the text.

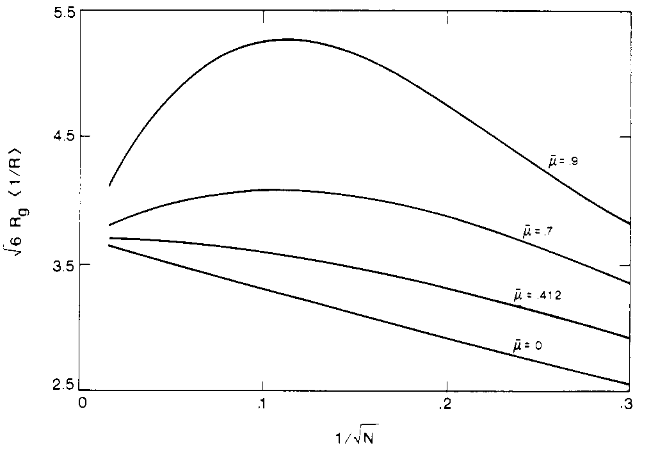

Figure 2. Product $6^{1/2}R_g\langle 1/R \rangle$ vs. $1/N^{1/2}$ for the various chain models. The shape of the figure is essentially the same as Figure 1 except for small N and large $\bar{\mu}$.

Figure 1 shows $(\alpha N)^{1/2}\langle 1/R \rangle$ as a function of $N^{1/2}$ for the models discussed above. The curves are calculated numerically by performing summations directly, rather than using the approximate analytical formulas derived above. The factor $(\alpha N)^{1/2}$ is the asymptotic, large-N form of R_g. Figure 1 shows that a simple scaling by the asymptotic form of R_g is not universal. In the experimental treatment of the data, one takes independently measured values of R_g and $\langle 1/R \rangle$ at a given molecular weight and forms their product.[11] To mimic this, we have plotted $6^{1/2}$ $R_g\langle 1/R \rangle$ vs. $1/N^{1/2}$ in Figure 2. The results are similar to those found in Figure 1 except for small N and high $\bar{\mu}$.

Modification of Hydrodynamic Interaction

Now we can consider the sensitivity of $\langle 1/R \rangle$ to modifications on the Oseen tensor at short distances. One could use the Rotne and Prager[21] model for the hydrodynamic interaction, but we use instead a simpler model that lends itself better to computations. We modify the Oseen tensor as

$$\langle \mathbf{T}^{ij} \rangle_{\text{eq}} = \frac{\mathbf{I}}{6\pi\eta}\left\langle \frac{1 - e^{-\zeta R_{ij}}}{R_{ij}} \right\rangle_{\text{eq}} \tag{26}$$

where ζ is an adjustable parameter. The conventional Oseen tensor results are recaptured when $\zeta \rightarrow \infty$ and the free drain limit (Oseen tensor equal to zero) when $\zeta = 0$. The divergence at $R_{ij} = 0$ is removed in the model when ζ is finite. The attractive feature of the model is that the equilibrium average in eq 26 can be calculated for a Gaussian chain analytically. Replacing $\langle 2/R_{ij} \rangle$ in eq 14 by $\langle [1 - \exp(-\zeta R_{ij})]/R_{ij} \rangle$, we obtain

$$bN^{1/2}\langle 1/R \rangle = \left(\frac{24}{\pi}\right)^{1/2} \frac{1}{(N+1)^{3/2}} \sum_{s=1}^{N} \frac{(N+1-s)}{s^{1/2}} \pi^{1/2} \chi_s e^{\chi_s^{\,2}} \operatorname{erfc}(\chi_s) \tag{27}$$

where $\chi_s = \zeta b s^{1/2}/6^{1/2}$. We calculated this summation numerically for values of N up to 31 000 for $\zeta b = \infty$, $\zeta b = 1$, and $\zeta b = 1.5$. The results are presented in Figure 3 along with the results for the freely jointed chain. The Monte Carlo results obtained by Guttman[11] et al. are also marked in the figure for comparison with analytical results. It is observed that the modification of the Oseen tensor at short distances has no effect on $\langle 1/R \rangle$ in the long-chain limit, but it tends to bring the Gaussian chain results closer to the Monte Carlo results for shorter chains.

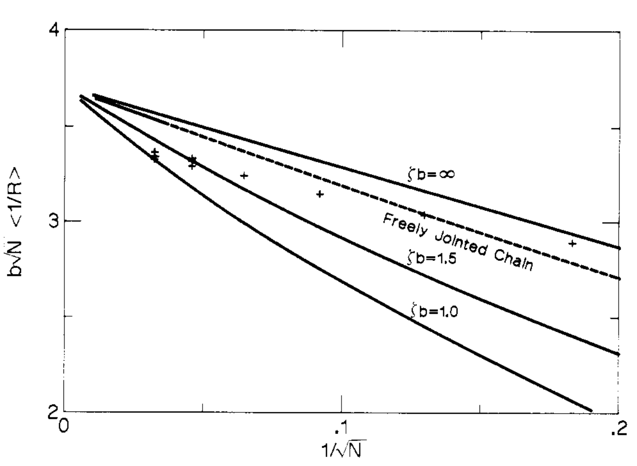

Figure 3. Effect of different choices of hydrodynamic interaction models at short separation distances on $\langle 1/R \rangle$. For $\zeta \rightarrow \infty$ we obtain the Gaussian chain with no modifications in the hydrodynamic interaction at short distances. For comparison the dashed line is the freely jointed chain. The + are the Monte Carlo data of Guttman et al.[11] For the Monte Carlo data N and b are in statistical units (see discussion in ref 11).

Discussion and Conclusions

We have shown that for two cases the expansion for $\langle 1/R \rangle$ is of the form

$$b\langle 1/R \rangle = \frac{A_0}{N^{1/2}} - \frac{A_1}{N} + \frac{A_2}{N^{3/2}}$$

We might expect other chain models which include only interactions with close neighbors along the chain and without excluded volume to have such an expansion. Fixman and Mansfield[13] and Martin[22] have discussed the perturbation expansion around the Gaussian chain in which the perturbation includes a term E_0 from partial exclusion and E_1 from nearest-neighbor attraction. In these expansions Fixman and Mansfield have argued that a term in $\langle 1/R \rangle$ of the form $\ln(N)/N$ appears at the Θ point. These terms seem to arise from both the exclusion and the attraction. This means that chain models described here without exclusion and attraction energies will not show the second term expected from the Fixman and Mansfield expansion. Their expansion may be considered as another model for the description of relatively short chains.

The flexible Gaussian (G) and freely jointed (FJ) chain models, both containing b and N as two adjustable parameters, can be made to coincide by requiring that the slopes of the expansion of $\langle 1/R \rangle$ in both cases be the same. This requirement leads to a connection between the statistical lengths b_G and b_{FJ}, or between N_G and N_{FJ} since the product of $bN^{1/2}$ must be the same for both models. From the numerical values given in Table I for the slopes, one finds

$$b_{FJ}/b_G = (N_G/N_{PJ})^{1/2} = 4.036/5.178 = 0.78 \quad (28)$$

Thus, the bond length to be used in the freely jointed chain model is 78% of the statistical length in the Gaussian model. With this choice, these two models become indistinguishable in their prediction of R_G and R_H as far as the first two terms in their large-N expansion in powers of $N^{-1/2}$ are concerned.

The Gaussian chain model with stiffness contains three adjustable parameters: b, N, and $\bar{\mu}$. Since the slope of $\langle 1/R \rangle$ as a function of $N^{-1/2}$ becomes positive when the chain stiffness is increased, it does not seem to be always possible to collapse this model to a two-parameter model with an effective b and N. It is observed in Figure 1 that $\langle 1/R \rangle$ and hence $1/R_H$ tend to the asymptotic limit more slowly when the chain stiffness is increased, as expected from persistence length considerations.

The substitution of the expansion of $\langle 1/R \rangle$ into eq 8 yields an expansion for the hydrodynamic radius in powers of $N^{-1/2}$

$$R_G(N)/R_H(N) = \frac{A_0}{6^{1/2}} - \frac{b\alpha^{1/2}}{6R_G(N)}[A_1 - B_1(\bar{\mu}) - (3/\pi)^{1/2}\alpha^{1/2}/h^*] + O(1/N) \quad (29)$$

in the stiff Gaussian chain model. Here we have eliminated $N^{1/2}$ using $R_G(N) = (N\alpha)^{1/2}b/6^{1/2} + O(1/N)$ in order to express the $R_G(N)/R_H(N)$ ratio in terms of measurable quantities. The right-hand side of eq 29 depends now on three parameters, b, $\bar{\mu}$, and h^*.

In the case of the flexible Gaussian chain model $\bar{\mu} = 0$, $B_1(\bar{\mu}) = 0$, eq 29 reduces to

$$R_G(N)/R_H(N) = 1.504 - [b/R_G(N)][0.673 - (1/2)(3\pi)^{-1/2}/h^*] + O(1/N) \quad (30)$$

where we have used the numerical values for A_0 and A_1 from Table I. This equation may be used to interpret R_G and R_H data for flexible, relatively short chains.

The main point we would like to make in conclusion is that the interpretation of the diffusion experiments on relatively short chains with molecular weights 10^6 or less presents difficulties when accuracies of the order of 10% are of concern, because the results of the experiment depend on the parameter of the chain model, details of the hydrodynamic interaction at short distances, and the draining parameter. Here we have attempted to quantify the effects of changing these parameters on R_G and R_H and proposed eq 29 and 30 to be used to interpret R_H data.

Acknowledgment. We thank Dr. F. L. McCrackin and Professor G. C. Summerfield for helpful discussions. This work was partially supported by National Science Foundation Grant No. CPE-8207308.

Appendix A

The problem is to expand

$$I(N) = \frac{4}{\pi}\frac{1}{N^{1/2}}\int_0^\infty \mathrm{d}x\ G_N(x/b)$$

into a power series in $N^{-1/2}$. In the case of Gaussian chains, we have

$$I(N) = \frac{4}{\pi}\frac{6^{1/2}}{N^{1/2}}\int_0^\infty \mathrm{d}x\ \frac{e^{-x^2}}{1 - \exp(-x^2)}\left[1 - \frac{1 - e^{-Nx^2}}{N[1 - \exp(-x^2)]}\right]$$

A change of variable $y = xN^{1/2}$ leads to

$$I(N) = \frac{4(6^{1/2})}{\pi}\frac{1}{N}\int_0^\infty \mathrm{d}y\ \frac{e^{-y^2/N}}{1 - \exp(-y^2/N)}\left[1 - \frac{1 - e^{-y^2}}{N[1 - \exp(-y^2/N)]}\right]$$

The limit as $N \to \infty$ is

$$A_0 = \frac{4(6^{1/2})}{\pi}\int_0^\infty \mathrm{d}y\ y^{-4}[y^2 - (1 - e^{-y^2})] = 8(2^{1/2})/3\pi \quad (A1)$$

The integration in eq A1 is performed by integration by parts twice. Now consider

$$I(N) - A_0 = \frac{4(6^{1/2})}{\pi}\int_0^\infty \mathrm{d}y\left[\frac{e^{-y^2/N}}{N(1 - e^{-y^2/N})} - \frac{1}{y^2}\right] - \frac{4(6^{1/2})}{\pi}\int_0^\infty \mathrm{d}y\left[\frac{e^{-y^2/N}}{N^2(1 - e^{-y^2/N})^2} - \frac{1}{y^4}\right](1 - e^{-y^2})$$

The limit of the first term can be obtained by letting $y = xN^{1/2}$ as $-A_1/N^{1/2}$

$$A_1 = \frac{4(6^{1/2})}{\pi}\int_0^\infty \mathrm{d}x\left[\frac{1}{x^2} - \frac{e^{-x^2}}{1 - e^{-x^2}}\right]$$

The second term also can be evaluated for large N as $A_3/N^{3/2} + O(1/N^2)$ by letting $y = xN^{1/2}$, where

$$A_3 = \frac{4(6^{1/2})}{\pi}\int_0^\infty \mathrm{d}x\left[\frac{1}{x^4} - \frac{e^{-x^2}}{(1 - e^{-x^2})}\right] = 0.5673$$

Then, the following expansion is found:

$$I(N) = A_0 - \frac{A_1}{N^{1/2}} + \frac{A_3}{N^{3/2}} - \frac{1}{N^2}\frac{1}{(6\pi)^{1/2}} + O(1/N^{5/2})$$

In the case of a freely jointed chain $I(N)$ is given by

$$I(N) = \frac{4}{\pi}\int_0^\infty \mathrm{d}y\ \frac{j_0(y/N^{1/2})}{N[1 - j_0(y/N^{1/2})]}\left[1 - \left(\frac{1}{N}\right)\frac{1 - j_0(y/N^{1/2})^N}{1 - j_0(y/N^{1/2})}\right] \quad (A2)$$

The large-N limit can be obtained by observing

$$N[1 - j_0(y/N^{1/2})] = \frac{y^2}{6}\left[1 - \frac{y^2}{20N} + \frac{y^4}{840N^2} + O(1/N^3)\right]$$

$$j_0(y/N^{1/2})^N = \exp\left[-\frac{y^2}{6} - \frac{y^4}{180N} + O(1/N^2)\right]$$

The latter can be verified by taking the logarithm of both sides. Substituting these expansions into eq A2 and letting $N \to \infty$, one finds that $I(\infty) = A_0$ as in the case of the

Gaussian chain, with the same A_0 given in eq A1.

To obtain the terms proportional to $1/N^{1/2}$ we again form

$$I(N) - A_0 = \frac{4}{\pi}\int_0^\infty \mathrm{d}y \left[\frac{j_0(y/N^{1/2})}{N[1 - j_0(y/N^{1/2})]} - \frac{6}{y_2} \right] - \frac{4}{\pi}\int_0^\infty \mathrm{d}y \left[\frac{j_0^2(y/N^{1/2})[1 - j_0(y/N^{1/2})^N]}{N^2[1 - j_0(y/N^{1/2})]^2} - \frac{36}{y^4}(1 - e^{-y^2/6}) \right] \tag{A3}$$

By letting $y = xN^{1/2}$, one can show that the first term is equal to $-B_1/N^{1/2}$ with

$$B_1 = \frac{4}{\pi}\int_0^\infty \mathrm{d}x \left[\frac{6}{x^2} - \frac{j_0(x)}{1 - j_0(x)} \right]$$

The second term requires closer attention, because it leads to a term proportional to $1/N$. Using the expansions given in eq A3 one can show after some algebra that the second term behaves as B_2/N where

$$B_2 = 4\pi\left[\frac{12}{5}\int_0^\infty \mathrm{d}y\, \frac{1 - e^{-y^2/6}}{y^2} - \frac{1}{5}\int_0^\infty \mathrm{d}y\, e^{-y^2/6} \right] = \frac{6}{5}\left(\frac{6}{\pi}\right)^{1/2}$$

Hence, in the case of a freely jointed chain, we find

$$I(N) = A_0 - \frac{B_1}{N^{1/2}} + \left(\frac{6}{\pi}\right)^{1/2}\frac{6}{5N} + O(1/N^{3/2})$$

A factor $[N_\mathrm{b}/(N_\mathrm{b} + 1)]^{1/2} \cong 1 - 1/(2N_\mathrm{b})$, where N_b is the number of beads in the chain, is needed to obtain the expansion coefficients in eq 15a and Table I. This factor affects only A_2, the coefficient of $1/N_\mathrm{b}$.

Appendix B

We want to construct a multidimensional Gaussian distribution

$$P(\mathbf{b}^N) = A \exp[-\tfrac{1}{2}M_{jl}\mathbf{b}_j\cdot\mathbf{b}_l]$$

such that

$$\langle \mathbf{b}_j\cdot\mathbf{b}_l \rangle = b^2\bar{\mu}^{|j-l|}$$

will strictly hold. This implies that the correlation matrix, which is the inverse of M_{jl}, must be of the following form

$$\mathbf{M}^{-1} = \frac{b^2}{3}\begin{bmatrix} 1 & \bar{\mu} & \bar{\mu}^2 & \cdots & \bar{\mu}^{N-1} \\ \bar{\mu} & 1 & \bar{\mu} & \cdots & \bar{\mu}^{N-2} \\ \cdot & & & & \\ \cdot & & & & \\ \cdot & & & & \\ \bar{\mu}^{N-1} & \bar{\mu}^{N-2} & \bar{\mu} & \cdots & 1 \end{bmatrix}$$

The inverse of this matrix can be verified to be

$$\mathbf{M} = \frac{3}{b^2}\frac{1}{1 - \bar{\mu}^2}\begin{bmatrix} 1 & -\bar{\mu} & & \\ -\bar{\mu} & 1 + \bar{\mu}^2 & & 0 \\ & & \ddots & \\ 0 & & 1 + \bar{\mu}^2 & -\bar{\mu} \\ & & -\bar{\mu} & 1 \end{bmatrix}$$

The normalization $A = \mathbf{M}^{3/2}/(2\pi)^{3N/2}$ is obtained by using

$$\mathbf{M} = [3/b^2(1 - \bar{\mu}^2)]^N(1 - \bar{\mu}^2)$$

Appendix C

Start with

$$I(\bar{\mu}) \equiv \frac{1}{N^2}\sum_{s=1}^{N}\frac{N - s}{[\alpha s - \beta(1 - \bar{\mu}^s)]^{1/2}}$$

and form

$$I(\bar{\mu}) - \frac{I(0)}{\alpha^{1/2}} = \frac{1}{\alpha^{1/2}}\frac{1}{N^2}\sum_{s=1}^{N}(N - s)[(s - \gamma(1 - \bar{\mu}^s))^{-1/2} - s^{-1/2}]$$

where

$$\gamma = \beta/\alpha$$

Use the trapezoidal rule to replace the summation by an integration

$$I(\bar{\mu}) - \frac{I(0)}{\alpha^{1/2}} = \frac{1}{(\alpha N)^{1/2}}\left\{\frac{1}{N^{3/2}}\int_1^N \mathrm{d}s\,(N - s)[\ldots] + \frac{1}{2}\,\frac{N - 1}{N^{3/2}}(\alpha^{1/2} - 1)\right\}$$

The last term is the usual end-point correction term. Since the integral of $s[\ldots]/N^{1/2}$ from one to infinity is finite due to the subtraction, its contribution is of the order of N^{-1}. Using $b\langle 1/R\rangle = 2(6/\pi)^{-1/2}I(\bar{\mu})$ one obtains eq 23.

References and Notes

(1) Schmidt, M.; Burchard, W. *Macromolecules* **1981**, *14*, 210.
(2) Yamakawa, H. "Modern Theory of Polymer Solutions"; Harper and Row: New York, 1971.
(3) Kurata, M.; Yamakawa, H. *J. Chem. Phys.* **1958**, *29*, 311.
(4) Zimm, B. H.; Roe, G. M.; Epstein, L. F. *J. Chem. Phys.* **1956**, *24*, 279.
(5) Horta, A.; Fixman, M. *J. Am. Chem. Soc.* **1968**, *90*, 3048.
(6) Zimm, B. H. *Macromolecules* **1980**, *13*, 592.
(7) Fixman, M. *Macromolecules* **1981**, *14*, 1706; *14*, 1710.
(8) Dubois-Violette, E.; de Gennes, P.-G. *Physics* (*Long Island City, N.Y.*) **1967**, *3*, 181.
(9) Mansfield, M. L. Ph.D. Dissertation, Dartmouth College, Hanover, NH, Nov 1980.
(10) Akcasu, A. Z. *Macromolecules* **1982**, *15*, 1321.
(11) Guttman, C. M.; McCrackin, F. L.; Han, C. C. *Macromolecules* **1982**, *15*, 1205.
(12) McCrackin, F. L.; Guttman, C. M.; Akcasu, A. Z. *Macromolecules* **1984**, *17*, 604.
(13) Fixman, M.; Mansfield, M. L. *Macromolecules* **1984**, *17*, 522.
(14) Akcasu, A. Z. *Polymer* **1981**, *22*, 1169.
(15) Akcasu, A. Z.; Benmound, M.; Hammoudd, B. *J. Chem. Phys.* **1984**, *80*, 2762.
(16) Burchard, W.; Kajiward, K.; Nerger, D.; Stockmayer, W. H. *Macromolecules*, **1984**, *17*, 222.
(17) Akcasu, A. Z.; Gürol, H. J. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 1.
(18) Akcasu, A. Z.; Higgins, J. S. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 1745.
(19) Jannink, G.; Summerfield, G. C. Proceedings of the Symposium on Neutron Inelastic Scattering, Grenoble, March 6–10, 1972, IAEA-SM-159/X-2.
(20) Kratky, R.; Porod, G. *Recl. Trav. Chim. Pays-Bas* **1949**, *68*, 1106.
(21) Rotne, J.; Prager, S. *J. Chem. Phys.* **1969**, *50*, 4831.
(22) Martin, J. *Macromolecules* **1984**, *17*, 1263.