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Translational Diffusion of Polymer Chains in Dilute Solution[†]

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ABSTRACT: The equations describing the diffusive motion of polymer chains in the rigid-body approximation have been examined in detail, and the situation in which the molecule has zero angular velocity is considered. It is treated in the Oseen approximation with strong and weak hydrodynamic interactions between chain segments and using the preaveraged Oseen tensor, which is unambiguously defined. The case of weak hydrodynamic interactions, independent of preaveraging, relates to the treatment of Kirkwood and Riseman and results in the Kirkwood equation. Thus, three cases are considered, the Oseen, the Kirkwood–Riseman (K–R) (weak interactions), and the preaveraged Oseen, and are used to interpret experimental diffusion coefficients of short polymethylene chains. The interpretation is in terms of ζ/f, where ζ is the segmental friction coefficient and f is the molecular friction coefficient, and uses the equation $\zeta/f = \langle {}^1/_3 \operatorname{Tr} (\mathbf{K}^{-1})\rangle_{\text{conf}}$. $\mathbf{K}^{-1}$ is a tensor related to the Oseen tensor $\mathbf{T}_{ij}$ for all pairs of segments i and j. $\langle ... \rangle_{\text{conf}}$ denotes configurational average, which was found by evaluating $\mathbf{K}^{-1}$ for samples of chain configurations generated for the longer chains by Monte Carlo methods using Metropolis sampling and for the shorter chains by using all possible configurations. The chain model used was the rotational-isomeric-state model due to Flory and co-workers. All three cases can be used to interpret the experimental data if ζ is allowed to vary approximately in proportion to the effective bond length of the chain. Approximate extrapolation of the differences between the K–R and Oseen values of ζ/f to infinite chain length indicates that the former underestimates f by 6–8% for the unperturbed PM chain in benzene at 25 °C. The underestimation is in broad agreement with previous correlations of experimental data on unperturbed poly(methyl methacrylate) and polystyrene chains of high molar mass and with calculations of Garcia de la Torre and Freire using related polymethylene chain models.

1. Introduction

The translational diffusion coefficient (D) of a solute molecule in dilute solution is a measure of the differential thermal motion of the center of mass of the molecule relative to that of the surrounding solvent molecules. For a macromolecular solute, where there are many centers of interaction with solvent, the only tractable method of predicting D is to assume that the solvent is a continuum characterized by its viscosity η_0. The centers of interaction or friction centers are then taken as segments of the polymer chain based on skeletal atoms or groups of skeletal atoms and are conventionally assumed to be spherical. The establishment of a relationship between D and the segment distribution of the molecule is a dynamical problem, with D characterizing the lowest normal mode of the molecule. Thus, D could be calculated from a molecular dynamics simulation incorporation hydrodynamic interactions between friction centers. In practice, this is not possible at present, as solving the equations of motion for a macromolecule requires a prohibitive amount of computer time.

Alternative approaches to the problem assume that the molecule diffuses as an instantaneously rigid body and compute D for an ensemble of such rigid bodies. Implicit here is the assumption that center-of-mass motion, as measured in classical boundary-spreading experiments, is separable from the internal modes of the molecule.[1] It is also assumed that the equilibrium segment distribution of the molecule is not perturbed by the solvent flow. Thus the mechanisms by which configurations interconvert,[1] which are important for the higher dynamical modes of macromolecule, are not considered, but the result of the interconversions (the ensemble of configurations) is employed. Historically, this was the approach used by Kirkwood and Riseman[2] and Kirkwood,[3] resulting in the well-known equation[3] for the diffusion coefficient of a polymer molecule of x segments

$$D = \frac{kT}{x\zeta} + \frac{kT}{6\pi\eta_0}\,\frac{[R^{-1}]}{x^2} \tag{1}$$

where ζ is the segmental friction coefficient, η_0 is the viscosity of the solvent, and $[R^{-1}] = \sum_i\sum_j\langle r_{ij}^{-1}\rangle$, $i \neq j$, with $\langle r_{ij}^{-1}\rangle$ denoting the average reciprocal separation of segments i and j. At high molar mass, there is little flow of solvent through the molecular domain, and the first term in eq 1 (the free-draining term) can be neglected. However, at low molar mass, correlations of measured diffusion coefficients for several polymer chains in a variety of

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solvents using eq 1 have shown that free-draining cannot be neglected[4,5] and that frictional forces on individual segments can depend strongly on the environment of the segments. For systems with relatively weak segment–solvent interactions, for example, polymethylene (PM) in a variety of solvents,[4] the *effective* segmental friction coefficient ζ depends on both chain length and solvent properties, principally η_0 and molar volume V_0. A dependence of ζ on molar mass and solvent structure at low molar mass may be expected simply from the treatment of the solvent as a continuum, but the hydrodynamic approximations in the derivation of eq 1 may also contribute to the variation of ζ with chain length. The usual derivation of eq 1 assumes that hydrodynamic interactions between point centers of friction in the molecule are given by the preaveraged Oseen tensor[6] and that the hydrodynamic interactions are weak. The meaning of these assumptions and their relative importance are discussed in detail in this paper.

Equation 1 can be recast to give[4,5]

$$\frac{1}{r_{\rm D}} = \frac{1}{r_{\rm F}} + \frac{1}{r_{\rm E}} \qquad (2)$$

where $r_{\rm D}$ is the Stokes–Einstein diffusion radius, $r_{\rm F} = xa$ (from $\zeta = 6\pi\eta_0 a$) is the free-draining radius, and $r_{\rm E} = x^2/[R^{-1}]$ is the effective impermeable diffusion radius. As $x \rightarrow \infty$, the free-draining term in eq 2 becomes negligible and $r_{\rm D} \cong r_{\rm E}$. For an unperturbed chain of infinite length (a Gaussian chain) the equilibrium radius of gyration $\langle s_0^2\rangle^{1/2}$ is related to $r_{\rm D}$ in the following way:[2]

$$\langle s_0^2\rangle^{1/2} = (8/3\pi^{1/2})r_{\rm D} \qquad (3)$$

In general,[4,5] $\langle s_0^2\rangle^{1/2}$ can be related to the impermeable hydrodynamic radius by the equation

$$\langle s_0^2\rangle^{1/2} = \psi_0(x)x^2/[R^{-1}] \qquad (4)$$

The functional form of $\psi_0(x)$ has been shown to depend on chain structure[5] for short chains, and $\psi_0(\infty)$ ($=8/3\pi^{1/2}$) can be identified with the parameter ρ introduced by other authors.[7,8] Correlations of independently measured values of $\langle s_0^2\rangle^{1/2}$ and $r_{\rm D}$ for high molar mass poly(methyl methacrylate)[7] (PMMA) and polystyrene[8] (PS) in a variety of Θ solvents have shown that $\psi_0(\infty)$ is smaller by about 23% (PMMA) and 15% (PS) than the Gaussian limiting value of $8/3\pi^{1/2}$. Thus, the limiting relationship between $\langle s_0^2\rangle^{1/2}$ and $r_{\rm D}$ is not predicted correctly by eq 3 and is dependent on chain structure. Several authors have attempted to improve on eq 3. Zimm[9] has treated a hypothetical freely jointed chain model based on a Gaussian distribution of the separation of contiguous friction centers. Garcia de la Torre, Jimenez, and Friere[10] and Garcia de la Torre and Friere[11] used a next higher order interaction tensor[12,13] and included a treatment of rotation. They applied their equations to model PM chains of varying flexibility and used the results to interpret experimental diffusion coefficients. Their work[10] indicates that eq 3 overestimates the value of $\psi_0(\infty)$ by an amount which increases with the hydrodynamic segment radius and with chain flexibility. For chains with excluded volume, eq 3 may be generalized to $\langle s^2\rangle^{1/2} = \psi(\infty)r_{\rm D}$, where $\psi(\infty)$ will, in general, not be equal to $8/3\pi^{1/2}$. However, no distinction between $\psi(\infty)$ and $\psi_0(\infty)$ was made.[10,11] A somewhat involved comparison with Zimm's results showed[10] approximate agreement, with an overestimation[9] of 13% in the Kirkwood–Riseman value of $\psi(\infty)$ using Zimm's hydrodynamic model and chain model and an overestimation of 14% in $\psi_0(\infty)$ using their hydrodynamic model, the freely jointed chain, and a value of the segment radius approximately equal to that used by Zimm. In order to investigate the rigid-body assumption, Fixman[14] has used an approximate dynamical method to compute D for so-called short Gaussian chains. This model may be termed[15] the wiggly hydrodynamic sphere (WHS). The conclusions suggest that by neglecting fluctuations in hydrodynamic interactions, eq 3 is in error by about 1%, thereby lending support to the rigid-body approach.

In the present paper, the equations describing the motion of a rigid body constituted of friction centers and moving with constant velocity in a solvent continuum are formulated. The formulation leads to two cases: first, when the molecule has random orientation and does not rotate and, second, when the molecule rotates about a particular axis during translation. The former case may be compared with the model used by Garcia de la Torre, Jimenez, and Freire,[10] excluding rotation, and the latter with that used by Zimm.[9] Only the first case is considered in detail in the present paper. The effects of various models of hydrodynamic interaction based on the Oseen tensor are investigated. In particular, the behavior of $\psi_0(\infty)$ for PM chains is investigated through numerical calculations using a realistic chain model and previous correlations[4,5] with experimental data.

2. Hydrodynamic Framework

2.1. Forces on Frictional Centers. The model of the polymer molecule assumed is the conventional one of x spherical frictional centers (numbered 1–x) connected by $x - 1$ frictionless bonds. An origin O is fixed in the molecule, and the vector describing the position of center i with respect to this origin is $\mathbf{r}_i$. Center i experiences forces $\mathbf{F}_i^{\rm B}$, $\mathbf{F}_i^{\rm L}$, and $\mathbf{F}_i^{\rm E}$, where $\mathbf{F}_i^{\rm B}$ is the force due to the bonds connecting the centers, $\mathbf{F}_i^{\rm L}$ is the force due to the surrounding liquid (solvent continuum), and $\mathbf{F}_i^{\rm E}$ is the resultant external force (including forces due to Brownian motion and to externally imposed forces such as gravity). The influence of the other friction centers in the molecule is formally represented in the expressions used for $\mathbf{F}_i^{\rm L}$.

The velocity is assumed to be sufficiently small for any acceleration of the centers to be ignored. Thus

$$\mathbf{F}_i^{\rm B} + \mathbf{F}_i^{\rm L} + \mathbf{F}_i^{\rm E} = 0, \qquad i = 1, 2, ..., x \qquad (5)$$

The significance of terms $\mathbf{F}_i^{\rm B}$ and $\mathbf{F}_i^{\rm E}$ is seen when summing over all friction centers to find the molecular force balance. First

$$\sum_{i=1}^{x}\mathbf{F}_i^{\rm B} = 0 \qquad (6)$$

since for the force on center k arising from its connection to center l, there is an equal and opposite force on center l due to its connection to center k. Second, the terms $\mathbf{F}_i^{\rm E}$ are summed to give the external force on the molecule, with

$$\sum_{i=1}^{x}\mathbf{F}_i^{\rm E} = \mathbf{F} \qquad (7)$$

Hence, summing over eq 5

$$\mathbf{F} = -\sum_{i=1}^{x}\mathbf{F}_i^{\rm L} \qquad (8)$$

The real quantity of debate is $\mathbf{F}_i^{\rm L}$. This is assumed to be proportional to the velocity of center i relative to that of the solvent at the position of center i if that center were removed. That is

$$\mathbf{F}_i^{\rm L} = -\zeta(\mathbf{u}_i - \mathbf{v}_i - \mathbf{v}_i') \qquad (9)$$

where $\mathbf{u}_i$ is the velocity of center i, $\mathbf{v}_i$ is that of the solvent at i if the whole molecule were removed, and $\mathbf{v}_i'$ is the perturbation in the velocity of the solvent at i due to the presence of the other $x - 1$ friction centers.

The functional form of $\mathbf{v}_i$ relates to the situation being considered. If it were viscous flow, $\mathbf{v}_i$ would be the velocity at a given point in the shear field. For translational and rotational diffusion and sedimentation, the motion of a single molecule in a stationary solvent is required, so that

$$\mathbf{v}_i = \mathbf{0} \tag{10}$$

For a dilute solution, the perturbation in velocity, $\mathbf{v}_i'$, is determined by the forces exerted on the liquid by the $x - 1$ other centers. In keeping with previous treatments,[1-3,6] it is assumed that force and velocity are proportional with

$$\mathbf{v}_i' = -\sum_{j=1}^{x}\mathbf{T}_{ij}\cdot\mathbf{F}_j^{\mathrm{L}}, \qquad j \neq i \tag{11}$$

where $\mathbf{T}_{ij}$ is a second-rank tensor describing hydrodynamic interactions and is determined by $\mathbf{r}_i - \mathbf{r}_j$. Various forms of $\mathbf{T}_{ij}$ are discussed later.

Substituting for $\mathbf{v}_i$ and $\mathbf{v}_i'$ in eq 9, one finds that

$$\mathbf{F}_i^{\mathrm{L}} + \zeta\sum_{j=1}^{x}\mathbf{T}_{ij}\cdot\mathbf{F}_j^{\mathrm{L}} = -\zeta\mathbf{u}_i \tag{12}$$

with the condition of $j \neq i$ of eq 11 satisfied by defining $\mathbf{T}_{ii} = \mathbf{0}$. Alternatively, one may write

$$\sum_{j=1}^{x}\mathbf{P}_{ij}\cdot\mathbf{F}_j^{\mathrm{L}} = -\zeta\mathbf{u}_i \tag{13}$$

where

$$\mathbf{P}_{ij} = \delta_{ij}\mathbf{I} + \zeta\mathbf{T}_{ij} \tag{14}$$

Consideration of eq 13 for all i gives a system of x equations which may be solved for the $\mathbf{F}_i^{\mathrm{L}}$; namely

$$\mathbf{F}_i^{\mathrm{L}} = -\zeta\sum_{j=1}^{x}\mathbf{Q}_{ij}\cdot\mathbf{u}_j \tag{15}$$

with

$$\sum_{k=1}^{x}\mathbf{P}_{ik}\cdot\mathbf{Q}_{kj} = \delta_{ij}\mathbf{I} \tag{16}$$

Equation 15 shows that $\mathbf{Q}_{ij}$ may be considered as the friction tensor describing the frictional force at center i due to the velocity of center j. Conversely, $\mathbf{P}_{ij}$ may be considered as the corresponding mobility tensor.

$\mathbf{P}_{ij}$ is defined in terms of $\mathbf{T}_{ij}$, and, through eq 16, the $\mathbf{Q}_{ij}$ can be related by an inversion process to the $\mathbf{P}_{ij}$ for the whole molecule. The process is defined in Appendix I, in which the $x \times x$ equations generated from eq 16 by taking $i, j = 1, 2, ..., x$ are transformed into the single matrix equation

$$\boldsymbol{P}_{uv}\cdot\boldsymbol{Q}_{vw} = \boldsymbol{I}_{uw} \tag{17}$$

$\boldsymbol{P}$, $\boldsymbol{Q}$, and $\boldsymbol{I}$ are matrices of order $3x \times 3x$, with

$$u = 3(i - 1) + \alpha$$

$$v = 3(j - 1) + \beta$$

and

$$w = 3(k - 1) + \gamma$$

where $i, j, k = 1, 2, ..., x$ and $\alpha, \beta, \gamma = 1, 2, 3$. $\boldsymbol{P}$ contains the $\mathbf{P}_{ij}$ as blocks of 3×3 elements, $\boldsymbol{Q}$ similarly contains the $\mathbf{Q}_{ij}$, and $\boldsymbol{I}$ is the unit matrix.

2.2. Molecular Motion. Since the molecule is a rigid body, the velocity of center i may be written as

$$\mathbf{u}_i = \mathbf{u} + \boldsymbol{\Omega} \times \mathbf{r}_i \tag{18}$$

with $\mathbf{u}$ the velocity of the molecular-fixed origin relative to laboratory-fixed axes and $\boldsymbol{\Omega}$ the angular velocity of the molecule relative to the same axes. Substitution in eq 15 gives

$$\mathbf{F}_i^{\mathrm{L}} = -\zeta\sum_{j=1}^{x}\mathbf{Q}_{ij}\cdot(\mathbf{u} + \boldsymbol{\Omega} \times \mathbf{r}_j) \tag{19}$$

The total force $\mathbf{F}$ on the molecule is given by eq 8, which, together with eq 19, gives

$$\mathbf{F} = \zeta\sum_{i,j}^{x}\mathbf{Q}_{ij}\cdot(\mathbf{u} + \boldsymbol{\Omega} \times \mathbf{r}_j) \tag{20}$$

The couple $\mathbf{G}$ about the molecular origin is given by the equation

$$\mathbf{G} = \sum_{i=1}^{x}\mathbf{r}_i \times \mathbf{F}_i^{\mathrm{E}} \tag{21}$$

In addition, corresponding to eq 6

$$\sum_{i=1}^{x}\mathbf{r}_i \times \mathbf{F}_i^{\mathrm{B}} = \mathbf{0} \tag{22}$$

Summation over the friction centers, using the balance condition of eq 5, gives

$$\mathbf{G} + \sum_{i=1}^{x}\mathbf{r}_i \times \mathbf{F}_i^{\mathrm{L}} = \mathbf{0} \tag{23}$$

or, from eq 19

$$\mathbf{G} = \zeta\sum_{i=1}^{x}\mathbf{r}_i \times \sum_{j=1}^{x}\mathbf{Q}_{ij}\cdot(\mathbf{u} + \boldsymbol{\Omega} \times \mathbf{r}_j) \tag{24}$$

Equations 20 and 24 are the equations of motion of the molecule at one instant in time. They may be used to determine its linear velocity $\mathbf{u}$ and angular velocity $\boldsymbol{\Omega}$ in terms of $\mathbf{F}$ and $\mathbf{G}$, the total force and total couple on the molecule.

$\mathbf{F}$ and $\mathbf{G}$ result from the external forces on the molecule, including the Brownian-motion forces due to the solvent molecules and any gravitational field. In the absence of explicit calculations of $\mathbf{F}$ and $\mathbf{G}$ in these terms, two extreme cases may be defined. One is when the random forces due to the Brownian motion of the surrounding molecules (the solvent continuum) are large. It may then be proposed that a definite rotation of the molecule is never estabilished. In terms of eq 20 and 24 this means that over any infinitesimal period of time the Brownian forces have caused sufficient random disturbances to give

$$\boldsymbol{\Omega} = \mathbf{0} \tag{25}$$

All orientations of the molecule in its translational motion are then equally probable. The second case is when the molecule is subject only to a unidirectional force such as gravity. Its development is deferred until a later publication. It leads to a description of the sedimentative motion of the molecule in the absence of Brownian motion and is similar to the situation described by Zimm.[9]

The molecular motion occurring depends on the tensor $\mathbf{T}_{ij}$. Subject to the choice of $\mathbf{T}_{ij}$ and subsequent manipulative approximations in treating the resulting equations, the condition $\boldsymbol{\Omega} = \mathbf{0}$ leads to expressions for D derived by several previous authors.[1-3,10,16] Various possibilities for the tensor $\mathbf{T}_{ij}$ are now discussed, followed by the derivation and investigation of the consequent expressions for D.

2.3. Forms of the Hydrodynamic Interaction Tensor $\mathbf{T}_{ij}$. In general, $\mathbf{T}_{ij}$ depends on the differences between the coordinates of friction centers i and j. It is convenient to scale the differences to a chain of unit skeletal bond length by writing

$$|\mathbf{r}_i - \mathbf{r}_j| = l\tilde{r}_{ij} \tag{26}$$

and

$$\mathbf{r}_i - \mathbf{r}_j = l\tilde{r}_{ij}\mathbf{n}_{ij} \tag{27}$$

l is the bond length, $\tilde{r}_{ij}$ is the magnitude of the distance between centers i and j for a chain of unit skeletal bond length, and $\mathbf{n}_{ij}$ is the unit vector from i to j. In addition, eq 14 shows that $\mathbf{T}_{ij}$ always occurs in the product $\zeta\mathbf{T}_{ij}$ and it is convenient to consider this as a single quantity.

Four forms of $\zeta\mathbf{T}_{ij}$ have been considered in previous treatments (in all cases $\zeta\mathbf{T}_{ii} = \mathbf{0}$):

(a)
$$\zeta\mathbf{T}_{ij} = \frac{\zeta}{8\pi\eta_0 l\tilde{r}_{ij}}(\mathbf{I} + \mathbf{n}_{ij}\mathbf{n}_{ij}) \tag{28}$$

This is the familiar Oseen tensor.[6] $\mathbf{n}_{ij}\mathbf{n}_{ij}$ denotes the direct product of the two vectors. The tensor assumes that interactions are between pairs of point centers and that the perturbation velocities decrease in inverse proportion to their distances apart.

(b)
$$\langle\zeta\mathbf{T}_{ij}\rangle_{\langle\text{Oseen}\rangle} = \frac{\zeta}{6\pi\eta_0 l\tilde{r}_{ij}}\mathbf{I} \tag{29}$$

is the preaveraged Oseen tensor. If the average of eq 28 is taken over all directions with equal probability then, because $\langle\mathbf{n}_{ij}\mathbf{n}_{ij}\rangle_{\text{preav}} = {}^1/_3\mathbf{I}$, eq 29 results. The reason for this procedure is the simplification it produces in the subsequent manipulation of equations. It could correspond to the case when every friction center is at the center of a spherically symmetric distribution of other centers. The orientation preaveraging is part of the preaveraging procedure frequently referred to[1-3,9-14,16] (see later).

(c)
$$\zeta\mathbf{T}_{ij} = \mathbf{0} \qquad \text{for all } i, j \tag{30}$$

gives free-draining flow with no perturbation of the solvent velocity field by the friction centers.

(d)
$$\zeta\mathbf{T}_{ij} = \frac{\zeta}{8\pi\eta_0 l\tilde{r}_{ij}}(\mathbf{I} + \mathbf{n}_{ij}\mathbf{n}_{ij}) + \frac{\zeta a^2}{24\pi\eta_0 l^3\tilde{r}_{ij}^{\,3}}(\mathbf{I} - 3\mathbf{n}_{ij}\mathbf{n}_{ij}) \tag{31}$$

This tensor has been used by several authors[10-13] for flexible chains. It retains a further term in Stokes' expression for the velocity field at a point produced by uniform flow over a sphere of radius a, giving a term involving the inverse cube of the distance. It also allows the parameter a to be used, which is taken as the finite radius of a friction center. Its use is somewhat inconsistent for the conventional model of a chain of friction centers as it relates to the perturbation produced by point forces on a sphere centered at $\mathbf{r}_j$ on point $\mathbf{r}_i$, rather than over a spherical surface centered at $\mathbf{r}_i$.

3. Translational Diffusion Coefficients of Rigid Chains with Random Molecular Orientation

Proceeding from eq 20 with the condition of eq 25 satisfied gives

$$\mathbf{F} = \zeta\Big(\sum_{i,j=1}^{x}\mathbf{Q}_{ij}\Big)\cdot\mathbf{u} \tag{32}$$

where $\mathbf{F}$ is the total force due to Brownian motion on the molecule in a particular orientation. Equation 32 may be rewritten

$$\mathbf{F} = \zeta\mathbf{K}\cdot\mathbf{u} \tag{33}$$

where

$$\mathbf{K} = \sum_{i,j=1}^{x}\mathbf{Q}_{ij} \tag{34}$$

The tensor $\mathbf{K}$ will generally imply that $\mathbf{u}$ and $\mathbf{F}$ lie along different directions. The component of $\mathbf{u}$ in the direction of $\mathbf{F}$ is

$$u_{\mathbf{F}} = \frac{1}{F}\mathbf{F}\cdot\mathbf{u} \tag{35}$$

and the average over all orientations of the molecule is

$$\langle u_{\mathbf{F}}\rangle_{\text{or}} = \frac{1}{F}\langle\mathbf{F}\cdot\mathbf{u}\rangle_{\text{or}} \tag{36}$$

The average velocity per unit force is $1/f$ ($=D/kT$), where f is the molecular friction coefficient, so that

$$\frac{D}{kT} = \frac{1}{f} = \frac{1}{F^2}\langle\mathbf{F}\cdot\mathbf{u}\rangle_{\text{or}} \tag{37}$$

From eq 33

$$\mathbf{u} = \frac{1}{\zeta}\mathbf{K}^{-1}\cdot\mathbf{F} \tag{38}$$

Hence

$$\frac{\zeta}{f} = \frac{1}{F^2}\langle\mathbf{F}\cdot\mathbf{K}^{-1}\cdot\mathbf{F}\rangle_{\text{or}} \tag{39}$$

and, defining $\mathbf{n}_F$ as the unit vector along $\mathbf{F}$

$$\frac{\zeta}{f} = \langle\mathbf{n}_F\cdot\mathbf{K}^{-1}\cdot\mathbf{n}_F\rangle_{\text{or}} \tag{40}$$

The quantity on the right-hand side of eq 40 is an average over all orientations of the molecule for a fixed direction of $\mathbf{F}$ (or $\mathbf{n}_F$). Equivalently, it can be evaluated as the average for a fixed orientation of the molecule over all possible directions $\mathbf{n}_F$, with the results that

$$\langle\mathbf{n}_F\cdot\mathbf{K}^{-1}\cdot\mathbf{n}_F\rangle_F = \tfrac{1}{3}\,\mathrm{Tr}\,(\mathbf{K}^{-1}) \tag{41}$$

and

$$\zeta/f = \tfrac{1}{3}\,\mathrm{Tr}\,(\mathbf{K}^{-1}) \tag{42}$$

The evaluation of ζ/f can now proceed by considering the various expressions for $\mathbf{K}^{-1}$ resulting from the different $\zeta\mathbf{T}_{ij}$, with $\mathbf{K}^{-1}$ and $\zeta\mathbf{T}_{ij}$ linked through the equations

$$\mathbf{P}_{ij} = \delta_{ij}\mathbf{I} + \zeta\mathbf{T}_{ij} \tag{14}$$

$$\sum_{k=1}^{x}\mathbf{P}_{ik}\cdot\mathbf{Q}_{kj} = \delta_{ij}\mathbf{I} \tag{16}$$

$$\mathbf{K} = \sum_{i,j=1}^{x}\mathbf{Q}_{ij} \tag{34}$$

It may be noted in passing that, while eq 20 with the condition of zero angular velocity leads to eq 42 for the translational friction or diffusion coefficient, eq 24 with the condition of zero translational velocity of the molecule leads to the rotational diffusion coefficient (cf. ref 16).

(a) Oseen Tensor. With $\zeta\mathbf{T}_{ij}$ given by eq 28 it does not seem possible, in general, to find $\mathbf{Q}_{ij}$ analytically. Hence, all the $\mathbf{Q}_{ij}$ must be evaluated numerically through eq 17. Subsequent evaluation of $\mathbf{K}^{-1}$ gives what may be termed the Oseen value of ζ/f.

However, considering eq 28, the factor $\zeta/8\pi n_0 l$ may be considered as a parameter (α) which scales the strength of hydrodynamic interaction, with

$$\alpha = \zeta/8\pi\eta_0 l \tag{43}$$

Then, for α small, $\zeta\mathbf{T}_{ij} \cong \mathbf{0}$, $\mathbf{P}_{ij} \cong \delta_{ij}\mathbf{I}$, and $\mathbf{P}_{ij}$ may be found as a series expansion in α. Retention of only the first power in α gives an analytical expression for $\mathrm{Tr}\,(\mathbf{K}^{-1})$ and hence D. In detail

$$\zeta \mathbf{T}_{ij} = \alpha \tilde{\mathbf{T}}_{ij} \tag{44}$$

where

$$\tilde{\mathbf{T}}_{ij} = \frac{1}{\tilde{r}_{ij}}(\mathbf{I} + \mathbf{n}_{ij}\mathbf{n}_{ij}) \qquad (\tilde{\mathbf{T}}_{ii} = \mathbf{0}) \tag{45}$$

giving

$$\mathbf{P}_{ij} = \delta_{ij}\mathbf{I} + \alpha\tilde{\mathbf{T}}_{ij} \tag{46}$$

Hence, since α is small, eq 16 and 34 give

$$\mathbf{Q}_{ij} = \delta_{ij}\mathbf{I} - \alpha\tilde{\mathbf{T}}_{ij} \tag{47}$$

and

$$\mathbf{K} = x\mathbf{I} - \alpha \sum_{i,j=1}^{x} \tilde{\mathbf{T}}_{ij} \tag{48}$$

Thus

$$\mathbf{K}^{-1} = \frac{1}{x}\left(\mathbf{I} + \frac{\alpha}{x}\sum_{i,j=1}^{x}\tilde{\mathbf{T}}_{ij}\right) \tag{49}$$

and

$$\tfrac{1}{3}\,\mathrm{Tr}\,(\mathbf{K}^{-1}) = \frac{1}{x} + \frac{\alpha}{3x^2}\sum_{i,j=1}^{x}\mathrm{Tr}\,(\tilde{\mathbf{T}}_{ij}) \tag{50}$$

However

$$\mathrm{Tr}\,(\tilde{\mathbf{T}}_{ij}) = 4/\tilde{r}_{ij} \tag{51}$$

Therefore

$$\left(\frac{\zeta}{f}\right)_{\text{K-R}} = \frac{1}{x} + \frac{\zeta}{6\pi\eta_0 l x^2}\sum_{i,j=1}^{x}\frac{1}{\tilde{r}_{ij}} \tag{52}$$

This is the expression previously obtained by Kirkwood,[3] although the present method of derivation is related more closely to that used earlier by Kirkwood and Riseman.[2] The assumption of α small was not used explicitly by them and they introduced a "preaveraged" form of the Oseen tensor together with Gaussian chain statistics, giving a result valid only for unperturbed chains of large x. The preaveraging process was not clearly defined but in fact included both orientation averaging and averaging over chain configurations. The present derivation shows that eq 52 holds for a rigid molecule and that it results directly from Oseen hydrodynamics coupled with random molecular orientation and weak hydrodynamic interactions. The value of ζ/f obtained with eq 52 may be termed the Kirkwood–Riseman (K–R) value.

(b) Preaveraged Oseen Tensor. The tensor of eq 29 when combined with eq 14 means that

$$\mathbf{P}_{ij} = p_{ij}\mathbf{I} \tag{53}$$

where

$$p_{ij} = \frac{\zeta}{6\pi\eta_0 l\tilde{r}_{ij}} \qquad \text{for } i \neq j \tag{54a}$$

$$p_{ij} = 1 \qquad \text{for } i = j \tag{54b}$$

To find $\mathbf{Q}_{ij}$ it is only necessary to invert the $x \times x$ matrix (p_{ij}), since eq 16 and 53 give the matrix (q_{ij}) as the inverse of (p_{ij}), with

$$\sum_{k=1}^{x} p_{ik}q_{kj} = \delta_{ij} \tag{55}$$

$$\mathbf{Q}_{ij} = q_{ij}\mathbf{I} \tag{56}$$

and

$$\mathbf{K} = q\mathbf{I} \tag{57}$$

where

$$q = \sum_{i,j=1}^{x} q_{ij} \tag{58}$$

In addition, eq 33 ($\mathbf{F} = \zeta\mathbf{K}\cdot\mathbf{u}$) shows that, because $\mathbf{K}$ is a scalar multiple of $\mathbf{I}$, $\mathbf{u}$ is parallel to $\mathbf{F}$ and the molecule moves in the direction of the external force.

The numerical evaluation of ζ/f through eq 42 and eq 53–58 leads to what may be termed the preaveraged Oseen (⟨Oseen⟩) value of ζ/f. Equations 42 and 57 show that the value of ζ/f obtained in this way is given by the equation

$$(\zeta/f)_{\langle\text{Oseen}\rangle} = 1/q \tag{59}$$

(c) Free-Draining Tensor. For the limiting case of free draining, eq 54 becomes

$$p_{ij} = \delta_{ij} \tag{60}$$

Hence

$$q_{ij} = \delta_{ij} \tag{61}$$

$$\mathbf{K} = x\mathbf{I} \tag{62}$$

and

$$(\zeta/f)_{\text{fd}} = 1/x \tag{63}$$

the free-draining value of ζ/f.

(d) Higher Order Interaction Tensor. Equation 31 has not been used in the numerical calculations to be reported. However, the method of evaluation of ζ/f would follow that for the Oseen and preaveraged Oseen tensors through the matrices $\boldsymbol{P}$ and $\boldsymbol{Q}$. One property of the tensor, noted by Yamakawa,[13] is that its preaveraged form contains no term in l^{-3} and hence the same value of ζ/f results as from the preaveraged Oseen tensor.

4. Correlations of Diffusion Coefficients of Polymethylene Chains

Oseen, ⟨Oseen⟩, and K–R values of ζ/f have been calculated for PM chains of 3–50 segments. For each value of x, an equilibrium ensemble of rigid configurations of the PM chain was generated using, for the longer chains, an established Monte Carlo procedure which employs Metropolis sampling.[4,5,17–19] The appropriate equations for ζ/f were then solved for each configuration, and the average value of ζ/f over all configurations was found, with eq 42 becoming

$$\zeta/f = \langle \tfrac{1}{3}\,\mathrm{Tr}\,(\mathbf{K}^{-1})\rangle_{\text{conf}} \tag{64}$$

The chain model used was the rotational-isomeric-state (RIS) model of Flory and co-workers,[20] and the calculations referred to a temperature of 298 K. Sample sizes varied from all the possible RIS configurations up to $x = 10$ (namely, 2187) to about 10 000 for $x = 14$ and down to about 500 for $x = 50$. Only relatively small samples could be used because of the amount of computer time required to manipulate the matrices $\boldsymbol{P}$ and $\boldsymbol{Q}$ in the Oseen calculation. However, as can be seen from Figures 1 and 2 (later), acceptable accuracy was achieved. This is because the calculations relate to a low-order moment of the intersegmental separations,[21] namely, $\langle r_{ij}^{-1}\rangle$, and because of the use of Metropolis sampling, which gives a more rapid convergence than random sampling.

In the case of K–R values of ζ/f, corresponding to weak hydrodynamic interaction, the average over configurations transforms eq 52 into Kirkwood's equation[3]

$$\frac{\zeta}{f} = \frac{1}{x} + \frac{\zeta}{6\pi\eta_0 l x^2}\sum_{i,j=1}^{x}\left\langle\frac{1}{\tilde{r}_{i,j}}\right\rangle_{\text{conf}} \tag{65}$$

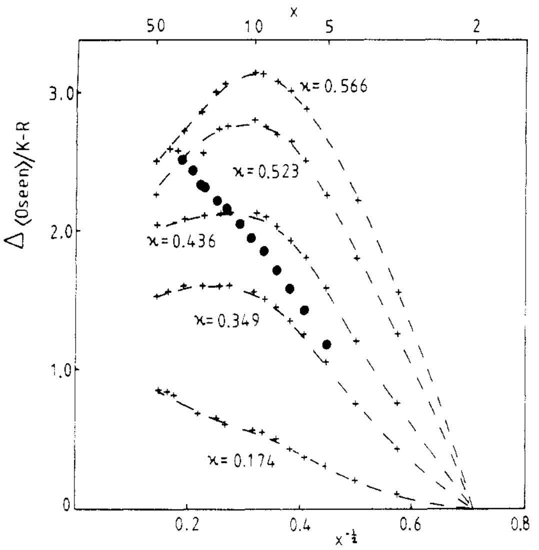

Figure 1. Percent between values of ζ/f for PM chains from ⟨Oseen⟩ and K-R treatments as a function of $x^{-1/2}$ (ordinate defined by eq 73): (+) percent differences at constant κ; (●) percent differences derived from experimental diffusion coefficients of PM in benzene at 25 °C, using ⟨Oseen⟩ values of κ from Table II.

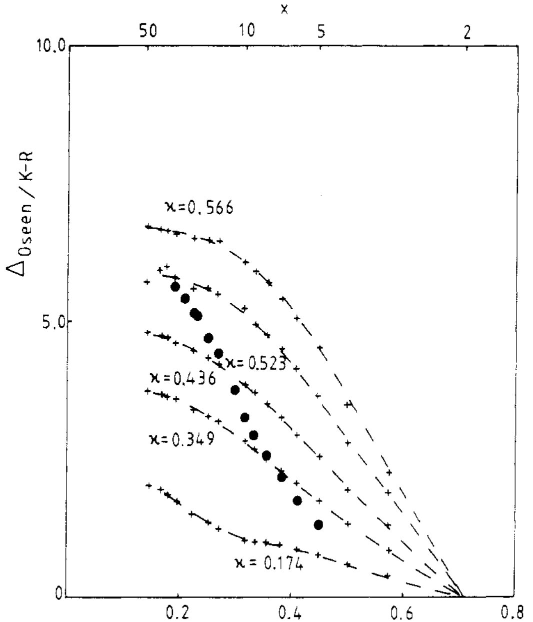

Figure 2. Percent difference between values of ζ/f for PM chains from Oseen and K-R treatments as a function of $x^{-1/2}$ (ordinate defined by eq 74): (+) percent differences at constant κ; (●) percent differences derived from experimental diffusion coefficients of PM in benzene at 25 °C, using Oseen values of κ from Table II.

which is an alternative form of eq 1. Further, eq 65 may be written

$$\frac{\zeta}{f} = \frac{1}{x} + \frac{\kappa[\tilde{R}^{-1}]}{x^2} \tag{66}$$

where the strength of the hydrodynamic interactions is now scaled through the parameter (cf. eq 43)

$$\kappa = \tfrac{4}{3}\alpha = \zeta/6\pi\eta_0 l \tag{67}$$

and

$$[\tilde{R}^{-1}] = \sum_{i,j=1}^{x} \langle 1/\tilde{r}_{ij}\rangle_{\text{conf}} \tag{68}$$

In addition, although explicit expressions for the configuration-average values of ζ/f in the Oseen and ⟨Oseen⟩ cases cannot be obtained, the parameter κ can be used in their calculation. Thus, for single configurations eq 28 and 29 become

$$\zeta\mathbf{T}_{ij} = \frac{3}{4}\,\frac{\kappa}{\tilde{r}_{ij}}(\mathbf{I} + \mathbf{n}_{ij}\mathbf{n}_{ij}) \tag{69}$$

and

$$\langle \zeta\mathbf{T}_{ij}\rangle_{\langle\text{Oseen}\rangle} = \frac{\kappa}{\tilde{r}_{ij}}\mathbf{I} \tag{70}$$

It has been shown previously[4,5] that experimental diffusion coefficients for short polymer chains can only be interpreted with eq 65 by allowing ζ to vary in proportion to b, the effective bond length of the chain, where $b = (\langle r_0^2\rangle/n)^{1/2}$, with $\langle r_0^2\rangle$ the mean-square end-to-end distance of an unperturbed chain of n bonds. (For PM,[4] $n = x - 1$, and for poly(dimethylsiloxane),[5] $n = 2x - 1$, as the $(CH_3)_2SiO$ unit was found to be the effective frictional center.) The variation of ζ with b, and therefore chain length, was represented by the equation

$$\zeta = c_b(6\pi\eta_0 b) \tag{71}$$

where c_b was found to be essentially independent of chain length but to depend on chain structure, solvent, and temperature. Assuming eq 65 to be correct, the variation was interpreted[4] as resulting from the actual discontinuous nature of the assumed solvent continuum, especially because c_b decreased as η_0 and/or molar volume of solvent increased. It may also[4] reflect the neglect of internal modes of the molecule, which give rise to local frictional effects, with the increase in ζ with chain length inferring that local segmental velocities decrease less rapidly with chain length than the center-of-mass velocity.

The apparent variation of ζ with chain length, of course, infers a variation of κ, and combining eq 67 and 71

$$\kappa = c_b b/l \tag{72}$$

Values of b and values of c_b and κ required to give agreement with experimental diffusion coefficients of PM in a variety of solvents on the basis of eq 65 are shown in Table I. The values of c_b, except those for carbon tetrachloride as solvent, are approximately equal to those from previous work,[4] which used a related RIS model.[21] Previously,[4] the erroneous value[22] of $\eta_0 = 0.938$ cP for carbon tetrachloride at 25 °C was used; Table I uses $\eta_0 = 0.900$ cP for this solvent. $\langle c_b\rangle$ denotes the average value for each system, neglecting the values of c_b for the shortest chain, where end effects will be more marked. The values of κ_∞ are derived by taking $\langle c_b\rangle$ and the known value[5,23] of b_∞ (=0.438 nm) for the infinite chain at 25 °C.

In view of the variation of κ with chain length, the calculations of the Oseen, K-R, and ⟨Oseen⟩ values of ζ/f were carried out with values of κ encompassing the range of values in Table I. Singularities in the solutions of the equations are expected[1,16,24,25] when κ becomes too large but these were not encountered in the present calculations. In addition, problems[9,10] associated with the "overlap" of friction centers, that is, r_{ij} becoming unrealistically small, did not occur with the present chain model. Some calculations at the higher values of κ and excluding configurations with $r_{ij} < 0.27$ nm[18,23] with $|i - j| > 4$ were performed. Negligible differences in the resulting values of ζ/f were found. This behavior probably results from the low statistical weight assigned to $g^{\pm}g^{\mp}$ pairs of contiguous conformations (at $|i - j| = 4$) in the RIS model used, with such pairs giving the majority of segment pairs with small values of r_{ij}. The fitting, by the three models, of the experimental

Table I
Values of c_b and κ Required To Give Agreement with Experimental Diffusion Coefficients for PM Chains in Various Solvents according to K-R Approximation[a]

		carbon tetrachloride/25 °C		benzene/25 °C		tetralin/22.2 °C		quinoline/25 °C		decalin/22.2 °C	
x	b/nm	c_b	κ	c_b	κ	c_b	κ	c_b	κ	c_b	κ
5	0.288	*0.314*	0.468	*0.267*	0.398	*0.160*	0.238	*0.148*	0.220	*0.135*	0.201
6	0.247	0.252	0.407	0.229	0.369	0.139	0.224	0.121	0.195	0.117	0.189
7	0.264	0.251	0.433	0.221	0.381	0.126	0.217	0.115	0.198	0.104	0.179
8	0.278	0.225	0.409	0.217	0.394			0.116	0.211	0.098	0.178
9	0.291			0.216	0.411	0.127	0.242	0.116	0.221	0.099	0.188
10	0.302	0.214	0.422	0.214	0.422			0.118	0.233	0.092	0.182
12	0.320	0.205	0.429	0.202	0.422	0.105	0.220	0.120	0.251	0.092	0.192
14	0.334					0.113	0.247			0.090	0.196
16	0.346	0.194	0.439	0.201	0.455			0.124	0.280		
18	0.355	0.253	0.587			0.108	0.251			0.094	0.218
19	0.360			0.199	0.468			0.134	0.315		
20	0.364	0.215	0.512								
24	0.376			0.214	0.526						
28	0.385	0.215	0.541	0.219	0.551	0.128	0.322			0.107	0.269
∞	0.438										
$\langle c_b \rangle$[b]		0.225		0.213		0.121		0.120		0.099	
κ_∞[c]			0.644		0.610		0.346		0.344		0.283

[a] See ref 4. [b] Average values neglecting italicized entries at shortest chain length. [c] Expected values for infinite chain.

Table II
Values of c_b and κ Required To Give Agreement with Experimental Diffusion Coefficients for PM Chains in Benzene at 25 °C according to K-R, ⟨Oseen⟩, and Oseen Treatments

		K-R		⟨Oseen⟩		Oseen	
x	b/nm	c_b	κ	c_b	κ	c_b	κ
5	0.228	*0.267*	0.398	*0.258*	0.384	*0.225*	0.335
6	0.247	0.229	0.369	0.224	0.361	0.215	0.347
7	0.264	0.221	0.381	0.216	0.372	0.208	0.359
8	0.278	0.217	0.394	0.211	0.383	0.202	0.357
9	0.291	0.216	0.411	0.211	0.402	0.198	0.376
10	0.302	0.214	0.422	0.208	0.410	0.194	0.383
12	0.320	0.202	0.422	0.197	0.411	0.187	0.392
16	0.346	0.201	0.455	0.195	0.440	0.179	0.405
19	0.360	0.199	0.468	0.192	0.451	0.179	0.422
24	0.376	0.214	0.526	0.208	0.510	0.185	0.454
28	0.385	0.219	0.551	0.213	0.537	0.197	0.496
∞	0.438						
$\langle c_b \rangle$[a]		0.213		0.208		0.194	
κ_∞[b]			0.610		0.604		0.555

[a] Average values neglecting italicized entries at shortest chain length. [b] Expected values for infinite chain.

diffusion coefficients for PM in benzene at 25 °C was also considered in detail, and the resulting values of c_b and κ required to reproduce the experimental values of D are given in Table II. Those for the K-R model are reproduced from Table I. It can be seen that, probably for the reasons stated earlier, reasonably constant values of c_b arise in all three cases so that κ still varies with chain length. For the limited chain lengths considered, the model effectively only changes the value of $\langle c_b \rangle$ and the resulting range of values of κ.

The percent differences in values of ζ/f from the K-R and ⟨Oseen⟩ treatments at given values of κ are shown in Figure 1 as functions of chain length. The ordinate

$$\Delta_{\langle\mathrm{Oseen}\rangle/\mathrm{K\text{-}R}} = 100((\zeta/f)_{\mathrm{K\text{-}R}} - (\zeta/f)_{\langle\mathrm{Oseen}\rangle})/(\zeta/f)_{\mathrm{K\text{-}R}} \quad (73)$$

Dashed curves are drawn through calculated points at constant κ, and the filled circles represent the differences obtained with the values of κ in Table II for the ⟨Oseen⟩ treatment, together with extra values interpolated at x = 14 and 20. If percent differences for the values of κ in Table II for the K-R treatment had been plotted, only small changes in the positions of the filled circles would result. The dashed curves represent the differences between the two models at different strengths of hydrodynamic interaction for PM chains in "idealized" solvent continuums where κ remains constant. The filled circles represent estimated differences between the two models for the particular system, unperturbed PM in benzene at 25 °C. Such differences will, through κ, be sensitive to polymer, solvent, and temperature.

The curves in Figure 1 indicate that the differences between the K-R and ⟨Oseen⟩ values of ζ/f increase with x for small x, but as $x \to \infty$ some approximately constant limiting value may be approached at the higher values of κ shown. Remembering that the estimated values of κ_∞ for the K-R and ⟨Oseen⟩ treatments are 0.610 and 0.604, respectively, the points show that the difference between the two models for PM chains in benzene at 25 °C is estimated to be 2–3% for infinite chain length. Finally, the larger values of κ in Table II for the K-R compared with the ⟨Oseen⟩ treatments mean that the K-R treatment gives the larger values of ζ/f (that is, $\Delta_{\langle\mathrm{Oseen}\rangle/\mathrm{K\text{-}R}}$ is positive).

Figure 2 shows similar plots to Figure 1, but comprising the Oseen and K-R treatments with

$$\Delta_{\mathrm{Oseen}/\mathrm{K\text{-}R}} = 100((\zeta/f)_{\mathrm{K\text{-}R}} - (\zeta/f)_{\mathrm{Oseen}})/(\zeta/f)_{\mathrm{K\text{-}R}} \quad (74)$$

The filled circles refer to the values of κ in Table II for the

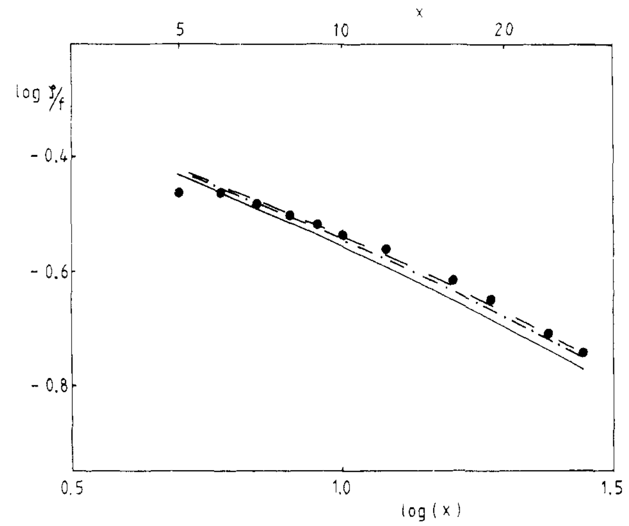

Figure 3. log (ζ/f) vs. log x for Oseen (—), ⟨Oseen⟩ (-·-), and K-R (---) treatments using values of κ which give agreement with K-R treatment. Curves calculated at $\kappa = \langle c_b \rangle b/l$ with $\langle c_b \rangle = 0.213$. (●) Calculated using experimental data and K-R values of c_b from Table II.

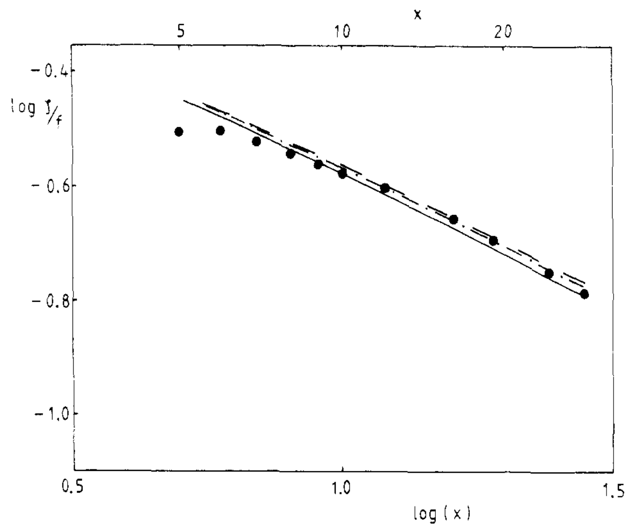

Figure 4. log (ζ/f) vs. log x for Oseen (—), ⟨Oseen⟩ (-·-), and K-R (---) treatments using values of κ which give agreement with Oseen treatment. Curves calculated at $\kappa = \langle c_b \rangle b/l$, with $\langle c_b \rangle = 0.194$. (●) Calculated using experimental data and Oseen values of c_b from Table II.

Oseen model again with extra values at $x = 14$ and 20. The differences increase monotonically with κ at all x and are larger than those between the K-R and ⟨Oseen⟩ models. Given the limiting values of κ_∞ for the K-R and Oseen models in Table II, the points indicate that the K-R model gives a value of ζ/f for the infinite PM chain in benzene at 25 °C which is the larger by somewhere between 6 and 8%. *Experimental* diffusion coefficients for longer chains would be needed to define this limiting difference more adequately. Given the impermeable behavior at infinite chain length and assuming that the Oseen treatment is correct, the limiting difference in ζ/f equals that in $\psi_0(\infty)$ (see eq 3 and 4) for the two cases. Thus, for the unperturbed PM chain, the present analysis of experimental data on short chains indicates that the K-R value of $\psi_0(\infty)$ is larger by some 6-8% than the true value. This is smaller than the experimentally derived differences[7,8] for PMMA and PS quoted earlier. The values of c_b and κ in Table I also indicate that there will be a sensitivity to solvent and temperature as well as chain structure. Garcia de la Torre, Jimenez, and Freire,[10] by considering results at constant κ from their PM chain models and hydrodynamic model, showed that the estimated error at infinite chain length was very sensitive to chain flexibility. Consideration of the subsequent intepretation of Garcia de la Torre and Freire[11] of the same experimental data as used in Table I for benzene and carbon tetrachloride shows that the predicted error in K-R value of $\psi_0(\infty)$ (or $\psi(\infty)$) would be about 4-5%. The result is strikingly similar to the present one, in spite of the use of a higher order interaction tensor and a different chain model containing some excluded-volume effects.

Figures 3 and 4 show log (ζ/f) vs. log x in order to examine the differences between the three treatments and the proposed constancy of $\langle c_b \rangle$ in interpreting experimental values of D. In Figure 3, the curves have been plotted with the values of κ chosen to fit the K-R equation to the experimental data; namely, from eq 72 and Table II, $\kappa = \langle c_b \rangle b/l = 0.213b/l$. The "experimental" points have correspondingly been plotted at

$$\log (\zeta/f) = \log (c_b b/r_D), \qquad (75)$$

using the K-R values of c_b from Table II. The differences between the two broken curves (K-R and ⟨Oseen⟩) are approximately proportional to the percentage differences plotted as filled circles in Figure 1. Apart from discrepancies at short chain lengths, the points in Figure 3 are represented satisfactorily by the K-R treatment with κ proportional to effective bond length and $c_b = 0.213$. This representation is effectively that given previously.[4]

Figure 4 gives the corresponding representation on the basis of the Oseen treatment with the curves plotted using $\kappa = 0.194b/l$ and the "experimental" points as log $(c_b b/r_D)$, using the Oseen values of c_b from Table II. The differences between the K-R and the Oseen curves are proportional to the percentage differences plotted as filled circles in Figure 2. Agreement between the "experimental" points and the Oseen curve appears to be slightly worse than that between "experiment" and the K-R curve in Figure 3. This could result from the short chain lengths considered, with Figure 4 indicating that "end effects" persist to longer chain lengths than would be deduced from Figure 3. Data at longer chain lengths are required to establish whether c_b eventually becomes constant, and from the limited range of x considered no definite conclusions can be drawn about the relative "goodness-to-fit" to the experimental data provided by the three treatments. At infinite chain length the resulting 6-8% difference between the K-R and Oseen treatments deduced from Figure 2 gives a difference in ordinate of 0.06 to 0.08 between the K-R and Oseen curves in Figure 4, and it should be possible to distinguish between their abilities to explain experimental data on unperturbed PM chains.

Garcia de la Torre and Freire[11] tentatively conclude, without the detailed fitting to experimental data presented here, that a constant value of κ provides a better explanation of the experimental data for short PM chains in benzene and carbon tetrachloride than a constant value of c_b. This conclusion is not borne out by the present work. In this context, it should be noted that the values of κ in Table II for the preaveraged case will be the same for the Oseen tensor as for the higher order interaction tensor used by Garcia de la Torre and Freire. The constancy of κ with chain length for this case is not indicated and a constancy for the Oseen treatment is unlikely using the present chain model with the higher order interaction tensor. Thus, the differences between the results of the present analysis and those of Garcia de la Torre and Freire probably reside in differences in the chain models and the methods of chain generation. Their chain model does not strictly refer to the unperturbed PM chain and their method of chain generation appears to employ a priori rather than conditional probabilities for determining successive conformations (see ref 4 and 21).

Conclusions

By careful definition of the equations of motion in the rigid-body approximation, the conventional representations of center-of-mass diffusion coefficients through Oseen hydrodynamics are seen to relate to the condition $\boldsymbol{\Omega} = \mathbf{0}$. This condition has been interpreted as resulting from overwhelming Brownian forces which, however, are assumed not to disturb the probabilities of the various configurations available to a flexible chain.

Satisfactory interpretations of experimental data on short PM chains can be made in the Oseen, K–R, and ⟨Oseen⟩ approximations provided that in all cases κ is allowed to vary with chain length. The empirical, approximate constancy of $\langle c_b \rangle$ is not seen to be a necessary requirement in defining this variation, which probably relates to the basic assumption of a solvent continuum and the neglect of internal modes implicit in the rigid-body approximation.[1,4,5] However, calculations using a consistently defined higher order interaction tensor could be carried out to examine the effects introduced by the use of the Oseen tensor.

On the basis of Oseen, rigid-body hydrodynamics it is estimated that the K–R value of $\psi_0(\infty)$ is too large by about 6–8% for the PM chain in benzene at 25 °C. In view of the previous and different discrepancies found[7,8] between the experimental and K–R values of $\psi_0(\infty)$ for PMMA and PS, it seems that this quantity is sensitive to chain structure. Sensitivity to chain environment (solvent and temperature) may also be inferred. From the values of κ listed in Table I, it may be deduced that, compared with PM in benzene, the discrepancies in $\psi_0(\infty)$ will be slightly larger for PM in carbon tetrachloride and smaller for PM in the other solvents listed. The detailed analysis of data from a variety of systems over a wide range of chain lengths is needed to investigate these points further, as distinctive variations of $\psi_0(x)$ with x occur for different chain structures,[5] solvents, and hydrodynamic approximations. Systems with strong segment–solvent interactions may, however, show effectively impermeable behavior at short chain lengths[4] and not be useful in this respect.

The physical picture which emerges is that at high molar mass the effective penetration of the molecular domain by solvent flow, defining the hydrodynamic radius relative to the equilibrium radius, depends on chain structure, solvent, and temperature.

Acknowledgment. We thank Mr. A. Appleyard for his assistance in developing and running some of the computer programs used in the work reported.

Appendix I

The tensors $\mathbf{Q}_{ij}$, $i, j = 1, 2, ..., x$, are defined by eq 16, viz.

$$\sum_{k=1}^{x} \mathbf{P}_{ik} \cdot \mathbf{Q}_{kj} = \delta_{ij} \mathbf{I} \qquad \text{(A1.1)}$$

where $\mathbf{P}_{ij}$ is a symmetric second-rank tensor in three dimensions and $\mathbf{P}_{ij} = \mathbf{P}_{ji}$. Let the components of $\mathbf{P}_{ij}$ and $\mathbf{Q}_{ij}$ with respect to suitable axes be $P_{ij}{}^{\alpha\beta}$ and $Q_{ij},{}^{\alpha\beta}$, where α, $\beta = 1, 2, 3$. Equation A1.1 may now be written in the form

$$\sum_{k=1}^{x} \sum_{\gamma=1}^{3} P_{ik}{}^{\alpha\gamma} Q_{kj}{}^{\gamma\beta} = \delta_{ij} \delta^{\alpha\beta} \qquad \text{(A1.2)}$$

Now let the matrices $\boldsymbol{P}$ and $\boldsymbol{Q}$ with elements $\boldsymbol{P}_{uv}$ and $\boldsymbol{Q}_{uv}$ be constructed such that

$$P_{ij}{}^{\alpha\beta} = \boldsymbol{P}_{uv} \qquad \text{(A1.3)}$$

$$Q_{ij}{}^{\alpha\beta} = \boldsymbol{Q}_{uv} \qquad \text{(A1.4)}$$

with u and v defined by the equations

$$u = 3(i - 1) + \alpha$$

and

$$v = 3(j - 1) + \beta$$

As i and j run over the values 1–x and α and β over the values 1, 2, 3, then u and v run over the values 1, 2, ..., $3x$. Equation A1.2 may be written as

$$\sum_{w=1}^{3x} \boldsymbol{P}_{uw} \boldsymbol{Q}_{wv} = \delta_{uv} \qquad \text{(A1.5)}$$

or

$$\boldsymbol{P} \cdot \boldsymbol{Q} = \boldsymbol{I} \qquad \text{(A1.6)}$$

where $\boldsymbol{I}$ is the $3x \times 3x$ unit matrix. Since $\mathbf{P}_{ij} = \mathbf{P}_{ji}$ and $\mathbf{P}_{ij}$ is a symmetric tensor, $\boldsymbol{P}$ is a symmetric matrix. Thus, $\boldsymbol{Q}$ is a symmetric matrix, $\mathbf{Q}_{ij} = \mathbf{Q}_{ji}$, and $\mathbf{Q}_{ij}$ is a symmetric tensor.

The use of $\boldsymbol{P}$ and $\boldsymbol{Q}$ and $\mathbf{P}_{2j}$ and $\mathbf{Q}_{2j}$ to evaluate the friction coefficients of a dipole of friction centers for the various hydrodynamic interaction tensors treated in the text is now given by way of illustration. Using the Oseen tensor, eq 14, 28, 43, and 45 shows that

$$\mathbf{P}_{ij} = \mathbf{I}, \qquad \text{for } i = j \qquad \text{(A1.7)}$$

$$P_{ij} = \frac{\alpha}{\tilde{r}_{ij}} (\mathbf{I} + \mathbf{n}_{ij} \mathbf{n}_{ij}), \qquad \text{for } i \neq j \qquad \text{(A1.8)}$$

For a dipole $i, j = 1, 2$, $\alpha = \zeta/(8\pi\eta_0 l)$, where l is the length of the dipole and $\tilde{r}_{12} = 1$. In addition, $\mathbf{n}_{ij}\mathbf{n}_{ij}$ may be replaced by $\mathbf{nn}$, where $\mathbf{n} = \mathbf{n}_{12} = -\mathbf{n}_{21}$. Thus, eq A1.8 becomes

$$\mathbf{P}_{12} = \mathbf{P}_{21} = \alpha(\mathbf{I} + \mathbf{nn}) \qquad \text{(A1.9)}$$

From eq A1.1, A1.7, and A1.9 it is possible to find explicit expressions for the $\mathbf{Q}_{ij}$ with

$$\mathbf{Q}_{11} = \mathbf{Q}_{22} = \lambda \mathbf{I} + (\mu - \lambda)\mathbf{nn} \qquad \text{(A1.10a)}$$

and

$$\mathbf{Q}_{12} = \mathbf{Q}_{21} = -\alpha\lambda \mathbf{I} - \alpha(2\mu - \lambda)\mathbf{nn} \qquad \text{(A1.10b)}$$

where

$$\lambda = 1/(1 - \alpha^2) \qquad \text{(A1.11a)}$$

and

$$\mu = 1/(1 - 4\alpha^2) \qquad \text{(A1.11b)}$$

Axes $Ox_1x_2x_3$ may be chosen so that $\mathbf{n}$ lies along Ox_1, when $\boldsymbol{P}$ and $\boldsymbol{Q}$ become

$$\boldsymbol{P} = \begin{pmatrix} 1 & 0 & 0 & 2\alpha & 0 & 0 \\ 0 & 1 & 0 & 0 & \alpha & 0 \\ 0 & 0 & 1 & 0 & 0 & \alpha \\ 2\alpha & 0 & 0 & 1 & 0 & 0 \\ 0 & \alpha & 0 & 0 & 1 & 0 \\ 0 & 0 & \alpha & 0 & 0 & 1 \end{pmatrix} \qquad \text{(A1.12)}$$

$$\boldsymbol{Q} = \begin{pmatrix} \mu & 0 & 0 & -2\alpha\mu & 0 & 0 \\ 0 & \lambda & 0 & 0 & \alpha\lambda & 0 \\ \sigma & 0 & \lambda & 0 & 0 & \alpha\lambda \\ -2\alpha\mu & 0 & 0 & \mu & 0 & 0 \\ 0 & \alpha\lambda & 0 & 0 & \lambda & 0 \\ 0 & 0 & \alpha\lambda & 0 & 0 & \lambda \end{pmatrix} \qquad \text{(A1.13)}$$

The fact that $\boldsymbol{Q}$ is the inverse of $\boldsymbol{P}$ may be checked directly.

The ratio of the segmental to molecular friction coefficients is defined by eq 42; namely

$$\zeta/f = \tfrac{1}{3}\,\mathrm{Tr}\,(\mathbf{K}^{-1}) \qquad (42)$$

with

$$\mathbf{K} = \sum_{i,j=1}^{x} \mathbf{Q}_{ij} \qquad (34)$$

In the present case

$$\mathbf{K} = 2\lambda(1-\alpha)\mathbf{I} + 2(\mu(1-2\alpha) - \lambda(1-\alpha))\mathbf{nn} \qquad (\mathrm{A1.14})$$

which, on substituting for λ and μ and using the axes $Ox_1x_2x_3$ defined, reduces to

$$\mathbf{K} = 2\ \mathrm{diag}\ (1/(1+2\alpha),\ 1/(1+\alpha),\ 1/(1+\alpha)) \qquad (\mathrm{A1.15})$$

Whence

$$\mathbf{K}^{-1} = (1/2)\ \mathrm{diag}\ (1+2\alpha,\ 1+\alpha,\ 1+\alpha) \qquad (\mathrm{A1.16})$$

and

$$(\zeta/f)_{\mathrm{Oseen}} = \tfrac{1}{2}(1 + 4\alpha/3) \qquad (\mathrm{A1.17})$$

This is the result also given by the K–R approximation, eq 52.

Using the preaveraged Oseen tensor, one has

$$\mathbf{P}_{ij} = p_{ij}\mathbf{I} \qquad (53)$$

with $p_{ij} = p_{ji}$ and, for the dipole

$$p_{11} = p_{22} = 1 \qquad (\mathrm{A1.18a})$$

and

$$p_{12} = p_{21} = 4\alpha/3 \qquad (\mathrm{A1.18b})$$

Equations 56 gives

$$\mathbf{Q}_{ij} = q_{ij}\mathbf{I} \qquad (56)$$

and, here

$$q_{11} = q_{22} = \tau \qquad (\mathrm{A1.19a})$$

$$q_{12} = q_{21} = -4\alpha\tau/3 \qquad (\mathrm{A1.19b})$$

with

$$\tau = 1/(1 - 16\alpha^2/9) \qquad (\mathrm{A1.20})$$

Use of eq 34 and 42 shows that

$$(\zeta/f)_{\mathrm{preav}} = \tfrac{1}{2}(1 + 4\alpha/3) \qquad (\mathrm{A1.21})$$

Thus, as is known, for the special case of a dipole, the Oseen, K–R, and ⟨Oseen⟩ approximations give the same value of ζ/f.

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Self-Diffusion of Polystyrenes by Forced Rayleigh Scattering

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ABSTRACT: The self-diffusion coefficients (D_s) of 4-(bromomethyl)azobenzene-labeled polystyrenes in tetrahydrofuran solution were measured for five molecular weights, from 32 000, to 360 000, in overlapping concentration ranges (in units of weight fraction) spanning from $c = 0.024$ g/g to $c = 0.648$ g/g. We have examined these measurements in the context of the Doi–Edwards theory, as extended by Graessley, and the de Gennes scaling theory. We found that for concentrations above c^*, the concentration for onset of semidilute behavior, the self-diffusion coefficient was well described by $D_s \propto M^{-2}$. On the other hand, the concentration dependence of D_s was neither described by a unique power law as in the de Gennes model nor directly proportional to $\eta_0^{-1}c^2$, where η_0 is the zero-shear viscosity of the solution, as predicted by Graessley using the Doi–Edwards model. Instead, we found the concentration dependence to be best described by Rouse theory, i.e., $D_s \propto \eta_0^{-1}c$. The absolute magnitudes of the diffusion coefficients agreed well with previous measurements by Léger et al. (*Macromolecules* 1981, *14*, 1732) for concentrations below 0.20 g/g, but there were substantial departures from their results at higher concentrations. The observed D_s values were found to be independent of label position and label concentration.

Introduction

W. H. Stockmayer's contributions to our present understanding of the chain dynamics of isolated macromolecules extends over 3 decades, and a tutorial on the subject marked by his usual incisive eloquence is given in Les Houches lectures.[2] The purpose here is to do our part, however small, in trying to extend the chain dynamics to concentrated solutions by examining chain self-diffusion

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