Diffusivity of Polymers in Dilute Solutions Undergoing Homogeneous Flows

In order to describe the translational diffusion of polymers in dilute solution, an elastic dumbbell model is used for which the effects of both hydrodynamic interaction and a nonlinear connector force are treated in a self-consistently averaged form. For this model, the diffusion tensor in the presence of a homogeneous flow field is obtained from (*i*) the mass flux caused by concentration gradients, (*ii*) the average polymer velocity caused by external forces, and (*iii*) the mean-square displacement of a polymer caused by the Brownian forces. From the second and third approaches the same expression for the diffusion tensor is found, whereas a different expression is obtained from the first approach. This means that the Nernst-Einstein equation cannot be generalized to the case of flowing solutions. The model predictions for the diffusion tensors in steady shear flow are discussed in detail.

Hans Christian Öttinger
Chemical Engineering Department and
Rheology Research Center
University of Wisconsin
Madison, WI 53706

Introduction

In a recent paper (Öttinger, 1987e) the translational diffusion tensor for polymers in dilute solution in the presence of a homogeneous solvent flow field was calculated by using a Hookean dumbbell model for the polymers. The restriction to *homogeneous flows* made possible an explicit and clear illustration of the following points:

1. The anisotropic solvent state due to the flow field leads to *anisotropic polymer diffusivity,* which needs to be described by a diffusion tensor instead of a diffusion coefficient.
2. The *Nernst-Einstein equation cannot be generalized to the diffusion of polymers in flowing solutions.* More explicitly, this means that the expressions for the diffusion tensor deduced from the polymer mass flux caused by external forces and by concentration gradients do not coincide. (The Nernst-Einstein equation for solutions at rest has been discussed by, among others, Bird et al., 1960, and Kops-Werkhoven et al., 1983.)
3. In the definition of the mass concentration of polymer it is crucial to treat the *polymers as spatially extended objects* (Bird et al., 1987; Brunn and Grisafi, 1985; Curtiss et al., 1976).

The translational diffusivity of polymers in homogeneous flows is not only an interesting problem in its own right, but the conclusions drawn for homogeneous flows are also very important for the investigation of the polymer-migration effect in nonhomogeneous flow situations (see references in Öttinger, 1987e).

It is the purpose of this paper:

1. To generalize previous results (Öttinger, 1987d, e) by including the effects of the finite polymer extensibility in the model.
2. To illustrate the diffusive behavior of polymers in steady shear flow in great detail.

For the model employed in this paper, an elastic dumbbell model with self-consistently averaged hydrodynamic interaction and nonlinear spring-force law (Öttinger, 1987c; Biller et al., 1986), we construct an expansion of the diffusion tensors in terms of the shear rate (for steady shear flow). The same method can also be used to derive expansions of the stress tensor and the viscometric functions in terms of the shear rate. The most striking new result of the calculations for steady shear flow is the strong shear-rate dependence of the diffusion tensor describing the time evolution of concentration gradients which, for moderate and high shear rates, surprisingly has a negative principal value.

Basic Equations

The discussion of the translational diffusivity of polymers in dilute solutions undergoing homogeneous flows in this paper is based on an elastic dumbbell model, in which the effects of the hydrodynamic interaction and a nonlinear spring-force law are accounted for in a self-consistently averaged form. Of course, a dumbbell model yields a rather oversimplified description of

---

The present address of the author is Fakultät für Physik der Universität Freiburg, D-7800 Freiburg im Breisgau, West Germany.

real polymers. In particular, it is known that, for the dumbbell model, inclusion of hydrodynamic interaction leads to an increase of the viscometric functions, whereas more realistic models show that hydrodynamic interaction decreases the viscometric functions. Previous investigations of the rheological behavior of bead-spring dumbbells and chains with self-consistently averaged hydrodynamic interactions and nonlinear spring forces (Öttinger, 1985, 1987a, b, c) showed, however, that the dumbbell results are qualitatively reasonable. For the calculation of diffusion tensors, it is crucial to treat the polymers as extended objects; note that this important aspect, the extensibility of the polymers, is fully accounted for in a dumbbell model. The effect of the *finite* extensibility of the polymers on their diffusive behavior, which is one of the main subjects of this paper, might well be more important than the more complicated internal motions present in chain models. For the rheological properties, the use of nonlinear instead of Hookean forces leads to a qualitative change of the dumbbell-model predictions, whereas Hookean dumbbells and chains predict the same qualitative behavior.

The configuration of a dumbbell is completely specified by two vectors $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$, which give the positions of the two beads with respect to a fixed origin. We assume that the two identical, spherical beads (with radius a) of a dumbbell are connected by a finitely extensible nonlinear elastic (FENE) spring (Warner, 1972; Bird et al., 1987). The velocity field of the incompressible Newtonian solvent in which these dumbbells are suspended is assumed to be homogeneous, that is, $\boldsymbol{v}(\boldsymbol{r}) = \boldsymbol{v}_o + \boldsymbol{\kappa}(t) \cdot \boldsymbol{r}$ with a constant vector $\boldsymbol{v}_o$ and a traceless tensor $\boldsymbol{\kappa}(t)$ independent of the position $\boldsymbol{r}$ but possibly dependent on the time t. On moving through this solvent the beads experience a hydrodynamic drag given by Stokes' law. The drag force on each bead is proportional to the velocity of the bead relative to the solvent, with the proportionality constant (or friction coefficient) ζ being given by $\zeta = 6\pi\eta_s a$, where η_s is the solvent viscosity. Furthermore, the number density of polymers n is presumed to be sufficiently small that various polymers do not interact with each other.

For dumbbell models one can easily separate the motion of the entire polymer in space and the internal motion. To this end we introduce the center of mass $\boldsymbol{R}$ and the connector vector $\boldsymbol{Q}$ in order to characterize the bead positions:

$$\boldsymbol{R} = \tfrac{1}{2}(\boldsymbol{r}_1 + \boldsymbol{r}_2), \quad \boldsymbol{Q} = \boldsymbol{r}_2 - \boldsymbol{r}_1 \tag{1}$$

Internal configurations

We first study the time evolution of the internal configurations. The dynamics of the connector vector is governed by the Brownian forces and the FENE spring force (Warner, 1972)

$$\boldsymbol{F}^c = H\boldsymbol{Q}/(1 - Q^2/Q_o^2) \tag{2}$$

where Q is the length of the vector $\boldsymbol{Q}$, Q_o is the maximum possible spring extension and H is the spring constant for $Q \ll Q_o$. In the limit $Q_o \rightarrow \infty$, we obtain a Hookean spring-force law with spring constant H.

The dumbbell model with consistently averaged hydrodynamic interaction and FENE spring force used in this paper is a special case of the bead-spring chain model studied by Öttinger (1987c). The consistently averaged FENE spring force is obtained by replacing the factor Q^2 in the denominator of Eq. 2 by its average value performed with the configurational distribution function, which needs to be determined self-consistently from the resulting dynamics. Similarly, the consistently averaged hydrodynamic interaction tensor is to be evaluated with the configurational distribution function, which itself depends on the averaged hydrodynamic interaction tensor (for details see Öttinger, 1985, 1986a, b, 1987a, b, c). For consistently averaged nonlinear effects, the internal configurational distribution function is a Gaussian distribution. The average of the connector vector over all internal configurations is zero ($\langle \boldsymbol{Q} \rangle = 0$), even in the presence of external forces (as long as the external forces on the two beads of a dumbbell are equal). The Gaussian distribution for the internal configurations is thus completely characterized by the dimensionless covariance $\boldsymbol{\sigma}$

$$\boldsymbol{\sigma} = \frac{b+3}{b}\frac{H}{kT}\langle \boldsymbol{QQ} \rangle \tag{3}$$

where $b = HQ_o^2/kT$ is the usual dimensionless finite-extensibility parameter (Bird et al., 1987), k is Boltzmann's constant, and T is the absolute temperature (the normalization in Eq. 3 is chosen to give $\boldsymbol{\sigma} = \boldsymbol{1}$ at equilibrium).

The time evolution of the tensor $\boldsymbol{\sigma}$ can be obtained by solving the following ordinary differential equation (Öttinger, 1987c):

$$\begin{aligned}\tilde{\lambda}_H \boldsymbol{\sigma}_{(1)} &= \tilde{\lambda}_H \left(\frac{d}{dt}\boldsymbol{\sigma} - \boldsymbol{\kappa} \cdot \boldsymbol{\sigma} - \boldsymbol{\sigma} \cdot \boldsymbol{\kappa}^T\right) \\ &= [\boldsymbol{1} - \sqrt{2}h\mathcal{H}(\boldsymbol{\sigma})] \cdot \left(\boldsymbol{1} - \frac{b}{b+3-tr\boldsymbol{\sigma}}\boldsymbol{\sigma}\right)\end{aligned} \tag{4}$$

where the first part of this equation is the definition of the codeformational time derivative $\boldsymbol{\sigma}_{(1)}$; $\tilde{\lambda}_H = [b/(b+3)]\zeta/4H$ is the basic time constant in the model; $h = a[(\pi kT/H)b/(b+3)]^{-1/2}$ is the dimensionless hydrodynamic interaction parameter; $tr\boldsymbol{\sigma}$ is the trace of the tensor $\boldsymbol{\sigma}$; and $\mathcal{H}(\boldsymbol{\sigma})$ is the *hydrodynamic interaction function* (Öttinger, 1987c):

$$\begin{aligned}\mathcal{H}(\boldsymbol{\sigma}) = \frac{3}{16\pi}[\det \boldsymbol{\sigma}]^{-1/2} \int \frac{1}{x}\left(\boldsymbol{1} + \frac{\boldsymbol{xx}}{x^2}\right) \\ \cdot \exp\left\{-\frac{1}{2}\boldsymbol{x} \cdot \boldsymbol{\sigma}^{-1} \cdot \boldsymbol{x}\right\} d\boldsymbol{x}\end{aligned} \tag{5}$$

The hydrodynamic interaction function in Eq. 5 results from the description of the interaction between the beads of a dumbbell through perturbations of the solvent flow field by the Oseen-Burgers tensor (Bird et al., 1987). For solving Eq. 4 analytically or numerically, it is very convenient to know that the function $\mathcal{H}(\boldsymbol{\sigma})$ can be expressed in terms of elliptic integrals (Öttinger, 1987c, Appendix B).

Equation 4 is the basic equation governing the time evolution of the internal configurations of elastic dumbbells with consistently averaged hydrodynamic interaction and FENE spring force.

Center-of-mass motion

The time evolution of the position of the center of mass of a polymer molecule in space can be obtained in exactly the same way as for the special case of infinitely extensible ($b = \infty$) Hookean dumbbells (Öttinger, 1987e). By calculating the average velocity of the center of mass with respect to the solvent caused by external forces in the presence of a homogeneous solvent flow field, we obtain the following diffusion tensor associated with the polymer mobility (note that we need to introduce a diffusion tensor rather than a diffusion coefficient because the average velocity of a polymer depends on the direction of the applied external force with respect to the flow field):

$$\boldsymbol{D}^{I} = \frac{kT}{2\zeta}[\boldsymbol{1} + \sqrt{2}h\boldsymbol{\mathcal{H}}(\boldsymbol{\sigma})] \tag{6}$$

As for Hookean dumbbells, the diffusion tensor obtained from the mean-square displacement of a single finitely extensible dumbbell caused by the stochastic Brownian forces is also given by Eq. 6. The diffusion tensor $\boldsymbol{D}^{I}$ thus describes the diffusive behavior of polymers in flowing, dilute solutions associated with both the polymer mobility and the Brownian forces.

On the other hand, the diffusion tensor deduced from the mass flux caused by concentration gradients is not given by Eq. 6 (even in the special case of Hookean dumbbells). In order to find an expression for the diffusion tensor associated with concentration gradients one needs to derive a diffusion equation for the mass concentration of polymer. This diffusion equation can be derived for the finitely extensible dumbbells of this paper by exactly the same procedure as for Hookean dumbbells (Öttinger, 1987e). In this manner we obtain:

$$\boldsymbol{D}^{II} = \frac{kT}{2\zeta}[\boldsymbol{1} + \sqrt{2}h\boldsymbol{\mathcal{H}}(\boldsymbol{\sigma}) + \tilde{\lambda}_{H}\boldsymbol{\sigma}_{(1)}] \tag{7}$$

The diffusion tensor $\boldsymbol{D}^{II}$ describes the diffusive behavior of polymers in flowing, dilute solutions associated with concentration gradients.

The discussion of translational diffusion in steady shear flow in the following sections is based on Eqs. 4, 6, and 7. The rheological properties of the polymer solution in the absence of concentration gradients can be obtained from the Kramers expression for the polymer contribution to the stress tensor (Bird et al., 1987):

$$\frac{\boldsymbol{\tau}^{p}}{nkT} = \boldsymbol{1} - \frac{b}{b + 3 - tr\boldsymbol{\sigma}}\boldsymbol{\sigma} \tag{8}$$

In the following discussion, Eq. 8 will be used to compare the diffusion tensors and the rheological properties predicted by the elastic dumbbell model with consistently averaged hydrodynamic interaction and FENE spring force.

Solution of Basic Equations for Steady Shear Flow

Before we can discuss the diffusion tensors or the stress tensor predicted by the model described in the preceding section we need to solve Eq. 4 for the covariance $\boldsymbol{\sigma}$. In this section, we show how Eq. 4 can be solved for steady shear flow by transforming to a coordinate system in which the matrix representation of $\boldsymbol{\sigma}$ is diagonal. We also construct an expansion of the principal values (or eigenvalues) of $\boldsymbol{\sigma}$ in powers of the shear rate.

Diagonalization

For steady shear flow, the matrix representation of the tensor $\boldsymbol{\kappa}$ in a fixed rectangular Cartesian coordinate system C is given by

$$\kappa_{C} = \dot{\gamma}\begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{9}$$

where $\dot{\gamma}$ is the shear rate. For this flow situation, we find that the matrix representation of the tensor $\boldsymbol{\sigma}$ introduced in Eq. 3 is of the form

$$\sigma_{C} = \begin{bmatrix} \sigma_{11} & \sigma_{12} & 0 \\ \sigma_{12} & \sigma_{22} & 0 \\ 0 & 0 & \sigma_{33} \end{bmatrix} \tag{10}$$

that is, the 3-axis of C is a principal axis of the symmetric tensor $\boldsymbol{\sigma}$. By rotating the coordinate system C by an angle ϕ ($0 \le \phi < \pi/2$) around its 3-axis we can find a rectangular Cartesian coordinate system C' in which the matrix representation of the tensor $\boldsymbol{\sigma}$ is diagonal. If the principal values of $\boldsymbol{\sigma}$ are σ_1, σ_2, and σ_3, we have from the invariants of the transformation from C to C':

$$\begin{gathered} \sigma_{11} + \sigma_{22} = \sigma_{1} + \sigma_{2} \\ \sigma_{11}\sigma_{22} - \sigma_{12}^{2} = \sigma_{1}\sigma_{2} \\ \sigma_{33} = \sigma_{3} \end{gathered} \tag{11}$$

In the coordinate system C', the off-diagonal components of the tensor $\boldsymbol{\mathcal{H}}(\boldsymbol{\sigma})$ defined in Eq. 5 vanish for reasons of symmetry so that, in this coordinate system C', the tensor $\boldsymbol{\mathcal{H}}(\boldsymbol{\sigma})$ is characterized by its principal values $\mathcal{H}_1$, $\mathcal{H}_2$, and $\mathcal{H}_3$. From Eq. 4, we then find that the matrix representation of the tensor $\boldsymbol{\sigma}_{(1)}$ in the coordinate system C' is also diagonal. Therefore, we have $\boldsymbol{\sigma} \cdot \boldsymbol{\sigma}_{(1)} = \boldsymbol{\sigma}_{(1)} \cdot \boldsymbol{\sigma}$. This commutation relation yields a relationship between the four nonzero components of $\boldsymbol{\sigma}$ in the coordinate system C:

$$2\sigma_{12}^{2} = \sigma_{22}(\sigma_{11} - \sigma_{22}) \tag{12}$$

Equation 12 is very valuable because it implies that $\boldsymbol{\sigma}$ has only three independent components in the coordinate system C. The three principal values σ_i therefore contain enough information to calculate the components of $\boldsymbol{\sigma}$ in C, which immediately give the viscometric functions, Eq. 8, and the directions of the two orthogonal principal axes of $\boldsymbol{\sigma}$ in the (1, 2) plane of the coordinate system C. The principal axes of the tensor $\boldsymbol{\sigma}$ are also the principal axes of tensor-valued functions of $\boldsymbol{\sigma}$, for instance, the diffusion tensors in Eqs. 6 and 7 and the stress tensor in Eq. 8. By exploiting Eq. 12 we obtain for the angle ϕ characterizing the directions of these principal axes:

$$\cos 2\phi = \left(\frac{\sigma_{11} - \sigma_{22}}{\sigma_{11} + \sigma_{22}}\right)^{1/2} = \frac{\sigma_{1} - \sigma_{2}}{\sigma_{1} + \sigma_{2}} \tag{13}$$

With Eqs. 11 and 12, one can also calculate the diagonal matrix of components of $\boldsymbol{\sigma}_{(1)}$ in the coordinate system C' in a straightforward manner. The basic Eq. 4 then yields the following three component equations:

$$-r\tilde{\lambda}_H\dot{\gamma}\sigma_1 = (1 - \sqrt{2}h\mathcal{H}_1)(1 - \sigma_1/\sigma_3) \tag{14a}$$

$$r\tilde{\lambda}_H\dot{\gamma}\sigma_2 = (1 - \sqrt{2}h\mathcal{H}_2)(1 - \sigma_2/\sigma_3) \tag{14b}$$

$$\sigma_3 = 1 - \frac{\sigma_1 + \sigma_2 - 2}{b + 1} \tag{14c}$$

where r is the ratio of the geometric and arithmetic means of σ_1 and σ_2, $r = 2\sqrt{\sigma_1\sigma_2}/(\sigma_1 + \sigma_2)$. It was shown by Öttinger (1987c, Appendix B) that the diagonal elements $\mathcal{H}_i$ can be expressed in terms of the σ_j by means of elliptic integrals. Equations 14 can then be solved by standard numerical techniques.

Expansion in powers of the shear rate

In order to complete the discussion of the basic Eq. 4 for the tensor σ in steady shear flow or, equivalently, of the component Eqs. 14, we now outline how an expansion of the solution of these equations in powers of the shear rate can be obtained. We write:

$$\sigma_1 = 1 + \sum_{i=1}^{\infty} c_i(\tilde{\lambda}_H\dot{\gamma})^i \tag{15a}$$

If we substitute $-\dot{\gamma}$ for $\dot{\gamma}$ in Eqs. 14 and exchange σ_1 and σ_2, we recover exactly the same set of equations. From this symmetry of Eqs. 14 we conclude

$$\sigma_2 = 1 + \sum_{i=1}^{\infty} c_i(-\tilde{\lambda}_H\dot{\gamma})^i \tag{15b}$$

and from Eq. 14c we then obtain:

$$\sigma_3 = 1 - \frac{2}{b + 1}\sum_{i=1}^{\infty} c_{2i}(\tilde{\lambda}_H\dot{\gamma})^{2i} \tag{15c}$$

The three principal values σ_i are thus characterized by a single set of coefficients c_j. In order to derive expansions of the quantities $\mathcal{H}_i$ in terms of the shear rate we can write (Öttinger, 1987c, Appendix B):

$$\mathcal{H}_1 = \frac{1}{\sqrt{\sigma_1}} f\left(1 - \frac{\sigma_2}{\sigma_1}, 1 - \frac{\sigma_3}{\sigma_1}\right) \tag{16}$$

with

$$f(x, y) = \sum_{i=0}^{\infty} (-1)^i \frac{3(i + 1)}{(2i + 1)(2i + 3)} \times \sum_{j=0}^{\infty} \binom{-1/2}{j}\binom{-1/2}{i - j} x^j y^{i-j}$$
$$= 1 + \frac{1}{5}(x + y) + \frac{9}{280}(3x^2 + 2xy + 3y^2) + \cdots. \tag{17}$$

Similar expressions for $\mathcal{H}_2$ and $\mathcal{H}_3$ can be obtained by permutations of the subscripts 1, 2, 3 in Eq. 16. If the coefficients $c_1 \ldots c_N$ in the expansions 15a–c are known, one can thus construct the coefficients $d_1 \ldots d_N$ in the expansion

$$\mathcal{H}_1 = 1 + \sum_{i=1}^{\infty} d_i(\tilde{\lambda}_H\dot{\gamma})^i \tag{18}$$

in a straightforward manner from Eqs. 16 and 17. Finally, in order to obtain the coefficient c_{N+1} we use Eq. 14a in the form

$$(\sigma_1 - \sigma_3)(1 - \sqrt{2}h) = \tilde{\lambda}_H\dot{\gamma}r\sigma_1\sigma_3 + \sqrt{2}h(\mathcal{H}_1 - 1)(\sigma_1 - \sigma_3) \tag{19}$$

From the Nth-order expansions of σ_1, σ_2, σ_3, and $\mathcal{H}_1$ one can obviously calculate the contribution of order $N + 1$ on the righthand side of Eq. 19, so that the lefthand side yields c_{N+1}. We thus have a recursive procedure to calculate all the coefficients c_i from the zero-order coefficient $c_o = 1$. The lowest order coefficients are:

$$c_1 = \frac{1}{1 - \sqrt{2}h} \tag{20a}$$

$$c_2 = \frac{1}{(1 - \sqrt{2}h)^2}\frac{b + 1}{b + 3}(1 + \tilde{h}) \tag{20b}$$

$$c_3 = \frac{1}{(1 - \sqrt{2}h)^3}\left[\frac{1}{2} - \frac{4}{b + 3} - \tilde{h}\left(\frac{1}{7} - \frac{6}{b + 3}\right) - 2\tilde{h}^2\left(1 - \frac{5}{b + 3}\right)\right] \tag{20c}$$

with $\tilde{h} = \sqrt{2}h/[10(1 - \sqrt{2}h)]$.

For given values of h and b, the procedure outlined above has been used to calculate the numerical values of the coefficients c_i on a VAX/VMS computer (note that even an exact, formal construction of the coefficients c_i as functions of h and b with a computer is possible). For $h = 0.15$ and $b = 50$, the results for the principal value σ_1 obtained from the numerical solution of Eqs. 14 and from various order expansions are compared in Figure 1. The number of coefficients c_i that could be evaluated was not restricted by the computer time or the number of storage locations available but rather by the accuracy of the results for c_i. By comparing the coefficients c_i from calculations with single and double precision, four-figure agreement was found for $i \leq 12$, three-figure agreement for $i \leq 16$, and completely different results were obtained for c_{19} (for $h = 0.15$ and $b = 50$ as well as for $h = 0.15$ and $b = 100$).

Figure 1 shows that at low shear rates the expansions of order

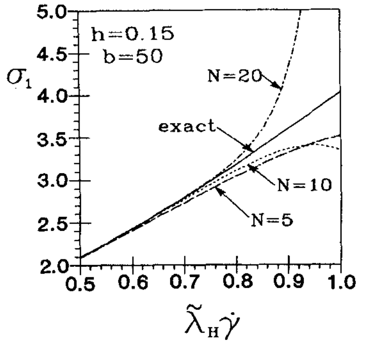

Figure 1. Prinicipal value σ_1 vs. dimensionless shear rate $\tilde{\lambda}_H\dot{\gamma}$.

Exact numerical solution of Eqs. 14 and Nth-order expansions of σ_1 in powers of shear rate for various N are displayed

5, 10, and 20 describe the exact behavior of σ_1 very well. At $\tilde{\lambda}_H\dot{\gamma} = 1$, the fifth-order expansion deviates roughly 10% from the exact result. The 10th-order expansion improves the fifth-order expansion for $\tilde{\lambda}_H\dot{\gamma} \lesssim 0.94$, whereas it yields a poorer approximation at higher shear rates. The 20th-order expansion is very good for $\tilde{\lambda}_H\dot{\gamma} \lesssim 0.75$ (less than 0.5% deviation from the exact result); however, it fails drastically for $\tilde{\lambda}_H\dot{\gamma} \gtrsim 0.9$. Expansions of high order are thus of very limited value.

Viscometric functions

As mentioned before, the principal values σ_i of the tensor σ also contain the complete information on the viscometric functions. Since we want to compare the behavior of the diffusion tensor and the viscometric functions in the next section, we briefly summarize the expressions for the viscometric functions in terms of the principal values σ_i. The polymer contribution to the viscosity η_p and the normal-stress coefficients ψ_1, ψ_2 are defined by $\tau^p_{12} = -\eta_p\dot{\gamma}$, $\tau^p_{11} - \tau^p_{22} = -\psi_1\dot{\gamma}^2$, and $\tau^p_{22} - \tau^p_{33} = -\psi_2\dot{\gamma}^2$. By using Eq. 8 for the stress tensor $\boldsymbol{\tau}^p$ and Eqs. 11, 12 to express the components of the tensor $\boldsymbol{\sigma}$ in terms of its principal values, we obtain the following expressions for η_p and ψ_1:

$$\eta_p = nkT\tilde{\lambda}_H \frac{1}{\sigma_3} \frac{2\sqrt{\sigma_1\sigma_2}}{\sigma_1 + \sigma_2} \frac{\sigma_1 - \sigma_2}{2\tilde{\lambda}_H\dot{\gamma}} \tag{21}$$

$$\psi_1 = 2nkT\tilde{\lambda}_H^2 \frac{1}{\sigma_3} \frac{2}{\sigma_1 + \sigma_2} \left(\frac{\sigma_1 - \sigma_2}{2\tilde{\lambda}_H\dot{\gamma}}\right)^2 \tag{22}$$

The second normal-stress coefficient can be obtained from the following relationship between the viscometric functions (Öttinger, 1986b):

$$2\eta_p^2 - nkT\psi_1 = \psi_1\psi_2\dot{\gamma}^2 \tag{23}$$

This generalization of the same relationship for Hookean dumbbells with consistently averaged hydrodynamic interaction can be derived from Eqs. 12 and 14c.

Equations 21–23 can be used to construct expansions for the viscometric functions from Eqs. 15. The second-order results for η_p and ψ_1 obtained from the coefficients c_i in Eq. 20 are in agreement with the third-order retarded-motion expansion for the more general case of chains of arbitrary length (Öttinger, 1987c). By the procedure outlined in the previous subsection one can easily construct higher order contributions to the viscometric functions for dumbbells.

Diffusion Tensors in Steady Shear Flow

For the discussion in this section the basic Eqs. 14 have been solved numerically for various values of the shear rate $\dot{\gamma}$, the hydrodynamic interaction parameter h, and the finite-extensibility parameter b (reasonable values for these parameters were discussed in detail by Öttinger, 1987c). We first study the dependence of the angle ϕ on the various parameters. This angle, which can be calculated from Eq. 13, characterizes the direction of the principal axes of the covariance σ and the diffusion tensors $\boldsymbol{D}^{I,II}$ in the (1, 2) plane (the precise meaning of the angle ϕ was explained after Eq. 10).

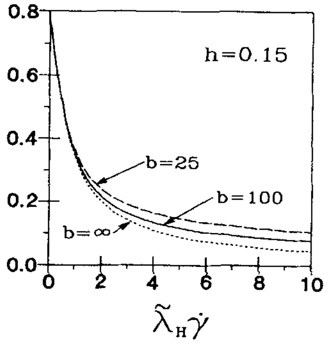

Figure 2. Angle ϕ, Eq. 13, vs. dimensionless shear rate $\tilde{\lambda}_H\dot{\gamma}$.

In the limit $\tilde{\lambda}_H\dot{\gamma} \rightarrow 0$, we find $\phi = \pi/4$ for all values of h and b. Figures 2 and 3 show that for increasing shear rate, ϕ decreases very rapidly. At a given shear rate, the angle ϕ decreases with increasing finite-extensibility parameter b, Figure 2, as well as with increasing hydrodynamic interaction parameter h, Figure 3. The small values of ϕ at high shear rates imply that the first principal axis of the tensors $\boldsymbol{\sigma}$ and $\boldsymbol{D}^{I,II}$ is almost parallel to the 1-axis of the laboratory coordinate system C.

Since the directions of the principal axes of the diffusion tensors $\boldsymbol{D}^{I,II}$ are completely characterized by ϕ, we now need to discuss only the three principal values of the diffusion tensors. We introduce the normalized principal values of the diffusion tensors $\boldsymbol{D}^{I,II}$ by

$$\boldsymbol{D}_{C'}^{I,II} = \frac{kT}{2\zeta}(1 + \sqrt{2}h)\begin{pmatrix} D_1^{I,II} & 0 & 0 \\ 0 & D_2^{I,II} & 0 \\ 0 & 0 & D_3^{I,II} \end{pmatrix} \tag{24}$$

This normalization implies $D_i^{I,II} = 1$ for shear rate zero. The normalized principal values in Eq. 24 can be calculated from Eqs. 6 and 7 and the solution of Eqs. 14.

Diffusion tensor $\boldsymbol{D}^I$

We first discuss the principal values of the diffusion tensor $\boldsymbol{D}^I$, which describes the polymer mass flux caused by external forces and the mean-square displacement of the center of mass of a polymer caused by the Brownian forces. For $h = 0.15$ and $b = 100$, Figure 4 shows that for increasing shear rate, the prin-

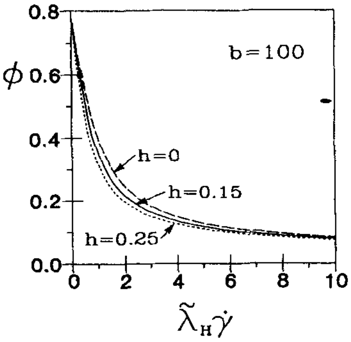

Figure 3. Angle ϕ, Eq. 13, vs. dimensionless shear rate $\tilde{\lambda}_H\dot{\gamma}$.

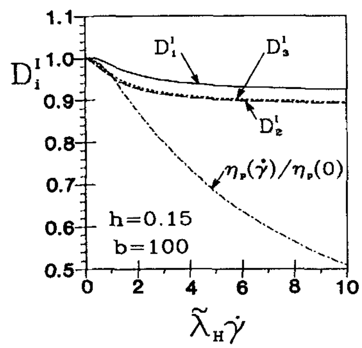

Figure 4. Normalized principal values D_i' vs. dimensionless shear rate $\tilde{\lambda}_H\dot{\gamma}$.

Relative polymer contribution to viscosity $\eta_p(\dot{\gamma})/\eta_p(0)$ is included for comparison

cipal values of the diffusion tensor D' change much less than the polymer contribution to the viscosity. With the exception of D_1' at very low shear rates, the normalized principal values of D' are slightly smaller than unity, thus indicating a reduced diffusivity of polymers in flowing solutions. With increasing shear rate, $D_{2,3}'$ decrease monotonically, whereas D_1' slightly increases at low shear rates before it starts to decrease for $\tilde{\lambda}_H\dot{\gamma} \gtrsim 0.2$. For a smaller b value ($h = 0.15$, $b = 50$), the behavior of D_1' is very similar; however, D_1' has a minimum near $\tilde{\lambda}_H\dot{\gamma} = 7$ and slowly increases again for higher shear rates, Figure 5.

The principal value D_1' decreases with increasing extensibility of the springs, Figure 5. For the rather stiff springs with $b = 25$, D_1' deviates in the entire range $0 \leq \tilde{\lambda}_H\dot{\gamma} \leq 10$ by less than some 3% from its zero shear rate value, whereas the polymer contribution to the viscosity decreases by more than 60%. For increasing hydrodynamic interaction parameter h, the change in the hydrodynamic interaction with the polymer extension caused by the flow field becomes more and more important. Therefore, the changes in D_1' increase with h, Figure 6. For $h = 0$, all principal values D_1' are independent of $\dot{\gamma}$ and b; see Eq. 6.

Changes in the parameters h and b affect the normalized principal values D_2' and D_3' in the same way as D_1'.

Diffusion tensor D''

We now discuss the principal values of the diffusion tensor D'', which describes the polymer mass flux caused by concentration gradients. By comparing Eqs. 6 and 7 one can conclude that $D_3' = D_3''$ for all values of b and h.

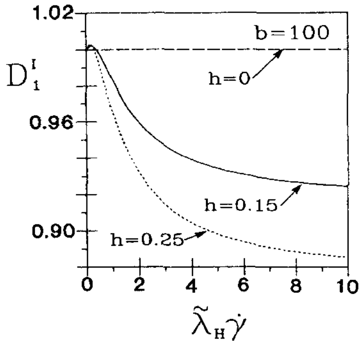

Figure 6. Normalized principal value D_1' vs. dimensionless shear rate $\tilde{\lambda}_H\dot{\gamma}$.

Figure 7 shows the normalized principal values D_i'' for $h = 0.15$ and $b = 100$. The slopes of $D_{1,2}''$ at $\tilde{\lambda}_H\dot{\gamma} = 0$ are opposite in sign to the slopes of $D_{1,2}'$ (Öttinger, 1987e). It is very surprising that the principal value D_1'' of the diffusion tensor D'' is negative for $\tilde{\lambda}_H\dot{\gamma} \gtrsim 0.6$. In order to understand the physical meaning of a negative principal value of D'' we need to remember that the diffusion tensor D'' was deduced from the polymer mass flux *with respect to the flow field* caused by concentration gradients. Even without taking diffusion into account, the flow field separates particles with different 2-components of the position vector in the laboratory coordinate system C and thus tends to smooth concentration gradients. A negative principal value of D'' indicates that the smoothing effect of the flow field is reduced. This reduced rate of concentration-gradient smoothing is caused by the springs, which connect the beads of a dumbbell: The springs hold the beads of a dumbbell together, whereas the flow field tries to separate them. By pulling together the beads separated by the flow field, the springs tend to preserve the local mass concentration and to oppose the smoothing of concentration gradients caused by the flow field. Since the flow field effects have been subtracted in the definition of D'', it is this concentration-preserving effect of the springs which leads to a negative principal value of the diffusion tensor D''.

Note that the principal value D_1'' in Figure 7 changes very rapidly with the shear rate (at $\tilde{\lambda}_H\dot{\gamma} = 2$, the polymer contribution to the viscosity is only some 12% below its zero shear rate value). The principal value D_2'' increases with shear rate until at

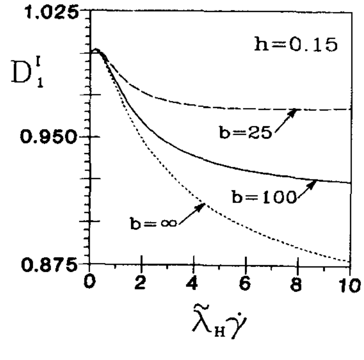

Figure 5. Normalized principal value D_1' vs. dimensionless shear rate $\tilde{\lambda}_H\dot{\gamma}$.

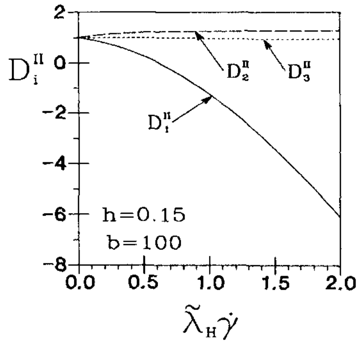

Figure 7. Normalized principal values D_i'' vs. dimensionless shear rate $\tilde{\lambda}_H\dot{\gamma}$.

$\tilde{\lambda}_H\dot{\gamma} \approx 2.6$ a maximum is reached. The maximum value of D_2^{II} is some 26% larger than the zero shear rate value. For higher shear rates, D_2^{II} decreases only very slowly.

As for the diffusion tensor $\boldsymbol{D}^{I}$, the principal values of $\boldsymbol{D}^{II}$ decrease for increasing finite-extensibility parameter b. However, the effect of b on D_2^{II} is very small (less than 2% for $h = 0$ and $b = 25, 100, \infty$). With increasing hydrodynamic interaction parameter h, D_1^{II} increases except for $0.5 \lesssim \tilde{\lambda}_H\dot{\gamma} \lesssim 1.5$ ($b = 100$), whereas D_2^{II} decreases for all shear rates.

The above discussion shows that the diffusion tensor $\boldsymbol{D}^{II}$ associated with concentration gradients is much more strongly affected by a steady shear flow field than the diffusion tensor $\boldsymbol{D}^{I}$ associated with external forces and Brownian forces.

Summary and Discussion

In this paper, an elastic dumbbell model has been employed to study the translational diffusivity of polymers in dilute solutions undergoing homogeneous flows. A generalization of the previously derived expressions for the diffusion tensors deduced from the polymer mass flux caused by external forces and concentration gradients as well as from the mean-square displacement of the center of mass of a polymer by the Brownian forces has been obtained by including the finite extensibility of polymers in a dumbbell model with consistently averaged hydrodynamic interaction. Like the hydrodynamic interaction, the finite polymer extensibility has been treated in a self-consistently averaged form.

We obtain the same expression for the diffusion tensor from the definitions associated with external forces and Brownian forces ($\boldsymbol{D}^{I}$), whereas a different expression follows from the definition associated with concentration gradients ($\boldsymbol{D}^{II}$). [Different diffusion tensors $\boldsymbol{D}^{I}$ and $\boldsymbol{D}^{II}$ in the presence of a homogeneous solvent flow field have previously been found even in the absence of finite-extensibility and hydrodynamic interaction effects (Öttinger, 1987e).] The fact that two different expressions for the diffusion tensor are deduced from the mass flux caused by external forces and by concentration gradients implies that the Nernst-Einstein equation cannot be generalized to flowing solutions.

For steady shear flow, the basic equations describing the model have been simplified by a transformation to a coordinate system in which the occurring tensors are represented by diagonal matrices. We have described how the diagonalized equations can be used to construct expansions for the diffusion tensors and the viscometric functions in powers of the shear rate in a very effective manner. However, such expansions have been found to be useful only at low shear rates.

The diffusion tensors $\boldsymbol{D}^{I}$ and $\boldsymbol{D}^{II}$ for steady shear flow have been discussed in great detail. The tensor $\boldsymbol{D}^{I}$ is not affected very strongly by the flow field, so that it will be very hard to detect the predicted shear-rate dependency of $\boldsymbol{D}^{I}$ in experiments on flowing polymer solutions. On the other hand, the tensor $\boldsymbol{D}^{II}$ changes very rapidly with the shear rate. For moderate and high shear rates, the diffusion tensor $\boldsymbol{D}^{II}$ has a negative principal value. This negative principal value does not lead to concentration gradients that increase in the corresponding principal direction in time. Concentration gradients are smoothed by the flow field; however, the springs, which prevent the beads of a dumbbell from being separated by the flow field, reduce the smoothing effect of the flow field. As the smoothing effect of the flow field has been subtracted in the definition of the diffusion tensor $\boldsymbol{D}^{II}$, the opposite effect of the springs leads to a negative principal value of $\boldsymbol{D}^{II}$. Since our model predicts a diffusion tensor $\boldsymbol{D}^{II}$ which changes very strongly (both quantitatively and qualitatively) with shear rate, it appears to be most interesting to obtain the diffusive properties of polymers in flowing solutions by investigating the time evolution of concentration gradients experimentally, for example, in steady shear flow.

Acknowledgment

I wish to thank J. D. Schieber for his helpful comments in the preparation of this manuscript. Financial support provided by the Max Kade Foundation is gratefully acknowledged.

Notation

a = bead radius
b = finite-extensibility parameter
c_i, d_i = coefficients in an expansion in powers of the shear rate
$\boldsymbol{D}^{I}$ = diffusion tensor (external force, Brownian diffusion)
D_i^{I} = normalized principal values of $\boldsymbol{D}^{I}$
$\boldsymbol{D}^{II}$ = diffusion tensor (concentration gradients)
D_i^{II} = normalized principal values of $\boldsymbol{D}^{II}$
f = function related to elliptic integrals
$\boldsymbol{F}^{c}$ = FENE spring force
h = hydrodynamic interaction parameter
$\tilde{h}$ = modified hydrodynamic interaction parameter
$\boldsymbol{\mathcal{H}}$ = hydrodynamic interaction function
$\mathcal{H}_i$ = principal values of $\boldsymbol{\mathcal{H}}$
H = spring constant at zero polymer extension
k = Boltzmann's constant
n = number density of polymers
N = order of expansions in powers of the shear rate
$\boldsymbol{Q}$ = connector vector
Q = length of connector vector
Q_o = maximum length of connector vector
r = ratio of geometric and arithmetic means of σ_1 and σ_2
$\boldsymbol{r}$ = position vector
$\boldsymbol{r}_1, \boldsymbol{r}_2$ = bead position vectors
$\boldsymbol{R}$ = center of mass
t = time
T = absolute temperature
$\boldsymbol{v}(\boldsymbol{r})$ = velocity field
$\boldsymbol{v}_o$ = constant velocity
x = integration variable

Greek letters

$\dot{\gamma}$ = shear rate
ζ = bead friction coefficient
η_s = solvent viscosity
η_p = polymer contribution to viscosity
$\boldsymbol{\kappa}$ = velocity gradients
$\tilde{\lambda}_H$ = time constant
$\boldsymbol{\sigma}$ = normalized dimensionless covariance
σ_i = principal values of $\boldsymbol{\sigma}$
σ_{ij} = components of $\boldsymbol{\sigma}$ in coordinate system C
$\boldsymbol{\tau}^{p}$ = polymer contribution to stress tensor
τ_{ij}^{p} = components of $\boldsymbol{\tau}^{p}$ in coordinate system C
ϕ = angle characterizing directions of principal axes of $\boldsymbol{\sigma}$, $\boldsymbol{\mathcal{H}}$, $\boldsymbol{D}^{I,II}$, and $\boldsymbol{\tau}^{p}$
$\psi_{1,2}$ = first, second normal-stress coefficient

Subscripts

C, C' = components of a tensor in coordinate system C, C'
(1) = codeformational time derivative

Superscripts

T = transposition
-1 = inverse tensor

Literature Cited

Biller, P., H. C. Öttinger, and F. Petruccione, "Consistently Averaged Hydrodynamic Interaction for Dumbbell Models in Elongational Flow," *J. Chem. Phys.*, **85**, 1672 (1986).

Bird, R. B., W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*, Wiley, New York, 568 (1960).

Bird, R. B., C. F. Curtiss, R. C. Armstrong, and O. Hassager, *Dynamics of Polymeric Liquids, 2: Kinetic Theory*, 2nd ed., Wiley, New York, Ch. 13, 17 (1987).

Brunn, P. O., and S. Grisafi, "Kinetic Theory of a Dilute Polymer Solution in a Small Channel: Equilibrium Results," *Chem. Eng. Commun.*, **36**, 367 (1985).

Curtiss, C. F., R. B. Bird, and O. Hassager, "Kinetic Theory and Rheology of Macromolecular Solutions," *Adv. Chem. Phys.*, **35**, 31 (1976).

Kops-Werkhoven, M. M., A. Vrij, and H. N. W. Lekkerkerker, "On the Relation Between Diffusion, Sedimentation, and Friction," *J. Chem. Phys.*, **78**, 2760 (1983).

Öttinger, H. C., "Consistently Averaged Hydrodynamic Interaction for Rouse Dumbbells in Steady Shear Flow," *J. Chem. Phys.*, **83**, 6535 (1985).

———, "Consistently Averaged Hydrodynamic Interaction for Rouse Dumbbells. Series Expansions," *J. Chem. Phys.*, **84**, 4068 (1986a).

———, "Consistently Averaged Hydrodynamic Interaction for Rouse Dumbbells: The Rheological Equation of State," *J. Chem. Phys.*, **85**, 1669 (1986b).

———, "A Generalization of the Rouse-Zimm Model," *Colloid Polym. Sci.*, **265**, 101 (1987a).

———, "Generalized Zimm Model for Dilute Polymer Solutions under Theta Conditions," *J. Chem. Phys.*, **86**, 3731 (1987b).

———, "A Model of Dilute Polymer Solutions with Hydrodynamic Interaction and Finite Extensibility. I: Basic Equations and Series Expansions," *J. Non-Newtonian Fluid Mech.*, **26**, 207 (1987c).

———, "Translational Diffusivity from the Zimm Model," *J. Chem. Phys.*, **87**, 3156 (1987d).

———, "Consistently Averaged Hydrodynamic Interaction for Rouse Dumbbells: Translational Diffusivity," *J. Chem. Phys.*, **87**, 6185 (1987e).

Warner, H. R. Jr., "Kinetic Theory and Rheology of Dilute Suspensions of Finitely Extendible Dumbbells," *Ind. Eng. Chem. Fundam.*, **11**, 379 (1972).

Manuscript received Oct. 12, 1987, and revision received Aug. 1, 1988.