

Calculation of Various Universal Properties for Dilute Polymer Solutions Undergoing Shear Flow

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ABSTRACT: A mechanical polymer model including hydrodynamic-interaction and excluded-volume effects is used to predict universal rheological and diffusive properties of dilute polymer solutions. For steady shear flow, explicit expressions for the shear-rate-dependent hydrodynamic-interaction contribution to the stress tensor and polymer diffusion tensors are obtained by employing a perturbation scheme. In the limit of long chains, these contributions are calculated systematically by using renormalization-group methods. The universal shear-rate-dependent predictions for the polymer contribution to the viscosity, the first normal-stress coefficient, the ratio of the second to the first normal-stress coefficient, and the polymer diffusion tensor are presented and discussed for good and for Θ solvents.

I. Introduction

Many properties of dilute solutions of linear polymers are independent of chemical details when expressed in suitably rescaled units.¹ For example, when the polymer contribution to the steady shear flow viscosity divided by its zero-shear-rate value is plotted as a function of shear rate times the longest polymer relaxation time, the curves for various polymer-solvent systems coincide (the product of shear rate and longest relaxation time corresponds to the reduced shear rate commonly used by experimentalists). Such *universal curves* are affected only by a very few, general characteristics of the polymer-solvent systems such as the solvent quality. It is the purpose of this paper to calculate the universal rheological and diffusive properties of dilute polymer solutions undergoing steady shear flow for both good and Θ solvents. The theoretical predictions are presented in a form that allows direct and convenient comparison with experimental results.

The theoretical investigation in this paper is based on the Rouse model^{2,3} in which the solvent is treated as a Newtonian liquid and the polymers are represented as linear chains of identical beads joined by Hookean springs. Two additional effects that are believed to determine the properties of dilute solutions and that are neglected in the traditional Rouse model are then incorporated into the model: hydrodynamic interaction and excluded volume. The hydrodynamic interaction is a consequence of the disturbance of the solvent velocity field caused by the bead motion and is hence always present in dilute solutions. The excluded-volume interaction between any pair of polymer segments coming close to each other in space affects the properties of polymers in good solvents. By reducing the temperature and thus making the solvent quality worse, one can reduce the effect of excluded-volume interactions between different segments of a polymer; at the so-called Θ temperature the excluded-volume effect is, roughly speaking, switched off, and the properties of Θ solutions are determined by hydrodynamic interaction alone. We therefore present the theoretical results for the models with both hydrodynamic interaction and excluded volume (good solvents) and with hydrodynamic interaction alone (Θ solvents).

Since we refer the reader to previous papers⁴⁻⁸ for a detailed description of the formulation of the hydrodynamic-interaction and excluded-volume effects, we only summarize here the basic steps and ideas underlying our calculations.

(1) Both hydrodynamic interaction and excluded volume are very complicated, nonlinear effects. If one wants to avoid mean-field-type calculations and computer simulations, the natural tool for attacking these problems is perturbation theory. All the results presented in this paper are based on first-order perturbation theory in the parameters characterizing the strength of the hydrodynamic and excluded-volume interactions.

(2) In constructing the perturbation theories of hydrodynamic interaction and excluded volume in three dimensions, it turns out that the parameters characterizing the strength of the hydrodynamic-interaction and excluded-volume effects are both proportional to $N_0^{1/2}$, where N_0 is the number of beads in a Rouse chain.^{9,10} When constructing a perturbation theory for long chains, expansion parameters proportional to $N_0^{1/2}$ are fatal, and the question comes up: how, if at all, can hydrodynamic interaction and excluded volume be treated by perturbation theory? The key observation for making perturbation theory applicable is that in $d > 3$ space dimensions, where d does not need to be an integer, the probability of contacts between different polymer segments decreases and disturbances of the solvent-velocity field decay more rapidly; in other words, the strength of both hydrodynamic-interaction and excluded-volume effects is reduced in $d > 3$ dimensions. In fact, for $d = 4 - \epsilon$ the parameters characterizing the strength of hydrodynamic interaction and excluded volume are both proportional to $N_0^{\epsilon/2}$, and perturbation theory becomes a useful tool for small ϵ , that is, near four dimensions.⁴⁻⁷ This is why the perturbation calculations presented here are performed in d -dimensional space.

(3) In order to describe high-molecular-weight polymers by a bead-spring model, one can arbitrarily introduce beads consisting of say 50, 100, or 200 monomers. If the model is to be useful in spite of this arbitrariness, all these choices should lead to the same physical results provided that the number of beads and the hydrodynamic-interaction and excluded-volume parameters are corre-

spondingly redefined in changing the size of the beads. This renormalization of the model parameters^{4,5,11,12} is a fundamental and natural step in the calculations; this step is inevitable and nontrivial because hydrodynamic interaction and excluded volume between different, small beads must eventually be incorporated into the renormalized parameters characterizing the properties of a single, larger bead when modeling the polymer chains by using progressively larger beads. In a practical calculation of the renormalization factors, it is convenient to choose the ratio of the sizes of the larger to smaller beads infinitely large, and in doing so also the corresponding renormalization constants occurring in the calculations become infinitely large. However, in the final results all singular terms are eliminated.

In proceeding from smaller to larger beads and renormalizing the model parameters, the hydrodynamic-interaction and excluded-volume parameters approach well-defined values, the so-called fixed-point values of the hydrodynamic-interaction and excluded-volume parameters.^{4,8} High-molecular-weight polymers can be represented by model chains with beads consisting of a large number of monomers or smaller beads, and the large beads are hence characterized by the fixed-point hydrodynamic-interaction and excluded-volume parameters. As a consequence, the predictions of the properties of high-molecular-weight polymers are independent of any adjustable model parameters, that is, universal.

Since the fixed-point values of the hydrodynamic-interaction and excluded-volume parameters⁴ are proportional to ϵ , the perturbation theory of hydrodynamic-interaction and excluded-volume effects turns out to be an expansion in the parameter ϵ . To obtain results for $d = 3$ from the ϵ expansion one must use an expansion parameter of order unity rather than the divergent expansion parameters in the original perturbation theory for $d = 3$.

(4) All the calculations in this paper are based on first-order perturbation theory. However, there exists a method for refining the first-order perturbation results by adding higher order contributions. The addition of higher order terms, which is of course by no means unique, is governed by the requirement that the results should exhibit a power-law dependence on chain length as required by very general considerations discussed elsewhere.^{4,6} The first-order perturbation theory results alone do not fulfil this requirement; however, by exponentiating the first-order results (thus adding higher order corrections) the requirement may be fulfilled.

In summary, calculation of the results presented in this paper is based on first-order perturbation expressions for the desired quantities in d dimensions which are then expressed in terms of renormalized parameters and refined by exponentiation.

The outline of this paper is as follows. In the next section, we briefly summarize the basic model equations. As an illustrative example we then discuss the procedure of calculating the diffusion tensor for the polymers in steady shear flow and present the results (section III). In section IV, we determine the shear-rate dependence of the viscometric functions and present detailed results. A brief summary concludes the paper. Detailed information about the evaluation of the first-order perturbation theory contributions at finite shear rates may be found in the Appendix. Readers interested only in the universal predictions for the shear-rate dependence of the viscometric functions for dilute polymer solutions may skip directly to section IV.B (the results are summarized in

Table I) and should, however, be aware of the limitations of the model discussed in section V.

II. Model Equations

The starting point for the discussion of the rheological behavior of dilute polymer solution in this work is the Rouse model¹⁻³ in d -dimensional space. In that model, the polymers are represented by linear chains of N_0 identical, spherical beads connected by $N_0 - 1$ Hookean springs with spring constant H . For the vector \mathbf{Q}_k pointing from the bead k to the bead $k + 1$ one usually writes $\mathbf{Q}_k = \mathbf{r}_{k+1} - \mathbf{r}_k$, where $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N_0}$ are the bead-position vectors with respect to a laboratory-fixed, rectangular, d -dimensional coordinate frame. The solvent, which is modeled as an incompressible Newtonian fluid completely characterized by its viscosity η_s , is assumed to undergo homogeneous flow; that is, the velocity field $\mathbf{v}(\mathbf{r})$ is of the form $\mathbf{v}(\mathbf{r}) = \kappa \cdot \mathbf{r}$. In this paper we restrict ourselves to the study of simple steady shear flow for which the tensor κ (in a laboratory-fixed, rectangular, d -dimensional coordinate system) has the matrix representation $\kappa_{ij} = \gamma \delta_{1i} \delta_{2j}$, where γ is the constant shear rate and δ_{ij} is the Kronecker delta function.

In conventional polymer kinetic theory³ the dynamics of a single polymer chain are described by the "diffusion equation". For homogeneous flows, it is reasonable to assume that the dynamics of the internal configurations of the polymer in dilute solution are independent of the location of the center of mass. Therefore, the solution of the d -dimensional "diffusion equation", the configurational distribution function for the Rouse model chains, depends on the $N_0 - 1$ connector vectors \mathbf{Q}_k only. One can immediately deduce that in steady shear flow the distribution function of the Rouse model is a Gaussian function of the connector vectors with zero mean values and second moments given by⁶

$$\langle \mathbf{Q}_j \mathbf{Q}_k \rangle = \frac{k_B T}{H} [\delta_{jk} \mathbf{1} + 2\lambda_H C_{jk}(\kappa + \kappa^T) + 8\lambda_H^2 C_{jk}^2 \kappa \cdot \kappa^T] \quad (1)$$

where k_B is Boltzmann's constant, T is the absolute temperature, and the $(N_0 - 1) \times (N_0 - 1)$ matrix $C_{jk} = \min(j, k) - jk/N_0$ is the usual Kramers matrix (C^2 is the second power of the Kramers matrix). The often-used time constant $\lambda_H = \zeta_0/(4H)$ is proportional to the bead-friction coefficient ζ_0 , and the angular brackets on the left-hand side of (1) denote an ensemble average. On the other hand, switching from the connector vectors \mathbf{Q}_k to the difference vectors $\mathbf{r}_{\mu\nu} = \mathbf{r}_\nu - \mathbf{r}_\mu$, which are sums of the connector vectors, $\mathbf{r}_{\mu\nu} = \sum_{j=\mu}^{\nu-1} \mathbf{Q}_j$ ($\nu > \mu$), one finds that the distribution of $\mathbf{r}_{\mu\nu}$ is also Gaussian with zero mean value and the covariances

$$\hat{\sigma}_{\mu\nu} = \frac{H}{k_B T} \frac{\langle \mathbf{r}_{\mu\nu} \mathbf{r}_{\mu\nu} \rangle}{|\mu - \nu|} = 1 + \lambda_H (\kappa + \kappa^T) \hat{S}_{\mu\nu}^{(1)} + 2\lambda_H^2 \kappa \cdot \kappa^T \hat{S}_{\mu\nu}^{(2)} \quad (2)$$

The auxiliary matrices $\hat{S}_{\mu\nu}^{(m)}$ occurring in (2) are defined as follows:

$$\hat{S}_{\mu\nu}^{(m)} = \frac{2^m}{|\mu - \nu|} \sum_{j,k=\min(\mu,\nu)}^{\max(\mu,\nu)-1} C_{jk}^m \quad (3)$$

where C_{jk}^m is the m th power of the Kramers matrix.

The Rouse model, which is an exactly solvable model,² neglects two important physical effects that should be included in a dynamical theory of dilute polymer solutions: hydrodynamic-interaction and excluded-volume effects. For long polymer chains near four dimensions perturbation

theory can be employed to investigate both the hydrodynamic and excluded-volume interactions and so to incorporate these effects into the model.^{6,7} In fact, in constructing a perturbation theory expansion of the hydrodynamic interaction in $d = 4 - \epsilon$ dimensions for long chains, the quantity $\zeta_0 N_0^{\epsilon/2}$ has been found to be the natural expansion parameter,⁶ whereas the expansion parameter in the perturbation theory of excluded-volume effects is $\nu_0 N_0^{\epsilon/2}$, where ν_0 is the excluded-volume parameter.⁷ The occurrence of the factor $N_0^{\epsilon/2}$ in these expansion parameters indicates that for consideration of the long-chain behavior it is crucial to perform the calculations in $d = 4 - \epsilon$ dimensions. In the following sections we construct a first-order perturbation theory of the hydrodynamic-interaction and excluded-volume effects for nonvanishing shear rate. All averages occurring in these first-order equations require the Gaussian configurational distribution function of the Rouse model characterized by the above-mentioned second moments (1) or (2).

Since we expect the observable quantities to be independent of the precise definition of the beads in the mechanical model, we replace the parameters ζ_0 and ν_0 which are associated with the beads by the dimensionless parameters ξ_0 and u_0 defined as usual:^{4,11}

$$\xi_0 = \frac{\zeta_0}{\eta_s} \left(\frac{k_B T}{H} \right)^{(\epsilon/2)-1} L^{\epsilon/2} \quad (4)$$

$$u_0 = \nu_0 \left(\frac{k_B T}{H} \right)^{(\epsilon/2)-2} L^{\epsilon/2} \quad (5)$$

In these equations, L is a dimensionless, phenomenological parameter. One may regard $L^{1/2}$ as the size of a polymer segment that consists of a large number of beads, and ξ_0 and u_0 as the hydrodynamic-interaction and excluded-volume parameters associated with such a segment.

III. Diffusive Properties

In order to illustrate the way in which renormalization-group calculations of the hydrodynamic-interaction effects at finite values of the shear rate can be performed, we discuss in this section the polymer contribution to the diffusion tensor. We outline the general idea of the method, leaving the calculational details to the Appendix. The results are presented in subsection III.B.

A. Diffusion Tensor. In the presence of a homogeneous flow field $\mathbf{v}(\mathbf{r}) = \kappa \cdot \mathbf{r}$ the diffusive properties of polymers depend on the direction relative to the characteristic directions of the flow field and hence need to be characterized by a tensor rather than by a scalar coefficient. A possible definition of the diffusion tensor \mathbf{D} associated with the mobility of polymers in the presence of external forces is related to the average velocity of the center of mass, \mathbf{r}_{cm} , caused by an external force, \mathbf{F}^e :

$$\frac{d}{dt} \langle \mathbf{r}_{cm} \rangle = \kappa \cdot \langle \mathbf{r}_{cm} \rangle + \frac{1}{k_B T} \mathbf{D} \cdot \mathbf{F}^e \quad (6)$$

The diffusion tensor \mathbf{D} can be obtained experimentally by measuring the relative velocities caused by an external force on the polymers in a dilute solution. Notice that in previous works on translational diffusivity of polymers in dilute solution (cf. refs 13–15) also diffusion tensors associated with the Brownian motion and the time evolution of polymer mass concentration gradients in flowing solutions are calculated. One important result of these investigations is that in nonequilibrium situations the Nernst–Einstein relation does not hold.

If one adopts the definition (6) to the first-order perturbation theory of the hydrodynamic-interaction and excluded-volume effects, then one finds no first-order corrections to the diffusion tensor due to excluded-volume interactions; the resulting corrections to the usual isotropic Rouse result stem from hydrodynamic interaction only:⁸

$$\mathbf{D} = \frac{k_B T}{\zeta_0 N_0} \left(1 + \frac{\zeta_0}{N_0} \sum_{\substack{\mu, \nu=1 \\ \mu \neq \nu}}^{N_0} \langle \Omega_{\mu\nu} \rangle \right) \quad (7)$$

where $\Omega_{\mu\nu} = \Omega(\mathbf{r}_\mu - \mathbf{r}_\nu)$ is the d -dimensional Oseen tensor describing the hydrodynamic interaction between beads μ and ν . In d dimensions the Oseen tensor can be constructed by solving the linearized, d -dimensional Navier–Stokes equation under the assumption that the solvent relaxation is very fast compared to polymer relaxation processes:⁴

$$\Omega(\mathbf{r}) = \frac{1}{(2\pi)^d} \int d^d \mathbf{k} \frac{1}{\eta_s k^2} \left(1 - \frac{\mathbf{k} \mathbf{k}}{k^2} \right) e^{i \mathbf{k} \cdot \mathbf{r}} \quad (8)$$

where k is the length of the vector \mathbf{k} and $\int d^d \mathbf{k} = \prod_{\alpha=1}^d \int dk_\alpha$ denotes a d -dimensional integral over all space.

The perturbation expansion (7), required as input for a renormalization-group (RG) analysis of the diffusion tensor, holds for arbitrary values of the shear rate. At equilibrium, this perturbation theory is found to develop $(1/\epsilon)$ singularities for long chains ($N_0 \rightarrow \infty$) near four dimensions.¹¹ Such divergences are related to the ambiguity in the definition of the beads and indicate that a renormalization of the model parameters is necessary. To this end, in the RG treatment bare model parameters N_0 and ξ_0 are replaced by the renormalized parameters:

$$N = Z_N N_0 / L \quad (9)$$

$$\xi = Z_\xi \xi_0 \quad (10)$$

$$u = Z_u u_0 \quad (11)$$

Although the expression (7) for the diffusion tensor is not modified by excluded-volume effects, we here study also the renormalization of the excluded-volume parameter u . (The reason for this will become clear later in this subsection.) For a suitable choice of the renormalization constants Z_N , Z_ξ , and Z_u defined by (9)–(11), the $(1/\epsilon)$ singularities in the first-order expansion in ξ and u can be removed from the expressions for all observable quantities. At equilibrium, the renormalization constants canceling all divergences to first order in ξ and u are well-known⁴

$$Z_N = Z_N(u) = 1 + \frac{1}{2\pi^2 \epsilon} u \quad (12)$$

$$Z_\xi = Z_\xi(\xi, u) = 1 - \frac{3}{8\pi^2 \epsilon} \xi - \frac{1}{2\pi^2 \epsilon} u \quad (13)$$

$$Z_u = Z_u(u) = 1 - \frac{2}{\pi^2 \epsilon} u \quad (14)$$

However, since we are interested in the nonequilibrium diffusion, the question arises as to whether these equilibrium constants, and thus the renormalization procedure, are affected by the presence of shear flow. A careful discussion of the occurring singular terms⁸ shows that for finite values of the reduced shear rate of the Rouse model

$$\beta_0 = \frac{N_0^2 \zeta_0}{12H} \dot{\gamma} \quad (15)$$

there are no additional $(1/\epsilon)$ singularities apart from those already present at equilibrium. Therefore, to first order

in ξ and u and for arbitrary values of β_0 , all appearing singularities are eliminated after introducing the renormalized parameters N and ξ formed with the equilibrium renormalization constants (12) and (13).

After inserting the renormalized parameters N and ξ into (7), one finds the final, renormalized, first-order perturbation theory results for the diffusion tensor in steady shear flow:

$$\mathbf{D} = \frac{k_B T}{\eta_s} \left(L \frac{k_B T}{H} \right)^{1-(d/2)} \frac{1}{\xi N} \left\{ 1 + \frac{3\xi}{16\pi^2} \left[\ln(2\pi N) - \frac{1}{6} \right] 1 + \frac{3\xi}{32\pi^2} \int_0^1 dx \int_0^1 dy \frac{\mathbf{H}(1 + h_1(x,y)(\hat{\kappa} + \hat{\kappa}^T) + h_2(x,y)\hat{\kappa}\hat{\kappa}^T) - 1}{|x-y|} \right\} \quad (16)$$

where the hydrodynamic-interaction function \mathbf{H} is closely related to the average of the Oseen tensor required in (7) and the functions $h_1(x,y)$ and $h_2(x,y)$ correspond for $N_0 \rightarrow \infty$ to the matrices $\hat{S}_{\mu\nu}^{(1)}$ and $\hat{S}_{\mu\nu}^{(2)}$:

$$h_1(x,y) = 3|x-y| \left\{ (x+y) - \frac{1}{3}|x-y| - \frac{1}{2}(x+y)^2 \right\} \quad (17)$$

and

$$h_2(x,y) = 3|x-y| \left\{ \frac{1}{15}|x-y|^3 - 3(x^3 + y^3) - 5xy(x+y) + (x+y)^2(x^2 + y^2 + 2) \right\} \quad (18)$$

The tensor $\hat{\kappa}$ corresponds to κ with $\dot{\gamma}$ replaced by the reduced shear rate $\beta = \eta_p \dot{\gamma} / n k_B T$ frequently used in experimental investigations of polymer rheology. Here η_p is the polymer contribution to the viscosity, and n denotes the number density of polymers. Because of the facts that (i) the reduced shear rate occurs only in the first-order perturbation-theory contribution and (ii) we perform all calculations to first order in ϵ only, it is permissible to use the reduced shear rate β_0 of the Rouse model when evaluating the double integral in (16). Following the discussion above, we separate in (16) the isotropic Rouse and equilibrium contributions in the first line of (16) from the nonequilibrium contribution which is represented by the double integral in (16). In order to calculate this integral we need a representation of the hydrodynamic-interaction function

$$\mathbf{H}(\sigma) = \frac{1}{(2\pi)^{d/2}} \frac{d(d-2)}{d-1} \int d^d \mathbf{k} \frac{1}{k^2} \left(1 - \frac{\mathbf{k}\mathbf{k}}{k^2} \right) \exp\left(-\frac{1}{2}\mathbf{k}\cdot\sigma\cdot\mathbf{k}\right) \quad (19)$$

in $d = 4$ dimensions where σ denotes a second-rank tensor and for the evaluation of the integral in (16) we have $\sigma = 1 + h_1(x,y)(\hat{\kappa} + \hat{\kappa}^T) + h_2(x,y)\hat{\kappa}\hat{\kappa}^T$. From our detailed calculation summarized in the Appendix, the needed explicit representation of \mathbf{H} in four dimensions can be derived (cf. eq B1). We skip this technical point here and note instead two important properties of the representation (B1) of \mathbf{H} : (i) at equilibrium ($\beta = 0$) the function \mathbf{H} is normalized to $\mathbf{H}(1) = 1$ and hence the double integral in (16) vanishes; (ii) for any arbitrary value of β the representation of the function \mathbf{H} is a function of x, y , and β and may be evaluated analytically. In conclusion, if one is interested in obtaining the nonequilibrium first-order perturbation-theory contributions to the diffusion tensor, one may calculate the double integral occurring in (16) numerically, which can be accomplished by standard methods, such as Simpson's rule.

For presenting the results for the diffusion tensor in a convenient manner, we transform the first-order pertur-

bation result (16) into a shear-rate-dependent rectangular coordinate system \mathbf{C} in which the hydrodynamic-interaction function \mathbf{H} is diagonal. Therefore, in that coordinate system the diffusion tensor will be completely characterized by its principal values. As pointed out in the Introduction, for long chains one expects the diffusion tensor to be proportional to a certain power of the number of segments N . Since such a power-law dependence is incompatible with the diagonalized first-order expression for the diffusion tensor, one usually exponentiates first-order results like the diagonal representation of (16). Upon diagonalizing (16), exponentiating, and normalizing to zero-shear-rate values, one obtains the universal RG result for the diffusion tensor:

$$\frac{D_i^C(\beta)}{D_i^C(0)} = \exp \left\{ \frac{3\xi^*}{32\pi^2} \int_0^1 dx \int_0^1 dy \times \frac{H_i^C(1 + h_1(x,y)(\hat{\kappa} + \hat{\kappa}^T) + h_2(x,y)\hat{\kappa}\hat{\kappa}^T) - 1}{|x-y|} \right\} \quad (20)$$

where D_i^C and H_i^C are the principal values of the diffusion tensor and the hydrodynamic-interaction function \mathbf{H} , respectively. The particular value ξ^* of the hydrodynamic-interaction parameter is frequently referred to as the fixed-point value. As has been pointed out in the Introduction, the fixed-point values of the renormalized model parameters characterize the behavior of long chains. In the absence of excluded-volume interactions, i.e., $u = 0$, the fixed-point value of the renormalized excluded-volume parameter u^* is zero and the fixed-point value of the hydrodynamic-interaction parameter ξ^* satisfies the equation $Z_\xi(\xi^*) = 0$. Thus, for Θ solvents we have⁴

$$u^* = 0, \quad \xi^* = \frac{8}{3}\pi^2\epsilon \quad (21)$$

For good solvents, the fixed-point values of the hydrodynamic-interaction and excluded-volume parameters must be determined from the following conditions:

$$Z_\xi(\xi^*, u^*) = 0, \quad Z_u(u^*) = 0 \quad (22)$$

These equations are satisfied by⁴

$$u^* = \frac{\pi^2}{2}\epsilon, \quad \xi^* = 2\pi^2\epsilon \quad (23)$$

It is important to note that since (22) introduces a coupling between the renormalized excluded-volume and hydrodynamic-interaction effects for long chains, the fixed-point value ξ^* for good solvents differs from that for Θ solvents. According to (16), the first-order expression for \mathbf{D} is not modified by explicit excluded-volume corrections. Notice, however, that since \mathbf{D} depends on ξ , the long-chain behavior of the RG result (20) characterized by the fixed-point value ξ^* is nevertheless affected by excluded-volume interactions. This is the reason why we need the excluded-volume parameter in the discussion of this section.

B. Results for the Diffusion Tensor. For a complete description of the diffusion tensor in three dimensions we need to give the relationship between the original laboratory-fixed coordinate system and the system \mathbf{C} in which \mathbf{H} is diagonal. For steady shear flow the coordinate system \mathbf{C} may be obtained by rotating the laboratory system by an angle ϕ ($0 \leq \phi < \pi/2$) around the 3-axes. Note that this shear-rate-dependent angle ϕ is independent of ξ ; thus an exponentiation procedure is not possible. In the present subsection, we discuss the shear-rate dependence of the angle ϕ and of the normalized principal values D_i^C ($i = 1, 2, 3$) of the diffusion tensor (20). We investigate

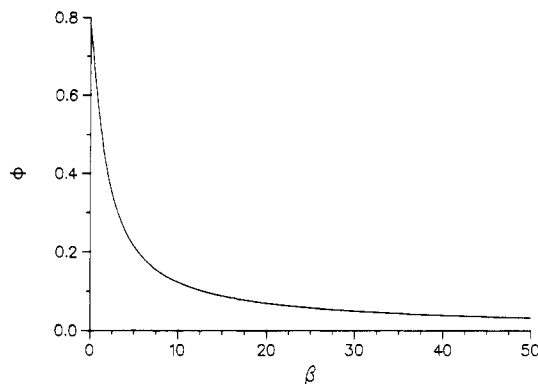


Figure 1. The angle ϕ characterizing the directions of the principal axes of the diffusion tensor \mathbf{D} vs the reduced shear rate β .

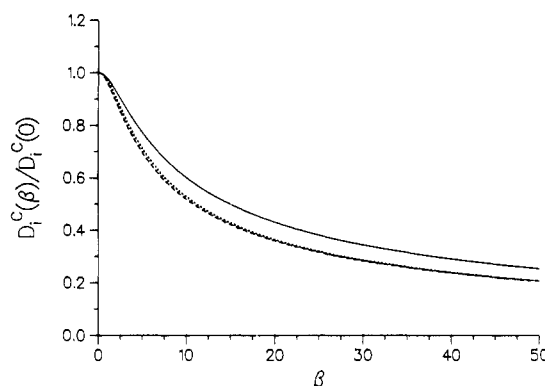


Figure 2. Normalized principal values $D_i^C(\beta)/D_i^C(0)$ of the diffusion tensor \mathbf{D} vs the shear rate β for good solvents. The continuous, dashed, and dotted curves belong to the 1,2,3 components of \mathbf{D} ($i = 1, 2, 3$) in the coordinate system C , respectively.

good solvents only, but the corresponding results for Θ solvents may always be recalculated by exploiting eqs 20 and 21, i.e., by raising the good-solvent results to the 4/3 power.

Figure 1 displays our RG result for the angle ϕ . In the limit of vanishing shear rate we find $\phi \rightarrow \pi/4$. Over the entire range of β plotted in Figure 1 ϕ decreases monotonically with increasing shear rate. The small values of ϕ at high shear rates indicate that the principal axes of the diffusion tensor are almost parallel to the axes of the laboratory coordinate system.

The shear-rate dependence of the normalized principal values $D_i^C(\beta)/D_i^C(0)$ of the diffusion tensor \mathbf{D} which describes the polymer mass flux caused by external forces is shown in Figure 2. The normalization implies $D_i^C(\beta)/D_i^C(0) = 1$ for shear rate zero. For small β , all principal values start to decrease monotonically, thus indicating a reduced diffusivity of polymers in flowing solution. At any given shear rate, the normalized principal value D_1^C associated with the 1-axis is slightly larger than the other two values, and the normalized results for D_3^C lie between the corresponding curves for D_1^C and D_2^C .

With the exception of D_1^C , we found good qualitative agreement between the predictions of the RG analysis and both the consistent-averaging method¹⁴ and the Gaussian approximation¹⁵ for Hookean dumbbells. For D_1^C the consistent-averaging method and the Gaussian approximation predict at low shear rates flow-enhanced diffusion, which is not observed in our RG calculation.

IV. Rheological Properties

We now turn to the study of the shear-rate-dependent viscometric functions for steady shear flow, which are

quantities of great experimental interest. We summarize here the basic steps while keeping details to a minimum. The results are presented in section IV.B. For a detailed description of the formulation of the excluded-volume and hydrodynamic-interaction effects for arbitrary values of the shear rate, we refer the reader to previous work⁶⁻⁸ and to Appendix B.

A. Stress Tensor and Viscometric Functions. For polymers modeled as noninteracting, linear Rouse chains with no internal constraints and suspended in a Newtonian solvent, the polymer contribution to the stress tensor τ^p for homogeneous flows is given by the Kramers expression (e.g., Table 15.2-1 or §18.4 of the textbook by Bird et al.³):

$$\tau^p = -nH \sum_{j=1}^{N_0-1} \langle \mathbf{Q}_j \mathbf{Q}_j \rangle + (N_0 - 1)nk_B T \mathbf{I} \quad (24)$$

which is a basic equation of conventional polymer kinetic theory. In this expression n denotes the number density of polymers, and a Maxwellian velocity distribution of the beads is assumed. All required information about the perturbation of the configurational distribution function caused by the hydrodynamic-interaction and excluded-volume effects (which should be used to perform the average occurring in the Kramers expression for τ^p) can be obtained from the time evolution equation for the second moments. In a d -dimensional space the form of the Kramers expression does not change.⁶ Moreover, derivations of hydrodynamic equations for dilute polymer solutions from a system of coupled Langevin equations for polymer and solvent (CLEPS) lead to a stress tensor that coincides with the expression (24) keeping only the lowest order terms in the polymer concentration.^{16,17} Therefore, the Kramers expression for the stress tensor constitutes a starting point for the RG calculation of the shear-rate-dependent polymer contribution to the viscosity η_p and the normal-stress coefficients Ψ_1 and Ψ_2 (cf. eqs D.5-1 to D.5-3 of the textbook by Bird et al.³):

$$\tau_{12}^p = -\dot{\gamma} \eta_p \quad (25)$$

$$\tau_{11}^p - \tau_{22}^p = -\dot{\gamma}^2 \Psi_1 \quad (26)$$

$$\tau_{22}^p - \tau_{33}^p = -\dot{\gamma}^2 \Psi_2 \quad (27)$$

Since the influence of the excluded-volume effects on the shear-rate dependence of the viscometric functions for dilute polymer solutions is discussed in great detail in a previous paper (cf. eqs 9 and 15–17 in ref 7), we skip the discussion of excluded volume until presentation of the results for good solvent in the following subsection and concentrate on the evaluation of corresponding expressions for the hydrodynamic interaction in this subsection. Actually, in deriving the first-order perturbation theory expansion, one can treat the effects of hydrodynamic interaction and excluded volume separately and add the respective contributions in the end because coupled effects are of second (or higher) order.

To determine the hydrodynamic-interaction corrections to first order in the strength of the hydrodynamic interaction, we note that there are two different contributions, which we analyze separately (cf. eqs A7–A11 in ref 8). In the first contribution, the hydrodynamic-interaction tensors are replaced by their averages; thus, keeping only this contribution corresponds to the self-consistent-averaging approximation.¹⁸ For conveniently presenting the self-consistently averaged hydrodynamic interaction in d dimensions, one may use the hydrodynamic-interaction function $\mathbf{H}(\sigma)$ defined in (19). The

Table I
Results for the Viscometric Functions

β	good solvents			Θ solvents		
	$\eta_p(\beta)/\eta_p(0)$	$\Psi_1(\beta)/\Psi_1(0)$	Ψ_2/Ψ_1	$\eta_p(\beta)/\eta_p(0)$	$\Psi_1(\beta)/\Psi_1(0)$	Ψ_2/Ψ_1
0.000	1.000	1.000	-0.00973	1.000	1.000	-0.01298
0.010	1.000	1.000	-0.00972	1.000	1.000	-0.01296
0.032	1.000	1.000	-0.00972	1.000	1.000	-0.01296
0.100	1.000	1.000	-0.00972	1.000	1.000	-0.01296
0.316	0.996	1.000	-0.00936	1.000	1.000	-0.01248
1.000	0.970	0.972	-0.00720	1.000	1.000	-0.00960
1.778	0.934	0.932	-0.00432	1.012	1.018	-0.00576
3.162	0.897	0.891	-0.00108	1.068	1.145	-0.00144
5.623	0.895	0.920	0.00072	1.233	1.584	0.00096
10.000	0.964	1.104	0.00108	1.609	2.855	0.00144
17.783	1.123	1.532	0.00072	2.360	6.407	0.00096
31.623	1.422	2.501	0.00036	3.865	17.798	0.00048

second contribution expresses the fact that it is not permissible to replace the hydrodynamic-interaction tensors with their averages and thus completely neglect the configurational dependence of the hydrodynamic-interaction tensor; in that sense, the second contribution takes into account the fluctuations of the hydrodynamic-interaction tensors around their averages.¹⁹ In order to investigate the effects of fluctuations in the hydrodynamic interaction, we introduce the d -dimensional fourth-rank tensor $\mathbf{K}(\sigma)$:

$$\mathbf{K}(\sigma) = \frac{-1}{(2\pi)^{d/2}} \frac{(d-2)(d+1)}{d-1} \int d^d \mathbf{k} \frac{1}{k^2} \mathbf{k} \left(1 - \frac{\mathbf{k} \cdot \mathbf{k}}{k^2} \right) \mathbf{k} \times \exp\left(-\frac{1}{2} \mathbf{k} \cdot \sigma \cdot \mathbf{k}\right) \quad (28)$$

where σ denotes a second-rank tensor. Useful general representations of the hydrodynamic-interaction functions $\mathbf{H}(\sigma)$ and $\mathbf{K}(\sigma)$ are given in Appendix A, whereas in Appendix B we present explicit, bare first-order perturbation expansions for the stress tensor required as an input in a RG analysis.

For the contribution caused by the consistently averaged hydrodynamic interaction it can be shown that even in the calculation of the zero-shear-rate polymer viscosity η_p and the first normal-stress coefficient Ψ_1 the bare corrections (cf. eq B6) diverge like $1/\epsilon$ as ϵ approaches zero and N_0 goes to infinity. In addition, it turns out that for finite values of the reduced shear rate β_0 no additional singularities occur. This observation suggests that for arbitrary β_0 we can renormalize the bare model parameters ζ_0 and N_0 by replacing them with ξ and N formed with the equilibrium renormalization constants (12) and (13). In order to investigate the shear-rate dependence of the renormalized consistently averaged contribution to η_p and Ψ_1 , we adopt the method described in the previous section for the diffusion tensor; we separate the equilibrium from the nonequilibrium contributions and calculate the latter numerically.

Turning to the contributions due to the fluctuations of the hydrodynamic interaction (cf. eq B7), we find that for arbitrary β_0 , including $\beta_0 = 0$, there are no $(1/\epsilon)$ singularities in the long-chain limit. The same holds true for the consistent-averaging contribution to the second normal-stress coefficient Ψ_2 in (B6). Therefore, we calculate the renormalized first-order perturbation theory corrections to these quantities by replacing the bare parameters ζ_0 and N_0 with the renormalized parameters ξ and N given by (10) and (9). The double integrals occurring in the long-chain limit in the corrections to viscometric functions related to the fluctuations and the consistent-averaging contribution to Ψ_2 may be evaluated numerically.

In summary, the final, renormalized, first-order perturbation-theory expansion of the hydrodynamic-interaction effect for the viscometric functions in steady shear flow can be evaluated for arbitrary values of β using the equilibrium renormalization constants (12) and (13). The numerical investigations can be reduced to a two-dimensional integral that can be performed by standard integration schemes such as Simpson's rule.

As has been pointed out in the Introduction, the standard RG analysis predicts a power-law dependence on N that is inconsistent with the renormalized first-order expression for the viscometric functions. We achieve the correct dependence of the viscometric functions on N by applying the method discussed in the previous section in connection with the diffusion tensor, namely, by exponentiating the renormalized first-order perturbation-theory results of the hydrodynamic-interaction and excluded-volume effects. Notice, however, that after expanding the exponentiated first-order expansion to first order in ξ and u , that is, taking the limit of small ξ and u , one recovers the original first-order expressions. Since one expects a power-law dependence of η_p and Ψ_1 on N only for very long chains which are characterized by the particular values ξ^* and u^* , we use the exponentiated first-order expressions only for these fixed-point values of ξ and u . Knowing this fact, one may always recalculate the first-order results from the final RG predictions, which will be presented in the following subsection.

B. Results for Good and Θ Solvents. In this subsection we present the RG predictions for the shear-rate-dependent rheological properties of dilute polymer solution undergoing steady shear flow. The results for the polymer contribution to the viscosity η_p and the first normal-stress coefficient Ψ_1 (normalized to their corresponding zero-shear-rate values) are based on an exponentiated first-order expansion in ϵ . We also discuss the universal ratio of the normal-stress coefficients Ψ_2/Ψ_1 . Our results for good and Θ solvents are summarized in Table I.

We start with the reduced polymer contribution to the viscosity shown in Figure 3. At low values of the shear rate we observe shear thinning for good-solvent conditions. This is plausible since the excluded-volume interactions become less important when the polymer stretching due to the imposed shear rate decreases. The Θ solution is not shear-thinned at all. On the other hand, the self-consistent averaging approximation of the Rouse model with hydrodynamic interaction¹⁸ and even the Gaussian approximation,¹⁹ which accounts for the fluctuations in the hydrodynamic interactions, predicts for chains consisting of a finite number of beads a shear-thinning effect at low shear rates.^{18,26-28}

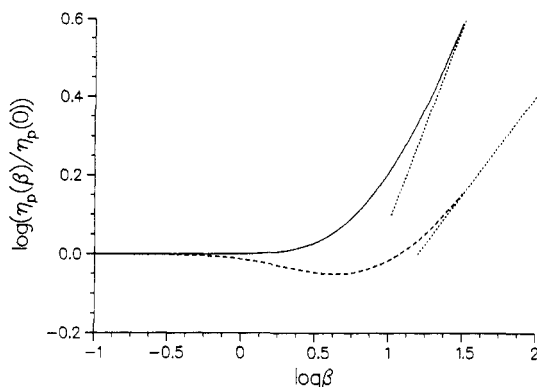


Figure 3. Normalized polymer contribution to the viscosity $\eta_p(\beta)/\eta_p(0)$ vs the reduced shear rate β for Θ (continuous) and good (dashed) solvents. The dotted lines represent the asymptotic behavior of $\eta_p(\beta)/\eta_p(0)$ in the limit of high reduced shear rates as found in ref 8.

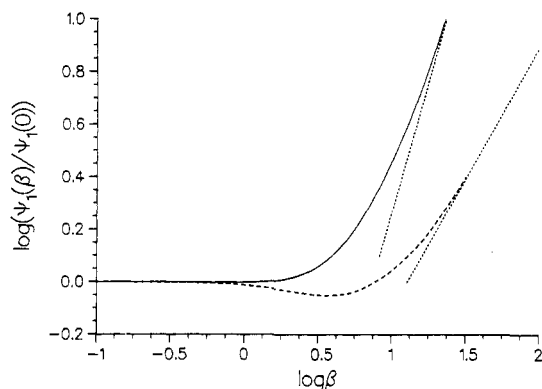


Figure 4. Normalized first normal-stress coefficient $\Psi_1(\beta)/\Psi_1(0)$ vs the reduced shear rate β for Θ (continuous) and good (dashed) solvents. The dotted lines represent the asymptotic behavior of $\Psi_1(\beta)/\Psi_1(0)$ in the limit of high reduced shear rates as found in ref 8.

The curves for the universal coefficient of the first normal-stress difference in Figure 4 show at low shear rate the same behavior as the polymer viscosity: again the solution thins for good solvents only. In the high-shear-rate regime the RG calculation predicts shear thickening. Both the reduced polymer viscosity and the reduced first normal-stress coefficient follow a power-law dependence on reduced shear rate.⁸ The shear-thickening effect arises because hydrodynamic interactions are partially switched off when the polymers become stretched at high shear rates (the viscosity for long, free-draining chains is much larger than for non-free-draining chains). The power-law behavior indicates that this "switching off" is incomplete and persists to arbitrarily high shear rates. Notice that for good solvents there are two contributions to the exponent governing the power-law dependence of the polymer viscosity and the first normal-stress coefficient which are of opposite sign: the negative contribution to the exponent due to excluded-volume effects and the (larger) positive contribution to the exponent stemming from hydrodynamic interactions.^{7,8} A power law characterized by a positive exponent is at variance with the prediction of the blob model²³ and the conclusions of ref 24 (for a further critical discussion of the high-shear-rate limit in the RG calculation, see ref 25) and seems to contradict experimental observation. An upturn on shear polymer viscosity and first normal-stress coefficient at large (but not arbitrarily large) β is also observed in approximate theoretical models for Θ solvents.^{18,27,28} Notice, however, that since the model uses elastic linear

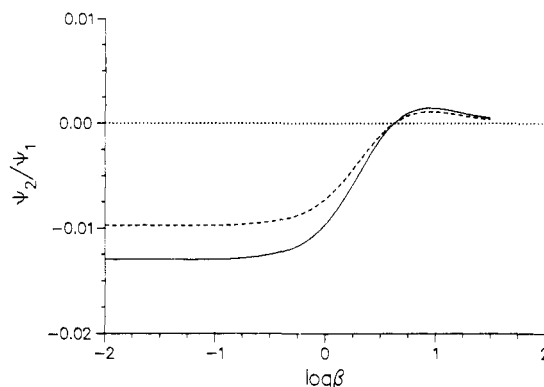


Figure 5. Ratio of the second to the first normal-stress coefficient Ψ_2/Ψ_1 vs the reduced shear rate β for Θ (continuous) and good (dashed) solvents. The dotted line corresponds to the prediction of the Rouse model.

springs connecting the beads, it is not clear that our results should give agreement with experiments at very high shear rate. Comparison of models including approximately nonlinear spring laws with experimental data indicates that finite extensibility of the polymer chains is crucial in describing polymer viscosity at large values of the imposed shear rate.²⁹

In Figure 5 we plot the universal ratio Ψ_2/Ψ_1 , which involves the second normal-stress coefficient. Since the Rouse value of Ψ_2 is zero, the exponentiation of the renormalized first-order expansion for Ψ_2 is not possible. Therefore, in calculating the ratio Ψ_2/Ψ_1 the first-order result for Ψ_1 should, for reasons of consistency, not be exponentiated either, but rather the lowest order (i.e., Rouse) value was used to obtain the curves in Figure 5. In three dimensions the RG analysis predicts a very small, negative ratio of the normal-stress differences for long chains in both Θ and good solvents. Notice that since the first-order corrections to Ψ_2 due to excluded-volume effects vanish⁷ and the ratio Ψ_2/Ψ_1 is evaluated by using the Rouse result for Ψ_1 , the solvent quality influences the result for Ψ_2/Ψ_1 only through the fixed-point value for ξ given in (23). For $\beta \rightarrow 0$ we find results that are small in magnitude and negative. According to the Appendix the zero-shear-rate results for Θ solvents may be evaluated analytically and are identical with those found in ref 6. As the shear rate increases, the magnitude of Ψ_2/Ψ_1 decreases, changes sign at $\beta \approx 4$, and reaches a maximum at $\beta \approx 9$. The maximum for Θ solvents is slightly larger than for good solvents. For higher shear rates Ψ_2/Ψ_1 decreases and vanishes at very high shear rates.

Some comparisons should be noted between the results for Ψ_2/Ψ_1 presented here and other approximate (numerical) results for the Θ -solvent case. The self-consistent-averaging approximation¹⁸ predicts a positive ratio of the second to the first normal-stress coefficient at equilibrium. At intermediate shear it changes its sign and vanishes as β becomes very large. In contrast, the behavior of Ψ_2/Ψ_1 predicted by the Gaussian approximation for a dumbbell²⁶ as well as for a chain model²⁷ is in qualitative agreement with our RG result. This similarity can be understood from a formal point of view. Both the RG calculation for Θ solvents and the Gaussian approximation are exact to first order in the strength of the hydrodynamic interaction, and (if the exponentiation procedure for the RG calculation is carried out) both account for an infinite number of higher order corrections. Moreover, at zero shear rate both methods can be handled analytically, whereas the shear-rate dependence needs to be calculated by numerical methods.

During the preparation of this work a preprint version of a RG study of rheological properties of dilute polymer solutions came to our attention.³⁵ In that investigation of non-Newtonian stress the viscometric functions for good and θ solvents were also calculated. Comparing the θ -solvent curves for the reduced polymer viscosity and the first normal-stress coefficient from ref 35 to those presented in Figures 3 and 4, we find good quantitative agreement. For good solvents, however, the agreement is only qualitative. In particular, the minimum value of reduced η_p calculated in ref 35 is ca. 12% lower than the minimum in Figure 3. Moreover, the minimum value for reduced Ψ_1 predicted in ref 35 is 57% lower than the corresponding minimum in Figure 4. The results for Ψ_2/Ψ_1 obtained in ref 35 are qualitatively the same as the curves shown in Figure 5. However, we should point out quantitative deviations that arise over the entire range of β . For vanishing shear rates ($\beta \rightarrow 0$) the result $\Psi_2/\Psi_1 \approx -0.03$, nearly independent of the solvent quality, has been found in ref 35. On the other hand, our prediction for good solvents (still for $\beta \rightarrow 0$) is $\Psi_2/\Psi_1 \approx -0.0097$ and $\Psi_2/\Psi_1 \approx -0.0130$ in the θ -solvent case. The latter result is in agreement with the values reported by other investigations of θ solvents using the RG approach.^{6,34} As shown in Figure 5, the ratio Ψ_2/Ψ_1 reaches a maximum at moderate β . The same qualitative behavior of Ψ_2/Ψ_1 has been found in ref 35. However, in contrast to the results plotted in Figure 5 the maximum value of Ψ_2/Ψ_1 for good solvents reported in ref 35 is larger than the corresponding maximum value for θ solvents. Since the RG procedure applied for the calculation of the viscometric functions in this work uses the same approach as used in ref 35, it is necessary to resolve the quantitative discrepancies by carefully examining the difficult calculations and the numerical results.

V. Summary and Limitations of the Model

One important purpose of this work is to extend the RG analysis for dilute polymer solutions undergoing steady shear flow to arbitrary values of the imposed reduced shear rate. To this end, we explicitly calculate the first-order perturbation theory corrections of hydrodynamic-interaction and excluded-volume effects to the diffusion and stress tensors. For finite values of the reduced shear rate β the divergences occurring for long chains near four dimensions can be removed by introducing renormalized parameters formed with the renormalization constants found at equilibrium. In terms of the renormalized model parameters, the diffusion tensor and the viscometric functions are regular functions of the friction coefficient ξ , the excluded-volume parameter u , the chain length N , and the reduced shear rate β . For intermediate reduced shear rates the shear-rate dependence of the hydrodynamic-interaction contributions to the viscometric functions has been expressed as a double integral which can be evaluated by numerical methods. After adding the corresponding renormalized first-order perturbation expansions resulting from the excluded-volume effects,⁷ which are regular functions of the excluded-volume parameter u , we exponentiate the first-order results and obtain theoretical predictions for universal rheological and diffusive properties. The predictions for the reduced polymer viscosity, the reduced first normal-stress coefficient, and the ratio of the second to the first normal-stress coefficient for both good and θ solvents are summarized in Table I. In the high-shear-rate regime and for vanishing shear rates our results coincide with the previously calculated expressions.⁶⁻⁸

While we have extended the Rouse model to include the hydrodynamic-interaction and excluded-volume effects, we have completely neglected the effects of finite extensibility of the polymer chains. A generalization of the elastic (Gaussian) Rouse model to account for these inelastic spring effects is very difficult, unless restriction is made to an approximate description of the finite extensibility of the springs connecting the beads.^{3,32} Two further effects that might be important in the presence of shear flow have also been neglected in the model: (i) the flow modifications of the hydrodynamic interactions and (ii) the effect of bead inertia. The effect of flow modification of the hydrodynamic-interaction tensor was analyzed in ref 20. Rough estimates of this effect based on ref 21 suggest that for fixed β the shear rate $\dot{\gamma}$ decays sufficiently fast with increasing N such that flow modification can be neglected even on the polymer scale. Although it is difficult to determine the importance of the bead-inertia effect in a rigorous manner, the following argument suggests that for fixed, finite reduced shear rate β it is permissible to neglect this effect. Noting that β describes the effect of the flow on the polymer scale, one can estimate the effect of the shear flow on the local scale (the bead scale) by making the shear rate $\dot{\gamma}$ dimensionless. To this end, one multiplies $\dot{\gamma}$ by the time scale for the corresponding local dynamics, which is independent of the chain length, and hence this product is small compared to β . For the finite but possibly large β values considered in our calculations the effect of shear flow on any local scale vanishes in the long-chain limit; the bead-inertia effect should hence be of roughly the same order as at equilibrium and thus negligible. The limitations resulting from the above-mentioned effects should be investigated in more detail. Thus, a systematic calculation based on the system of coupled Langevin equations for polymer and solvent (CLEPS)²² would certainly be desirable.

Finally, it should be noted that our starting point for the RG analysis of universal nonequilibrium properties of dilute polymer solutions undergoing steady shear flow is basically conventional polymer kinetic theory generalized to d space dimensions. To a certain extent, the basic equation used in conventional polymer kinetic theory can be justified by CLEPS,³³ which are used for RG calculations of rheological properties, too.³⁴ In that sense, the calculations in this paper may be considered to be based on the CLEPS, and the results are expected to agree with those obtained by employing the coupled-Langevin equation approach.³⁶

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Appendix

In the following appendices we study the first-order perturbation theory expansion in the strength of the hydrodynamic interaction needed for the RG calculations from a technical point of view. To this end, we discuss in Appendix A the d -dimensional hydrodynamic-interaction functions defined by eq 19 and 28 in a more general form. In Appendix B we summarize the details of the first-order perturbation contributions to the shear-rate-dependent stress and diffusion tensors in d dimensions.

A. Hydrodynamic-Interaction Functions. In evaluating the first-order perturbation expansion in the hydrodynamic-interaction parameter for Hookean chains for arbitrary shear rates, the hydrodynamic-interaction

functions $\mathbf{H}(\sigma)$ and $\mathbf{K}(\sigma)$ play a crucial rule. Here we discuss some properties of these functions and give general representations for arbitrary symmetric second-rank tensors σ in a d -dimensional space.

The function $\mathbf{H}(\sigma)$ is, as well as its argument, a positive-definite, symmetric second-rank tensor and was introduced in discussing the diffusion tensor. It describes the self-consistently averaged hydrodynamic interaction in d dimensions. On the other hand, the fluctuations in the hydrodynamic interaction are closely related to the fourth-rank tensor $\mathbf{K}(\sigma)$. In $d = 3$ dimensions there exists an explicit representation of the function $\mathbf{H}(\sigma)$ in terms of elliptic integrals in a coordinate system \mathbf{C} in which σ is diagonal.³² However, a representation of the function $\mathbf{K}(\sigma)$ is still unknown. We now construct a representation of the hydrodynamic-interaction functions in an arbitrary coordinate system by evaluating the integrals appearing in (19) and (28) for arbitrary dimension $d \geq 3$.

In the first step we consider the integral

$$\mathbf{F}^{(s)} = \frac{1}{(2\pi)^{d/2}} \int d^d \mathbf{k} \frac{1}{k^{2s}} \exp\left(-\frac{1}{2} \mathbf{k} \cdot \sigma \cdot \mathbf{k}\right) \quad (\text{A1})$$

where $s \geq 1$. For $s = 1$ one finds that (apart from a d -dependent prefactor) $\mathbf{F}^{(s)}$ corresponds to the isotropic part of the hydrodynamic-interaction function $\mathbf{H}(\sigma)$ defined in (19). We express $1/k^{2s}$ in terms of the Γ function, which is given by $\Gamma(s) = \int_0^\infty du u^{s-1} \exp(-u)$. By performing a substitution one has the identity

$$\frac{1}{k^{2s}} = \frac{1}{\Gamma(s)2^s} \int_0^\infty du u^{s-1} \exp\left(-\frac{1}{2} k^2 u\right) \quad (\text{A2})$$

Inserting this expression into (A1) and interchanging the order of the \mathbf{k} and u integrations, we obtain

$$\mathbf{F}^{(s)} = \frac{1}{(2\pi)^{d/2} \Gamma(s) 2^s} \int_0^\infty du u^{s-1} \int d^d \mathbf{k} \times \exp\left(-\frac{1}{2} \mathbf{k} \cdot (1u + \sigma) \cdot \mathbf{k}\right) = \frac{1}{\Gamma(s) 2^s} \int_0^\infty du \frac{u^{-1}}{\sqrt{\det \mathbf{A}}} \quad (\text{A3})$$

where we set $\mathbf{A} = 1u + \sigma$. We now want to show that the remaining nonisotropic terms in the hydrodynamic-interaction functions $\mathbf{H}(\sigma)$ and $\mathbf{K}(\sigma)$ can be evaluated in the same manner. To this end, one derives in the general case the identity

$$\frac{1}{(2\pi)^{d/2}} \int d^d \mathbf{k} \frac{1}{k^{2s}} k_\alpha f(\mathbf{k}) \exp\left(-\frac{1}{2} \mathbf{k} \cdot \sigma \cdot \mathbf{k}\right) = \frac{1}{\Gamma(s) 2^s} \sum_{\beta=1}^d \int_0^\infty du \frac{u^{s-1}}{\sqrt{\det \mathbf{A}}} A_{\alpha\beta}^{-1} \left\langle \frac{\partial f(\mathbf{k})}{\partial k_\beta} \right\rangle_{\mathbf{A}} \quad (\text{A4})$$

where $\alpha, \beta = 1, 2, \dots, d$ and the function $f(\mathbf{k})$ is a polynomial. The angular brackets in A4 denote a Gaussian momentum average that should be performed with the covariance (in momentum space) \mathbf{A}^{-1} . To obtain this result, (A2) has been inserted and we have changed the integration order. Finally, the following general decomposition rule for the moments of a Gaussian distribution has been used:

$$\langle k_\alpha f(\mathbf{k}) \rangle = \sum_{\beta=1}^d \langle k_\alpha k_\beta \rangle \left\langle \frac{\partial f(\mathbf{k})}{\partial k_\beta} \right\rangle \quad (\text{A5})$$

From (A4) and (A3) the various terms occurring in (19) and (28) can be constructed by a suitable choice of the function $f(\mathbf{k})$.

For odd dimensions d the integrals involved in the functions $\mathbf{H}(\sigma)$ and $\mathbf{K}(\sigma)$ are closely related to elliptic integrals in the form proposed by Carlson³¹ and need to

be evaluated numerically. For this numerical calculation the representation of the hydrodynamic-interaction functions in terms of \mathbf{A} is very useful because in many software libraries there exist fast implementations of elliptic integrals based on Carlson's forms. On the other hand, performing the substitution $t = (1 + u)^{-1/2}$, one arrives at expressions that are more convenient for even dimensions d :

$$\mathbf{H} = \frac{d(d-2)}{d-1} \int_0^1 dt \frac{t^{d-3}}{\sqrt{\det \mathbf{E}}} \left(1 - \frac{1-t^2}{2} \mathbf{E}^{-1}\right) \quad (\text{A6})$$

where we introduced the second-rank tensor $\mathbf{E}(t) = 1 - (1 - \sigma)t^2$. For the function $\mathbf{K}(\sigma)$ one obtains the following representation:

$$K_{\alpha\beta\gamma\delta} = \frac{-(d-2)(d+1)}{d-1} \int_0^1 dt \frac{t^{d-1}}{\sqrt{\det \mathbf{E}}} \left(E_{\alpha\delta}^{-1} E_{\beta\gamma}^{-1} - \frac{1-t^2}{2} (E_{\alpha\beta}^{-1} E_{\gamma\delta}^{-1} + E_{\alpha\gamma}^{-1} E_{\beta\delta}^{-1} + E_{\alpha\delta}^{-1} E_{\beta\gamma}^{-1}) \right) \quad (\text{A7})$$

where $\alpha, \beta, \gamma, \delta = 1, 2, \dots, d$. Equations A6 and A7 constitute the explicit representation of the hydrodynamic-interaction functions $\mathbf{H}(\sigma)$ and $\mathbf{K}(\sigma)$ in a $d \geq 3$ -dimensional space. We have already pointed out that for odd d the integrals contained in the hydrodynamic-interaction functions $\mathbf{H}(\sigma)$ and $\mathbf{K}(\sigma)$ are related to elliptic integrals. If d is even the integrals involved in the representations (A6) and (A7) can be expressed in terms of elementary functions.

B. Explicit First-Order Perturbation-Theory Contributions. In this Appendix we compile explicit expressions for the first-order perturbation-theory expansions in the hydrodynamic-interaction parameter in the presence of steady shear flow for the stress tensor and, therefore, for the shear-rate-dependent viscosity, and first and second normal-stress coefficients for Hookean chains consisting of an arbitrary number of beads. These expressions correspond to eqs A7–A11 in ref 8 for $m = 0$ and are the starting point for RG calculations presented in previous sections.

We first denote the explicit representation of the hydrodynamic-interaction function $\mathbf{H}(\hat{\sigma}_{\mu\nu})$ in d dimensions:

$$\mathbf{H}(\hat{\sigma}_{\mu\nu}) = \frac{d(d-2)}{2(d-1)} \{ [I_{d-3}^{(1)} + I_{d-1}^{(1)} + \lambda_H^2 \dot{\gamma}^2 (2(I_{d-1}^{(1)} + I_{d+1}^{(1)}) \hat{\mathbf{S}}_{\mu\nu}^{(2)} - (I_{d+1}^{(1)} + I_{d+3}^{(1)}) \hat{\mathbf{S}}_{\mu\nu}^{(1)} \hat{\mathbf{S}}_{\mu\nu}^{(1)})] 1 + [I_{d-1}^{(1)} - I_{d+1}^{(1)}] \hat{\mathbf{S}}_{\mu\nu}^{(1)} \lambda_H (\kappa + \kappa^T) + 2[I_{d-1}^{(1)} - I_{d+1}^{(1)}] \hat{\mathbf{S}}_{\mu\nu}^{(2)} \lambda_H^2 \kappa \cdot \kappa^T - [I_{d+1}^{(1)} - I_{d+3}^{(1)}] \hat{\mathbf{S}}_{\mu\nu}^{(1)} \hat{\mathbf{S}}_{\mu\nu}^{(1)} \lambda_H^2 (\kappa + \kappa^T)^2 \} \quad (\text{B1})$$

where $\hat{\sigma}_{\mu\nu}$ and $\hat{\mathbf{S}}_{\mu\nu}^{(m)}$ are defined by (2) and (3), respectively. For reasons that will be clear later we generalize the integrals $I_n^{(1)}$ occurring in (B1) which are functions of the shear rate and the bead numbers μ and ν and define the set of integrals

$$I_n^{(k)}(\mu, \nu, \dot{\gamma}) = \int_0^1 dt \frac{t^n}{\sqrt{\det \mathbf{E}_{\mu\nu}^{2k+1}}} \quad (\text{B2})$$

where n and k are nonnegative integers. Since for steady shear flow $\hat{\sigma}_{\mu\nu}$ is given by (2), the determinant of $\mathbf{E}_{\mu\nu} = 1 - (1 - \hat{\sigma}_{\mu\nu})t^2$ is a generalization of the function $e(\dot{\gamma})$ introduced in ref 7 in connection with the first-order excluded-volume contribution:

$$\det \mathbf{E}_{\mu\nu} = 1 + t^2 (2\hat{\mathbf{S}}_{\mu\nu}^{(2)} - t^2 \hat{\mathbf{S}}_{\mu\nu}^{(1)} \hat{\mathbf{S}}_{\mu\nu}^{(1)}) \lambda_H^2 \dot{\gamma}^2 \quad (\text{B3})$$

The integrals $I_n^{(k)}$ can be reduced by standard methods to

a sum of rational functions of the integrals $I_0^{(0)}, I_2^{(0)}$ (n odd), and $I_1^{(0)}$ (n even). Since the calculation of the $I_n^{(k)}$ in this paper needs to be performed in four dimensions, one can use the reduction formulas from ref 30, eq 2.263.1–3 and 2.264.5–8. The remaining integral $I_1^{(0)}$ may also be found analytically (cf. eq 2.261 in ref 30). Unfortunately, these reduction formulas are valid for nonequilibrium only. Therefore, near equilibrium we use the following expansion of the $I_n^{(k)}$ which can be derived directly from the definition (B2):

$$I_n^{(k)} = \sum_{m=0}^{\infty} \beta_0^{2m} \binom{-k-1/2}{m} \sum_{l=0}^m \binom{m}{l} \frac{(-1)^l}{n+2(m+l)+1} \times h_2^{m-l}(x,y) h_1^{2l}(x,y) \quad (\text{B4})$$

where the limit of large N_0 is already performed. The functions $h_1(x,y)$ and $h_2(x,y)$, which for large values of N_0 are closely related to the matrices $\hat{S}_{\mu\nu}^{(1)}$ and $\hat{S}_{\mu\nu}^{(2)}$, are given by (17) and (18). Notice that at equilibrium ($\beta_0 = 0$) as well as for $\mu = \nu$ the integrals $I_n^{(k)}$ are independent of k and therefore regular:

$$I_n^{(k)}(\mu = \nu, \dot{\gamma} = 0) = \frac{1}{n+1} \quad (\text{B5})$$

This relation is useful in verifying the viscometric functions in the limit of zero shear rate ($\beta_0 = 0$). Performing the long-chain limit ($N_0 \rightarrow \infty$) in (B1), we obtain a representation of \mathbf{H} that was used for the evaluation of the shear-rate dependence of the polymer contribution to the diffusion tensor in section III.A. Notice that by means of the reduction formulas and the expansion (B4) all integrals incorporated into the calculations by the hydrodynamic-interaction function \mathbf{H} can be evaluated analytically in four dimensions. The same is true for integrals incorporated by $\mathbf{K}(\sigma)$.

We now turn to the explicit first-order contributions to the polymer stress tensor due to hydrodynamic interactions. The general result for the consistent-averaging contribution, which is characterized by the hydrodynamic-interaction function $\mathbf{H}(\hat{\sigma}_{\mu\nu})$, can be written in the following form:

$$\begin{aligned} \tau^{\text{p(CA)}} = & \frac{1}{(2\pi)^{d/2}} \frac{nH\zeta_0}{\eta_s} \left(\frac{k_B T}{H} \right)^{\epsilon/2} \sum_{\substack{\mu, \nu=1 \\ \mu \neq \nu}}^{N_0} \frac{(BB^T)_{\mu\nu}}{|\mu - \nu|^{1-(\epsilon/2)}} \times \\ & \{ [I_{d-3}^{(1)} + I_{d-1}^{(1)} + \lambda_H^2 \dot{\gamma}^2 (I_{d+1}^{(1)} + 3I_{d-1}^{(1)}) \hat{S}_{\mu\nu}^{(2)} - \\ & 2I_{d+1}^{(1)} \hat{S}_{\mu\nu}^{(1)} \hat{S}_{\mu\nu}^{(1)} + 4(I_{d-1}^{(1)} - I_{d+1}^{(1)}) \hat{S}_{\mu\nu}^{(1)} (BB^T)_{\mu\nu}] \lambda_H (\kappa + \kappa^T) + \\ & 4(BB^T)_{\mu\nu} [2I_{d-3}^{(1)} + 2I_{d-1}^{(1)} + \lambda_H^2 \dot{\gamma}^2 (7I_{d-1}^{(1)} + I_{d+1}^{(1)}) \hat{S}_{\mu\nu}^{(2)} - \\ & 4I_{d+1}^{(1)} \hat{S}_{\mu\nu}^{(1)} \hat{S}_{\mu\nu}^{(1)} + 4(I_{d-1}^{(1)} - I_{d+1}^{(1)}) \hat{S}_{\mu\nu}^{(1)} (BB^T)_{\mu\nu}] \lambda_H^2 \kappa \cdot \kappa^T + \\ & [I_{d-1}^{(1)} - I_{d+1}^{(1)}] \hat{S}_{\mu\nu}^{(1)} \lambda_H^2 (\kappa + \kappa^T)^2 \} \quad (\text{B6}) \end{aligned}$$

where the $N_0 \times (N_0 - 1)$ matrix B is defined by $B_{\mu j} = j/N_0 - \theta(j - \mu)$ and $\theta(x)$ is the Heaviside step function; i.e., $\theta(x) = 1$ for $x \geq 0$ and $\theta(x) = 0$ for $x < 0$.

Since the representation of the hydrodynamic-interaction function $\mathbf{K}(\hat{\sigma}_{\mu\nu})$ is given by (A7), the first-order contribution of fluctuations in the hydrodynamic interaction to the stress tensor in steady shear flow can be constructed in exactly the same manner as worked out for the consistent-averaging contribution. However, because the expression becomes quite lengthy, we prefer to write

this contribution in the following form:

$$\begin{aligned} \tau^{\text{p(Fluc)}} = & \frac{-1}{(2\pi)^{d/2}} \frac{nH\zeta_0}{\eta_s} \left(\frac{k_B T}{H} \right)^{\epsilon/2} \sum_{\substack{\mu, \nu=1 \\ \mu \neq \nu}}^{N_0} |\mu - \nu|^{\epsilon/2} \{ \hat{R}_{\mu\nu}^{(1)} \cdot \hat{Z}_{\mu\nu} + \\ & 2\lambda_H (\kappa \cdot \hat{R}_{\mu\nu}^{(2)} \cdot \hat{Z}_{\mu\nu} + \hat{R}_{\mu\nu}^{(2)} \cdot \hat{Z}_{\mu\nu} \cdot \kappa^T) + 8\lambda_H^2 \kappa \cdot \hat{R}_{\mu\nu}^{(3)} \cdot \hat{Z}_{\mu\nu} \cdot \kappa^T \}_{\text{sym}} \quad (\text{B7}) \end{aligned}$$

The subscript sym in (B7) indicates that the right-hand side of (B7) must be symmetrized (alternatively, one could symmetrize $\tau^{\text{p(Fluc)}}$ instead). The second-rank tensors $\hat{R}_{\mu\nu}^{(m)}$ ($m = 0, 1, 2, 3, \dots$) and $\hat{Z}_{\mu\nu}$ occurring in (B7) are defined as follows:

$$\hat{R}_{\mu\nu}^{(m)} = (1 - \delta_{m0}) \hat{W}_{\mu\nu}^{(m-1)} \mathbf{1} + 2\lambda_H (\kappa + \kappa^T) \hat{W}_{\mu\nu}^{(m)} + 8\lambda_H^2 \kappa \cdot \kappa^T \hat{W}_{\mu\nu}^{(m+1)} \quad (\text{B8})$$

and

$$\begin{aligned} \hat{Z}_{\mu\nu} = & \frac{1-d}{(d-1)(d+1)} \mathbf{K}(\hat{\sigma}_{\mu\nu}) : \hat{R}_{\mu\nu}^{(0)} = ((2 + \det \hat{\sigma}_{\mu\nu}) \hat{f}_{\mu\nu}^{(d+3)} - \\ & 2\hat{f}_{\mu\nu}^{(d+5)} \cdot \hat{R}_{\mu\nu}^{(0)} + \det \hat{\sigma}_{\mu\nu} (\hat{f}_{\mu\nu}^{(d+5)} - \hat{f}_{\mu\nu}^{(d+3)}) \cdot \hat{R}_{\mu\nu}^{(0)} \cdot \hat{\sigma}_{\mu\nu}^{-1} + (\hat{f}_{\mu\nu}^{(d+1)} - \\ & 2\hat{f}_{\mu\nu}^{(d+3)} + \hat{f}_{\mu\nu}^{(d+5)}) \cdot \hat{R}_{\mu\nu}^{(0)} \cdot \hat{\sigma}_{\mu\nu} - 2\lambda_H^2 \dot{\gamma}^2 [(2\hat{W}_{\mu\nu}^{(1)} (\hat{f}_{\mu\nu}^{(d-1)} - \hat{f}_{\mu\nu}^{(d+1)}) - \\ & \hat{S}_{\mu\nu}^{(1)} \hat{W}_{\mu\nu}^{(0)} (\hat{f}_{\mu\nu}^{(d+1)} - \hat{f}_{\mu\nu}^{(d+3)}) - \hat{S}_{\mu\nu}^{(2)} (\hat{f}_{\mu\nu}^{(d+3)} - \hat{f}_{\mu\nu}^{(d+5)}) \cdot \hat{R}_{\mu\nu}^{(0)})] \quad (\text{B9}) \end{aligned}$$

where the second-rank tensors $\hat{f}_{\mu\nu}^{(n)}$ appearing in (B9) are, for steady shear flow, given by

$$\begin{aligned} \hat{f}_{\mu\nu}^{(n)} = & \int_0^1 dt \frac{t^n}{\sqrt{\det \mathbf{E}_{\mu\nu}}} \mathbf{E}_{\mu\nu}^{-1} = (I_n^{(2)} + (I_{n+2}^{(2)} \hat{S}_{\mu\nu}^{(2)} - \\ & I_{n+4}^{(2)} \hat{S}_{\mu\nu}^{(1)} \hat{S}_{\mu\nu}^{(1)}) \lambda_H^2 \dot{\gamma}^2) \mathbf{1} - I_{n+2}^{(2)} \hat{S}_{\mu\nu}^{(2)} \lambda_H (\kappa + \kappa^T) - \\ & 2I_{n+2}^{(2)} \hat{S}_{\mu\nu}^{(2)} \lambda_H^2 \kappa \cdot \kappa^T + I_{n+4}^{(2)} \hat{S}_{\mu\nu}^{(1)} \hat{S}_{\mu\nu}^{(1)} \lambda_H^2 (\kappa + \kappa^T)^2 \quad (\text{B10}) \end{aligned}$$

and the integrals $I_n^{(k)}$ have been introduced in (B2). Furthermore, one needs the auxiliary matrices $\hat{W}_{\mu\nu}^{(m)}$

$$\hat{W}_{\mu\nu}^{(m)} = \frac{1}{|\mu - \nu|} \sum_{j=\min(\mu, \nu)}^{\max(\mu, \nu)-1} (BC^m)_{\mu j} \quad (\text{B11})$$

Notice that the $\hat{W}_{\mu\nu}^{(m)}$ are regular, not symmetric functions of μ, ν . Both the calculation of the explicit expressions of the $\hat{W}_{\mu\nu}^{(m)}$ ($m = 0, 1, 2, 3, 4$) and the expressions themselves are very lengthy. We have carried out these calculations in the limit $N_0 \rightarrow \infty$. This allows us to rewrite the sum occurring in the definition (B11) and the sums containing in the m th power of the Kramers matrix C_{ij}^m into integrals which have been evaluated analytically. However, we suppose that for $m \geq 3$ it is more convenient first to diagonalize the C_{jk} before evaluating the relevant matrices $\hat{W}_{\mu\nu}^{(m)}$. Notice that the diagonalization of the Kramers matrix corresponds to the introduction of Rouse modes which have been used in the RG study of the polymer stress tensor in ref 35.

Equations B6 to (B11) are the basic results of this Appendix and hold for arbitrary space dimension d . In the special case $d = 4$ we obtain explicit expressions that are needed for the RG calculation of the viscometric functions presented in the previous sections of this paper.

References and Notes

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