Renormalization of various quantities for dilute polymer solutions undergoing shear flow

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We discuss the renormalization of the stress, gyration, and diffusion tensors for polymers in dilute solution in the presence of steady shear flow. For all finite values of the reduced shear rate, the first-order perturbation theory of hydrodynamic-interaction and excluded-volume effects yields regular functions of the renormalized model parameters. In the high-shear-rate limit, the power-law dependence of various quantities on the reduced shear rate can be evaluated explicitly.

I. INTRODUCTION

Renormalization-group (RG) theory is a powerful tool for calculating the properties of polymer solutions.[1-4] Although computational complexity usually makes it necessary to base RG calculations on perturbative methods, the RG predictions for various observable quantities—such as the radius of gyration, the osmotic pressure, and the zero-shear-rate viscosity—are remarkably accurate.

Since the pioneering RG calculations of polymer properties were based on the existence of a formal relationship between the statistical mechanics of long polymer chains and of magnetic systems near their critical points, it is clear why almost only equilibrium properties have up to now been calculated by the RG method. It is the purpose of this paper to discuss the behavior of an infinite number of quantities—among these the stress and gyration tensors—under steady shear flow. In particular, we show that after renormalization of the basic parameters all these quantities are well behaved, and we give explicit results for their shear-rate dependence at high shear rates. Furthermore, we separately discuss the shear-rate-dependent diffusion tensor.

In principle, there exists a widely accepted starting point for the RG calculation of nonequilibrium properties of dilute polymer solutions, namely, a system of coupled Langevin equations for the polymers and the solvent.[5] Since these coupled equations are extremely complicated, the analysis of this paper is based on a diffusion (or Fokker-Planck) equation for the polymers alone which can be derived from the coupled Langevin equations near four dimensions (more precisely, to first order in $\epsilon=4-d$, where d is the space dimensionality).[6-8] The procedure for calculating shear-rate-dependent quantities is then exactly the same as in the conventional polymer kinetic theory[9] based on Kirkwood's diffusion equation except that all calculations need to be performed in d-dimensional space.[10,11]

In Sec. II we present the results of the first-order perturbation theory of hydrodynamic-interaction and excluded-volume effects for an infinite set of shear-rate-dependent quantities in the long-chain limit. These perturbation-theory expressions are then expressed in terms of renormalized parameters (Sec. III), and explicit results are given in the high-shear-rate limit (Sec. IV). Since the renormalization constant for the excluded-volume parameter is not found in the course of eliminating singularities from the quantities studied in this paper, we separately calculate this renormalization constant in order to make it possible to evaluate the fixed-point values of the renormalized model parameters in the presence of shear flow (Sec. V). After calculating also the diffusion tensor for polymers in dilute solutions undergoing shear flow (Sec. VI), we conclude this paper with several remarks.

II. PERTURBATION THEORY FOR LONG CHAINS

The starting point for the discussion of the flow behavior of dilute polymer solutions in this paper is the Rouse model.[12] In that model the polymers are represented by linear chains of N_0 identical, spherical "beads" connected by N_0-1 Hookean "springs." The solvent is modeled by an incompressible, Newtonian fluid which is completely characterized by its viscosity η_s, and it is assumed to undergo homogeneous simple shear flow, that is, the velocity field is of the form $v_1=\dot\gamma r_2$, $v_j=0$ for $j\geq 2$, where $\dot\gamma$ is the shear rate, $\mathbf{v}$ the velocity, and $\mathbf{r}$ the position vector. For homogeneous flows, the internal configuration of a polymer is independent of the location of the center of mass of the chain. The configurations may hence be characterized by the N_0-1 connector vectors $\mathbf{Q}_j$ pointing from bead j to $j+1$ ($j=1,\ldots,N_0-1$).

The Rouse model in which hydrodynamic-interaction and excluded-volume effects are neglected is an exactly solvable model.[12] This model is the starting point for a perturbation theory of the above-mentioned complicated, nonlinear effects.[10,11] Hydrodynamic-interaction effects are described in the Oseen-tensor approximation which can be justified only near four dimensions. The expansion parameter in the perturbation theory of hydrodynamic-interaction effects is $\zeta_0 N_0^{\epsilon/2}$, where ζ_0 is the bead-friction coefficient. The excluded-volume interactions are usually described by a potential-energy contribution $V(\mathbf{r}_\nu-\mathbf{r}_\mu)=k_B T v_0 \delta(\mathbf{r}_\nu-\mathbf{r}_\mu)$ for every pair of beads μ and

ν where k_B is Boltzmann's constant, T the absolute temperature, and v_0 the excluded-volume parameter. The expansion parameter in the perturbation theory of excluded-volume effects is $v_0 N_0^{\epsilon/2}$. The occurrence of the factor $N_0^{\epsilon/2}$ in the above expansion parameters for hydrodynamic-interaction and excluded-volume effects indicates that in discussing the long-chain behavior it is crucial to perform the calculations in $d=4-\epsilon>3$ dimensions.

In the following we study an infinite set of quantities $\mathcal{Q}^{(m)}(m=0,1,\ldots)$, which are defined as follows:

$$\mathcal{Q}^{(m)}=N_0^{1-2m}\sum_{j,k=1}^{N_0-1} C_{kj}^m\langle \mathbf{Q}_j\mathbf{Q}_k\rangle \ , \tag{1}$$

where the angular brackets denote an ensemble average and the $(N_0-1)\times(N_0-1)$ matrix $C_{jk}=\min(j,k)-jk/N_0$ is the usual Kramers matrix[9] (C^m is the mth power of the Kramers matrix). Among the tensors $\mathcal{Q}^{(m)}$ there are several important quantities. The tensor $\mathcal{Q}^{(0)}$ is closely related to the polymer contribution to the stress tensor,

$$\tau^p=-\frac{nH}{N_0}\mathcal{Q}^{(0)} \ , \tag{2}$$

where n is the number density of polymers and H the Hookean spring constant. In (2) and in the remainder of this paper, isotropic contributions to the stress tensor are neglected because they do not contribute to the rheological behavior of incompressible fluids. The quantity $\mathcal{Q}^{(1)}$ is directly observable: $\mathcal{Q}^{(1)}$ is the mean gyration tensor, and its trace is the mean-square radius of gyration.

The perturbation expansion for the quantities $\mathcal{Q}^{(m)}$ in terms of $\zeta_0 N_0^{\epsilon/2}$ and $v_0 N_0^{\epsilon/2}$ can be constructed in exactly the same manner as worked out for the stress tensor in Refs. 10 and 11. The results for chains of arbitrary length are compiled in the Appendix. In the limit of very long chains ($N_0\to\infty$), these perturbation-theory results are found to develop singularities near four dimensions. These singular terms can be explicitly evaluated for all values of m and of the dimensionless quantity

$$\beta_0=\frac{N_0^2\zeta_0}{12H}\dot\gamma \ , \tag{3}$$

which is the Rouse-model result for the reduced shear rate β frequently used in experimental investigations of dilute solutions,

$$\beta=\frac{\eta_p}{nk_BT}\dot\gamma \ , \tag{4}$$

where $\eta_p=-\tau_{12}^p/\dot\gamma$ is the polymer contribution to the viscosity at zero shear rate. Notice that the parameter β_0 involves unobservable, bare model parameters, whereas β is an observable quantity. For $m\geq 1$, one obtains the following result:

$$\begin{aligned}\mathcal{Q}^{(m)}=\frac{k_BT}{H}N_0\left[1+\frac{u_0}{2\pi^2}\left[\frac{1}{\epsilon}+\tfrac{1}{2}\ln\frac{2\pi N_0}{L}\right]\right]\Bigg\{&t_m\mathbf{1}+\left[1+\left[\frac{u_0}{2\pi^2}-\frac{3\xi_0}{8\pi^2}\right]\left[\frac{1}{\epsilon}+\tfrac{1}{2}\ln\frac{2\pi N_0}{L}\right]\right]6t_{m+1}(\hat{\boldsymbol\kappa}_0+\hat{\boldsymbol\kappa}_0^T)\\&+\left[1+2\left[\frac{u_0}{2\pi^2}-\frac{3\xi_0}{8\pi^2}\right]\left[\frac{1}{\epsilon}+\tfrac{1}{2}\ln\frac{2\pi N_0}{L}\right]\right]72t_{m+2}\hat{\boldsymbol\kappa}_0\cdot\hat{\boldsymbol\kappa}_0^T\\&+u_0\boldsymbol{\mathcal{f}}^{(m)}(\beta_0)+\xi_0\boldsymbol{\mathcal{g}}^{(m)}(\beta_0)\Bigg\} \ ,\end{aligned} \tag{5}$$

where the transposed velocity gradient tensor $\hat{\boldsymbol\kappa}_0$ is characterized by the components $\hat\kappa_{0,ij}=\beta_0\delta_{1i}\delta_{2j}$, that is, the shear rate determining the velocity gradients is replaced by the reduced shear rate for the Rouse model, and where the dimensionless friction and excluded-volume parameters ξ_0 and u_0 are defined as usual:[1,2]

$$\xi_0=\frac{\zeta_0}{\eta_s}\left[\frac{k_BT}{H}\right]^{1-(d/2)}L^{\epsilon/2} \ , \tag{6}$$

and

$$u_0=v_0\left[\frac{k_BT}{H}\right]^{-d/2}L^{\epsilon/2} \ . \tag{7}$$

In these equations, L is a dimensionless, phenomenological parameter. One may regard $L^{1/2}$ as the size of a polymer segment which consists of a large number of beads,[10] and ξ_0 and u_0 as the hydrodynamic-interaction and excluded-volume parameters associated with such a segment. The functions $\boldsymbol{\mathcal{f}}^{(m)}(\beta_0)$ and $\boldsymbol{\mathcal{g}}^{(m)}(\beta_0)$ are well behaved (i.e., nonsingular near four dimensions), tensor-valued functions of β_0 alone,

$$\begin{aligned}\boldsymbol{\mathcal{f}}^{(m)}(\beta_0)=&\hat f_1^{(m)}(\beta_0)\mathbf{1}+\hat f_2^{(m)}(\beta_0)(\hat{\boldsymbol\kappa}_0+\hat{\boldsymbol\kappa}_0^T)\\&+\hat f_3^{(m)}(\beta_0)\hat{\boldsymbol\kappa}_0\cdot\hat{\boldsymbol\kappa}_0^T+\hat f_4^{(m)}(\beta_0)(\hat{\boldsymbol\kappa}_0+\hat{\boldsymbol\kappa}_0^T)^2 \ ,\end{aligned} \tag{8}$$

and the function $\boldsymbol{\mathcal{g}}^{(m)}(\beta_0)$ has the same structure. Finally, the number t_m for $m\geq 0$ is closely related to the trace of the mth power of the Kramers matrix, $t_m=\mathrm{Tr}(C^m)/N_0^{2m}$. In the long-chain limit ($N_0\to\infty$), the numbers t_m for $m\geq 1$ are independent of N_0:

$$t_m=\frac{2^{2m-1}}{(2m)!}|B_{2m}| \ , \tag{9}$$

where the B_j are the Bernoulli numbers [see Eqs. (9.71) of Ref. 13]:

$$|B_2|=\tfrac{1}{6},\quad |B_4|=\tfrac{1}{30},\quad |B_6|=\tfrac{1}{42},\quad |B_8|=\tfrac{1}{30} \ . \tag{10}$$

Equation (5) shows the structure of the perturbation-theory result in the long-chain limit. The functions $\mathcal{f}^{(m)}(\beta_0)$ and $\mathcal{g}^{(m)}(\beta_0)$ can be evaluated explicitly from the results compiled in the Appendix.

III. RENORMALIZATION OF THE PERTURBATION-THEORY RESULTS

The $1/\epsilon$ singularities in the first-order perturbation expressions (5) are related to the ambiguity in the definition of the beads. In a RG treatment, these singularities are eliminated by introducing renormalized parameters,

$$N=Z_N N_0/L \ , \tag{11}$$

$$u=Z_u u_0 \ , \tag{12}$$

$$\xi=Z_\xi \xi_0 \ , \tag{13}$$

and by suitably choosing the renormalization constants Z_N, Z_u, and Z_ξ. At equilibrium, the renormalization constants canceling all singularities to first order in ξ and u are well known:[1]

$$Z_N=Z_N(u)=1+\frac{1}{2\pi^2\epsilon}u \ , \tag{14}$$

$$Z_u=Z_u(u)=1-\frac{2}{\pi^2\epsilon}u \ , \tag{15}$$

$$Z_\xi=Z_\xi(\xi,u)=1-\frac{3}{8\pi^2\epsilon}\xi-\frac{1}{2\pi^2\epsilon}u \ . \tag{16}$$

In steady shear flow it is both for experimental and for theoretical investigations very convenient to introduce the reduced shear rate (4). In the presence of hydrodynamic and excluded-volume interactions, the first-order expression for β is

$$\beta=\beta_0\left[1-\frac{3\xi_0}{8\pi^2}\left[\frac{1}{\epsilon}-\frac{7}{9}+\frac{1}{2}\ln\frac{2\pi N_0}{L}\right]+\frac{u_0}{2\pi^2}\left[\frac{1}{\epsilon}-\frac{13}{24}+\frac{1}{2}\ln\frac{2\pi N_0}{L}\right]\right] , \tag{17}$$

where the reduced shear rate for the Rouse model, β_0, was defined in (3). As can be seen from (4), the factor in square brackets results directly from the bare first-order perturbation expression for the polymer contribution to the zero-shear-rate viscosity.[1,11] The reduced shear rate β corresponds to the parameter $w\propto\dot\gamma N^{\nu d}$ introduced in the discussion of Ref. 7 (see also Ref. 2) as the natural parameter describing the effect of shear flow on the polymers (here, ν is the well-known exponent characterizing the chain-length dependence of the size of a single polymer).

After introducing the renormalized parameters N,ξ,u, and the observable reduced shear rate β into (5) and keeping only first-order terms in ξ and u, one obtains for $m\geq 1$:

$$\mathcal{Q}^{(m)}=L\frac{k_BT}{H}N\left[1+\frac{u}{4\pi^2}\ln(2\pi N)\right]\{[1-uf_1^{(m)}(\beta)+\xi g_1^{(m)}(\beta)]t_m 1+[1-uf_2^{(m)}(\beta)+\xi g_2^{(m)}(\beta)]6t_{m+1}(\hat\kappa+\hat\kappa^T)$$
$$+[1-uf_3^{(m)}(\beta)+\xi g_3^{(m)}(\beta)]72t_{m+2}\hat\kappa\cdot\hat\kappa^T+[uf_4^{(m)}(\beta)-\xi g_4^{(m)}(\beta)](\hat\kappa+\hat\kappa^T)^2\} \ , \tag{18}$$

where $f_j^{(m)}(\beta)$ and $g_j^{(m)}(\beta)$ are well-behaved functions of β and the tensor $\hat\kappa$ corresponds to $\hat\kappa_0$ with β_0 replaced by β, that is, $\hat\kappa_{ij}=\beta\delta_{1i}\delta_{2i}$. From (18) it is clear that after introducing the renormalized parameters into the first-order perturbation results, all quantities $\mathcal{Q}^{(m)}$ for $m\geq 1$ are regular functions of N, ξ, u, and β. It is important to notice that the renormalization constants (14) and (16) required for eliminating the $1/\epsilon$ singularities are not affected by shear flow (for finite values of the reduced shear rate β). The definition (1) of $\mathcal{Q}^{(m)}$ has been chosen such that no renormalization of $\mathcal{Q}^{(m)}$ is necessary for $m\geq 1$.

We have so far discussed only the quantities $\mathcal{Q}^{(m)}$ for $m\geq 1$. However, according to (2), $\mathcal{Q}^{(0)}$ is related to the stress tensor and hence is a very interesting quantity, too. For $m=0$, there are additional singular terms in the excluded-volume contributions to $\mathcal{Q}^{(0)}$ (see Appendix). These additional singularities can be accounted for by omitting the first factor in square brackets on the right-hand side of (5) (except for an irrelevant, isotropic contribution to the stress tensor). Notice, however, that $\mathcal{Q}^{(0)}$ is not an observable quantity and that, for the experimentally accessible stress tensor, Eq. (2) implies that the prefactor $(k_BT/H)N_0$ in (5) depending on the arbitrary definition of the beads is replaced by the observable factor $-nk_BT$. For $m=0$, one therefore finds, instead of (18),

$$\tau^p=-nk_BT\{[1-uf_2^{(0)}(\beta)+\xi g_2^{(0)}(\beta)]6t_1(\hat\kappa+\hat\kappa^T)+[1-uf_3^{(0)}(\beta)+\xi g_3^{(0)}(\beta)]72t_2\hat\kappa\cdot\hat\kappa^T+[uf_4^{(0)}(\beta)-\xi g_4^{(0)}(\beta)](\hat\kappa+\hat\kappa^T)^2\} \ . \tag{19}$$

According to (19), the stress tensor for long chains is a function of ξ, u, and β only—independent of the chain length N. This does not imply that the viscometric functions are independent of N because these material functions are obtained by dividing certain components of the stress tensor by the shear rate $\dot\gamma$ (or $\dot\gamma^2$) rather than by the reduced shear rate β. One hence finds for the molecular-weight dependence of the polymer contribution to the viscosity and of the normal-stress coefficients at arbitrary reduced shear rates $\eta_p(\beta)\propto N^{\nu d}$ and $\Psi_j(\beta)\propto N^{2\nu d}(j=1,2)$, respectively.

In the standard RG treatment, the factors of the form $[1-uf_j^{(m)}(\beta)+\xi g_j^{(m)}(\beta)]$ occurring in (18) and (19) are usually exponentiated, that is, replaced with

$\exp[-uf_j^{(m)}(\beta)+\xi g_j^{(m)}(\beta)]$ in order to obtain expressions consistent with general scaling laws.[1-3]

IV. HIGH-SHEAR-RATE LIMIT

Calculation of the functions $f_j^{(m)}(\beta)$ and $g_j^{(m)}(\beta)$ occurring in (18) and (19) for arbitrary β from the first-order perturbation results compiled in the Appendix is in general a very complicated problem that can be solved only numerically.[14] In the high-shear-rate limit, however, these functions can be calculated analytically.

The key observation for discussing the high-shear-rate limit is that the dominating contributions in (18) and (19) come from pairs of beads μ and ν with $|\mu-\nu|/N_0 \approx \beta^{-2}$ (in discussing the first-order correction terms in u and ξ, there is no need to distinguish between β and β_0). For smaller values of $|\mu-\nu|$, that is, for more local effects, a finite reduced shear rate β constitutes only a negligible perturbation of the equilibrium situation; for larger values of $|\mu-\nu|$, the corresponding beads are so far separated that excluded-volume and hydrodynamic interactions are suppressed. A detailed calculation confirms the above observation and shows that the high-shear-rate behavior is obtained by subtracting a term $(\ln\beta_0)$ from each $[\frac{1}{2}\ln(2\pi N_0/L)]$ in (5). One hence obtains for large β after renormalization and exponentiation of the first-order perturbation expression,

$$\mathcal{Q}^{(m)}=L\frac{k_BT}{H}N\left(\frac{2\pi N}{\beta^2}\right)^{2\nu-1}[t_m\mathbf{1}+\beta^x 6t_{m+1}(\hat{\boldsymbol{\kappa}}+\hat{\boldsymbol{\kappa}}^T) +\beta^{2x}72t_{m+2}\hat{\boldsymbol{\kappa}}\cdot\hat{\boldsymbol{\kappa}}^T +O(\epsilon)(\hat{\boldsymbol{\kappa}}+\hat{\boldsymbol{\kappa}}^T)^2], \tag{20}$$

with

$$\nu=\frac{1}{2}+\frac{u^*}{8\pi^2},\quad x=\frac{3\xi^*}{8\pi^2}-\frac{u^*}{2\pi^2}, \tag{21}$$

where ξ^* and u^* are the fixed-point values of ξ and u which govern the long-chain behavior.

Equation (20) holds only for $m\geq 1$. For $m=0$, the stress tensor is from (19) found by an analogous procedure to be

$$\boldsymbol{\tau}^p=-nk_BT[\beta^x 6t_1(\hat{\boldsymbol{\kappa}}+\hat{\boldsymbol{\kappa}}^T)+\beta^{2x}72t_2\hat{\boldsymbol{\kappa}}\cdot\hat{\boldsymbol{\kappa}}^T +O(\epsilon)(\hat{\boldsymbol{\kappa}}+\hat{\boldsymbol{\kappa}}^T)^2]. \tag{22}$$

The finite corrections to the leading-order $\ln\beta_0$ behavior in the perturbation results, of course, lead after exponentiation to prefactors of order 1 multiplying the power-law terms in β in (20) and (22).

In particular, we obtain for the high-shear-rate behavior of the polymer contribution to the viscosity and of the first normal-stress coefficient,

$$\eta_p\propto\beta^x,\quad \Psi_1\propto\beta^{2x}. \tag{23}$$

The exponent x is evaluated in Sec. V.

After discussing the high-shear-rate limit in this section, we must point out that (at least) two effects that might be important at high shears rates are neglected in the model underlying the calculations of this paper: (i) the inertia of the beads and (ii) the flow modification of hydrodynamic interactions. To discuss the relevance of these two effects it is important to note that in studying the "high-shear-rate limit" we have considered large, finite values of the reduced shear rate. Even if the reduced shear rate β which describes the effect of the flow on the polymers on the scale of the polymer size is large, the shear rate $\dot{\gamma}$ for long chains is very small [notice that η_p in (4) is proportional to $N^{\nu d}$]. To estimate the effect of shear flow on a local scale, one has to make $\dot{\gamma}$ dimensionless by multiplying it with the time scale for the corresponding local dynamics that is independent of the chain length N and hence small compared to β. In other words, for finite β the effect of shear flow on any local scale vanishes in the long-chain limit. For the small shear rates $\dot{\gamma}$ considered here, even in the discussion of the large-β limit, bead-inertia effects should hence be of roughly the same order as at equilibrium and should thus be negligible (for a detailed discussion of the effect of bead inertia on the viscometric functions for the Rouse model, see Ref. 15). Even if the concept of hydrodynamic-interaction tensors, which relies on the linearization of the Navier-Stokes equation for perturbations of the solvent flow field, is assumed to be reasonable, hydrodynamic interactions are affected by the imposed homogeneous flow field.[16] Although it is difficult to determine the importance of this flow modification of the Oseen tensor in a rigorous manner, rough estimates based on Ref. 7 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.

V. RENORMALIZATION OF THE EXCLUDED-VOLUME PARAMETER

In order to evaluate the exponents ν and x occurring in (20), one needs to calculate the fixed-point values ξ^* and u^* in shear flow. These values are to be determined as those particular values of ξ and u for which $Z_\xi=Z_u=0$. The analysis of the preceding sections shows that Z_N and Z_ξ are not affected by shear flow (for finite β). However, since u_0 does not occur in the zeroth-order (or Rouse) expressions for the quantities studied in this paper, u_0 may simply be replaced by u in the first-order perturbation corrections and the renormalization constant Z_u in shear flow remains undetermined. In order to evaluate Z_u we follow Ref. 1 and use the following expression for the renormalization constant at equilibrium as a starting point for our discussion:

$$Z_u(u)=1-\frac{u}{(2\pi)^4\epsilon}\lim_{\epsilon\to 0}\epsilon\int_0^a dx\int_0^a dy\int d^dk\,4\tilde{G}_0(x,\mathbf{k})\times\tilde{G}_0(y,\mathbf{k}), \tag{24}$$

where $\tilde{G}_0(x,\mathbf{k})$ is the Fourier-transformed Rouse distribution for two segments separated by $x=|\mu-\nu|$ along the chain [here, the Fourier variable $\mathbf{k}$ is made dimensionless by means of the length scale $(k_BT/H)^{1/2}$]. The limit $\epsilon\to 0$ is introduced to extract the singular part in an

unambiguous manner [in a more rigorous notation, one should introduce ϵ' and $d'=4-\epsilon'$ under the limit in (24) and let ϵ' go to zero]. Since only the singular part of the integrals is relevant, the result should be independent of the parameter a which characterizes the maximum size of self-interaction loops (a should be small compared to the number of beads, N_0).

At equilibrium, one has

$$\tilde{G}_0(x,\mathbf{k})=\exp(-\tfrac{1}{2}xk^2)\ , \tag{25}$$

and the integrals and limit in the above expression for the renormalization constant can easily be performed to reproduce (15). In the presence of shear flow, one has to replace $\tilde{G}_0(x,\mathbf{k})$ by $\tilde{G}_0(\sigma,x,\mathbf{k})$ which depends also on the position $\sigma\in[0,N_0]$ of the small loop within the chain (and, of course, on the shear rate). For the Rouse model one has

$$\tilde{G}_0(\sigma,x,\mathbf{k})=\exp[-\tfrac{1}{2}\mathbf{k}\cdot\mathcal{M}(\sigma,x)\cdot\mathbf{k}]\ , \tag{26}$$

with

$$\mathcal{M}(\sigma,x)=x\,1+\frac{6x^2}{N_0}s(1-s)(\hat{\boldsymbol{\kappa}}_0+\hat{\boldsymbol{\kappa}}_0^T)+\frac{24x^2}{N_0}s^2(1-s)^2\hat{\boldsymbol{\kappa}}_0\cdot\hat{\boldsymbol{\kappa}}_0^T\ , \tag{27}$$

and $s=\sigma/N_0$. As a consequence of the dependence of small loop contributions on their position within the chain, one has to replace $4\tilde{G}_0(x,\mathbf{k})\tilde{G}_0(y,\mathbf{k})$ in the expression (24) for Z_u with $2\tilde{G}_0(\sigma,x,\mathbf{k})\tilde{G}_0(\tau,y,\mathbf{k})+\tilde{G}_0(\sigma,x,\mathbf{k})\tilde{G}_0(\sigma,y,\mathbf{k})+\tilde{G}_0(\tau,x,\mathbf{k})\tilde{G}_0(\tau,y,\mathbf{k})$ [cf. the diagrams on p. 336 of Oono's review article (Ref. 1)]. The renormalization factor in shear flow might hence in principle depend on the positions σ and τ of the beads ($\sigma,\tau\in[0,N_0]$) between which the renormalized excluded-volume interaction is considered.

To obtain Z_u one has to calculate integrals of the form

$$\int d^dk\ \tilde{G}_0(\sigma,x,\mathbf{k})\tilde{G}_0(\tau,y,\mathbf{k})=\frac{4\pi^2}{\sqrt{\det[\mathcal{M}(\sigma,x)+\mathcal{M}(\tau,y)]}}\ . \tag{28}$$

With the above expression for $\mathcal{M}(\sigma,x)$, one obtains

$$\det[\mathcal{M}(\sigma,x)+\mathcal{M}(\tau,y)]=(x+y)^d+\frac{24\beta_0^2}{N_0}(x+y)^{d-1}\times[x^2s^2(1-s)^2+y^2t^2(1-t)^2]-\frac{36\beta_0^2}{N_0^2}(x+y)^{d-2}[x^2s(1-s)+y^2t(1-t)]^2\ . \tag{29}$$

For fixed β_0, the limit $N_0\to\infty$ should be performed first, and afterwards the limit $\epsilon\to0$ should be carried out. The correction terms containing β_0 in (29) disappear for $N_0\to\infty$. This expresses merely the fact that, *on the local scale* of self-interaction loops, every finite reduced shear rate corresponds to *weak shear flow*. Therefore, the renormalization constant Z_u is not affected by shear flow. In particular, it is independent of the positions σ and τ of the interacting beads within the chain. Our result for Z_u seems to conflict with a very recent note,[17] which arrives at the conclusion that steady shear flow induces a crossover from a self-avoiding-walk fixed point with $\nu=0.59$ to a new, strong-shear fixed point with classical exponent $\nu=\frac{1}{2}$ and $u^*=0$. In Ref. 17, however, the shear rate $\dot{\gamma}$ describing the effect of shear flow on a local scale is kept constant (see the discussion at the end of Sec. IV). In performing a large number of iterated rescalings and going to increasingly larger spatial scales, in Ref. 17, the effect of shear flow becomes more and more important; the parameter characterizing the strength of the shear flow on the polymer scale (which is the reduced shear rate β) is infinitely large when the shear rate $\dot{\gamma}$ is kept constant and the long-chain limit is considered [cf. (4)]. For the finite (but possibly large) reduced shear rates β assumed in this paper, the shear rate $\dot{\gamma}$ in the long-chain limit has to go to zero and the discussion of Ref. 17 is not applicable.

Since neither Z_ξ nor Z_u is affected by steady shear flow with finite reduced shear rate, the fixed-point values ξ^* and u^* are also unaffected by shear flow,

$$u^*=\frac{\pi^2\epsilon}{2},\quad \xi^*=2\pi^2\epsilon\ . \tag{30}$$

For the exponents ν and x introduced in Sec. IV we hence obtain

$$\nu=\frac{1}{2}+\frac{\epsilon}{16},\quad x=\frac{\epsilon}{2}\ . \tag{31}$$

The exponent ν is the usual end-to-end-distance exponent in the presence of excluded-volume interactions. The exponent x governs, for example, the shear-rate dependence of the polymer contribution to the viscosity and the first normal-stress coefficient at high shear rates [cf. (23)]. The observation that the linear combination of ξ^* and u^* in the expression for x in (21) results directly from the occurrence of the same linear combination in the first-order perturbation expression for the viscosity [cf. (17)] suggests writing the exponent x as $x=4-2\nu d$. Notice that the exponent x is positive and thus describes shear thickening at high shear rates. This shear-thickening phenomenon arises because hydrodynamic interactions are partially switched off when the polymers become more and more 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 only partial and persists to arbitrarily high reduced shear rates. Notice, however, that the excluded-volume contribution to the exponent x is negative.[11] A positive exponent x is at variance with a prediction based on a blob argument.[18] In our detailed calculation summarized in the Appendix, the scale in which shear becomes relevant for the suppression of hydrodynamic interactions ($|\mu-\nu|\approx N_0/\beta^2$) is much smaller than the size of the blobs in Ref. 18 ($|\mu-\nu|\approx N_0/\beta^{1/(\nu d)}$).[19]

VI. DIFFUSION TENSOR

In the presence of a homogeneous flow field $\mathbf{v}(\mathbf{r})=\boldsymbol{\kappa}\cdot\mathbf{r}$ (for shear flow, one has $\kappa_{ij}=\dot{\gamma}\delta_{1i}\delta_{2j}$), the diffusive prop-

erties of polymers depend on the direction relative to the characteristic directions of the flow field and hence need to be characterized by a diffusion tensor rather than by a scalar diffusion coefficient. A possible definition of the diffusion tensor $\mathcal{D}$ is related to the average velocity of the center of mass, $\mathbf{r}_{\text{c.m.}}$ caused by an external force $\mathbf{F}^e$ (cf. Refs. 20–22),

$$\frac{d}{dt}\langle \mathbf{r}_{\text{c.m.}} \rangle = \boldsymbol{\kappa}\cdot\langle \mathbf{r}_{\text{c.m.}} \rangle + \frac{1}{k_B T}\mathcal{D}\cdot\mathbf{F}^e \ . \tag{32}$$

The diffusion tensor $\mathcal{D}$ can be calculated by falling back upon Kirkwood's diffusion equation which characterizes the time evolution of all bead-position vectors and hence also of the center-of-mass position. After keeping only first-order perturbation corrections to the corresponding Rouse result, one finds

$$\mathcal{D} = \frac{k_B T}{\zeta_0 N_0}\left[1 + \frac{1}{N_0}\sum_{\substack{\mu,\nu=1 \\ \mu\neq\nu}}^{N_0}\langle \zeta_0 \boldsymbol{\Omega}_{\mu\nu}\rangle\right] , \tag{33}$$

where $\boldsymbol{\Omega}_{\mu\nu}$ is the d-dimensional Oseen tensor describing the hydrodynamic interactions between beads μ and ν.[1] Since in (33) averaging is only required in the perturbation contribution, the averages of the Oseen tensors may be performed with the Gaussian Rouse distribution and are hence closely related to the hydrodynamic-interaction function $\mathcal{H}$ defined in the Appendix. For steady shear flow, one can write

$$\mathcal{D} = \frac{k_B T}{\zeta_0 N_0}\left[1 + \frac{3\xi_0}{8\pi^2}\left(\frac{1}{\epsilon} - \frac{1}{12} + \frac{1}{2}\ln\frac{2\pi N_0}{L}\right)\right]\left[1 + \frac{3\xi_0}{32\pi^2}\int_0^1 dx \int_0^1 dy \frac{\mathcal{H}(1 + h_1(x,y)(\hat{\boldsymbol{\kappa}}_0 + \hat{\boldsymbol{\kappa}}_0^T) + h_2(x,y)\hat{\boldsymbol{\kappa}}_0\cdot\hat{\boldsymbol{\kappa}}_0^T) - 1}{|x-y|}\right] , \tag{34}$$

where the hydrodynamic-interaction function $\mathcal{H}$ may be evaluated in four dimensions and the functions $h_1(x,y)$ and $h_2(x,y)$ are closely related to the matrices $\hat{S}^{(1)}_{\mu\nu}$ and $\hat{S}^{(2)}_{\mu\nu}$ introduced in the Appendix:[11]

$$h_1(x,y) = 3|x-y|[(x+y) - \tfrac{1}{3}|x-y| - \tfrac{1}{2}(x+y)^2] , \tag{35}$$

$$h_2(x,y) = 3|x-y|[\tfrac{1}{5}|x-y|^3 - 3(x^3+y^3) - 5xy(x+y) + (x+y)^2(x^2+y^2+2)] . \tag{36}$$

Notice that the double integral in (34) is convergent because for $|x-y| \to 0$ the functions h_1 and h_2 and hence also the numerator of the integrand are of order $|x-y|$.

At equilibrium ($\hat{\boldsymbol{\kappa}}_0 = \mathbf{0}$), the integrand of the double integral in (34) vanishes due to the normalization $\mathcal{H}(\mathbf{1}) = \mathbf{1}$, and the diffusion tensor is hence isotropic and reproduces the well-known equilibrium diffusion coefficient.[2] For arbitrary values of the reduced shear rate, the $1/\epsilon$ singularity in (34) is canceled after introducing the renormalized parameters N and ξ formed with the equilibrium renormalization constants (14) and (16),

$$\mathcal{D} = \frac{k_B T}{\eta_s}\left[L\frac{k_B T}{H}\right]^{1-(d/2)}\frac{1}{\xi N}\left[1 + \frac{3\xi}{16\pi^2}(\ln 2\pi N - \tfrac{1}{6})\mathbf{1} + \frac{3\xi}{32\pi^2}\int_0^1 dx \int_0^1 dy \frac{\mathcal{H}(1 + h_1(x,y)(\hat{\boldsymbol{\kappa}} + \hat{\boldsymbol{\kappa}}^T) + h_2(x,y)\hat{\boldsymbol{\kappa}}\cdot\hat{\boldsymbol{\kappa}}^T) - 1}{|x-y|}\right] . \tag{37}$$

Equation (37) is the final, renormalized, first-order perturbation-theory result for the diffusion tensor in steady shear flow. For $\hat{\boldsymbol{\kappa}} \neq \mathbf{0}$, the double integral in this equation must be evaluated numerically.[14] The high-shear-rate limit for the diffusion tensor can be discussed in the same way as for the quantities $\mathcal{Q}^{(m)}$ in Sec. IV. In this limit, the diffusion tensor

$$\mathcal{D} \propto \frac{1}{N}\left[\frac{N}{\beta^2}\right]^{3\epsilon/8}\mathbf{1} , \tag{38}$$

becomes isotropic and follows a power-law dependence both on molecular weight and on reduced shear rate. For a fixed reduced shear rate, the molecular-weight dependence of the diffusion tensor can to first order in ϵ be rewritten in the more familiar form $\mathcal{D} \propto N^{-(d-2)\nu}\mathbf{1}$.

VII. CONCLUDING REMARKS

We have shown explicitly that in steady shear flow the first-order perturbation theory of hydrodynamic-interaction and excluded-volume effects for the stress, gyration, and diffusion tensors (and an infinite set of further quantities) yields well-behaved expressions in terms of the renormalized model parameters. All the above quantities are regular functions of the chain length N, the friction coefficient ξ, the excluded-volume parameter u, and the reduced shear rate β. All renormalization constants are found to be independent of the reduced shear rate. For high shear rates, the various quantities exhibit a power-law dependence on the reduced shear rate, and the corresponding exponents have been calculated analytically to first order in $\epsilon = 4-d$. The resulting exponents indicate that the decrease of hydrodynamic interactions leads to shear thickening for the viscosity at high shear rates. For intermediate shear rates, the various universal material functions introduced in this paper need to be evaluated by numerical methods.[14]

The starting point for the discussion in this paper was Kirkwood's diffusion equation for the polymers generalized to d-dimensional space. In that approach, hydrodynamic interactions are described in the Oseen-tensor

approximation which, near equilibrium, can be justified to first order in ϵ. We here assume that the Oseen tensor yields a reasonable description of the polymer dynamics also at high shear rates, and we hence neglect the flow modification of the Oseen tensor.[16] We furthermore neglect the effect of bead inertia. The limitations resulting from neglecting the above-mentioned effects should be investigated in more detail, and a more systematic calculation based on the coupled Langevin equations for polymers and solvent[5] would certainly be desirable. However, calculations of the viscometric functions based on the coupled Langevin equations are very complicated even in cases where approximations are made that imply that the results must be equivalent to those obtained by the approach employed in this paper.[23]

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APPENDIX

For the quantities $\mathcal{Q}^{(m)}$ $(m \geq 0)$ defined in (1), the first-order contributions in the excluded-volume and hydrodynamic-interaction parameters, $\mathcal{Q}_{\rm EV}^{(m)}$ and $\mathcal{Q}_{\rm HI}^{(m)}$, respectively, are summarized in this appendix. These corrections are to be added to the corresponding Rouse expression,

$$\mathcal{Q}_R^{(m)} = N_0^{1-2m}\frac{k_B T}{H}[1\,\mathrm{Tr}(C^m) + 2\lambda_H(\boldsymbol{\kappa}+\boldsymbol{\kappa}^T)\mathrm{Tr}(C^{m+1}) + 8\lambda_H^2 \boldsymbol{\kappa}\cdot\boldsymbol{\kappa}^T \mathrm{Tr}(C^{m+2})] , \tag{A1}$$

where C is the Kramers matrix, $\boldsymbol{\kappa}$ is the transposed velocity gradient tensor for steady shear flow, and $\lambda_H = \zeta_0/(4H)$ is the basic time constant. The results for $\mathcal{Q}_{\rm EV}^{(m)}$ and $\mathcal{Q}_{\rm HI}^{(m)}$ presented below are straightforward generalizations of the first-order perturbation theory for the stress tensor developed in Refs. 10 and 11.

We first present the excluded-volume contribution. The general result for $m \geq 0$ can be written in the following form:

$$\begin{aligned}
\mathcal{Q}_{\rm EV}^{(m)} = {} & \frac{v_0 N_0^{1-2m}}{2^{m+1}\sqrt{(2\pi)^d}}\left[\frac{k_B T}{H}\right]^{(\epsilon/2)-1} \\
& \times \sum_{\substack{\mu,\nu=1 \\ \mu\neq\nu}}^{N_0} \frac{1}{|\mu-\nu|^{2-(\epsilon/2)}\sqrt{e_{\mu\nu}(\dot\gamma)^3}} \\
& \times \{[\hat S_{\mu\nu}^{(0)}\hat S_{\mu\nu}^{(m)} + \lambda_H^2\dot\gamma^2(2\hat S_{\mu\nu}^{(2)}\hat S_{\mu\nu}^{(m)} - \hat S_{\mu\nu}^{(1)}\hat S_{\mu\nu}^{(1)}\hat S_{\mu\nu}^{(m)})]1 \\
& + [2\hat S_{\mu\nu}^{(0)}\hat S_{\mu\nu}^{(m+1)} - \hat S_{\mu\nu}^{(1)}\hat S_{\mu\nu}^{(m)} + \lambda_H^2\dot\gamma^2(3\hat S_{\mu\nu}^{(2)}\hat S_{\mu\nu}^{(m+1)} - 2\hat S_{\mu\nu}^{(1)}\hat S_{\mu\nu}^{(1)}\hat S_{\mu\nu}^{(m+2)})]\lambda_H(\boldsymbol{\kappa}+\boldsymbol{\kappa}^T) \\
& + [3\hat S_{\mu\nu}^{(0)}\hat S_{\mu\nu}^{(m+2)} - \hat S_{\mu\nu}^{(1)}\hat S_{\mu\nu}^{(m+1)} - \hat S_{\mu\nu}^{(2)}\hat S_{\mu\nu}^{(m)} + \lambda_H^2\dot\gamma^2(3\hat S_{\mu\nu}^{(2)}\hat S_{\mu\nu}^{(m+2)} - 2\hat S_{\mu\nu}^{(1)}\hat S_{\mu\nu}^{(m+3)})]2\lambda_H^2\boldsymbol{\kappa}\cdot\boldsymbol{\kappa}^T \\
& + (\hat S_{\mu\nu}^{(1)}\hat S_{\mu\nu}^{(1)}\hat S_{\mu\nu}^{(m)} - \hat S_{\mu\nu}^{(1)}\hat S_{\mu\nu}^{(m+1)})\lambda_H^2(\boldsymbol{\kappa}+\boldsymbol{\kappa}^T)^2\} ,
\end{aligned} \tag{A2}$$

where

$$e_{\mu\nu}(\dot\gamma) = 1 + (2\hat S_{\mu\nu}^{(0)}\hat S_{\mu\nu}^{(2)} - \hat S_{\mu\nu}^{(1)}\hat S_{\mu\nu}^{(1)})\lambda_H^2\dot\gamma^2 , \tag{A3}$$

and the matrices

$$\hat S_{\mu\nu}^{(m)} = \frac{2^m}{|\mu-\nu|}\sum_{j,k=\min(\mu,\nu)}^{\max(\mu,\nu)-1} C_{jk}^m \tag{A4}$$

are equal to the matrices $S_{\mu\nu}^{(m)}$ defined in Eq. (18) of Ref. 11 divided by $|\mu-\nu|$. Since the matrices $\hat S_{\mu\nu}^{(m)}$ for $m \geq 1$ contain a further factor of $|\mu-\nu|$ (at least in the long-chain limit), the only terms in (A2) which lead to $1/\epsilon$ singularities near four dimensions are those terms consisting of two factors $\hat S$, one of which with superscript "(0)" (notice that $\hat S_{\mu\nu}^{(0)} = 1$).

Notice that from (A2) one can conclude that the quantity $2\lambda_H(\boldsymbol{\kappa}\cdot\mathcal{Q}_{\rm EV}^{(1)} + \mathcal{Q}_{\rm EV}^{(1)}\cdot\boldsymbol{\kappa}^T)$ is equal to the nonisotropic part of $\mathcal{Q}_{\rm EV}^{(0)}$. One therefore has a close relationship between the excluded-volume contributions to the gyration tensor and to the viscometric functions. This relationship which may be used to calculate the equilibrium radius of gyration from the excluded-volume contribution to the zero-shear-rate viscosity is closely related to the validity of the Giesekus expression for the stress tensor in the absence of hydrodynamic interactions.[9]

For conveniently presenting the hydrodynamic-interaction contribution $\mathcal{Q}_{\rm HI}^{(m)}$ it is necessary to introduce the hydrodynamic-interaction functions $\mathcal{H}(\boldsymbol{\sigma})$ and $\mathcal{K}(\boldsymbol{\sigma})$. Both the argument and the values of the function $\mathcal{H}(\boldsymbol{\sigma})$ are second-rank tensors:

$$\mathcal{H}(\vec\sigma) = \frac{1}{\sqrt{(2\pi)^d}}\frac{d(d-2)}{d-1}\int d^d k \frac{1}{k^2}\left[1 - \frac{\mathbf{k}\mathbf{k}}{k^2}\right] \times \exp(-\tfrac{1}{2}\mathbf{k}\cdot\boldsymbol{\sigma}\cdot\mathbf{k}) . \tag{A5}$$

The self-consistently averaged hydrodynamic interactions in d dimensions are described by this function $\mathcal{H}(\boldsymbol{\sigma})$, whereas the fluctuations in the hydrodynamic interactions are closely related to the fourth-rank tensors $\mathcal{K}(\boldsymbol{\sigma})$:[10]

$$\mathcal{H}(\sigma)=\frac{-1}{\sqrt{(2\pi)^d}}\frac{(d-2)(d+1)}{d-1}\int d^dk\frac{1}{k^2}\mathbf{k}\left[1-\frac{\mathbf{kk}}{k^2}\right]\mathbf{k}\times\exp\left[-\tfrac{1}{2}\mathbf{k}\cdot\boldsymbol{\sigma}\cdot\mathbf{k}\right]. \tag{A6}$$

In these definitions, the d-dependent prefactors have been chosen in the same way as in Ref. 10; most of these d-dependent factors are canceled in the expression for $\mathcal{Q}_{\rm HI}^{(m)}$ given below [cf. (A8)]. With these hydrodynamic-interaction functions the contribution $\mathcal{Q}_{\rm HI}^{(m)}$ can be written as

$$\mathcal{Q}_{\rm HI}^{(m)}=N_0^{1-2m}[\mathcal{C}^{(m+1)}+2\lambda_H(\boldsymbol{\kappa}\cdot\mathcal{C}^{(m+2)}+\mathcal{C}^{(m+2)}\cdot\boldsymbol{\kappa}^T)+8\lambda_H^2\boldsymbol{\kappa}\cdot\mathcal{C}^{(m+3)}\cdot\boldsymbol{\kappa}^T], \tag{A7}$$

where the tensors $\mathcal{C}^{(m)}$ for $m\geq 1$ are defined as follows:

$$\mathcal{C}^{(m)}=-\frac{(d-1)\zeta_0}{d(d-2)\sqrt{(2\pi)^d}\eta_s}\left[\frac{k_BT}{H}\right]^{\epsilon/2}\sum_{\substack{\mu,\nu=1\\ \mu\neq\nu}}^{N_0}\left\{\hat{\mathcal{P}}_{\mu\nu}^{(m)}\cdot\frac{\mathcal{H}(\hat{\boldsymbol{\sigma}}_{\mu\nu})}{|\mu-\nu|^{1-(\epsilon/2)}}+\frac{d}{d+1}|\mu-\nu|^{\epsilon/2}\hat{\mathcal{R}}_{\mu\nu}^{(m)}\cdot\mathcal{H}(\hat{\boldsymbol{\sigma}}_{\mu\nu}):\hat{\mathcal{R}}_{\mu\nu}^{(0)}\right\}_{\rm sym}. \tag{A8}$$

The subscript "sym" in the last equation indicates that the right-hand side of (A8) must be symmetrized because the tensors $\mathcal{C}^{(m)}$ should be symmetric [alternatively, one could use nonsymmetrized tensors $\mathcal{C}^{(m)}$ and symmetrize the tensors $\mathcal{Q}_{\rm HI}^{(m)}$ resulting from (A7)]. The tensors $\hat{\boldsymbol{\sigma}}_{\mu\nu}$, $\hat{\mathcal{P}}_{\mu\nu}^{(m)}$, and $\hat{\mathcal{R}}_{\mu\nu}^{(m)}$ occurring in (A8) are defined as follows:

$$\hat{\boldsymbol{\sigma}}_{\mu\nu}=1+\lambda_H(\boldsymbol{\kappa}+\boldsymbol{\kappa}^T)\hat{S}_{\mu\nu}^{(1)}+2\lambda_H^2\boldsymbol{\kappa}\cdot\boldsymbol{\kappa}^T\hat{S}_{\mu\nu}^{(2)}, \tag{A9}$$

$$\hat{\mathcal{P}}_{\mu\nu}^{(m)}=2\lambda_H(\boldsymbol{\kappa}+\boldsymbol{\kappa}^T)(BB^T)_{\mu\nu}^m+8\lambda_H^2\boldsymbol{\kappa}\cdot\boldsymbol{\kappa}^T(BB^T)_{\mu\nu}^{m+1}, \tag{A10}$$

$$\hat{\mathcal{R}}_{\mu\nu}^{(m)}=\frac{1}{|\mu-\nu|}\sum_{j=\min(\mu,\nu)}^{\max(\mu,\nu)-1}[1(1-\delta_{m0})(BC^{m-1})_{\mu j}+2\lambda_H(\boldsymbol{\kappa}+\boldsymbol{\kappa}^T)(BC^m)_{\mu j}+8\lambda_H^2\boldsymbol{\kappa}\cdot\boldsymbol{\kappa}^T(BC^{m+1})_{\mu j}]. \tag{A11}$$

In (A10) and (A11), the $N_0\times(N_0-1)$ matrix B is defined by $B_{\mu j}=(j/N_0)-\Theta(j-\mu)$, where $\Theta(x)$ is the Heaviside step function, i.e., $\Theta(x)=0$ for $x<0$ and $\Theta(x)=1$ for $x\geq 0$ (in terms of B, the Kramers matrix C can be written as $C=B^TB$). Notice that the tensors $\hat{\mathcal{R}}_{\mu\nu}^{(m)}$ are regular for $\nu=\mu$. Therefore, the term involving the hydrodynamic-interaction function $\mathcal{H}$ in (A8) does not lead to $1/\epsilon$ singularities near four dimensions.

Equations (A1), (A2), and (A7) constitute the rigorous first-order perturbation expansion in the excluded-volume and hydrodynamic-interaction parameters for Hookean chains consisting of an arbitrary number of beads and for arbitrary shear rates.

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