PHYSICAL REVIEW A VOLUME 41, NUMBER 12 15 JUNE 1990

Dilute polymer solution in steady shear flow: Non-Newtonian stress

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(Received 11 October 1989)

An expression for the stress tensor of a dilute polymer solution under shear has been derived via renormalization-group theory. It is valid to first order in $\epsilon(=4-d$, where d is the spatial dimensionality) to arbitrary flow rates. The polymeric contribution to the viscosity exhibits shear thinning for intermediate values of the shear. This thinning depends sensitively on the solvent quality (amount of excluded volume): for good solvents, the thinning is greatly enhanced, as is observed experimentally. The first and second normal stresses are also calculated. The ratio of the second to first normal stress for low shear is found to be a small negative quantity, approximately -0.03, nearly independent of solvent quality. This is in reasonable agreement with the sparse experimental results. A discussion of the Fokker-Planck operator and steady-state correlation functions for the Rouse theory is provided.

I. INTRODUCTION

At present there exist few first-principles theoretical results for polymer systems under finite shear. For example, only recently has the correct dependence of the nonequilibrium steady-state end-to-end distance of a polymer chain on the molecular weight been determined by Bird *et al.*[1] and later investigated via renormalization-group[2] (RG) theory. In this work, we provide a systematic calculation of the non-Newtonian rheological properties of a dilute solution of macromolecules under steady shear.

A dynamical theory of dilute polymer solution under shear should include a description of hydrodynamic and excluded-volume effects. Starting from an extensively studied dynamical model that incorporates these effects, we perform a first-principles calculation of the stress tensor via RG theory to first order in ϵ $(=4-d$, where d is the spatial dimensionality). This allows us to evaluate the reduced viscosity and first and second normal stresses. The starting point for the calculation is a coupled system of linear Langevin equations describing the chain and solvent.[3] In the dilute regime, renormalization-group studies on this model (without flow) have already yielded low-shear transport properties, such as the intrinsic viscosity[4] and the relaxation spectrum,[5,6] as well as time correlation functions.[7] Very recently Wang[8] and Öttinger[9] have calculated zero-shear rheological quantities in various good and poor solvent limits.

Less work has been done on this model for the case in which the solvent flow field has a finite, constant gradient. Yamazaki and Ohta[10] calculated the steady state properties of a polymer in uniaxial elongational flow. Later, Puri, Schaub, and Oono[2] calculated the time-dependent end-to-end distance of a polymer after the onset of simple elongational or shear flows. Rabin and Kawasaki[11] have also recently performed some preliminary investigations of the model in the case of strong shear.

We find the following results. For low-shear rates, the solution is thinned due to the flow, whereas at very high shear, the model predicts a shear thickening. The solvent quality (temperature) is seen to affect the non-Newtonian properties. For example, the thinning is greatly enhanced for good solvents in contrast to poor solvents. This result is reminiscent of the early results of Fixman,[12] obtained from unrenormalized expansions.

We are able to calculate analytically some of the lowest-order effects of the flow. For example, we determine the second normal stress in the limit of vanishing flow. This is found to be negative, and in semiquantitative agreement with experimental results. It should be noted that, for long chains, some researchers have calculated positive second normal stress[13,14] both analytically and numerically.

The paper is organized as follows. In Sec. II, we introduce the dynamical model and derive the Fokker-Planck (FP) equation governing the probability distribution function for the chain dynamics. In Sec. III, the equation governing the polymeric contribution to the stress tensor is derived to lowest order in ϵ and solved. Plots are presented for the reduced viscosity and the first and second normal stress coefficients. In Sec. IV we discuss the behavior for low flow rates, in which case we can determine the second normal stress analytically. Section V interprets the results physically and gives a brief comparison with experimental studies on polymer systems. Other theories are critically reviewed, and a discussion and conclusion are presented.

Many important results are derived or reviewed in the appendices. Appendix A sketches a derivation of the FP equation for a polymer chain under shear. Appendix B reviews aspects of the solution to this FP equation for the Rouse theory. Appendix C is a calculation of the monomer-monomer correlation functions and the stress matrix in the Rouse theory. Appendix D gives the explicit form of the quantities necessary to calculate the stress matrix to order ϵ. In Appendix E we present the renormalized form of the dimensionless flow rate, and discuss the solutions to the RG equation for quantities appearing within the theory. Readers interested in results and a qualitative discussion need to read only Secs. II, III, and V.

II. COUPLED LANGEVIN EQUATIONS FOR GAUSSIAN CHAIN AND SOLVENT

We begin with the usual system of coupled Langevin equations describing the chain and solvent.[3] Our aim is to provide further justification for the elimination of the solvent degrees of freedom in favor of an Oseen tensor description of the polymer. We outline the approach here, and provide greater depth in Appendix A.

The equation for the chain reads:

$$\partial_t \mathbf{R}(\tau,t)=\mathbf{v}(\mathbf{R}(\tau,t))-\frac{1}{\zeta_0}\frac{\delta\mathcal{H}}{\delta\mathbf{R}(\tau,t)}+\mathbf{u}(\mathbf{R}(\tau,t),t)+\boldsymbol{\theta}(\tau,t)\ . \tag{2.1}$$

Here $\mathbf{R}(\tau,t)$ represents the position of the chain at time t a distance τ along the chain contour $(0<\tau<N_0)$; ζ_0 is the bare monomer friction constant. $\mathcal{H}$ is the Edwards Hamiltonian:

$$\mathcal{H}=\mathcal{H}_0+\mathcal{H}_{\text{int}}\ , \tag{2.2}$$

$$\mathcal{H}_0=\frac{1}{2}\int_0^{N_0}d\tau\left[\frac{d\mathbf{R}(\tau)}{d\tau}\right]^2\ , \tag{2.3}$$

$$H_{\text{int}}=\frac{v_0}{2}\int_0^{N_0}\int_0^{N_0}d\tau\, d\sigma\, \delta(\mathbf{R}(\tau)-\mathbf{R}(\sigma))\ . \tag{2.4}$$

The white noise $\boldsymbol{\theta}$ satisfies the fluctuation-dissipation theorem:

$$\langle\boldsymbol{\theta}(\tau,t)\boldsymbol{\theta}(\sigma,s)\rangle=2\zeta_0^{-1}\delta(t-s)\delta(\tau-\sigma)\underline{I}\ , \tag{2.5}$$

where $\underline{I}$ is the unit matrix, and energy units are such that $k_BT=1$.

The total solvent velocity field at a point $\mathbf{r}$ in the fluid is given by $\mathbf{v}(\mathbf{r})+\mathbf{u}(\mathbf{r},t)$. Here $\mathbf{v}(\mathbf{r})$ is the systematic part of the solvent velocity field, and $\mathbf{u}(\mathbf{r},t)$ is the fluctuating part. The velocity field obeys a Navier-Stokes type equation which includes a force term due to the presence of polymers. After eliminating the pressure from this equation, one arrives at the following Langevin equation (for the solvent):

$$D_t\mathbf{u}(\mathbf{r},t)=\eta_0\nabla^2\mathbf{u}(\mathbf{r},t)-\left[\int_0^{N_0}d\tau\frac{\delta\mathcal{H}}{\delta\mathbf{R}(\tau,t)}\delta(\mathbf{r}-\mathbf{R}(\tau,t))\right]_\perp+\mathbf{f}(\mathbf{r},t)\ , \tag{2.6}$$

with

$$D_t\mathbf{u}(\mathbf{r},t)\equiv\partial_t\mathbf{u}(\mathbf{r},t)+[(\mathbf{u}+\mathbf{v})\cdot\nabla(\mathbf{u}+\mathbf{v})]_\perp\ . \tag{2.7}$$

Here η_0 is the bare solvent viscosity, and $[\ ]_\perp$ selects the transverse part. Also $\mathbf{f}$ is a transverse Gaussian white noise with mean zero and correlations (in momentum space) given by

$$\langle\mathbf{f}(\mathbf{k},t)\mathbf{f}(-\mathbf{k}',s)\rangle=+2\eta_0k^2\left[\underline{I}\frac{\mathbf{kk}}{k^2}\right]\delta(\mathbf{k}-\mathbf{k}')\delta(t-s)\ . \tag{2.8}$$

In this study, we concentrate on simple shear flow and thus represent the systematic velocity field by

$$\mathbf{v}(\mathbf{r})=g\underline{A}\cdot\mathbf{r}\ , \tag{2.9}$$

where $\underline{A}$ is a $d\times d$ dimensionless matrix having one nonzero entry of value unity

$$A_{ij}=\delta_{i1}\delta_{j2}\ , \tag{2.10}$$

with δ the Kronecker delta. We consider the dynamics to take place in a generalized d-dimensional space, since ultimately the presence of the excluded volume necessitates studying the system in a perturbation approach about $d=4$.

To derive a FP operator for the chain, we employ a projection operator method similar to that used originally in the study of the critical fluid by Onuki and Kawasaki,[15] and later in polymer dynamics by Lee, Baldwin, and Oono.[16] The derivation is standard and presented in Appendix A. We argue there that the convective terms appearing in Eq. (2.7) may be neglected for the case of simple shear. A simplified argument is presented below.

Consider the convective parts of the derivative appearing in Eq. (2.7). The $\mathbf{v}\cdot\nabla\mathbf{v}$ term vanishes identically. How does the magnitude of the $\mathbf{v}\cdot(\nabla\cdot\mathbf{u})$ and $\mathbf{u}\cdot(\nabla\cdot\mathbf{v})$ terms compare with the dissipative term $\eta_0\nabla^2\mathbf{u}$? The dimensionless ratio which we may form by comparing these two terms is equal to the time scale of the solvent divided by the time scale of the shear flow. Thus,

$$\frac{\tau_{\text{solv}}}{\tau_{\text{sh}}}=\frac{\tau_{\text{solv}}}{\tau_{\text{poly}}}\frac{\tau_{\text{poly}}}{\tau_{\text{sh}}}\ . \tag{2.11}$$

The dimensionless quantity proportional to the shear rate is equal to $\tau_{\text{poly}}/\tau_{\text{sh}}$. Since $\tau_{\text{solv}}/\tau_{\text{poly}}$ is very small, it is consistent to neglect the convective terms, unless the shear rate is extraordinarily high. Note that Puri *et al.*[2] argued that the convective terms do not contribute to order g^2 in the calculation of the end-to-end distance, however we have given a quite general argument not to consider these terms.

The resulting equation governing the probability distribution $P\{\mathbf{R},t\}$ for the chain dynamics has the usual Oseen tensor form

$$\partial_tP=\mathcal{L}_F^*P\ , \tag{2.12}$$

where

$$\mathcal{L}_F^*=\frac{1}{2N_0\zeta_0}\sum_{q=0}^{\infty}\sum_{p=0}^{\infty}\left[\frac{\partial}{\partial\mathbf{R}_p}\cdot\left(\overleftrightarrow{\mathbf{D}}_{p,q}\cdot\frac{\partial\mathcal{H}}{\partial\mathbf{R}_q}-2gN_0\zeta_0\underline{A}\cdot\mathbf{R}_p\right]+\frac{\partial}{\partial\mathbf{R}_p}\cdot\overleftrightarrow{\mathbf{D}}_{p,q}\cdot\frac{\partial}{\partial\mathbf{R}_q}\right]\ . \tag{2.13}$$

Here

$$\overleftrightarrow{\mathrm{D}}_{p,q}=\underline{I}(1+\delta_{p,0})\delta_{p,q}+\frac{2\zeta_0}{\eta_0 N_0}\int^{\mathbf{k}}\frac{1}{k^4}(k^2\underline{I}-\mathbf{kk})\int_0^{N_0}\int_0^{N_0}d\tau\, d\sigma\, e^{i\mathbf{k}\cdot[\mathbf{R}(\sigma)-\mathbf{R}(\tau)]}\cos\frac{p\pi\tau}{N_0}\cos\frac{q\pi\sigma}{N_0}\ . \tag{2.14}$$

We have used an implied summation convention over q in Eq. (2.13) $\sum_{q=1}^{\infty}$ as we will henceforth. Note $(\partial/\partial\mathbf{R}_p)\cdot\overleftrightarrow{\mathrm{D}}_{p,q}=0$. Equation (2.13) introduces the Rouse modes $\mathbf{R}_p$ defined in Appendix C 1 in the usual way. For momentum integrals we use the standard shorthand

$$\int^{\mathbf{k}}\equiv\int d^dk\frac{1}{(2\pi)^d}\ .$$

The presence of the flow introduces many subtleties into the solution of the FP equation. Johnson[17] has shown that one cannot completely study the time dependence of a Rouse chain under flow by considering an eigenvalue equation for some diagonalizable operator. Moreover, constructing perturbatively the steady-state distribution function for the full system with hydrodynamics and excluded volume becomes extremely difficult. For completeness, we include a discussion in Appendix B.

III. CALCULATION OF THE STRESS MATRIX

In this section we perform a calculation of the polymeric contribution to the stress tensor $\overleftrightarrow{\sigma}^{\,\mathrm{poly}}$ of the solution to order ϵ. The presence of excluded-volume and hydrodynamic interactions necessitates a renormalized perturbation theory for polymer dynamics. (For a nice review see Oono.[18]) In this procedure, molecular parameters are divided into factors depending sensitively on microscopic details and factors that do not. This leads to a non-Rouse dependence of the polymer time scale on the chain length. After renormalization, the hydrodynamic interaction and the excluded volume interaction contribute to order ϵ. This provides a convenient way to solve for the stress tensor in terms of perturbation theory in ϵ, as we shall see later.

Following Doi and Edwards,[19] the stress tensor $\overleftrightarrow{\sigma}^{\,\mathrm{poly}}$ may be found by considering the average internal forces of a polymer chain spanning an imaginary plane. This leads to the expression (in our notation)

$$\overleftrightarrow{\sigma}^{\,\mathrm{poly}}=c_P\int_0^{N_0}d\tau\left\langle\frac{\delta\mathcal{H}}{\delta\mathbf{R}(\tau)}\mathbf{R}(\tau)\right\rangle\ , \tag{3.1}$$

which in Rouse modes reads

$$\overleftrightarrow{\sigma}^{\,\mathrm{poly}}=c_P\sum_{q=1}^{\infty}\overleftrightarrow{\sigma}_q\ , \tag{3.2}$$

where we have defined a tensor $\overleftrightarrow{\sigma}_q$ through

$$\overleftrightarrow{\sigma}_q=\left\langle\frac{\partial\mathcal{H}}{\partial\mathbf{R}_q}\mathbf{R}_q\right\rangle^S\ . \tag{3.3}$$

We do not provide a derivation for the expression (3.1). There is no reason to expect that (3.1) is a more reliable result than the Oseen tensor description of the polymer solution, particularly in the nonequilibrium situation.

In Eqs. (3.1)–(3.3), c_P denotes the number of polymers per unit volume, and the superscript S when it appears denotes a symmetrization of a matrix quantity. Also, $\langle Q\rangle=\int\mathcal{D}\{\mathbf{R}\}QW$ denotes a steady-state average of property Q, where W is the steady-state distribution function solving $\mathcal{L}_F^*W=0$. Note that the tensor $\overleftrightarrow{\sigma}^{\mathrm{poly}}$ must be symmetric,[19] so we have explicitly symmetrized $\overleftrightarrow{\sigma}_q$.

We begin the derivation of a stress tensor equation with

$$\int\mathcal{D}\{R\}\mathbf{R}_{p'}\mathbf{R}_{p'}\mathcal{L}^*W=0\ . \tag{3.4}$$

Using Eqs. (2.13) and (3.4) in the steady state, and differentiating by parts, yields

$$\left\langle\mathbf{R}_p\overleftrightarrow{\mathrm{D}}_{p,q}\cdot\frac{\partial\mathcal{H}}{\partial\mathbf{R}_q}\right\rangle-g\overleftrightarrow{\mathrm{A}}\cdot\langle\mathbf{R}_p\mathbf{R}_p\rangle 2N_0\zeta_0-\langle\overleftrightarrow{\mathrm{D}}_{p,p}\rangle\overset{S}{=}0\ . \tag{3.5}$$

Here we have defined the symbol $\overset{S}{=}$, to mean that only the symmetric part of the matrix equality holds. We now substitute

$$2\langle\mathbf{R}_p\mathbf{R}_p\rangle=\left[\frac{1}{\pi p}\right]^2N_0\left[\overleftrightarrow{\sigma}_p-\left\langle\mathbf{R}_p\frac{\partial\mathcal{H}_{\mathrm{int}}}{\partial\mathbf{R}_p}\right\rangle^S\right]\ , \tag{3.6}$$

which can be derived from Eqs. (2.2) and (3.3). Eqs. (3.5) and (3.6) yield

$$\left\langle\mathbf{R}_p\overleftrightarrow{\mathrm{D}}_{p,q}\cdot\frac{\partial\mathcal{H}}{\partial\mathbf{R}_q}\right\rangle-G(p)\underline{A}\cdot\overleftrightarrow{\sigma}_p+G(p)\underline{A}\cdot\left\langle\mathbf{R}_p\frac{\partial\mathcal{H}_{\mathrm{int}}}{\partial\mathbf{R}_q}\right\rangle^S-\langle\overleftrightarrow{\mathrm{D}}_{p,p}\rangle\overset{S}{=}0\ , \tag{3.7}$$

where

$$G(p)=\frac{G}{(\pi p)^2}\ ,\qquad G=g\zeta_0N_0^2\ . \tag{3.8}$$

What we would like to do is to derive a closed equation for the quantity $\overleftrightarrow{\sigma}_p$. Remarkably, this is possible to lowest order in ϵ. In order to derive such a closed equation, we make extensive use of the fact that the $\epsilon=0$ theory is Gaussian and employ Gaussian decoupling formulas.

In the absence of the excluded volume and hydrodynamic interactions Eq. (3.7) yields

$$[\underline{I}-G(p)\underline{A}]\cdot\overleftrightarrow{\sigma}_p\overset{S}{=}\underline{I}\ . \tag{3.9}$$

This is essentially the lowest order equation for $\overleftrightarrow{\sigma}_p$ and its solution is simple [see Eqs. (C3) or (3.14)]. To acquire a solution for $\overleftrightarrow{\sigma}_p$ from Eq. (3.7), our scheme is to move to the right-hand side (RHS) of the equation most terms that are of order ϵ. However, the presence of the excluded volume and hydrodynamic interactions changes the dependence of the time scale of the polymer on the chain length. Therefore we will maintain on the left-hand side (LHS) of the equation those terms which lead to the renormalization of the dimensionless flow rate $G(p)$. This quantity is the only remaining variable in the problem and it explicitly involves the time scale. We are lead ultimately to Eq. (3.12) which should be compared with Eq. (3.9).

We begin this program by dividing the friction tensor into a part preaveraged in zero flow and a remainder

$$\overleftrightarrow{\mathrm{D}}_{p,q}=D(p,q)\underline{I}+\overleftrightarrow{\mathrm{D}}'_{p,q}\ , \tag{3.10}$$

where

$$D(p,q)\underline{I}=\langle\overleftrightarrow{\mathrm{D}}_{p,q}\rangle_{g=0}\ . \tag{3.11}$$

We can write to order ϵ that

$$[\underline{I}-G_R(p)\underline{A}]\cdot\overleftrightarrow{\sigma}_p\overset{S}{=}\overleftrightarrow{\mathrm{S}}_p\ , \tag{3.12}$$

where $G_R(p)$ is the renormalized dimensionless flow field,

$$G_R(p)=G(p)\left[1-[D(p,p)-1]\right.$$
$$\left.-\frac{1}{2d}N_0\left[\frac{1}{p\pi}\right]^2\left\langle\frac{\partial}{\partial\mathbf{R}_p}\cdot\frac{\partial\mathcal{H}_{\mathrm{int}}}{\partial\mathbf{R}_p}\right\rangle_{g=0}\right]\ , \tag{3.13}$$

and $\overleftrightarrow{\mathrm{S}}_p$ is equal to the unit tensor plus ϵ terms, as is given in appendix D. The ϵ terms of $\overleftrightarrow{\mathrm{S}}_p$ may be evaluated using the standard Rouse correlation functions (Appendix C). After renormalization (Appendix E), $G_R(p)$ becomes proportional to $gN^{d\nu}$, where ν is the critical exponent governing the scaling between the end-to-end distance and the contour length. This is the dynamical scaling result.

The solution to Eq. (3.11) is given by

$$\overleftrightarrow{\sigma}_p=\overleftrightarrow{\mathrm{S}}_p+\frac{G_R(p)}{2}(\underline{A}\cdot\overleftrightarrow{\mathrm{S}}_p+\overleftrightarrow{\mathrm{S}}_p\cdot\underline{A}^T)+\frac{G_R^2(p)}{2}\underline{A}\cdot\overleftrightarrow{\mathrm{S}}_p\cdot\underline{A}^T\ . \tag{3.14}$$

The stress tensor may be evaluated from eqs. (3.2) and (3.14), after performing the sum on p. Three important rheological quantities summarize knowledge of the stress tensor. The intrinsic polymeric contribution to the shear viscosity is defined as

$$[\eta]=\frac{[\overleftrightarrow{\sigma}^{\,\mathrm{poly}}]_{xy}}{gc_P\eta_0M}\ , \tag{3.15}$$

where M is the molecular weight of the polymer molecule. The first and second normal stress coefficients are defined, respectively, as

$$[\psi_1]=\frac{[\overleftrightarrow{\sigma}^{\,\mathrm{poly}}]_{xx}-[\overleftrightarrow{\sigma}^{\,\mathrm{poly}}]_{yy}}{c_Pg^2}\ , \tag{3.16}$$

$$[\psi_2]=\frac{[\overleftrightarrow{\sigma}^{\,\mathrm{poly}}]_{xy}-[\overleftrightarrow{\sigma}^{\mathrm{poly}}]_{zz}}{c_Pg^2}\ . \tag{3.17}$$

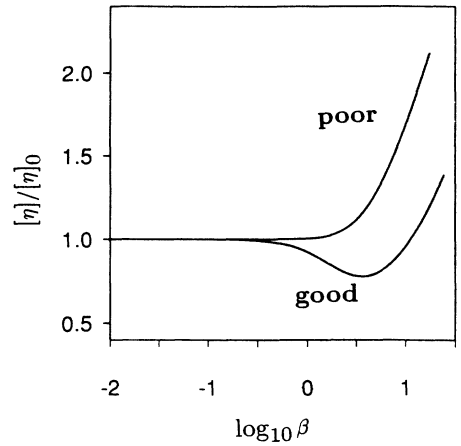

FIG. 1. The reduced viscosity as a function of flow rate for the good ($Z=\infty$) and poor ($Z=0.0$) solvent cases.

In Figs. 1–3, we have plotted dimensionless groupings of these variables $[\eta]/[\eta]_0$, $[\psi_1]/[\psi_1]_0$, and $[\psi_2]/[\psi_1]$, where

$$[\eta]_0=\lim_{G_R\to0}[\eta] \tag{3.18}$$

and

$$[\psi_1]_0=\lim_{G_R\to0}[\psi_1]\ . \tag{3.19}$$

Thus Figs. 1 and 2 are normalized to unity in the limit of vanishing shear rate. The Z variable describes the crossover from the poor solvent case ($Z=0$, Gaussian fixed point) to the good solvent case ($Z=\infty$, self avoiding fixed point). In the aforementioned plots, we have introduced the dimensionless time scale β as

$$\beta=g\eta_0M[\eta]_0\ . \tag{3.20}$$

Since we derive the stress tensor as a function of G_R, we must determine the linear relation between G_R and β, the quantity used most often by experimentalists. Using Eqs. (3.15), (3.18), and (3.20), it is straightforward to derive the following relation:

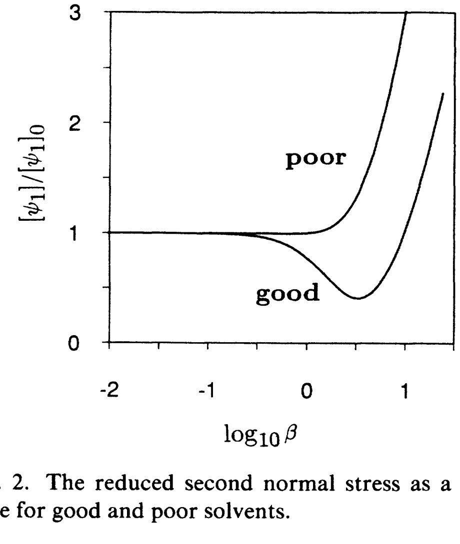

FIG. 2. The reduced second normal stress as a function of low rate for good and poor solvents.

$$\beta/G_R=\lim_{G_R\to 0}\frac{[\overleftrightarrow{\sigma}^{\text{poly}}]_{xy}}{G_R c_P}\ . \tag{3.21}$$

The RHS of the equation is a constant which may be determined numerically from our result for the stress tensor (the Rouse value is $\frac{1}{12}=0.0833$). We present the relation for both the good and poor solvent limits:

$$\beta=(8.72\times 10^{-2})G_R,\quad \text{poor solvents} \tag{3.22}$$

$$\beta=(8.04\times 10^{-2})G_R,\quad \text{good solvents}\ . \tag{3.23}$$

We discuss the curves in some detail in Sec. V.

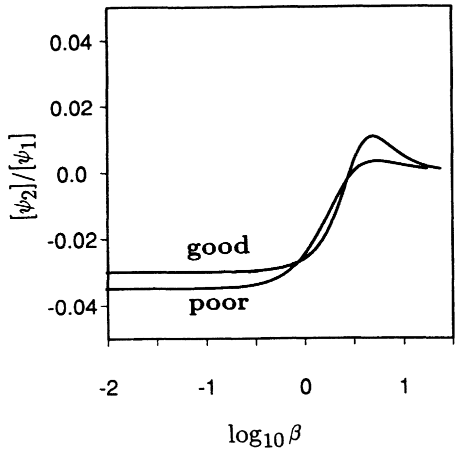

FIG. 3. The ratio of the second to the first normal stress for good and poor solvent cases.

IV. LOWEST-ORDER EFFECTS OF FLOW

In this section we solve for the second normal stress coefficient in the limit of zero shear. To lowest order in ϵ one may use Appendix D and expand in powers of the flow rate to write

$$[\overleftrightarrow{\sigma}_p]_{22}-[\overleftrightarrow{\sigma}_p]_{33}=[\overleftrightarrow{S}_p]_{22}-[\overleftrightarrow{S}_p]_{33} \tag{4.1}$$

$$=-\frac{G_R^2}{12}\frac{\zeta_0}{4\pi^2\eta_0}\int_0^1 dv\int_0^{1-v}dw \tag{4.2}$$

$$\times\left[\frac{1}{24\pi^2p^2}[\tfrac{3}{2}(1-v^2)-w]\{\cos[p\pi(1+v)]+\cos(p\pi w)\}+\frac{1}{2\pi^4p^4}\frac{1}{w}R(p,w,v)-\frac{1}{24\pi^2p^2}[\tfrac{3}{2}(1-v^2)-w]R(p,w,v)\right],$$

where

$$R(p,w,v)=2(+\{1-\cos[p\pi(1+v)]\}[1-\cos(p\pi w)]-v\{\sin[p\pi(1+v)]\sin(p\pi w)\})\ . \tag{4.3}$$

To arrive at the total stress, we must perform sums on p. Thus we need (for $0<v,w<1$):

$$\sum_{p=1}^{\infty}\frac{1}{(p\pi)^2}\{\cos[p\pi(1+v)]+\cos(p\pi w)\}=\frac{1}{3}-\frac{w}{2}+\frac{w^2}{4}-\frac{1-v^2}{4}\ , \tag{4.4}$$

$$\sum_{p=1}^{\infty}\frac{1}{(p\pi)^4}R(p,w,v)=w(1-v^2)\left[-\frac{v^2}{6}+\frac{w}{4}-\frac{w^2}{6}\right], \tag{4.5}$$

$$\sum_{p=1}^{\infty}\frac{1}{(p\pi)^2}R(p,w,v)=w(1-v^2)\ . \tag{4.6}$$

This leaves us with

$$\frac{1}{c_P}([\overleftrightarrow{\sigma}^{\text{poly}}]_{22}-[\overleftrightarrow{\sigma}^{\text{poly}}]_{33})$$

$$=-\frac{1}{12}\frac{\zeta_0}{4\pi^2\eta_0}G_R^2\int_0^1 dv\int_0^{1-v}dw \tag{4.7}$$

$$\times\left[\frac{1}{24}\left[\frac{3}{2}(1-v^2)-w\right]\left[\frac{1}{3}-\frac{w}{2}+\frac{w^2}{4}-\frac{1-v^2}{4}\right]+\frac{1}{2}(1-v^2)\left[-\frac{v^2}{6}+\frac{w}{4}-\frac{w^2}{6}\right]-\frac{1}{24}\left[\frac{3}{2}(1-v^2)-w\right]w(1-v^2)\right]. \tag{4.8}$$

After performing the v and w integrations, one finds

$$\frac{1}{c_p}([\overleftrightarrow{\sigma}^{\,\text{poly}}]_{22}-[\overleftrightarrow{\sigma}^{\,\text{poly}}]_{33})$$

$$=\frac{\zeta_0}{4\pi^2\eta_0}G_R^2\left[\frac{1}{720\times24\times12}-\frac{7}{864\times12}-\frac{163}{2160\times14\times12}\right]$$

$$=-\frac{\zeta_0}{4\pi^2\eta_0}G_R^2(2.211\times10^{-4})\ . \tag{4.9}$$

This agrees with the results of Öttinger and Wang.[11]

For long chains we find that in terms of the crossover variables of the RG flow (to lowest order in ϵ):

$$\frac{\zeta_0}{\eta_0}=2\pi^2\epsilon\frac{Z}{1+Z}\frac{1}{1-(1+Z)^{-3/4}}\ . \tag{4.10}$$

The variable Z represents the crossover from the Gaussian fixed point $Z=0$ to the self-avoiding fixed point $Z=\infty$. Thus for poor $(Z=0)$ and good solvents $(Z=\infty)$ one finds

$$\frac{1}{c_p}([\overleftrightarrow{\sigma}^{\,\text{poly}}]_{22}-[\overleftrightarrow{\sigma}^{\,\text{poly}}]_{33})=-(1.94\times10^{-2})\beta^2\epsilon,\ \text{poor solvents} \tag{4.11}$$

$$\frac{1}{c_p}([\overleftrightarrow{\sigma}^{\,\text{poly}}]_{22}-[\overleftrightarrow{\sigma}^{\,\text{poly}}]_{33})=-(1.71\times10^{-2})\beta^2\epsilon,\ \text{good solvents}\ , \tag{4.12}$$

where we have used the relation between G_R and β from Sec. III.

V. COMPARISON WITH DATA AND DISCUSSION

Starting from a well-accepted dynamical model for the chain and solvent, we have performed a calculation of the stress tensor for polymer dilute solution that is exact to first order in ϵ (where $\epsilon=4-d$). Our dynamical model has been extensively studied via RG theory, and incorporates the hydrodynamic and excluded volume effects. The only first principles calculation of this kind previously performed are those of Wang[8] and Öttinger[9] who expanded the stress tensor to second order in the flow rate, in order to find expressions for the normal stresses.

Figure 1 is a plot of the reduced viscosity as a function of the shear rate. For low values of the shear rate, the solution is thinned. This thinning depends sensitively on the quality of the solvent (the magnitude of the excluded volume interaction). For good solvents, the thinning is greatly enhanced. This is a natural result, since the excluded volume suppresses the mobility, and the stretching decreases the importance of the excluded volume interaction.

A comparison with data is shown in Figs. 4 and 5. In Fig. 4, the reduced viscosity for good solvents is plotted as a function of shear rate, and compared with the data of Noda and Yamada.[20] We see semiquantitative agreement up to relatively high shear. From recent calculations by Öttinger,[13] Bird,[21] and others, it seems that the finite extensibility of a chain is crucial in governing the very high shear rate non-Newtonian properties. For example, Öttinger has found that for finitely extensible chains, the solution thins indefinitely at high shear. Since our model does not incorporate this important effect, it is not clear that our results should give reliable agreement with experiment for very high shear. This may explain the discrepancy between our theory and the available experimental data. For good solvents, at the shear rates at which our data deviates from experiment, we estimate that the chains are stretched to approximately five times their original end-to-end distance. In Fig. 5, we see that

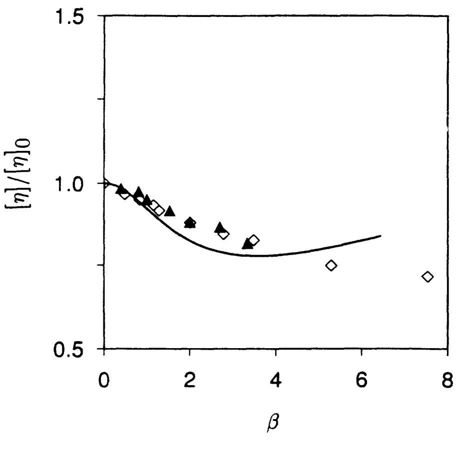

FIG. 4. The reduced viscosity as a function of the dimensionless flow rate for good solvents. The curve represents our theoretical result. The data is ◇ poly(α-methylstyrene) (sample S-16: $M=13.6\times10^6$) in toluene at 25 °C, Noda and Yamada (Ref. 20); ▲, polystyrene (sample S-9: $M=7.14\times10^6$) in benzene at 30.0 °C, Suzuki, Kotaka, and Inagaki (Ref. 29).

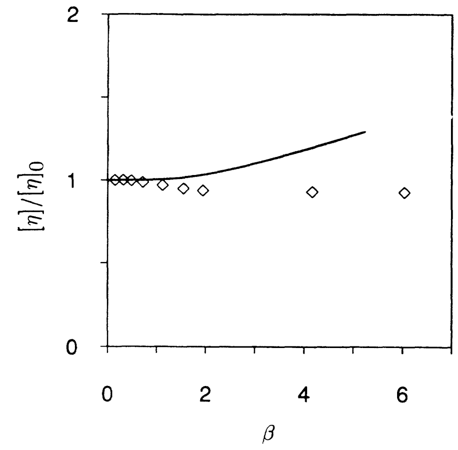

FIG. 5. The reduced viscosity as a function of the dimensionless flow rate for poor solvents. The curve represents our theoretical result. The data is from Noda and Yamada (Ref. 20): polystyrene (sample S-H: $M=13.6\times10^6$) in decalin at 15.4 °C.

both theory and experiment show virtually no shear thinning. Thus the thinning is primarily due to the excluded volume effects.

A formula commonly found in the literature[22] is

$$\frac{[\eta]_0}{[\eta]} = 1 + \text{const} \times \beta^{1/2} , \tag{5.1}$$

governing primarily the experimentally observed high-shear rate behavior of the shear thinning. Actually, our theory predicts that as the shear rate is increased to very high values, the solution ultimately thickens. We have no clear physical interpretation for this thickening mechanism. Approximate numerical solutions of Magda *et al.*[14] and Öttinger[13] also find thickening. We discuss their findings in some detail below.

In Fig. 3, we have plotted the ratio of the second to first normal stress coefficients. We find that for low-shear rates

$$\lim_{G \to 0} \frac{\Psi_2}{\Psi_1} \approx -0.03 , \tag{5.2}$$

with only slight dependence on solvent quality. According to Larson,[23] there is a broad range of values that has been reported for this ratio at low shear, with most workers finding values between (-0.05) and (-0.3). Recently a value of -0.02 has also been reported.[24] Our results are in reasonable agreement with these experiments in that this quantity is both small and negative. Keentok *et al.*[25] find that the ratio decreases as concentration decreases.

Finally, let us critically review other theories and numerical works. Öttinger and Magda *et al.* have numerically studied the same Fokker-Planck equation in the absence of excluded volume. Since correlation functions depend on the steady-state distribution function and the steady-state distribution function depends in turn on the conformational properties of the chain, analytically it is very difficult to solve for the stress tensor. However, these researchers preaverage the diffusion matrix, so that the distribution function governing the chain dynamics is Gaussian. This enables them to solve for the distribution function and the correlation functions numerically in a self-consistent manner. Magda *et al.* and Öttinger's results for the first normal stress are similar to ours. However, they find a positive sign for the second normal stress, that is, not in keeping with our results (and may be due to preaveraging[11]). They find a very small shear thinning in semiquantitative agreement with our results for the theta solvent case. Since they cannot incorporate the excluded volume, they are unable to study the solvent quality effects.

Fixman[12] studied the effect of excluded volume on the stress tensor, but considered only the lowest-order effects of the flow rate. His results are similar to ours: the excluded volume enhances the thinning effects. However, in Fixman's calculation the excluded volume parameter may increase indefinitely with increasing solvent quality, so that any degree of shear thinning may be achieved. Our procedure is less arbitrary in that increasing the solvent quality drives the excluded volume parameter to a well-defined fixed point, and so the thinning may not be arbitrarily great.

In summary, we have performed a systematic calculation for the non-Newtonian properties of a dilute solution of polymers. Our result is exact to first order in the small parameter ϵ, using a RG approach. The model incorporates excluded volume and hydrodynamic interaction, but does not include the effects of finite extensibility.

ACKNOWLEDGMENTS

We would like to thank Dr. Ronald Larson for many helpful conversations and insights, as well as Professor John D'Angelo for informing him of the status of certain aspects of the theory of nilpotent operators in Hilbert spaces.

APPENDIX A: PROJECTION OPERATOR METHOD

Here we use the Kawasaki formula to derive the Fokker-Planck operator for the chain under flow. We show how it is possible to neglect the convective terms. The Oseen tensor description for the critical fluid was first derived by the reduction of kinetic models by Kawasaki (see Ref. 15 and references therein). His formula yields the effective generator of the dynamics of the probability distribution for the appropriate field variable, by projecting out the solvent variables. Let $\mathcal{L}^*$ be the Fokker-Planck operator governing the probability distribution for the dynamical system given by the chain-solvent system given by Eqs. (2.1) and (2.6). The $\mathcal{L}_F^*$ governing the chain variables

$$\partial_t P(\{\mathbf{R}\},t) = \mathcal{L}_F^* P(\{\mathbf{R}\},t) \tag{A1}$$

is given by the formula (see Appendix D of Onuki-Kawasaki):

$$\mathcal{L}_F^* = \langle \mathcal{L}^* \rangle_{\mathrm{u}} + \langle \mathcal{L}^* \mathcal{Q}(\delta - \mathcal{Q}\mathcal{L}^*\mathcal{Q})^{-1}\mathcal{Q}\mathcal{L}^* \rangle_{\mathrm{u}} , \tag{A2}$$

where δ is an infinitesimal number and we define projection operators $\mathcal{P}$, $\mathcal{Q}$ such that

$$\mathcal{Q} = 1 - \mathcal{P} , \tag{A3}$$

$$\mathcal{P} = \frac{W(\{\mathbf{R}\},\{\mathbf{u}\})}{W(\{\mathbf{R}\})} \int \mathcal{D}\{\mathbf{u}\} , \tag{A4}$$

$$W(\{\mathbf{R}\}) = \int \mathcal{D}\{\mathbf{u}\} W(\{\mathbf{R}\},\{\mathbf{u}\}) , \tag{A5}$$

and $W(\{\mathbf{R}\},\{\mathbf{u}\})$ is the steady-state distribution function satisfying $\mathcal{L}^* W = 0$. Also in Eq. (A2), the average of a quantity Q over solvent velocity flow field variables is given by

$$\langle Q \rangle_{\mathrm{u}} \equiv \int \mathcal{D}\{\mathbf{u}\} Q \frac{W(\{\mathbf{R}\},\{\mathbf{u}\})}{W(\{\mathbf{R}\})} . \tag{A6}$$

Precisely the same arguments which are used in deriving the effective Fokker-Planck equation in the case without flow allow us to replace the second term on the RHS of Eq. (A2) by

$$\langle \mathcal{L}_{\mathrm{int}}^* \mathcal{Q}(\delta - \mathcal{Q}\mathcal{L}_0^*\mathcal{Q})^{-1}\mathcal{Q}\mathcal{L}_{\mathrm{int}}^* \rangle , \tag{A7}$$

where $\mathcal{L}_0^*$ governs the full $\epsilon = 0$ dynamics of chain and solvent and $\mathcal{L}^*_{\text{int}}$ governs the mode-coupling terms between the chain and solvent.

In the exposition given by Lee, Baldwin, and Oono,[16] the Oseen tensor description is derived via Eqs. (A2) and (A7) for the case without flow. The only subtle point in the case we discuss here is that the $\mathcal{L}^*_0$ of Eq. (A7) involves terms due to the flow. We may compare the magnitude of the flow terms to the magnitude of the term governing the dissipation of the solvent field. If the flow is microscopically weak, then the terms due to the chain are irrelevant.

Let us then compare the magnitude of the convective terms to the dissipative terms. In momentum space the convective terms are given by

$$-g\underline{A}\cdot\mathbf{u}(\mathbf{k})+g\mathbf{k}\cdot\underline{A}\cdot\frac{\partial}{\partial\mathbf{k}}\mathbf{u}(\mathbf{k})\ , \tag{A8}$$

whereas the dissipative term is given by

$$-\eta_0k^2\mathbf{u}(\mathbf{k})\ . \tag{A9}$$

Since the chain length sets the distance scale in the problem, the dimensionless grouping we can form by considering a ratio of the convective terms to the dissipative term is

$$\frac{gN_0}{\eta_0}=g\zeta_0N_0^2\left[\frac{1}{\eta_0\zeta_0N_0}\right]\ . \tag{A10}$$

The second grouping of Eq. (A10) is neglected under the usual Markov assumption (it represents the ratio between the time scale of the polymer and the time scale of the chain). The conclusion is that the neglect of the convective terms is consistent with the usual Markov assumption, unless the flow rate is microscopically strong. Note that our findings disagree with that of Puri, Schaub, and Oono,[2] who found that the Markov description was correct only to order g^2.

Equation (A7) with Eq. (A2) now yield the $\mathcal{L}^*_F$ of Eq. (2.13) in the usual[16] way. The operator $\mathcal{L}^*_F$ corresponds to the conventional Oseen description. A more complete derivation of the above results will be given elsewhere.[26]

APPENDIX B: NOTES ON THE FOKKER-PLANCK OPERATOR IN ROUSE THEORY

Here we discuss the Fokker-Planck operator for the Rouse chain (no hydrodynamic or excluded volume interactions) under steady shear flow. We show below that for each mode p we can find a proportionality between the dynamical operator $-\mathcal{L}^*$ governing the probability distribution of the Rouse chain under shear in the x,y plane and the operator H:

$$H=N+D\ , \tag{B1}$$

$$D=a^\dagger a+b^\dagger b\ , \tag{B2}$$

$$N=-\alpha a^\dagger b\ , \tag{B3}$$

with

$$[b,b^\dagger]=[a,a^\dagger]=1\ , \tag{B4}$$

and all other commutators vanishing. Here

$$\alpha=\frac{G(p)}{(1+G^2(p)/4)^{1/2}} \tag{B5}$$

is a constant which depends in a nonlinear way on the flow. By inspection N and D commute, and D is diagonal in the familiar harmonic oscillator states. It is thus clear that H cannot be diagonalized. Moreover N is nilpotent in any finite-dimensional subspace constructed from the invariant subspaces of D. To see the ramifications of this last observation, consider first Q such that $\partial_tQ=-DQ$. Time-dependent solutions for Q are easily found from an eigenvalue equation for D. Then solutions for P (governing each mode p at $\epsilon=0$) are given formally by

$$P=e^{-Nt}Q\ . \tag{B6}$$

Note that the steady-state distribution function for the Rouse chain is stationary, because the lowest eigenvalue of D is zero and N annihilates the "ground state". However the higher states mix as a function of time (although they all decay exponentially fast to the steady state). Thus for the Rouse chain, we cannot completely study the time dependence of the higher states by considering a spectral representation for some diagonalizable operator. (For a complete exposition, see Johnson.[17]) Indeed the α of Eq. (B5) should be thought of as a transition rate, between (certain) eigenstates of D with the same eigenvalue.

That the problem with shear immediately brings us to the most subtle points of the study of Fokker-Planck operators is not at all surprising; indeed the study of unbounded linear operators in Hilbert spaces is still an area of intensive research. Even the generalization of the primary decomposition theorem (which for linear operators in finite-dimensional vector spaces states that any linear operator may be uniquely decomposed into a pair of mutually commuting operators such that one of the operators may be diagonalized and the other is nilpotent) to Hilbert spaces is unknown. As is well known, it is qualitatively incorrect to think of unbounded linear operators in Hilbert spaces as infinite-dimensional matrices, so that much of our intuition built from the theory of matrices breaks down.

We now construct the proportionality between $\mathcal{L}^*$ and H and give the form of a, $a^\dagger$, b, and b^+ of Eqs. (B1)–(B5). The Fokker-Planck operator governing the Rouse chain under flow may be written as

$$-\mathcal{L}^*_{\text{Rouse}}=\sum_{p=1}^{\infty}\frac{(p\pi)^2}{\zeta_0N_0^2}H_p'\ , \tag{B7}$$

where

$$H_p'=-\partial_{\mathbf{T}_p}\cdot[\underline{I}-G(p)\underline{A}]\cdot\mathbf{T}_p-\partial^2_{\mathbf{T}_p} \tag{B8}$$

and $\mathbf{T}_p$ is directly proportional to the Rouse mode

$$\mathbf{T}_p=\left[\frac{2(p\pi)^2}{N_0}\right]^{1/2}\mathbf{R}_p\ . \tag{B9}$$

Examining the form of Eq. (B8) shows that we only need consider the x and y parts of the equation, since that involves the only subtleties. This leaves us to consider the eigenvalues of the operator H_p given by

$$H_p=-2-\mathbf{T}_p\cdot[\underline{I}-G(p)\underline{A}^T]\cdot\partial_{\mathbf{T}_p}-\partial^2_{\mathbf{T}_p} \; . \tag{B10}$$

We will write

$$D_p=-2-\mathbf{T}_p\cdot\partial_{\mathbf{T}_p}-\partial_{\mathbf{T}_p}\cdot\overleftrightarrow{\sigma}_p\cdot\partial_{\mathbf{T}_p} \; , \tag{B11}$$

$$N_p=H_p-D_p \tag{B12}$$

$$=G(p)\partial_{\mathbf{T}_p}\cdot\underline{A}\cdot\mathbf{T}_p+\partial_{\mathbf{T}_p}\cdot(\overleftrightarrow{\sigma}_p-\underline{I})\cdot\partial_{\mathbf{T}_p} \tag{B13}$$

with $\overleftrightarrow{\sigma}_p$ defined in Eq. (C3). By inspection D_p, H_p, N_p all commute with one another.

We will proceed to construct a, $a^\dagger$, b, and $b^\dagger$. Consider a coordinate transformation

$$\mathbf{T}_p=\overleftrightarrow{\sigma}_p^{1/2}\cdot\overleftrightarrow{\mathbf{M}}\cdot\mathbf{V}_p \; , \tag{B14}$$

where $\overleftrightarrow{\mathbf{M}}$ is a rotation, as yet, unspecified. Note that since $\overleftrightarrow{\sigma}_p$ is a positive symmetric matrix, it has a unique positive square root $\overleftrightarrow{\sigma}_p^{1/2}$. In these coordinates,

$$\begin{aligned} D_p&=-2-\mathbf{V}_p\cdot\partial_{\mathbf{V}_p}-\partial_{\mathbf{V}_p}\cdot\partial_{\mathbf{V}_p} \; , \\ N_p&=G(p)\partial_{\mathbf{V}_p}\cdot\overleftrightarrow{\mathbf{M}}^T\cdot\overleftrightarrow{\sigma}_p^{-1/2}\cdot\underline{A}\cdot\overleftrightarrow{\sigma}_p^{1/2}\cdot\overleftrightarrow{\mathbf{M}}\cdot\mathbf{V}_p \\ &\quad+\partial_{\mathbf{V}_p}\cdot(\underline{I}-\overleftrightarrow{\mathbf{M}}^T\overleftrightarrow{\sigma}_p^{-1}\overleftrightarrow{\mathbf{M}})\cdot\partial_{\mathbf{V}_p} \; . \end{aligned} \tag{B15}$$

The first part of the transformation of Eq. (B14) brings D_p to a familiar harmonic oscillator form, which is unchanged by the further rotation. The rotation $\overleftrightarrow{\mathbf{M}}$ is chosen such that N_p and D_p are given by Eqs. (B1)–(B15) with

$$\begin{aligned} a&=V_x+\partial_{V_x} \; , \\ a^\dagger&=-\partial_{V_x} \; , \\ b&=V_y+\partial_{V_y} \; , \\ b^\dagger&=-\partial_{V_y} \; . \end{aligned} \tag{B16}$$

The construction of the rotation $\overleftrightarrow{\mathbf{M}}$ is left to the interested reader as a straightforward but tedious exercise.

APPENDIX C: ROUSE THEORY: STEADY-STATE CORRELATIONS

1. Rouse modes: definition

We find it convenient to introduce Rouse modes in our exposition and so we list here the definitions of Rouse modes and the transformations from Rouse modes back to chain coordinates:

$$\mathbf{R}_q=\frac{1}{N_0}\int_0^{N_0}d\sigma\,\mathbf{R}(\sigma)\cos\frac{q\pi\sigma}{N_0} \; , \tag{C1}$$

$$\mathbf{R}(\tau)=\mathbf{R}_0+2\sum_{q=1}^{\infty}\mathbf{R}_q\cos\frac{q\pi\tau}{N_0} \; . \tag{C2}$$

Introducing this transform allows us to decouple the modes in the absence of excluded volume and hydrodynamics.

2. Steady-state correlations

Here we calculate some correlation functions for the Rouse chain under flow, namely $\overleftrightarrow{\sigma}_p,\overleftrightarrow{\sigma}^{\text{poly}},\langle[\mathbf{R}(\tau)-\mathbf{R}(\sigma)][\mathbf{R}(\tau)-\mathbf{R}(\sigma)]\rangle$, as well as $\langle(d\mathbf{R}/d\tau)(d\mathbf{R}/d\tau)\rangle_{\text{dev}}$. We also include expressions for the sums that are necessary to evaluate these correlations.

In the absence of excluded volume and hydrodynamic interactions, the quantity $\overleftrightarrow{\sigma}_p$ may be evaluated using Eq. (3.19) at $\epsilon=0$. Thus we have $\overleftrightarrow{\mathbf{S}}_p=\underline{I}$, and the solution is given by

$$\overleftrightarrow{\sigma}_p=\underline{I}+\frac{G(p)}{2}(\underline{A}+\underline{A}^T)+\frac{G^2(p)}{2}\underline{A}\cdot\underline{A}^T \; , \tag{C3}$$

with

$$G(p)=\frac{G}{(\pi p)^2}, \quad G=g\zeta_0N_0^2 \; . \tag{C4}$$

Using Eq. (3.6) at $\epsilon=0$, one obtains

$$\frac{2}{N_0}\langle\mathbf{R}_p\mathbf{R}_p\rangle=\left[\frac{1}{\pi p}\right]^2\overleftrightarrow{\sigma}_p \; . \tag{C5}$$

This implies

$$\frac{1}{N_0}\overleftrightarrow{\mathbf{Q}}(\tau,\sigma)\equiv\frac{1}{N_0}\langle[\mathbf{R}(\tau)-\mathbf{R}(\sigma)][\mathbf{R}(\tau)-\mathbf{R}(\sigma)]\rangle \tag{C6}$$

$$=\frac{4}{N_0}\sum_{p=1}^{\infty}\langle\mathbf{R}_p\mathbf{R}_p\rangle\left[\cos\frac{p\pi\tau}{N_0}-\cos\frac{p\pi\sigma}{N_0}\right]^2 \; . \tag{C7}$$

Using Eqs. (C3), (C5), and (C6) yields

$$\begin{aligned} \frac{1}{N_0}\overleftrightarrow{\mathbf{Q}}(\tau,\sigma)&=r_2(\tau,\sigma)\underline{I}+r_4(\tau,\sigma)\frac{G}{2}(\underline{A}+\underline{A}^T) \\ &\quad+r_6(\tau,\sigma)\frac{G^2}{2}\underline{A}\cdot\underline{A}^T \; , \end{aligned} \tag{C8}$$

where

$$r_j(\tau,\sigma)=2\sum_{p=1}^{\infty}\frac{[\cos(p\pi\tau/N_0)-\cos(p\pi\sigma/N_0)]^2}{(p\pi)^j} \; . \tag{C9}$$

We evaluate Eq. (C8) in several steps. First we define

$$f_j(\mu)=2\sum_{p=1}^{\infty}\frac{1-\cos p\pi\mu}{(p\pi)^j}, \quad |\mu|\le 1 \; . \tag{C10}$$

Using the standard results for Bernoulli sums one may calculate[27]

$$\begin{aligned} f_2(\mu)&=|\mu|-\tfrac{1}{2}\mu^2 \; , \\ f_4(\mu)&=\tfrac{1}{6}(\mu^2-|\mu|^3+\tfrac{1}{4}\mu^4) \; , \\ f_6(\mu)&=\tfrac{1}{720}(8\mu^2-10\mu^4+6|\mu|^5-\mu^6) \; . \end{aligned} \tag{C11}$$

This in turn yields

$$\begin{aligned} r_2(\tau,\sigma)&=|w| \; , \\ r_4(\tau,\sigma)&=\tfrac{1}{6}w^2[-|w|+\tfrac{3}{2}(1-v^2)] \; , \\ r_6(\tau,\sigma)&=\tfrac{1}{120}w^2[|w|^3+\tfrac{5}{2}(1-v^2)(1-v^2-w^2)] \; , \end{aligned} \tag{C12}$$

where

$$w=\frac{\tau-\sigma}{N_0}\,,\qquad v=\frac{\tau+\sigma-N_0}{N_0}\,. \tag{C13}$$

Notice that the two natural symmetries of the problem change the sign of either v or w. Namely, the interchange of the chain coordinates reverses the sign of w, whereas the relabeling of the chain ends reverses the sign of v. Obviously the correlation function given by Eq. (C6) is unchanged under these symmetries.

Finally, from Eqs. (C7) and (C11), we arrive at

$$\frac{1}{N_0}\overleftrightarrow{Q}(\tau,\sigma)=|w|\underline{I}+\frac{G}{12}(\underline{A}+\underline{A}^T)w^2[-|w|+\tfrac{3}{2}(1-v^2)]+\frac{G^2}{240}\underline{A}\cdot\underline{A}^Tw^2[|w|^3+\tfrac{5}{2}(1-v^2)(1-v^2-w^2)]\,. \tag{C14}$$

We will also need the following results in Appendix D ($w>0$):

$$\det|\overleftrightarrow{Q}(\tau,\sigma)|=(|w|N_0)^d\left[1+G^2\left[\frac{|w|(1-v^2)^2}{96}-\frac{w^2(1-v^2)^2}{64}+\frac{|w|^3(1-v^2)}{96}-\frac{w^4}{360}\right]\right]. \tag{C15}$$

The inverse of $\overleftrightarrow{\mathrm{Q}}(\tau,\sigma)$ is proportional to the following matrix which we define as

$$\begin{aligned}|w|\underline{Y}(\tau,\sigma)&\equiv\overleftrightarrow{\mathrm{Q}}^{-1}(\tau,\sigma)\det|\overleftrightarrow{\mathrm{Q}}(\tau,\sigma)|(|w|N_0)^{1-d}\\&=|w|\underline{I}-\frac{G}{12}(\underline{A}+\underline{A}^T)w^2[-|w|+\tfrac{3}{2}(1-v^2)]+\frac{G^2}{240}\underline{A}^T\cdot\underline{A}w^2[|w|^3+\tfrac{5}{2}(1-v^2)(1-v^2-w^2)]\,,\end{aligned} \tag{C16}$$

so that $\underline{Y}$ is unity in the absence of flow. We will need this quantity in the expression for $\overleftrightarrow{\mathrm{S}}_p$.

We also may calculate

$$\begin{aligned}N_0\left\langle\frac{d\mathbf{R}(\tau)}{d\tau}\frac{d\mathbf{R}(\tau)}{d\tau}\right\rangle_{\text{dev}}&=N_0\lim_{\sigma\to\tau}\frac{1}{(\tau-\sigma)^2}[\overleftrightarrow{\mathrm{Q}}(\tau,\sigma)-|\tau-\sigma|\underline{I}]\\&=\frac{G}{2}\frac{\tau(N_0-\tau)}{N_0^2}(\underline{A}+\underline{A}^T)+\frac{G^2}{6}\left[\frac{\tau(N_0-\tau)}{N_0^2}\right]^2\underline{A}\cdot\underline{A}^T\,.\end{aligned} \tag{C17}$$

We see that the stress along the chain backbone is peaked near the center of the chain. The implication is that, due to the flow, the translational symmetry along the chain is lost. The translational symmetry greatly simplifies the calculation of equilibrium properties in certain approximation schemes.

Finally we may sum the last equation over all the monomers, leading to

$$\begin{aligned}\int_0^{N_0}d\tau\left\langle\frac{d\mathbf{R}(\tau)}{d\tau}\frac{d\mathbf{R}(\tau)}{d\tau}\right\rangle_{\text{dev}}&=\sum_{p=1}^{\infty}(\overleftrightarrow{\sigma}_p-\underline{I})\\&=\frac{G}{12}(\underline{A}+\underline{A}^T)+\frac{G^2}{180}\underline{A}\cdot\underline{A}^T\,.\end{aligned} \tag{C18}$$

The final result of Eq. (C18) may be derived directly from Eqs. (C17) or (C3). The last quantity is proportional to the polymeric contribution to the deviatoric stress in the absence of excluded volume and hydrodynamic interactions.

APPENDIX D: EXPRESSION OF STRESS

Here we explicitly evaluate $\overleftrightarrow{\mathrm{S}}_p$, which arises in the expression for the stress. To first order in ϵ we find

$$\overleftrightarrow{\mathrm{S}}_p=\underline{I}+\overleftrightarrow{\mathrm{S}}_p^{\text{pre}}+\overleftrightarrow{\mathrm{S}}_p^{\text{non}}+\overleftrightarrow{\mathrm{S}}_p^{\text{ex}}\,, \tag{D1}$$

$$\overleftrightarrow{\mathrm{S}}_p^{\text{pre}}\overset{S}{=}-(\langle\overleftrightarrow{\mathrm{D}}'_{p,p}\rangle)\cdot(\overleftrightarrow{\sigma}_p-\underline{I})\,, \tag{D2}$$

$$(\overleftrightarrow{\mathrm{S}}_p^{\text{non}})^{\alpha\beta}\overset{S}{=}-\frac{N_0}{2}\sum_{q=1}^{\infty}\left[\frac{1}{\pi p}\right]^2\left\langle\frac{\partial^2\overleftrightarrow{\mathrm{D}}_{p,q}^{\alpha\gamma}}{\partial\mathbf{R}_p^{\mu}\partial\mathbf{R}_q^{\delta}}\right\rangle\sigma_q^{\delta\gamma}\sigma_p^{\mu\beta}\,, \tag{D3}$$

$$\begin{aligned}\overleftrightarrow{\mathrm{S}}_p^{\text{ex}}\overset{S}{=}&-\frac{N_0}{2}G(p)\left[\frac{1}{\pi p}\right]^2\\&\times\left\{\underline{A}\cdot\left[\left[\left\langle\frac{\partial^2\mathcal{H}_{\text{int}}}{\partial\mathbf{R}_p\partial\mathbf{R}_p}\right\rangle\right.\right.\right.\\&\left.\left.\left.\qquad-\left\langle\frac{\partial^2\mathcal{H}_{\text{int}}}{\partial\mathbf{R}_p\partial\mathbf{R}_p}\right\rangle_{g=0}\right]\cdot\overleftrightarrow{\sigma}_p\right]^S\right\}.\end{aligned} \tag{D4}$$

The $\underline{I}$ on the right hand side of Eq. (D1) corresponds to the Rouse theory; the remaining terms are of order ϵ. The second and third terms are from the hydrodynamic interaction and the fourth from the excluded volume. The second term in all that arises if the diffusion matrix is preaveraged (hence the nomenclature "pre" and "non"). Conventionally the nonpreaveraged term is considered to be small and is often neglected. The mathematics of the dynamical theory is far easier in its absence. However we find that $\overleftrightarrow{\mathrm{S}}_p^{\text{non}}$ has a flow dependence which is both significantly larger than and of opposite sign to $\overleftrightarrow{\mathrm{S}}_p^{\text{pre}}$.

The bulk of the work involved in this paper is in evaluating the above expression. Ultimately Eq. (D1) can be reduced to three integrations. Two of these integrations will involve the chain coordinates. A further integration will arise in the following way. Consider the form of $\overleftrightarrow{D}_{p,q}$ given by Eq. (2.14). We wish to reduce Eq. (D1) by a series of Gaussian conformational averages and by Gaussian integrations [involving the **k** integral of Eq. (2.14)]. To this end we introduce an identity to reexpress the $1/k^4$ term of Eq. (2.14):

$$\left[\frac{1}{\frac{1}{2}N_0k^2}\right]^2=\int_0^1\frac{d\beta}{\beta^3}(1-\beta)e^{-1/2N_0k^2/\beta}e^{1/2N_0k^2} . \qquad \text{(D5)}$$

This is more transparent on making the substitution $\beta=1/(1+\alpha)$. It is the form Eq. (D5) which will be most suitable for computer integrations.

The results are

$$\overleftrightarrow{S}_p^{\text{pre}}\overset{S}{=}-\frac{\zeta_0}{4\pi^2\eta_0}\int_0^1\beta(1-\beta)d\beta\int_0^1 dv\int_0^{1-v}dwJ_{\text{pre}}(p,v,w)\left[3\beta\frac{\Delta}{w}\underline{I}+(1+\Delta)\left[\frac{\text{tr}\underline{H}'}{w}\underline{I}-\frac{\underline{H}'}{w}\right]\right]\cdot(\overleftrightarrow{\sigma}_p-\underline{I}) , \qquad \text{(D6)}$$

and

$$\overleftrightarrow{S}_p^{\text{non}}\overset{S}{=}\frac{\zeta_0}{4\pi^2\eta_0}\int_0^1 d\beta\,\beta(1-\beta)\int_0^1 dv\int_0^{1-v}dw\frac{4}{(\pi p)^2}\frac{1+\Delta}{w^2}[\overleftrightarrow{J}_{\text{non}}\cdot\underline{H}_\beta(\text{tr}\underline{H}_\beta)+2\overleftrightarrow{J}_{\text{non}}\cdot\underline{H}_\beta\cdot\underline{H}_\beta$$
$$-2\underline{H}_\beta\cdot\overleftrightarrow{J}_{\text{non}}\cdot\underline{H}_\beta-\underline{H}_\beta\text{tr}(\underline{H}_\beta\cdot\overleftrightarrow{J}_{\text{non}})]\cdot\overleftrightarrow{\sigma}_p . \qquad \text{(D7)}$$

In order to arrive at the expression (D7), we needed to perform a sum over q, hence we used f_2,f_4,f_6 of Appendix C. Finally

$$\overleftrightarrow{S}_p^{\text{ex}}\overset{S}{=}v_0\frac{G(p)}{2\pi^2}\frac{1}{(p\pi)^2}\int_0^1 dv\int_0^{1-v}dw\frac{J_{\text{ex}}}{w^3}\left[\left[\frac{\underline{Y}}{(\det\underline{Y})^{3/2}}-\underline{I}\right]\cdot\overleftrightarrow{\sigma}_p\right]^S . \qquad \text{(D8)}$$

Definitions made in Eqs. (D6)–(D8) are

$$J_{\text{pre}}=\tfrac{1}{2}\{\cos[p\pi(1+v)]+\cos(p\pi w)\} , \qquad \text{(D9)}$$

$$\overleftrightarrow{J}_{\text{non}}=\{\cos[p\pi(1+v)]-1\}[\cos(p\pi w)-1]\left[\frac{-w}{16}G(\underline{A}+\underline{A}^T)+\frac{-w^2}{96}G^2\underline{A}\,\underline{A}^T[\tfrac{3}{2}(1-v^2)-w]\right]$$
$$+\{\sin[p\pi(1+v)]\sin(p\pi w)\}\left[\frac{wv}{16}G(\underline{A}+\underline{A}^T)+\frac{wv}{96}G^2\underline{A}\cdot\underline{A}^T(1-v^2-w^2)\right] , \qquad \text{(D10)}$$

$$J_{\text{ex}}=2\{1-\cos[p\pi(1+v)]\}\sin^2\left[\frac{p\pi w}{2}\right] . \qquad \text{(D11)}$$

Also,

$$\underline{H}_\beta=\underline{I}+\beta\underline{H}' . \qquad \text{(D12)}$$

The matrix $\underline{H}'$ is only nonzero in the upper 2×2 block where it is given by

$$\underline{H}'=\begin{bmatrix}-bG^2+\beta a^2G^2 & -aG\\ -aG & \beta a^2G^2\end{bmatrix}(1+\Delta)^2 , \qquad \text{(D13)}$$

where

$$a=\frac{1}{2|w|}r_4(w,v) , \qquad \text{(D14)}$$

$$b=\frac{1}{2|w|}r_6(w,v) , \qquad \text{(D15)}$$

$$\Delta=\frac{1}{(1+\beta bG^2-\beta^2a^2G^2)^{1/2}}-1 . \qquad \text{(D16)}$$

Finally r_4,r_6 as well as $\underline{Y},\overleftrightarrow{\sigma}_p$ are given in Appendix C; Eqs. (D6)–(D8) (and the subsequent definitions) then yield (D1). Equation (4.10) may be used to express $\overleftrightarrow{S}_p$ solely as a function of Z and p.

APPENDIX E: RENORMALIZATION

Here we renormalize the expression for the dimensionless flow rate. The exposition is by now standard,[18] and we keep details to a minimum. In the Z limit the hydrodynamic interaction and the excluded volume interaction become functions of the one variable Z. With Appendices D and E in hand the stress tensor may be evaluated numerically.

We wish first to evaluate Eq. (3.13). This equation reads

$$G_R(p)=G(p)\left[1-[D(p,p)-1]-\frac{1}{2d}N_0\left[\frac{1}{p\pi}\right]^2\left\langle\frac{\partial}{\partial\mathbf{R}_p}\cdot\frac{\partial\mathcal{H}_{\text{int}}}{\partial\mathbf{R}_p}\right\rangle_{g=0}\right] . \qquad \text{(E1)}$$

The correlation function of Eq. (E1) is evaluated at zero shear rate. From Eqs. (2.14) and (3.11), we find

$$D(p,p)-1=\frac{\zeta_0}{\eta_0}(2\pi N_0)^{\epsilon/2}\left[\frac{d-1}{d}\right]\left[\frac{1}{d-2}\right]\left[\frac{1}{4\pi^2}\right]2\int_0^1 dv\int_0^{1-v}dw\frac{J_{\text{ex}}}{w^3}\frac{\cos[p\pi(1+v)]+\cos(p\pi w)}{w^{1-\epsilon/2}}\ ,$$

$$=\frac{3\zeta_0}{8\pi^2\eta_0}\frac{1}{\epsilon}+\frac{5\zeta_0}{32\pi^2\eta_0}+\frac{3\zeta_0}{16\pi^2\eta_0}\left[f_{\text{hyd}}(p)+\ln\left[\frac{2N_0}{p}\right]\right]\ . \qquad \text{(E2)}$$

Also

$$\frac{N_0}{2d}\frac{1}{(p\pi)^2}\left\langle\frac{\partial}{\partial\mathbf{R}_p}\cdot\frac{\partial\mathcal{H}_{\text{int}}}{\partial\mathbf{R}_p}\right\rangle_{g=0}=-\frac{8}{(p\pi)^2}v_0(2\pi)^{-d/2}N_0^{\epsilon/2}\int_0^1 dw\int_0^{1-w}dv\frac{1}{w^{d/2-1}}\frac{\sin^2(p\pi w/2)\sin^2[p\pi(1+v)/2]}{w^2}\ ,$$

$$=-v_0(2\pi)^{-2}\left[\frac{2}{\epsilon}+\ln(4N_0/p)+f_{\text{ex}}(p)\right]\ , \qquad \text{(E3)}$$

correct to first order in ϵ. The quantities $f_{\text{hyd}}(p)$ and $f_{\text{ex}}(p)$ which appear in Eqs. (E2) and (E3) are given by

$$f_{\text{hyd}}(p)=\int_0^1 dw\frac{\cos w-1}{w}+\int_1^{p\pi}dw\frac{\cos w}{w}-\frac{1}{p\pi}\int_0^{p\pi}dw\frac{\sin w}{w}\ , \qquad \text{(E4)}$$

and

$$f_{\text{ex}}(p)=\int_0^1 dw\frac{\sin^2 w-w^2}{w^3}+\int_1^{p\pi/2}dw\frac{\sin^2 w}{w^3}+\frac{2}{p\pi}\int_0^{p\pi/2}dw\frac{\sin^2 w}{w^2}\left[\frac{\sin 2w}{2w}-1\right]\ . \qquad \text{(E5)}$$

In order to absorb the divergences appearing in Eqs. (E2) and (E4), we introduce first the standard dimensionless parameters u_0, ξ_0,

$$\begin{aligned} v_0&=u_0L^{-\epsilon/2}\ ,\\ \zeta_0&=\eta_0\xi_0L^{-\epsilon/2}\ , \end{aligned} \qquad \text{(E6)}$$

and then renormalization factors and renormalized variables (the latter appear on the RHS)

$$\begin{aligned} N_0&=(Z_N)^{-1}N\ ,\\ u_0&=(Z_u)^{-1}u\ ,\\ \zeta_0&=Z_\zeta^{-1}\zeta\ ,\\ \xi_0&=Z_\zeta^{-1}\xi\ . \end{aligned} \qquad \text{(E7)}$$

The renormalization factor Z_u may be determined by second-order perturbation theory and Z_N by calculating the end-to-end distance. Note that the flow should not affect the renormalization factors, as long as the flow is microscopically weak. Knowing Z_N and Z_u, we may determine Z_ξ by removing the divergences that appear in the expression for G_R. The results are

$$\begin{aligned} Z_N&=1+\frac{u}{2\pi^2\epsilon}\ ,\\ Z_u&=1-\frac{2u}{\pi^2\epsilon}\ ,\\ Z_\zeta&=1-\frac{u}{2\pi^2\epsilon}-\frac{3\xi}{8\pi^2\epsilon}\ . \end{aligned} \qquad \text{(E8)}$$

Combining Eqs. (E1)–(E3) and (E6)–(E8) yields to first order in ϵ:

$$G_R(p)=\left[\frac{1}{\pi p}\right]^2 G_R p^{-(\epsilon/8)(u/u^*)+(3\epsilon/8)(\xi/\xi^*)}\times\left[1+\frac{\epsilon}{8}\left[\frac{u}{u^*}[f_{\text{ex}}(p)-f_{\text{ex}}(p=1)]-\frac{3\xi}{\xi^*}[f_{\text{hyd}}(p)-f_{\text{hyd}}(p=1)]\right]\right]\ , \qquad \text{(E9)}$$

where

$$G_R=g\zeta N^2\left[\frac{2N}{L}\right]^{(\epsilon/8)(u/u^*)-(3\epsilon/8)(\xi/\xi^*)}\times\left[1+\frac{\epsilon}{8}\left[\frac{u}{u^*}[f_{\text{ex}}(p=1)]-\frac{3\xi}{\xi^*}[f_{\text{hyd}}(p=1)]\right]\right]\ , \qquad \text{(E10)}$$

which is correct to first order in ϵ. Here u^* and ξ^* are the fixed points of the renormalization group transformation: $u^*=\pi^2\epsilon/2$, $\xi^*=2\pi^2\epsilon$.

In order to find the appropriate scaling variables one writes the renormalization-group equation for $\overleftrightarrow{\sigma}_p$:

$$\left[L\frac{\partial}{\partial L}+\beta_u(u)\frac{\partial}{\partial u}+\beta_\xi(u,\xi)\frac{\partial}{\partial\xi}+\gamma_N(u)N\frac{\partial}{\partial N}\right]\bigg|_{\text{bare}}\overleftrightarrow{\sigma}_p=0\ , \qquad \text{(E11)}$$

where

$$\begin{aligned} \beta_u(u)&=L\frac{\partial}{\partial L}u\bigg|_{\text{bare}}=\frac{u\epsilon}{2}[(u^*-u)/u^*]\ ,\\ \beta_\xi(\xi,u)&=L\frac{\partial}{\partial L}\xi\bigg|_{\text{bare}}=\frac{\xi\epsilon}{2}\left[\frac{3}{4}\frac{\xi^*-\xi}{\xi^*}+\frac{1}{4}\frac{u^*-u}{u^*}\right]\ ,\\ \gamma N(u)&=L\frac{\partial}{\partial L}\ln Z_N\bigg|_{\text{bare}}=\frac{\epsilon}{8}(u/u^*)\ . \end{aligned} \qquad \text{(E12)}$$

We may derive the results for the beta functions from Eqs. (E6) and (E7). Here $|_{\text{bare}}$ signifies that the bare microscopic parameters v_0, ζ_0, and N_0 have been held fixed.

We seek solutions to the renormalization-group equation (E10):

$$\overleftrightarrow{\sigma}_p=\overleftrightarrow{\sigma}_p(L,N,u,\xi,g,p)\ , \tag{E13}$$

where recall g is the flow rate, u is the renormalized excluded volume parameter, and ξ is the renormalized friction coefficient. The solution has the form

$$\overleftrightarrow{\sigma}_p=\overleftrightarrow{\sigma}_p\left[Lw^{-2/\epsilon},N(1+w)^{-1/4},(1+w)^{3/4}\frac{1-\hat{z}}{\hat{z}},g,p\right]\ , \tag{E14}$$

where

$$w=u/(u^*-u)\ ,$$
$$\hat{z}=(\xi/\xi^*)/(u/u^*)\ . \tag{E15}$$

The solution must be invariant under the reparametrization of the model. Let [ ] denote the engineering dimension of a quantity with respect to the chain variable τ. Then

$$[\tau]=[N]=[L]=C\ , \tag{E16}$$

$$[g]=C^{-d/2}\ . \tag{E17}$$

Hence we can write

$$\overleftrightarrow{\sigma}_p=\overleftrightarrow{\sigma}_p\left[CLw^{-2/\epsilon},CN(1+w)^{-1/4},(1+w)^{3/4}\frac{1-\hat{z}}{\hat{z}},gC^{-d/2}\right]\ . \tag{E18}$$

If we choose

$$CN(1+w)^{-1/4}=1\ , \tag{E19}$$

after some algebraic manipulations we can write

$$\overleftrightarrow{\sigma}_p=\overleftrightarrow{\sigma}_p\left[(2\pi N/L)^{\epsilon/2}w(1+w)^{-\epsilon/8},\delta,gN^{d/2}\left[\frac{2\pi N}{L}\right]^{-(\epsilon/4)(u/u^*)},p\right]\ , \tag{E20}$$

where

$$\delta=(1+w)^{3/4}(1-\hat{z})/\hat{z}\ . \tag{E21}$$

In the Z limit $N\to\infty$ with $uN^{1/2}$ fixed, we can incorporate the solvent effects into a single variable Z defined by

$$Z=(2\pi N/L)^{\epsilon/2}\frac{u}{u^*-u}\ , \tag{E22}$$

so that

$$\overleftrightarrow{\sigma}_p=\overleftrightarrow{\sigma}_p\left[Z,gN^{d/2}\left[\frac{2\pi N}{L}\right]^{-(\epsilon/4)(u/u^*)},p\right]\ . \tag{E23}$$

In terms of Z then

$$\frac{\xi}{\xi^*}=\left[\frac{Z}{1+Z}\right]\left[\frac{1}{1-(1+Z)^{-3/4}}\right]\left[\frac{2\pi N}{L}\right]^{-(\epsilon/2)(1/1+Z)+(3\epsilon/8)(Z/1+Z)[(1+Z)^{-3/4}/1-(1+Z)^{-3/4}]}\ , \tag{E24}$$

$$\frac{u}{u^*}=\frac{Z}{1+Z}\left[\frac{2\pi N}{L}\right]^{-(\epsilon/2)(1/1+Z)}\ . \tag{E25}$$

One can then show that Eq. (E9) may be rewritten

$$G_R\propto gN^{d/2}(2\pi N/L)^{(e/4)(u/u^*)}\propto gN^{d\nu}\ , \tag{E26}$$

with

$$\nu=\frac{1}{2}+\frac{\epsilon}{16}\frac{u}{u^*} \tag{E27}$$

being the critical exponent.

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[27] There is a relation between these quantities which allows one to construct the f_{2k}. For the k integer: $f''_{2k}(\mu) = -f_{2(k-1)}(\mu) + [\int_0^1 dw\, f_{2(k-1)}(w)]$, with $f'_{2k}(0) = f_{2k}(0) = 0$. Since f''_2 is easily computed, we may solve for f_2 and then generate all the higher f_{2k}'s from the above relation.

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