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Nonlinear force and tensorial mobility in a kinetic theory for polymer liquids

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A stochastic differential equation for the global length and orientation of a flexible macromolecule is studied. A non-Hookean internal force law, a tensorial mobility, and an approximate form of the hydrodynamic interaction are taken into consideration. An equation for the equal-time correlation function is obtained in mean-field approximation, the constitutive equation is derived and the material functions are calculated for steady elongational and shear flows.

I. INTRODUCTION

The rheological properties of polymer fluids are determined by the constitutive equation, i.e., the relationship between the stress tensor and the velocity gradient. It is one of the aims of the kinetic theory of polymer solutions to substantiate or improve the constitutive equations which are usually modeled within a pure phenomenological approach. The simplest kinetic model is the Rouse model. According to this model the fluid is considered as an ensemble of noninteracting flexible macromolecules suspended in a Newtonian fluid. These macromolecules are idealized as chains of beads joined by Hookean springs. In addition to these internal Hookean forces the beads experience a hydrodynamic drag proportional to their velocity relative to the Newtonian solvent and stochastic, Brownian motion forces due to the thermal fluctuations of the solvent.

If one takes into consideration only the global orientation and length of the macromolecules as degrees of freedom each macromolecule can be regarded as a flexible dumbbell, characterized by a vector $\mathbf{x}(t)$. Neglecting the acceleration terms the equation of motion for $\mathbf{x}(t)$ reads

$$\dot{\mathbf{x}}(t) = \boldsymbol{\kappa}\mathbf{x}(t) - \frac{2}{\zeta}\mathbf{F}(\mathbf{x}(t)) + \boldsymbol{\eta}(t). \tag{1.1}$$

Here ζ is the friction coefficient appearing in Stokes' law for the hydrodynamical drag and $\mathbf{F}$ is the internal force, which is Hookean

$$\mathbf{F}(\mathbf{x}) = H\mathbf{x}. \tag{1.2}$$

The rate of deformation tensor $\boldsymbol{\kappa}$ is considered to be independent of position (homogeneous flow), but may depend on time. It occurs in the representation of the velocity field in the form

$$\mathbf{v}(\mathbf{r}) = \mathbf{v}_0 + \boldsymbol{\kappa}\mathbf{r}, \tag{1.3}$$

where $\mathbf{v}_0$ is a constant. Finally $\boldsymbol{\eta}(t)$ represents the stochastic Brownian motion force with a Gaussian distribution for each time and with the two-time correlation

$$\langle \eta_i(t)\eta_j(t')\rangle = D\delta_{ij}\delta(t-t'), \tag{1.4}$$

where

$$D = \frac{4kT}{\zeta}. \tag{1.5}$$

(T is the temperature and k is Boltzmann's constant.) The stress tensor is generally defined by

$$\tau_{ij}(t) = -\langle x_i(t)F_j(t)\rangle + kT\delta_{ij}, \tag{1.6}$$

and in the Rouse model it can directly be expressed by the two-point correlation function

$$G_{ij}(t,t') = \langle x_i(t)x_j(t')\rangle \tag{1.7}$$

at equal times via $[(\boldsymbol{\delta})_{ij} = \delta_{ij}]$

$$\boldsymbol{\tau}(t) = -H\mathbf{G}(t,t) + kT\boldsymbol{\delta}. \tag{1.8}$$

In Eqs. (1.6) and (1.8) we have dropped a factor n which is the number density of polymers, this will be done also in all material functions.

In steady simple shear flow where $\boldsymbol{\kappa}$ is

$$\boldsymbol{\kappa} = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}\dot{\gamma}, \tag{1.9}$$

the Rouse model leads to material functions independent of the shear rate $\dot{\gamma}$, namely for the viscosity η defined by

$$\tau_{12} = -\eta\dot{\gamma} \tag{1.10}$$

one obtains

$$\eta = kT\lambda_H, \quad \lambda_H = \zeta/4H, \tag{1.11}$$

and for the first normal-stress coefficient defined by

$$\tau_{11} - \tau_{22} = -\Psi_1\dot{\gamma}^2 \tag{1.12}$$

one gets

$$\Psi_1 = 2kT\lambda_H^2. \tag{1.13}$$

Finally the second normal-stress coefficient Ψ_2 defined by

$$\tau_{22} - \tau_{33} = -\Psi_2\dot{\gamma}^2 \tag{1.14}$$

is exactly zero. These results of the Rouse model are in contradiction to the experiments according to which all material functions strongly depend on $\dot{\gamma}$ and the second normal-stress coefficient though small is nonzero and mostly negative.

There have been a lot of modifications and generalizations of the simple Rouse model to meet the experimental findings, the FENE -model[1,2] (with finitely extendable nonlinear elastic dumbbells), models with the inclusion of the hydrodynamic interaction[1,3,4] and most recently the generalizations by Curtiss and Bird[5–9] and by Giesekus,[10–13] which are designed also for concentrated solutions.

In Ref. 14 the authors have shown that by inclusion of a cubic term in the law for the internal force, thus giving up the pure Hookean law [Eq. (1.2)], the material functions η and Ψ_1 show up the desired $\dot{\gamma}$ dependence, though Ψ_2 remains strictly zero. Furthermore, by standard field theoretical methods also the two-time correlation functions (1.7) for

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simple steady shear flow could be calculated in two different approximations, the mean-field and the Schwinger–Dyson approximation. In situations where exact results could be obtained by simulating the stochastic equation on a computer it was demonstrated that these exact results always lie between the approximate ones, all curves lying close together. The same situation is found for steady elongational flow.

In this paper we want to combine these ideas with the concept of deformation dependent tensorial mobility developed by Giesekus.[10–13] By generalizing the mobility $1/\zeta$ to a tensor depending on the equal time-correlation function, the second normal-stress coefficient becomes nonzero. In this manner we obtain a nonlinear model which includes Giesekus' important concept of tensorial mobility, which, however, is also based on a stochastic differential equation [a Langevin equation similar to Eq. (1.1)] so that also two-time correlation functions could be calculated by the above mentioned approximations.

In Sec. II we develop the stochastic equation of motion by generalizing Eq. (1.1). Then we derive the constitutive equations in the mean-field approximation. In Sec. III we discuss various special cases of these equations. In Secs. IV and V we calculate the material functions for simple steady elongational and shear flows, whereas in Sec. VI we discuss our results.

II. GENERALIZATIONS OF THE ROUSE MODEL

In Secs. II A–II C, we discuss three different generalizations of the Rouse model for a flexible dumbbell. Taking all three generalizations into account we derive the constitutive equations in Sec. II D.

A. The non-Hookean internal force

For higher shear rates or for strong deformations of the macromolecule one suggests that the pure Hookean law (1.2) for the internal force is not valid any more. In order to introduce a finite extensibility of the dumbbell the FENE model has been developed. Another force law which exhibits also a stiffness with increasing elongation is

$$\mathbf{F}(\mathbf{x}) = H\mathbf{x} + g\mathbf{x}^2\mathbf{x}, \quad g = \text{const}, \tag{2.1}$$

which is easier to utilize in calculating the correlation functions as was demonstrated in Ref. 14.

Furthermore, this force law represents the simplest modification of the Hookean law which is often introduced also in other branches of physics (e.g., the Ginzburg–Landau equation).

In the present context this is also a very reasonable modification. Namely, if one calculates the entropy force between two centers of a macromolecule by means of a random walk model beyond the first order term (which leads to the Hookean law) such a third-order term arises. If the two centers are separated by N flexible units, the coupling constant of the third-order term is proportional to $1/N$ while the coupling constants of all higher order corrections vanish at least as $1/N^2$.

As was already mentioned in the Introduction this modification of the internal law leads to $\dot\gamma$-dependent material functions η and Ψ_1 in steady shear flow, but the second normal-stress coefficient remains zero. In steady elongational flow the singularities of the Trouton viscosity are removed by the nonlinear force law (compare Sec. IV).

B. The hydrodynamic interaction

The hydrodynamic interaction first introduced by Kirkwood and Riseman[3] into polymer kinetic theory takes into account, that the motion of one bead influences the velocity field at the position of the other bead. As discussed frequently in the literature the consideration of this leads to the replacements

$$\frac{2}{\zeta} \to \frac{2}{\zeta}(\boldsymbol{\delta} - \zeta\boldsymbol{\Omega}), \tag{2.2}$$

$$D\boldsymbol{\delta} \to \frac{4kT}{\zeta}(\boldsymbol{\delta} - \zeta\boldsymbol{\Omega}) \tag{2.3}$$

in Eqs. (1.1) and (1.4), respectively, where $\boldsymbol{\Omega}$ is the Oseen tensor

$$\boldsymbol{\Omega} = \frac{1}{8\pi\eta_s r}\left(\boldsymbol{\delta} + \frac{\mathbf{rr}}{r^2}\right) = \frac{1}{8\pi\eta_s r^3}(r^2\boldsymbol{\delta} + \mathbf{rr}), \tag{2.4}$$

η_s is the viscosity of the solvent.

The considerable complication due to the nonlinear dependence of $\boldsymbol{\Omega}$ on $\mathbf{r}$ will usually be avoided[1] by replacing $\boldsymbol{\Omega}$ by an "equilibrium-averaged" Oseen tensor

$$\langle\boldsymbol{\Omega}\rangle_{\text{eq}} = \int d^3r\, \boldsymbol{\Omega}\psi_{\text{eq}}(\mathbf{r}) = A\cdot\boldsymbol{\delta},$$

where ψ_{eq} is the normalized distribution function at equilibrium ($\boldsymbol{\kappa} = 0$). Because A is constant, this modifies only $1/\zeta$ independently of $\dot\gamma$ so that the defects of the Rouse model are not cured. Öttinger[15] has introduced a consistently averaged hydrodynamic interaction by replacing ψ_{eq} by the true distribution function which has to be determined consistently. In this manner he obtained $\dot\gamma$-dependent material functions, but a positive second normal-stress coefficient.

In this paper we also want to replace $\boldsymbol{\Omega}$ by an average, namely by

$$\langle\boldsymbol{\Omega}\rangle' = \alpha'[\text{tr}\,\mathbf{G}(t,t)\boldsymbol{\delta} + \rho\mathbf{G}(t,t)][\text{tr}\,\mathbf{G}(t,t)]^{-3/2}, \tag{2.5}$$

where tr $\mathbf{G}$ means the trace of the matrix $\mathbf{G}$. The coefficient α' measures the strength of the hydrodynamic interaction. As one recognizes immediately the nominator and the denominator of $\boldsymbol{\Omega}$ have been averaged separately in order to obtain an approximate expression for $\langle\boldsymbol{\Omega}\rangle'$ which involves only $\mathbf{G}(t,t)$. Furthermore, a factor ρ has been introduced in order to improve this rather crude approximation (reasonable values for ρ are discussed in Sec. III).

Approximation (2.5) has two important advantages as compared to preaveraging. First, the off-diagonal components of $\langle\boldsymbol{\Omega}\rangle'$ are allowed to be nonzero and the different diagonal components do not have to be equal. Secondly, for widely separated beads in strong flows $\langle\boldsymbol{\Omega}\rangle'$ decreases due to an increase in tr $\mathbf{G}(t,t)$. Therefore, e.g., one obtains shear rate dependent material functions and a nonvanishing second normal-stress coefficient for Rouse dumbbells in steady shear flow.

C. The tensorial mobility

The consideration of the hydrodynamic interaction already leads to the fact that the factor $2/\zeta$ in front of the internal force in Eq. (1.1) is replaced by a tensor which depends on the correlation function and therefore also on $\dot{\gamma}$. According to Curtiss and Bird[5–9] and to Giesekus[10–13] there is another reason for replacing ζ or $1/\zeta$ by a tensor. For higher concentrations the hydrodynamic drag or the mobility becomes nonisotropic. This is an effect which certainly depends somehow on the correlation function and it is reasonable to take this into consideration by the replacement

$$\frac{2}{\zeta} \rightarrow \frac{2}{\zeta}\left[\boldsymbol{\delta} + \alpha \frac{H}{kT}(\mathbf{G} - \mathbf{G}^0)\right], \tag{2.6}$$

where $\mathbf{G}^0$ is $\mathbf{G}$ at $\kappa = 0$ and α measures the strength of this anisotropy. As the mobility tensor in Eq. (2.6) has to be positive definite or at least semidefinite, the condition $0 \leqslant \alpha \leqslant 1$ must be fulfilled.[10] By this ansatz the modifications due to the tensorial mobility and the hydrodynamic interaction take a similar form.

D. The constitutive equations

By considering all three modifications we now obtain the stochastic equation

$$\dot{\mathbf{x}}(t) = \boldsymbol{\kappa}\mathbf{x}(t) - \frac{2}{\zeta}\boldsymbol{\beta}\mathbf{F}(\mathbf{x}(t)) + \boldsymbol{\eta}(t) \tag{2.7}$$

instead of Eq. (1.1), where

$$\boldsymbol{\beta} = \boldsymbol{\delta} + \alpha \frac{H}{kT}[\mathbf{G}(t,t) - \mathbf{G}^0(t,t)] - \zeta\alpha' \times [\boldsymbol{\delta}\,\mathrm{tr}\,\mathbf{G}(t,t) + \rho\mathbf{G}(t,t)][\mathrm{tr}\,\mathbf{G}(t,t)]^{-3/2}, \tag{2.8}$$

$$\mathbf{F}(\mathbf{x}) = H\mathbf{x} + g\mathbf{x}\mathbf{x}^2, \tag{2.9}$$

and

$$\langle \eta_i(t)\eta_j(t')\rangle = \frac{4kT}{\zeta}\beta_{ij}(t)\delta(t-t'). \tag{2.10}$$

With this equation of motion for $\mathbf{x}(t)$, we want to derive an equation for $\mathbf{G}(t,t')$: We obtain

$$\frac{\partial}{\partial t}\langle x_i(t)x_j(t')\rangle = \kappa_{ik}(t)\langle x_k(t)x_j(t')\rangle - \frac{2}{\zeta}\beta_{ik}\langle F_k(t)x_j(t')\rangle + \langle \eta_i(t)x_j(t')\rangle \tag{2.11}$$

and

$$\frac{\partial}{\partial t'}\langle x_i(t)x_j(t')\rangle = \langle x_i(t)x_k(t')\rangle\kappa^T_{kj}(t') - \frac{2}{\zeta}\langle x_i(t)F_k(t')\rangle\beta^T_{kj} + \langle x_i(t)\eta_j(t')\rangle. \tag{2.12}$$

Adding these equations and taking the limit $t' \rightarrow t$ leads to

$$\frac{\mathscr{D}}{\mathscr{D}t}\mathbf{G}(t,t) = \frac{2}{\zeta}[\boldsymbol{\beta}(t)\boldsymbol{\tau}(t) + \boldsymbol{\tau}(t)\boldsymbol{\beta}^T(t)] + \mathbf{r}(t) + \mathbf{r}^T(t) - \frac{2kT}{\zeta}[\boldsymbol{\beta}(t) + \boldsymbol{\beta}^T(t)], \tag{2.13}$$

where the definition of the stress tensor (1.6) has been used, $\mathbf{r}$ is defined by

$$[\mathbf{r}(t)]_{ij} = \langle \eta_i(t)x_j(t)\rangle, \tag{2.14}$$

and we have introduced the upper convected time derivative

$$\frac{\mathscr{D}}{\mathscr{D}t}\mathbf{G} = \frac{\partial}{\partial t}\mathbf{G} - \boldsymbol{\kappa}\mathbf{G} - \mathbf{G}\boldsymbol{\kappa}^T. \tag{2.15}$$

From the stochastic equation (2.7), it can be inferred that

$$\mathbf{r} = \frac{2kT}{\zeta}\boldsymbol{\beta}, \tag{2.16}$$

so that finally

$$\frac{\mathscr{D}}{\mathscr{D}t}\mathbf{G}(t,t) = \frac{2}{\zeta}[\boldsymbol{\beta}(t)\boldsymbol{\tau}(t) + \boldsymbol{\tau}(t)\boldsymbol{\beta}^T(t)] \tag{2.17}$$

represents the equation from which the stress tensor has to be calculated. Apart from our slight generalization of the tensor $\boldsymbol{\beta}$ this equation is identical with the corresponding equation used by Giesekus[10] ($\boldsymbol{\tau} \rightarrow -\mathbf{S}$). Because of the Hookean relationship between $\boldsymbol{\tau}$ and $\mathbf{G}$ in Ref. 10 this equation serves as an equation for $\boldsymbol{\tau}$ *and* for $\mathbf{G}$. In our case the equation for $\mathbf{G}$, however, is more complicated. In order to derive this we have to determine the correlation function

$$\langle F_i(t)x_j(t')\rangle = HG_{ij}(t,t') + g\langle x_i(t)\mathbf{x}^2(t)x_j(t')\rangle, \tag{2.18}$$

where now a four-point correlation function appears. According to the standard rules we can decompose this term into a sum of products of two-point correlation functions and a cumulant, which in field theoretical language is called the connected four-point function:

$$\langle x_i(t)\mathbf{x}^2(t)x_j(t')\rangle = G_{ij}(t,t')\,\mathrm{tr}\,\mathbf{G}(t,t) + 2[\mathbf{G}(t,t)\mathbf{G}(t,t')]_{ij} + \langle\langle x_i(t)\mathbf{x}^2(t)x_j(t')\rangle\rangle. \tag{2.19}$$

In Ref. 14 we have used a systematic approximation scheme which in the simplest case leads to an expression for the cumulant $\langle\langle\cdots\rangle\rangle$ in terms of the correlation function and a response function. This constitutes the Schwinger–Dyson approximation. The mean-field approximation corresponds to setting the cumulant equal to zero. In the following we will restrict ourselves to this case. Then we obtain the following equation for the stress tensor:

$$\boldsymbol{\tau}(t) = -H\mathbf{G}(t,t) - g\{[\mathrm{tr}\,\mathbf{G}(t,t)]\mathbf{G}(t,t) + 2\mathbf{G}^2(t,t)\} + kT\boldsymbol{\delta}. \tag{2.20}$$

An equation for $\mathbf{G}(t,t)$ alone can now be derived by inserting Eq. (2.20) into Eq. (2.17) and using that $\boldsymbol{\beta}$ is a function of $\mathbf{G} = \mathbf{G}^T$ only:

$$\frac{\mathscr{D}G}{\mathscr{D}t} + \frac{4}{\zeta}\boldsymbol{\beta}[H\mathbf{G} + g(\mathbf{G}\,\mathrm{tr}\,\mathbf{G} + 2\mathbf{G}^2)] = \frac{4kT}{\zeta}\boldsymbol{\beta}. \tag{2.21}$$

This is the basic equation for $\mathbf{G}(t,t)$ which will be solved in the following for various flows. We could have equally written down the equations for $\mathbf{G}(t,t')$ for $t' \neq t$, but we will restrict ourselves in this paper to the discussion of the constitutive equations (2.20) and (2.21).

III. THE SPECIAL CASES

(i) Let us first consider the case $\alpha = \alpha' = 0$, i.e., we have an isotropic mobility, neglect the hydrodynamic interaction and consider only the non-Hookean force law. We have then

$$\beta = \delta, \quad \mathbf{r} = D\delta/2. \tag{3.1}$$

For this case see Ref. 14.

(ii) The case $\alpha' = g = 0$ is treated by Giesekus,[10–13] only the tensorial mobility is taken into account. We obtain, directly from Eq. (2.20),

$$\tau = -H\mathbf{G} + kT\delta = -kT\left(\frac{H}{kT}\mathbf{G} - \delta\right). \tag{3.2}$$

This is a Hookean relationship between τ and $\mathbf{G}$. Equation (2.21) for $\mathbf{G}$ reduces to

$$\frac{\mathscr{D}}{\mathscr{D}t}\mathbf{G} + \frac{4H}{\zeta}\beta(\mathbf{G} - \mathbf{G}^0) = 0 \tag{3.3}$$

with

$$\beta = \delta + \alpha\frac{H}{kT}(\mathbf{G} - \mathbf{G}^0),$$

where we have used that

$$H\mathbf{G}^0 = kT\delta. \tag{3.4}$$

Equation (3.3) is identical with Eq. (9) by Giesekus, Ref. 10.

(iii) In the case $\alpha = g = 0$ only the hydrodynamic interaction is considered. Now we have

$$\beta = \delta - \zeta\alpha'(\delta \operatorname{tr}\mathbf{G} + \rho\mathbf{G})(\operatorname{tr}\mathbf{G})^{-3/2} \tag{3.5}$$

and again

$$\tau = -H\mathbf{G} + kT\delta.$$

Characterizing the strength of the hydrodynamic interaction by

$$h = \frac{3+\rho}{3}\left(\frac{H}{6kT}\right)^{1/2}\zeta\alpha' \tag{3.6}$$

instead of α', one obtains for the material functions η and Ψ_1 at $\dot\gamma = 0$ the same values as by preaveraging. The result for Ψ_2 at $\dot\gamma = 0$ depends on the parameter ρ, for $\rho = 1/3$ one obtains the value predicted by consistent averaging.[15] If one wishes to reproduce the correct quadratic $\dot\gamma$ dependence of η for small $\dot\gamma$ (as predicted by consistent averaging) one has to chose ρ slightly less than 1/2.

(iv) In Ref. 16 Hess develops in a phenomenological approach a mean-field approximation, which corresponds, in our language, to using a tensorial Hookean law

$$\mathbf{F}(\mathbf{x}) = \mathbf{H}\cdot\mathbf{x}, \tag{3.7}$$

where the tensor $\mathbf{H}$ depends on $(\operatorname{Tr}\mathbf{G})\delta$ and $\mathbf{G}$ with coefficients $\kappa_\parallel$ and $\kappa_\perp$. His mobility, on the other hand, is still isotropic, so that the second normal-stress coefficient vanishes identically. The results of this work for the special case

$$\kappa_\parallel = 3\kappa_\perp$$

[compare Eqs. (2.10) and (3.7) of Ref. 16 with (2.21)] can be produced in our model if we set

$$\alpha = \alpha' = 0, \quad \text{i.e.,} \quad \beta = \delta \tag{3.8}$$

and

$$\kappa_\perp \sim g(4/\zeta). \tag{3.9}$$

IV. STEADY ELONGATIONAL FLOW

In this case $\mathbf{G} = \mathbf{G}(t,t)$ is time independent because of time translation invariance, the rate of deformation tensor

$$\kappa = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & -\frac{1}{2} \end{pmatrix}\dot\epsilon \tag{4.1}$$

is a constant matrix. With the ansatz

$$\mathbf{G} = \frac{kT}{H}\begin{pmatrix} G_{11} & 0 & 0 \\ 0 & G_{33} & 0 \\ 0 & 0 & G_{33} \end{pmatrix}, \tag{4.2}$$

we obtain from Eq. (2.21) the following two equations:

$$[\beta_{11} + 4\tilde g(3G_{11} + 2G_{33})\beta_{11} - 2\lambda_H\dot\epsilon]G_{11} = \beta_{11}, \tag{4.3a}$$

$$[\beta_{33} + 4\tilde g(G_{11} + 4G_{33})\beta_{33} + \lambda_H\dot\epsilon]G_{33} = \beta_{33}, \tag{4.3b}$$

where (for $\alpha' = 0$)

$$\beta_{11} = 1 + \alpha(G_{11} - G^0_{11}), \tag{4.4a}$$

$$\beta_{33} = 1 + \alpha(G_{33} - G^0_{33}), \tag{4.4b}$$

and

$$\tilde g = g\cdot\frac{kT}{H}\frac{\lambda_H}{\zeta}. \tag{4.5}$$

The equilibrium value $\mathbf{G}^0$ for $\dot\epsilon = 0$ can easily be calculated. One obtains

$$G^0_{11} = G^0_{33} = w(\tilde g) = \frac{\sqrt{1+80\tilde g} - 1}{40\tilde g}. \tag{4.6}$$

Notice that $w(0) = 1$ and $w(\tilde g) < 1$ for $\tilde g > 0$. The condition $0 \leqslant \alpha \leqslant 1/w(\tilde g)$ must be fulfilled in order to guarantee that the tensor β is positive definite.

On the other hand, we conclude from Eq. (2.17),

$$\beta_{11}\frac{\tau_{11}}{kT} = -2\lambda_H\dot\epsilon G_{11}, \tag{4.7a}$$

$$\beta_{33}\frac{\tau_{33}}{kT} = \lambda_H\dot\epsilon G_{33}. \tag{4.7b}$$

The Trouton viscosity then reads

$$T(\dot\epsilon) = \frac{1}{\lambda_H\dot\epsilon}\frac{\tau_{33} - \tau_{11}}{kT} = \frac{G_{33}}{\beta_{33}} + 2\frac{G_{11}}{\beta_{11}}. \tag{4.8}$$

For $\tilde g = 0$ equations (4.3) have been solved by Giesekus.[10] In this special case the normalized Trouton viscosity T as a function of $\lambda_H\dot\epsilon$ either adopts a minimum at negative values of $\lambda_H\dot\epsilon$ (for $0 < \alpha < 1/2$) or a maximum at positive values of $\lambda_H\dot\epsilon$ (for $1/2 < \alpha < 1$). Only for $\alpha = 1/2$ T is a monotonically increasing function of $\lambda_H\dot\epsilon$. For the Rouse model ($\alpha = 0$) T diverges at $\lambda_H\dot\epsilon = -1$ and $1/2$.

In general, Eqs. (4.3) cannot be solved exactly. However, a numerical solution can easily be obtained by an iterative procedure. In this way the change in the function $T(\dot\epsilon)$ due to the nonlinear force law has been investigated for sev-

eral values of the parameter α (still $\alpha' = 0$). For all values of α the Trouton viscosity decreases with increasing $\tilde{g}$, where the exact value for $T(0)$ is given by $3w(\tilde{g})$.

Figures 1(a)–1(d) show the functions $T(\dot{\epsilon})$ for $\tilde{g} = 0$, 0.02, 0.04, and 0.06 and for four different values of α.

The singularities at $\lambda_H \dot{\epsilon} = -1$ and $1/2$ for $\alpha = 0$ [Fig. 1(a)] are removed by the nonlinear force law. Even for very small values of $\tilde{g}$ the Trouton viscosity is drastically changed. For $0 < \alpha < 1$ the limiting values

$$T(\dot{\epsilon}) = \begin{cases} 2/\alpha & \text{for } \lambda_H \dot{\epsilon} \to \infty \\ 1/\alpha & \text{for } \lambda_H \dot{\epsilon} \to -\infty \end{cases},$$

and the qualitative form of the curves remain unchanged; however, the curves are more and more smoothed with increasing $\tilde{g}$, the maxima and minima become less pronounced.

V. STEADY SHEAR FLOW

Steady shear flow is characterized by the time independent matrix

$$\kappa = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \dot{\gamma}. \tag{5.1}$$

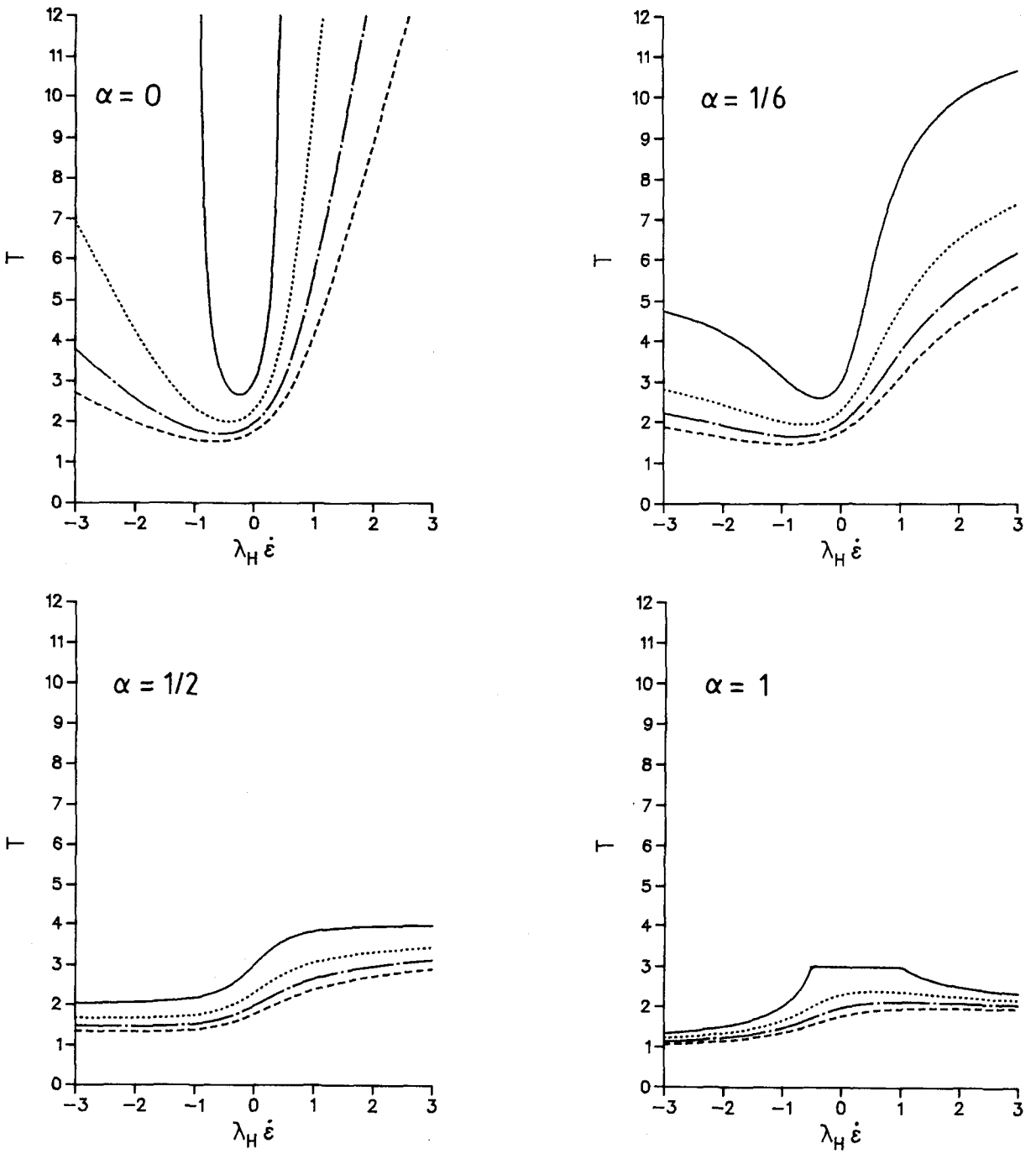

FIG. 1. Trouton viscosity vs dimensionless elongational rate for (a) $\alpha = 0$, (b) $\alpha = 1/6$, (c) $\alpha = 1/2$, and (d) $\alpha = 1$. In all figures the continuous line is the result for $\tilde{g} = 0$ [this special case has been investigated by Giesekus (Ref. 10)], the dotted line for $\tilde{g} = 0.02$, the chain-dotted line for $\tilde{g} = 0.04$, and the dashed line for $\tilde{g} = 0.06$.

For reasons of symmetry one can write

$$\mathbf{G} = \frac{kT}{H}\begin{pmatrix} G_{11} & G_{12} & 0 \\ G_{12} & G_{22} & 0 \\ 0 & 0 & G_{33} \end{pmatrix} \tag{5.2}$$

and by inserting (5.2) in the constitutive equation (2.21) one obtains the following four equations (for $\alpha' = 0$):

$$\alpha(G_{11}^2 + G_{12}^2)(1 + 4\tilde{g}[3G_{11} + G_{22} + G_{33}]) + 8\alpha\tilde{g}G_{12}^2(G_{11} + G_{22}) + (1 - \alpha w - \alpha)G_{11}$$
$$+ (1 - \alpha w)(4\tilde{g}\{G_{11}[3G_{11} + G_{22} + G_{33}] + 2G_{12}^2\} - 1) - 2\lambda_H\dot{\gamma}G_{12} = 0, \tag{5.3a}$$

$$\alpha(G_{22}^2 + G_{12}^2)(1 + 4\tilde{g}[G_{11} + 3G_{22} + G_{33}]) + 8\alpha\tilde{g}G_{12}^2(G_{11} + G_{22}) + (1 - \alpha w - \alpha)G_{22}$$
$$+ (1 - \alpha w)(4\tilde{g}\{G_{22}[G_{11} + 3G_{22} + G_{33}] + 2G_{12}^2\} - 1) = 0, \tag{5.3b}$$

$$\alpha G_{33}^2(1 + 4\tilde{g}[G_{11} + G_{22} + 3G_{33}]) + (1 - \alpha w - \alpha)G_{33} + (1 - \alpha w)(4\tilde{g}G_{33}[G_{11} + G_{22} + 3G_{33}] - 1) = 0, \tag{5.3c}$$

$$\alpha G_{12}(G_{11} + G_{22})(1 + 4\tilde{g}[G_{11} + G_{22} + G_{33}]) + 8\alpha\tilde{g}G_{12}(G_{11}^2 + G_{22}^2 + G_{12}^2$$
$$+ G_{11}G_{22}) + (1 - \alpha w - \alpha)G_{12} + (1 - \alpha w)4\tilde{g}G_{12}[3G_{11} + 3G_{22} + G_{33}] - \lambda_H\dot{\gamma}G_{22} = 0. \tag{5.3d}$$

For $\tilde{g} = 0$ Eqs. (5.3) have been solved exactly by Giesekus.[10] In the general case a numerical solution of these equations can easily be obtained. Then, the material functions η, Ψ_1, and Ψ_2 can be calculated from the expression for the stress tensor (2.20).

We introduce dimensionless material functions by using the dimensionless quantities τ_{ij}/kT and $\lambda_H\dot{\gamma}$ in the definitions (1.10,12,14). Then their values for $\dot{\gamma} = 0$ can be calculated exactly by solving Eq. (5.3) for small $\dot{\gamma}$. One obtains

$$\eta(0) = w(\tilde{g}), \tag{5.4a}$$

$$\Psi_1(0) = \frac{2w(\tilde{g})}{1 + 28\tilde{g}w(\tilde{g})}, \tag{5.4b}$$

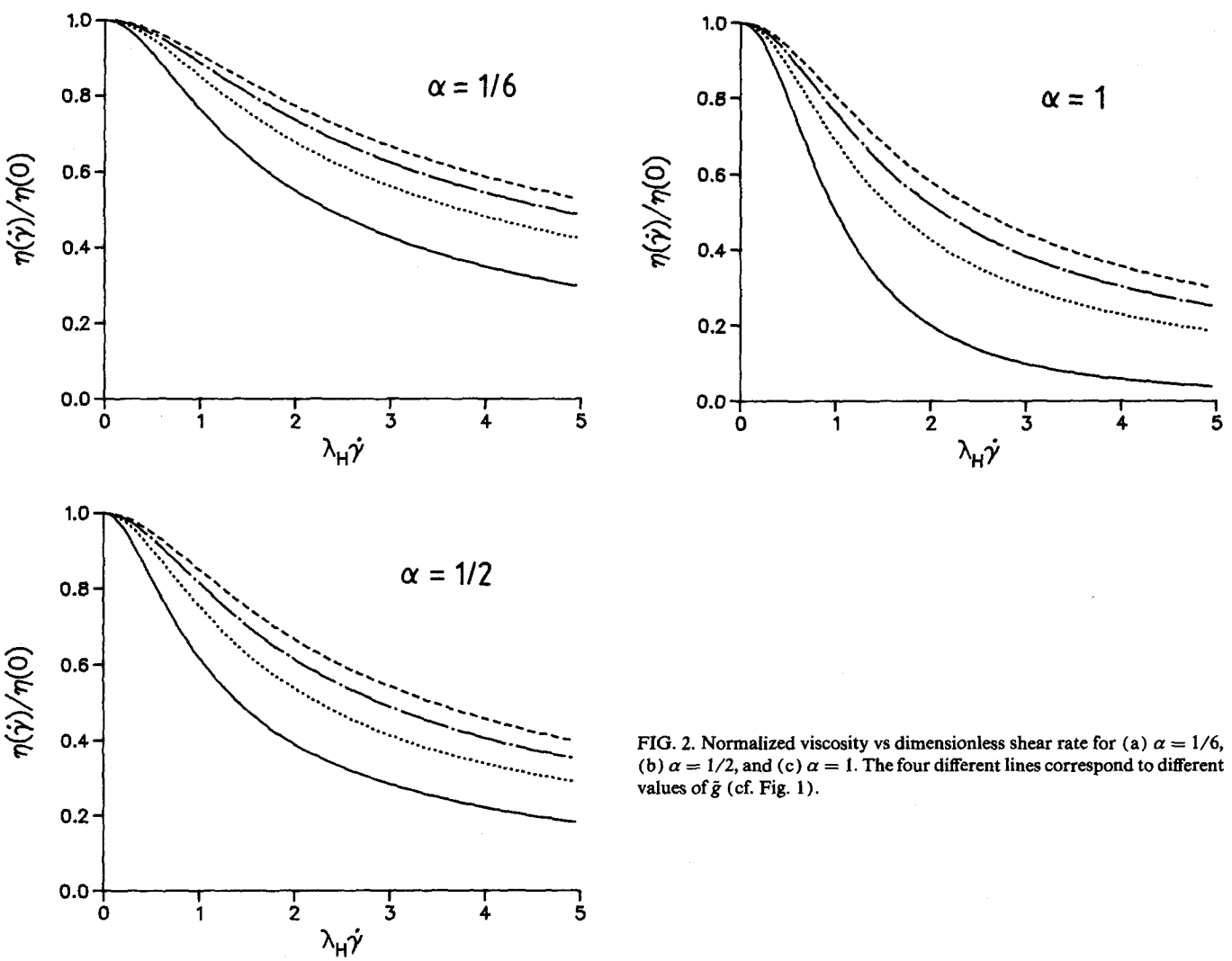

FIG. 2. Normalized viscosity vs dimensionless shear rate for (a) $\alpha = 1/6$, (b) $\alpha = 1/2$, and (c) $\alpha = 1$. The four different lines correspond to different values of $\tilde{g}$ (cf. Fig. 1).

$$\frac{\Psi_2(0)}{\Psi_1(0)} = -\frac{\alpha}{2} w(\tilde{g}). \tag{5.4c}$$

Figures 2(a)–2(c) shows the functions $\eta(\dot{\gamma})/\eta(0)$ for $\tilde{g} = 0$, 0.02, 0.04, and 0.06 for three different values of α. With increasing $\tilde{g}$ these curves become more and more flattened. The behavior of the functions $\Psi_1(\dot{\gamma})/\Psi_1(0)$ is very similar [Figs. 3(a)–3(c)]. For all curves with $\tilde{g} \neq 0$ and $\alpha \neq 0$ the asymptotic behavior can be shown to be

$$\eta(\dot{\gamma}) \sim (\lambda_H \dot{\gamma})^{-6/7} \tag{5.5a}$$

$$\Psi_1(\dot{\gamma}) \sim (\lambda_H \dot{\gamma})^{-10/7} \quad \text{for } \lambda_H \dot{\gamma} \to \infty \tag{5.5b}$$

with prefactors depending on $\tilde{g}$ and α. On the other hand, the asymptotic behavior of $\Psi_2(\dot{\gamma})$ is independent of α and $\tilde{g}$:

$$\Psi_2(\dot{\gamma}) = \frac{-1}{(\lambda_H \dot{\gamma})^2} \quad \text{for } \lambda_H \dot{\gamma} \to \infty. \tag{5.5c}$$

Figure 4 shows the curves $-\Psi_2(\dot{\gamma})/\Psi_1(\dot{\gamma})$ for $\alpha = 1/2$ and four different values of $\tilde{g}$. With increasing $\tilde{g}$ the curves are more and more lowered without appreciable change in the shape.

VI. CONCLUSIONS

We have discussed three different mechanisms by which the simple Rouse model can be modified in order to reflect the physical situation of a macromolecule in a solvent more realistically.

By keeping a stochastic differential equation as a basis of the model a framework results in which all correlation functions can be calculated if only sufficiently good approximation schemes are available. In Ref. 14 the authors have shown that the mean-field and the Schwinger–Dyson approximation lead to results which, e.g., for not too high shear rates are very close to those which can be obtained by a numerical simulation. Provided with this experience the study of the influence of a nonlinearity in the internal force is now possible also in models where a tensorial mobility has been introduced in order to adapt them to concentrated solutions.

In steady elongational flows we obtain with the nonlinearity alone already a Trouton viscosity $T(\dot{\epsilon})$ which is nondivergent contrary to the pure Rouse model. For a fixed mobility coefficient α the nonlinearity lowers the value of

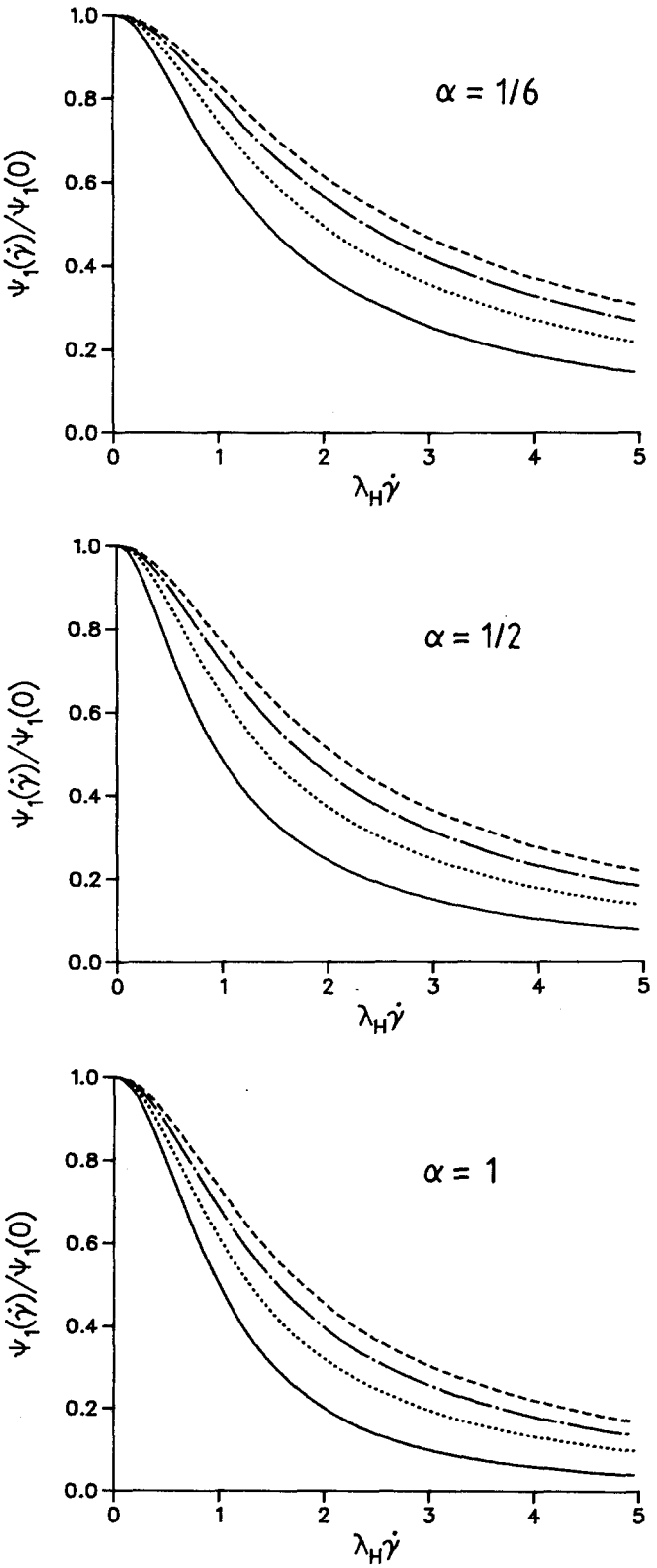

FIG. 3. Normalized first normal-stress coefficient vs dimensionless shear rate for (a) $\alpha = 1/6$, (b) $\alpha = 1/2$, and (c) $\alpha = 1$. The four different lines correspond to different values of $\tilde{g}$ (cf. Fig. 1).

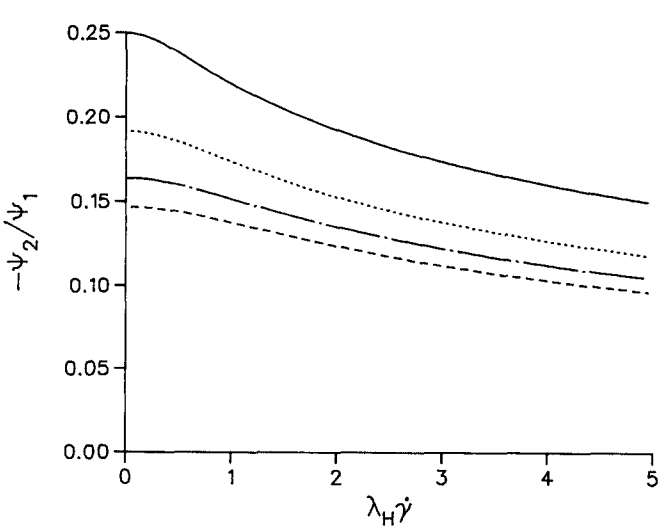

FIG. 4. The ratio of normal-stress coefficients $-\Psi_2/\Psi_1$ vs dimensionless shear rate for $\alpha = 1/2$. The four different lines correspond to different values of $\tilde{g}$ (cf. Fig. 1).

$T(0)$ by a factor $w(\tilde{g}) = (\sqrt{1+80\tilde{g}} - 1)/40\tilde{g}$ (where $\tilde{g}$ measures the strength of the nonlinear contribution to the internal force law) and diminishes the slope of $T(\dot{\epsilon})$ for small $\lambda_H \dot{\epsilon}$. On the other hand the asymptotic values for $\lambda_H \dot{\epsilon} \to \infty$ are independent of $\tilde{g}$.

In steady shear flow the nonlinearity alone is not able to produce a nonzero second normal-stress coefficient, but already leads to a $\dot{\gamma}$ dependence of the other material functions which seem to be close to experimental values. For fixed tensorial mobility α the inclusion of a nonlinearity again reduces the slope of the curves for $\eta(\dot{\gamma})/\eta(0)$ and $\Psi_1(\dot{\gamma})/\Psi_1(0)$, the influence of $\tilde{g}$ competes with that of α. The slope of the curve for $\Psi_2(\dot{\gamma})/\Psi_1(\dot{\gamma})$ is not changed appreciably, the whole curve is lowered with increasing $\tilde{g}$, at $\dot{\gamma} = 0$ again by a factor $w(\tilde{g})$.

Though in this paper we have discussed the modification of the constitutive equations also by the hydrodynamic interaction we have not studied its consequences in combination with the other two mechanisms. We have focused our attention on the interplay of the nonlinearity in the internal force law and the tensorial mobility. Both mechanisms are relevant for concentrated solutions, whereas for dilute solutions one should study the hydrodynamic interaction in combination with the nonlinear internal force law.

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