

Bead-Spring Macromolecules That Perturb the Solvent: Scleronomic, Monogenic, Molecular Forces

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SYNOPSIS

When linear, conservative, molecular forces are used in this bead-spring model of a polymer solution, a viscoplastic constitutive equation results. Using nonlinear intramolecular forces removes this viscoplasticity. The analysis shows that the anisotropy of the normal stresses is related to the anisotropy of the molecular forces. At the theta temperature the anisotropy of the intramolecular force alone determines the normal stress anisotropy. Nonlinear molecular forces are necessary for the analysis to predict a shear rate dependence for the stress in steady homogeneous flow. The symmetry of the stress tensor constrains the Hooke's law constants used to model the molecular forces. No overshoot is predicted for the stress response to a step change in shear rate when linear forces are used. Using linear forces, the stress response to a unit step shear rate shows a tendency of the polymer solution to undergo plastic deformation and to take a set.

INTRODUCTION

Lodge¹ has called to the attention of polymer scientists the need for a model of a polymer solution in which the macromolecules perturb the solvent. In a previous study,² we attempted to satisfy that need in a general fashion. That analysis substituted the usual friction coefficient force coupling between the solvent and the polymer with an arbitrary dispersion force based interaction. To apply this model, the form of the inter- and intramolecular forces must be specified. In this paper, we report the predictions yielded by the model when linear, anisotropic, conservative, and monogenic nonconservative forces are used.

We recognize that linear molecular forces are an unrealistic prediction for the actual forces both within a macromolecule and between the macromolecules and the solvent. However, we believe it is prudent to first analyze using linear forces before undertaking the more formidable task of using nonlinear ones. The wisdom of this approach is twofold. By examining the consequences of using linear forces, we gain insight into the relationship between the rheological behavior of the polymer solution and a set of simplified molecular parameters unemcum-

bered by tedious mathematics. It also gives us the opportunity to evaluate what, if anything, the use of nonlinear force laws would add to the analysis.

Our primary objective is to determine what form of the molecular force laws best predicts the normal stress anisotropy observed in shear flow experiments. While doing so, we hope to achieve a better understanding of this phenomenon on a molecular level. The example given in our earlier study² showed that using isotropic linear forces predicts a second normal stress difference equal to the negative of the first for simple shear flow. This prediction is inconsistent with experiments, which show that the second normal stress difference has a magnitude much smaller than that of the first. Therefore, we now evaluate the consequences of using anisotropic linear forces.

We also point out that our previous example used a homogeneous force law, i.e., the force law contained no constant term. A homogeneous (linear) force law precludes evaluating the stresses in anyway other than as a relationship between them. Mathematically, this results because a homogeneous force law yields a homogeneous system of equations for the stresses. Physically, this results because these force laws consist always of either attraction or repulsion only, i.e., the force does not change sign.

A homogeneous intramolecular force law is useful

in the Rouse³-Zimm⁴ models because they include a Brownian motion force that extends the springs of the polymer chain when the solution is at equilibrium. Mathematically, the Brownian motion force provides the nonhomogeneous terms in the system of equations governing the stresses. In this paper we use nonhomogeneous force laws and show how the stresses are expressed in terms of their parameters.

When specifying the molecular forces, we include the possibility that the stress tensor may be asymmetric. Although no experiments have yet measured any asymmetry for the stress tensor, including the possibility enables us to evaluate what influence the molecular forces have in maintaining a symmetric stress. Curtiss⁵ shows how the rotational motion of nonspherical molecules leads to an asymmetric contribution to the stress tensor. Green⁶ points out that the intramolecular force exerted by nonspherical molecules need not have spherical symmetry. Since polymer molecules in solution, and especially when the solution is in motion, will not generally have spherical symmetry, it interests us to see what constraints, if any, must be imposed on anisotropic molecular forces so that they predict a symmetric stress.

We begin the analysis with a brief review of the model. Initially, we analyze using conservative forces. We evaluate the polymer's intramolecular contribution to the total stress using nonhomogeneous linear forces for both the intramolecular interaction between adjacent beads on the polymer chain and the intermolecular interaction between each bead on the chain and the solvent. We then restrict ourselves to consider steady homogeneous flow and report the equations governing the asymmetric intramolecular contribution to the total stress.

To reduce the number of molecular parameters to a set that experimental data could fix, we use the concept of a theta solvent. We derive a constraint on the intramolecular forces to form a symmetric stress tensor. We report the steady state stresses in terms of the molecular force parameters and the time variation of the stress responding to a step change in the shear rate. Then we extend the analysis to include the use of monogenic nonconservative forces. We end by assessing what improvements the use of nonlinear forces could add to the analysis.

DEVELOPMENT

Review

We begin with a review of the model.² The total stress in the polymer solution consists of a contri-

bution each from the solvent and the solute. For a Newtonian solvent, the total stress has the form

$$\mathbf{T} = -P_s \delta + \eta_s \dot{\gamma} + \sigma^{(k)} \delta + \sigma \quad (1)$$

where P_s is the solvent's contribution to the isotropic pressure and η_s is its viscosity. δ is the unit tensor and $\dot{\gamma}$ is twice the rate of strain tensor. The polymer's contribution to the total stress consists of the sum of the isotropic kinetic contribution $\sigma^{(k)}$ and the intramolecular contribution σ .

The polymer's kinetic contribution to the total stress is given by

$$\sigma^{(k)} = -2n_p k_B T \quad (2)$$

where n_p is the local polymer density, k_B is Boltzmann's constant, and T is the absolute temperature. For our present needs, we neglect all concentration gradients and thereby take n_p as constant.

The intramolecular contribution is the sum of contributions from each spring of the bead-spring chain. For a chain composed of α beads we have

$$\sigma = \sum_{k=1}^{\alpha-1} \sigma'_k \quad (3a)$$

where

$$\sigma'_k = \langle \langle \mathbf{Q}'_k \partial \Phi / \partial \mathbf{Q}'_k \rangle \rangle \quad (3b)$$

A prime on a variable signifies a transformation into the normal modes. \mathbf{Q}_k is the spring vector or relative position vector between two adjacent beads. Φ is the intramolecular potential that binds two adjacent beads. The double backward slashes signify a joint solvent-polymer ensemble average.

The governing equation for σ'_k is

$$m_p D\sigma'_k / Dt + (\partial \mathbf{u} / \partial \mathbf{r})^{-1} : \sum_{i=1}^{\alpha-1} a_i \times \langle \langle \partial(\Gamma + \Phi) / \partial \mathbf{Q}'_i \partial(\mathbf{Q}'_k \partial \Phi / \partial \mathbf{Q}'_k) / \partial \mathbf{Q}'_i + \partial^2(\Gamma + \Phi) / \partial \mathbf{Q}'_i \partial \mathbf{Q}'_i \mathbf{Q}'_k \partial \Phi / \partial \mathbf{Q}'_k \rangle \rangle = 0 \quad (4)$$

where the a_i are the eigenvalues of the Rouse³ matrix, m_p is the mass of a bead, $\partial \mathbf{u} / \partial \mathbf{r}$ is the bulk flow velocity gradient, and Γ is the intermolecular potential between the solvent and the beads of the polymer chain. Equation (4) was derived using the restriction that the molecular forces arising from both Γ and Φ are conservative. In the first part of this Development section we maintain this restric-

tion. In the latter part we relax it to include monogenic nonconservative forces.

Anisotropic Forces

Nonhomogeneous Linear Forces

The analysis of the intramolecular contribution to the total stress requires that we specify both Γ and Φ . We consider linear force laws of the form

$$\partial\Gamma/\partial\mathbf{Q}'_i = \mathbf{I} \cdot (\mathbf{Q}'_i - \mathbf{b}) \quad (5a)$$

$$\partial\Phi/\partial\mathbf{Q}'_i = \mathbf{H} \cdot (\mathbf{Q}'_i - \mathbf{d}) \quad (5b)$$

where \mathbf{I} , \mathbf{H} , \mathbf{b} , and \mathbf{d} are all arbitrary (constant) parameters.

Since the force laws given by eqs. (5) are conservative, we may use them in eq. (4) to find

$$\begin{aligned} m_p D\sigma'_k/Ddt + 2(\alpha - 1)(\partial\mathbf{u}/\partial\mathbf{r})^{-1} : (\mathbf{I} + \mathbf{H})\sigma'_k \\ + a_k(\partial\mathbf{u}/\partial\mathbf{r})^{-1} : (\mathbf{I} + \mathbf{H}) \cdot \langle\langle \mathbf{Q}'_k \delta \partial\Phi/\partial\mathbf{Q}'_k \rangle\rangle \\ + \mathbf{Q}'_k(\mathbf{Q}'_k - \mathbf{d})\mathbf{H} \cdot \langle\langle \mathbf{Q}'_k \rangle\rangle = a_k(\partial\mathbf{u}/\partial\mathbf{r})^{-1} \\ : [\mathbf{I} \cdot \mathbf{b} \delta \mathbf{H} \cdot \langle\langle \mathbf{Q}'_k \rangle\rangle - \mathbf{d} + \mathbf{I} \cdot (\mathbf{b} \cdot \langle\langle \mathbf{Q}'_k \rangle\rangle \\ - \langle\langle \mathbf{Q}'_k \rangle\rangle \cdot \mathbf{d}) \mathbf{H} - \mathbf{H} \cdot \langle\langle \mathbf{Q}'_k \rangle\rangle \cdot \mathbf{d} \mathbf{H}] \quad (6) \end{aligned}$$

The quantity $\langle\langle \mathbf{Q}'_k \rangle\rangle$ appears in the above equation so we must derive and solve the governing equation for it.

$\langle\langle \mathbf{Q}'_k \rangle\rangle$ represents the ensemble average configuration of a spring in the polymer chain. To obtain its governing equation, we may either derive it from the equation governing the polymer configuration space distribution, in a manner similar to that shown for $\langle\langle \mathbf{Q}'_k \delta \Phi/\partial\mathbf{Q}'_k \rangle\rangle$ in Grisafi,² or we may replace $\partial\Phi/\partial\mathbf{Q}'_k$ in eq. (4) with scalar unity. Either way, the governing equation for $\langle\langle \mathbf{Q}'_k \rangle\rangle$ is

$$\begin{aligned} m_p D\langle\langle \mathbf{Q}'_k \rangle\rangle/Dt + (\partial\mathbf{u}/\partial\mathbf{r})^{-1} \\ : [a_k \langle\langle \partial(\Gamma + \Phi)/\partial\mathbf{Q}'_k \rangle\rangle \delta + \sum_{i=1}^{\alpha-1} a_i \\ \times \langle\langle \partial^2(\Gamma + \Phi)/\partial\mathbf{Q}'_i \partial\mathbf{Q}'_i \mathbf{Q}'_k \rangle\rangle] = 0 \quad (7) \end{aligned}$$

To simplify the notation, we let \mathbf{R}_k designate $\langle\langle \mathbf{Q}'_k \rangle\rangle$. Substituting the force laws of eq. (5) into (7) yields

$$\begin{aligned} m_p D\mathbf{R}_k/Dt + a_k(\partial\mathbf{u}/\partial\mathbf{r})^{-1} : (\mathbf{I} + \mathbf{H}) \cdot \mathbf{R}_k \delta \\ + 2(\alpha - 1)(\partial\mathbf{u}/\partial\mathbf{r})^{-1} : (\mathbf{I} + \mathbf{H})\mathbf{R}_k \\ = a_k(\partial\mathbf{u}/\partial\mathbf{r})^{-1} : (\mathbf{I} \cdot \mathbf{b} + \mathbf{H} \cdot \mathbf{d}) \delta \quad (8) \end{aligned}$$

Equation (8) must first be solved when solving (6).

Steady Homogeneous Flow

To evaluate the consequences of the force laws given by (5), we consider steady homogeneous flow. We let $\dot{\gamma}$ be the (constant) shear rate of this flow so that the velocity gradient is

$$\partial\mathbf{u}/\partial\mathbf{r} = \dot{\gamma}\delta_2\delta_1 \quad (9)$$

where δ_1 and δ_2 are the unit vectors in the flow and shear directions, respectively. The primary restriction in this case is that of stationary conditions. No matter what the actual bulk flow velocity field may be, the velocity profile that the macromolecules experience can usually be approximated with a linear one.

Regardless of whether or not any one macromolecule can distinguish between a homogeneous or a nonhomogeneous flow, the symmetry of viscometric flow requires that we set $\sigma_{23} = \sigma_{32} = \sigma_{13} = \sigma_{31} = 0$ because the stress tensor must be invariant with respect to a rotation of the coordinate axes. As a consequence of this, we must also set $H_{23} = H_{32} = H_{13} = H_{31} = 0$. The intermolecular force constants remain completely arbitrary; \mathbf{I} may be symmetric or asymmetric, isotropic or anisotropic. Although it must have the restriction given above, \mathbf{H} need not be symmetric, i.e., H_{21} need not equal H_{12} .

With the restriction on σ , (6) yields a system of five linear equations for the unknowns σ_{12} , σ_{21} , σ_{11} , σ_{22} , and σ_{33} . The five equations are:

11 component

$$\begin{aligned} 2(\alpha - 1)/a_k(\sigma'_{11})_k + H_{11}/H_{22}(\sigma'_{22})_k \\ + H_{11}/H_{12}(I_{11} + H_{11})/(I_{12} + H_{12})(\sigma'_{12})_k \\ = H_{11}(R_2)_k(I_{11}b_1 + I_{12}(b_2 - d_2) \\ + I_{13}b_3 - H_{12}d_2)/(I_{12} + H_{12}) \quad (10a) \end{aligned}$$

22-component

$$\begin{aligned} H_{21}/H_{11}(I_{11} + H_{11})/(I_{12} + H_{12})(\sigma'_{11})_k + (\sigma'_{21})_k \\ + 2H_{22}/H_{12}(I_{11} + H_{11})(\sigma'_{12})_k \\ + (2(\alpha - 1)/a_k + 1)(\sigma'_{22})_k \\ = H_{22}(R_2)_k[I_{11}b_1 + I_{12}(b_2 - d_2) \\ + I_{13}b_3 - H_{12}d_2]/(I_{12} + H_{12}) \\ + (I_{11}b_1 + I_{12}b_2 + I_{13}b_3)/(I_{12} + H_{12}) \\ \times \{H_{22}[(R_2)_k - d_2] - H_{21}d_1\} \quad (10b) \end{aligned}$$

33-component

$$\begin{aligned}
& 2(\alpha - 1)/a_k(\sigma'_{33})_k + H_{33}/H_{22}(\sigma'_{22})_k \\
& \quad + H_{33}/H_{12}(I_{11} + H_{11})/(I_{12} + H_{12})(\sigma'_{12})_k \\
& = H_{33}(R_2)_k[I_{11}b_1 + I_{12}(b_2 - d_2) \\
& \quad + I_{13}b_3 - H_{12}d_2]/(I_{12} + H_{12}) \quad (10c)
\end{aligned}$$

12-component

$$\begin{aligned}
& H_{12}/H_{22}(\sigma'_{22})_k + [2(\alpha - 1)/a_k \\
& \quad + (I_{11} + H_{11})/(I_{12} + H_{12})](\sigma'_{12})_k \\
& = H_{12}(R_2)_k[I_{11}b_1 + I_{12}(b_2 - d_2) \\
& \quad + I_{13}b_3 - H_{12}d_2]/(I_{12} + H_{12}) \quad (10d)
\end{aligned}$$

21-component

$$\begin{aligned}
& (I_{11} + H_{11})/(I_{12} + H_{12})(\sigma'_{11})_k \\
& \quad + [2(\alpha - 1)/a_k + H_{11}/H_{21}](\sigma'_{21})_k \\
& \quad + (1 + H_{21}/H_{12})(I_{11} + H_{11})/(I_{12} + H_{12}) \\
& \quad \quad \times (\sigma'_{12})_k + (H_{12} + H_{21})/H_{22}(\sigma'_{22})_k \\
& = H_{21}(R_2)_k[I_{11}b_1 + I_{12}(b_2 - d_2) \\
& \quad + I_{13}b_3 - H_{12}d_2]/(I_{12} + H_{12}) \\
& \quad + (I_{11}b_1 + I_{12}b_2 + I_{13}b_3)/(I_{12} + H_{12}) \\
& \quad \quad \times \{H_{12}[(R_2)_k - d_2] - H_{11}d_1\} \quad (10e)
\end{aligned}$$

where $(R_2)_k$ is the shear direction component of \mathbf{R}_k and

$$\mathbf{R} = \sum_{k=1}^{\alpha-1} \mathbf{R}_k \quad (11)$$

is the mean configuration of the polymer chain.

The parameters \mathbf{I} , \mathbf{H} , \mathbf{b} , and \mathbf{d} provide the model with more degrees of freedom than experimental data can fix. We need to consider physical situations that reduce the number of force constants to those that could be fitted to experimental data. For this purpose we consider a theta solvent. But, first, we note that solving for σ_{12} , σ_{21} , σ_{11} , σ_{22} , and σ_{33} in terms of the complete set of force constants is tedious, but straightforward. The resulting expressions are long and will not be reported here other than to report that

$$\sigma_{11} = H_{11}/H_{33}\sigma_{33} \quad (12)$$

This shows that, regardless of the intermolecular force between the solvent and the polymer, if H_{11}

= H_{33} , the model predicts that the second normal stress difference equals the negative of the first. Thus, it would appear that the intramolecular Hooke's law constants have greater bearing on the normal stress anisotropy than do the intermolecular constants.

Theta Solvent

The effect of the intermolecular force is to perturb the configuration of the macromolecule. For a poor solvent, it may occur that the macromolecule attains its unperturbed dimensions. This occurs at the so-called theta temperature. We expect that $\mathbf{H} \gg \mathbf{I}$ for a poor solvent. Therefore, we consider the limit where \mathbf{I} goes to zero and call this condition that of a theta solvent. Physically, this amounts to immersing the polymer in a solvent field of constant potential energy, the value of which is, of course, irrelevant.

For simplicity, we assume that \mathbf{H} is symmetric, but anisotropic;

$$\begin{aligned}
\mathbf{H} = & H_{11}\delta_1\delta_1 + H_{22}\delta_2\delta_2 + H_{33}\delta_3\delta_3 \\
& + H(\delta_2\delta_1 + \delta_1\delta_2) \quad (13)
\end{aligned}$$

Also, we take \mathbf{d} to be isotropic;

$$\mathbf{d} = d(\delta_1 + \delta_2 + \delta_3) \quad (14)$$

With these simplifications, the mean configuration of a spring on the polymer chain in steady homogeneous flow is

$$\begin{aligned}
\mathbf{R}_k = & (R_2)_k\delta_2 \\
= & a_k/[2(\alpha - 1) + a_k]d(1 + H_{11}/H)\delta_2 \quad (15)
\end{aligned}$$

Equations (10) governing the steady state stress are greatly simplified for a theta solvent. We simplify them further by equating σ_{12} and σ_{21} , thereby creating a symmetric stress. Doing so reduces the number of unknowns in eqs. (10) to four and reduces the system of equations to four equations plus one constraint.

The constraint restrains the values of the ratio H_{22}/H to those of H_{11}/H for each value of α . The constraint is

$$\begin{aligned}
& [4 - 1/(\alpha - 1)](H_{11}/H)^2 + (1 + H_{22}/H)H_{11}/H \\
& \quad + (\alpha + 1)H_{22}/H + 1/(\alpha - 1) - \alpha - 3 = 0 \quad (16a)
\end{aligned}$$

where we have used

$$\sum_{k=1}^{\alpha-1} a_k^2 = 6(\alpha - 1) - 2 \quad (16b)$$

By using only those ordered pairs of values for H_{11}/H and H_{22}/H that satisfy (16a), we maintain the symmetry of the stress tensor.

The steady state intramolecular contributions to the symmetric stress in homogeneous flow with a theta solvent are

$$(\sigma'_{12})_k = (1 + H_{11}/H)Hd^2/[\tau_k^2(\beta_1)_k(\beta_2)_k] \quad (17a)$$

$$\sigma_{11} = H_{11}/H\sigma_{12} \quad (17b)$$

$$(\sigma'_{22})_k = -H_{22}(R_2)_k d - H_{22}/H[2(\alpha - 1)/a_k + H_{11}/H](\sigma'_{12})_k \quad (17c)$$

$$\sigma_{33} = H_{33}/H\sigma_{12} \quad (17d)$$

where

$$\begin{aligned} \tau_k(\beta_1)_k = & -\left\{1 + \frac{1}{2}H_{11}/H + 2(\alpha - 1)/a_k \right. \\ & \left. + \frac{1}{2}[(H_{11}/H)^2 + 4(1 + H_{11}/H + H/H_{22} \right. \\ & \left. + H_{11}/H_{22})]^{1/2}\right\} \quad (17e) \end{aligned}$$

$$\begin{aligned} \tau_k(\beta_2)_k = & -\left\{1 + \frac{1}{2}H_{11}/H + 2(\alpha - 1)/a_k \right. \\ & \left. - \frac{1}{2}[(H_{11}/H)^2 + 4(1 + H_{11}/H + H/H_{22} \right. \\ & \left. + H_{11}/H_{22})]^{1/2}\right\} \quad (17f) \end{aligned}$$

and H_{22}/H is constrained to H_{11}/H by eq. (16a).

Equations (17) have five degrees of freedom. Measurements of the unperturbed dimension of the linear macromolecules can be used to fix d by using eq. (5). This leaves the intramolecular Hooke's law constants H , H_{11} , H_{22} , and H_{33} to be specified. Measurements of the ratio of the shear stress to the first normal stress difference can fix H_{11}/H . Measurements of the ratio of the first to the second normal stress difference can then fix H_{33}/H . The material functions can then all be scaled to the appropriate magnitude by fixing the value of H with an absolute measurement of the shear stress. So, using the concept of the theta solvent reduces the degrees of freedom to a set that is experimentally verifiable.

Response to a Unit Step Shear Rate

We now consider a transient approach to the steady state considered in the previous subsections. For all time prior to that which we call time zero, we assume an absence of stress and no preferred configuration for the polymer molecules. At time zero, we impose a unit step shear rate. This requires that we consider the transient equations governing \mathbf{R} and σ .

The governing equations for the components of each spring vector contributing to \mathbf{R} in a theta solvent are

$$\tau_k D(R_1)_k/Dt + 2(\alpha - 1)/a_k(R_1)_k = 0 \quad (18a)$$

$$\begin{aligned} \tau_k D(R_2)_k/Dt + [1 + 2(\alpha - 1)/a_k](R_2)_k \\ = (1 + H_{11}/H)d - H_{11}/H(R_1)_k \quad (18b) \end{aligned}$$

$$\tau_k D(R_3)_k/Dt + 2(\alpha - 1)/a_k(R_3)_k = 0 \quad (18c)$$

where

$$\tau_k = m_p \dot{\gamma}_0 / (Ha_k) \quad (18d)$$

is the time constant for the vibration mode corresponding to a_k and $\dot{\gamma}_0$ is the magnitude of the applied shear rate.

The initial conditions for these differential equations are

$$(R_1)_k = (R_2)_k = (R_3)_k = 0. \quad (18e)$$

Solving the equations with these conditions yields the time variation of the mean chain length to be

$$\begin{aligned} \mathbf{R} = (1 + H_{11}/H)d \sum_{k=1}^{\alpha-1} a_k/[2(\alpha - 1) + a_k] \\ \times (1 - \exp\{-t/\tau_k[1 + 2(\alpha - 1)/a_k]\})\delta_2 \quad (19) \end{aligned}$$

Equation (19) predicts a monotonic approach to the steady state value for \mathbf{R} .

The governing equations for the transient response of all the vibrational modes contributing to the intramolecular stress are

$$\begin{aligned} \tau_k D(\sigma'_{12})_k/Dt + [2(\alpha - 1)/a_k + H_{11}/H](\sigma'_{12})_k \\ + H/H_{22}(\sigma'_{22})_k = -H(R_2)_k d \quad (20a) \end{aligned}$$

$$\begin{aligned} \tau_k D(\sigma'_{11})_k/Dt + 2(\alpha - 1)/a_k(\sigma'_{11})_k + (H_{11}/H)^2 \\ \times (\sigma'_{12})_k + H_{11}/H_{22}(\sigma'_{22})_k = -H_{11}(R_2)_k d \quad (20b) \end{aligned}$$

$$\begin{aligned} \tau_k D(\sigma'_{22})_k/Dt + [2 + 2(\alpha - 1)/a_k](\sigma'_{22})_k \\ + [1 + 2H_{11}H_{22}/H^2](\sigma'_{12})_k + (\sigma'_{11})_k \\ = -H_{22}(R_2)_k d \quad (20c) \end{aligned}$$

$$\begin{aligned} \tau_k D(\sigma'_{33})_k/Dt + 2(\alpha - 1)/a_k(\sigma'_{33})_k \\ + H_{11}H_{33}/H^2(\sigma'_{12})_k + H_{33}/H_{22}(\sigma'_{22})_k \\ = -H_{33}(R_2)_k d \quad (20d) \end{aligned}$$

where H_{11}/H and H_{22}/H are constrained by eq. (16a).

The initial conditions are $\sigma'_k = \mathbf{0}$ for $t \leq 0$. The response of the stresses to the applied shear rate is

$$\begin{aligned}
(\sigma'_{12})_k &= Hd^2/\tau_k^2(1 + H_{11}/H)(1/[(\beta_1)_k(\beta_2)_k] \\
&+ \exp[(\beta_1)_k t]/\{(\beta_1)_k[(\beta_1)_k - (\beta_2)_k]\} \\
&+ \exp[(\beta_2)_k t]/\{(\beta_2)_k[(\beta_2)_k - (\beta_1)_k]\}) \quad (21a)
\end{aligned}$$

$$\sigma_{11} = H_{11}/H\sigma_{12} \quad (21b)$$

$$\begin{aligned}
(\sigma'_{22})_k &= -H_{22}d^2(1 + H_{11}/H)[a_k/[2(\alpha - 1) + a_k] \\
&\times (1 - \exp\{-t/\tau_k[1 + 2(\alpha - 1)/a_k]\}) \\
&+ [H_{11}/H + 2(\alpha - 1)/a_k]/[\tau_k^2(\beta_1)_k(\beta_2)_k] \\
&+ \{(\beta_1)_k + [H_{11}/H + 2(\alpha - 1)/a_k]/\tau_k\} \\
&\times \exp[(\beta_1)_k t]/\{\tau_k(\beta_1)_k[(\beta_1)_k - (\beta_2)_k]\} \\
&+ \{(\beta_2)_k + [H_{11}/H + 2(\alpha - 1)/a_k]/\tau_k\} \\
&\times \exp[(\beta_2)_k t]/\{\tau_k(\beta_2)_k[(\beta_2)_k - (\beta_1)_k]\} \quad (21c)
\end{aligned}$$

$$\sigma_{33} = H_{33}/H\sigma_{12} \quad (21d)$$

From eqs. (21) we obtain the time variation of the first and second normal stress differences as well as that of the shear stress. Figures 1, 2, and 3 show these results normalized to their steady state values of some values of the parameters. Note that the graphs show no overshoot for the transient response. Also, since the steady state stresses are independent of the shear rate, eqs. (21) predict that the polymer solution is viscoplastic: The polymer solution deforms plastically and takes a set.

Monogenic Nonconservative Forces

Purpose

In the preceding subsection of the Development section, we show that the steady state intramolecular contribution to the total stress in homogeneous flow is independent of the shear rate when linear forces are used. A consequence of this is that it predicts that the polymer viscosity is shear thinning in proportion to the reciprocal of an increasing shear rate. We also saw that no overshoot is predicted for the stress responding to a unit step in the shear rate. The question arises as to whether these predictions result from the linearity of the molecular forces or from their conservative nature.

One cannot say with certainty whether or not the use of nonlinear forces would predict the steady state stresses to be anything other than independent of the shear rate without having first developed a mathematical proof for the general class of nonlinear functions suitable as models of the molecular forces. An easier route to take is to extend the analysis to include nonconservative forces and then assess the changes made to the constitutive equation.

We need to explain the distinction between conservative and nonconservative forces. So that we may retain the concept of a molecular potential, e.g., Γ , Φ , and E , we consider only those nonconservative forces that are derivable from a single scalar function. Following Lanczos,⁷ we call such forces monogenic. According to Lanczos,⁷ if a molecular potential does not depend explicitly upon time, it is said to be scleronomic. The total energy of a scleronomic mechanical system is a constant of its motion. This holds true whether or not the forces between the particles depend upon the velocities. However, if they do, we need to distinguish between the potential energy of the system and its work function. As Lanczos⁷ points out, the work function is really the fundamental quantity in analytical mechanics. When the forces depend upon the velocities, the mechanical system still obeys a conservation law, but now the work function is no longer equal to the negative of the potential energy. For simplicity, we

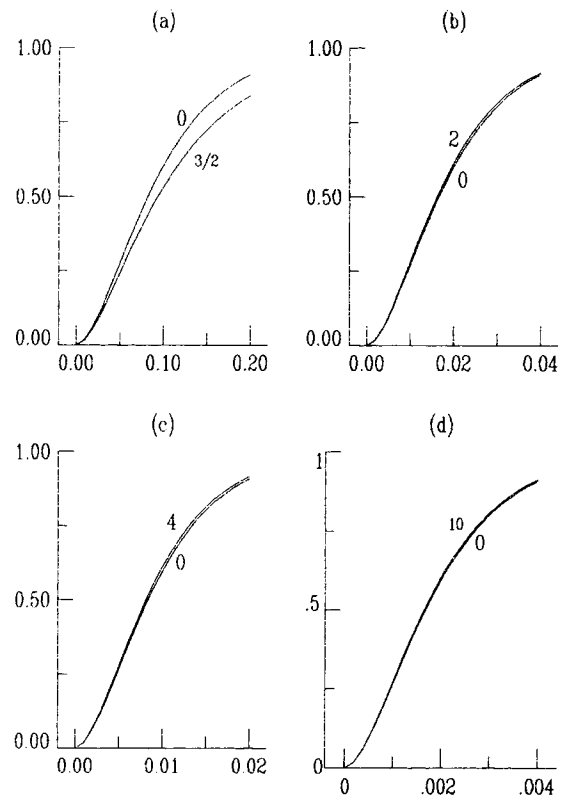


Figure 1 Dimensionless intramolecular contribution to the shear stress responding to a unit step shear rate. Part (a) is for a polymer chain composed of 10 beads; part (b) is for 50 beads; (c) is for 100 beads; (d) is for 500 beads. The ordinate of each graph is the shear stress normalized by its steady state value. The abscissa is dimensionless time: $tH/(m_p\dot{\gamma}_0)$. Each curve is marked by its value of the parameter H_{11}/H .

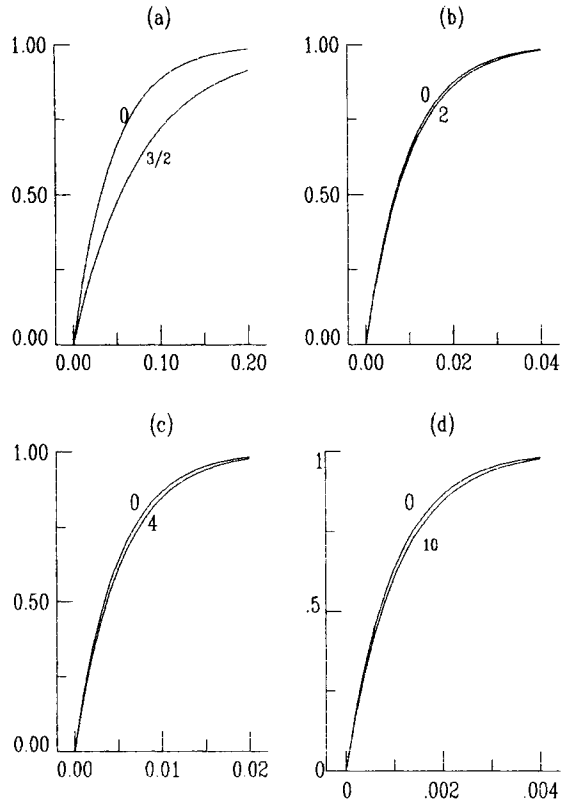


Figure 2 Dimensionless first normal stress difference responding to a unit step shear rate. Part (a) is for a polymer chain composed of 10 beads; part (b) is for 50 beads; (c) is for 100 beads; (d) is for 500 beads. The ordinate of each graph is the stress difference normalized by its steady state value. The abscissa is dimensionless time: $tH/(m_p\dot{\gamma}_0)$. Each curve is marked by its value of the parameter H_{11}/H .

retain the use of the molecular potentials Γ , Φ , and E , but refer to them as nonconservative when they depend upon the molecular velocities.

Lagrangian Mechanics

When considering velocity dependent molecular potentials the forces arising from them are not obvious. We must abandon the vectorial approach to mechanics and rely upon Lagrangian mechanics to conserve momentum. We define the Lagrangian for our system as

$$L = \frac{1}{2}m_s\dot{\mathbf{r}}_s \cdot \dot{\mathbf{r}}_s + \frac{1}{2}m_p \sum_{\mu=1}^{\alpha} \dot{\mathbf{r}}_{\mu} \cdot \dot{\mathbf{r}}_{\mu} - \Gamma - \Phi - E \quad (22)$$

where the subscript s signifies the solvent.

The Lagrangian equations of motion for the beads of the polymer chain are

$$d(\partial L/\partial \dot{\mathbf{r}}_{\mu})/dt - \partial L/\partial \mathbf{r}_{\mu} = 0 \quad (23)$$

for $\mu = 1, 2, 3, \dots, \alpha$. Using the Lagrangian for our system in (23) yields

$$m_p \ddot{\mathbf{r}}_{\mu} = d[\partial(\Gamma + \Phi + E)/\partial \dot{\mathbf{r}}_{\mu}]/dt - \partial(\Gamma + \Phi + E)/\partial \mathbf{r}_{\mu} \quad (24a)$$

where

$$\ddot{\mathbf{r}}_{\mu} = d\dot{\mathbf{r}}_{\mu}/dt - \frac{1}{2}(\dot{\mathbf{r}}_{\mu} \cdot \partial \dot{\mathbf{r}}_{\mu}/\partial \mathbf{r}_{\mu} + \partial \dot{\mathbf{r}}_{\mu}/\partial \mathbf{r}_{\mu} \cdot \dot{\mathbf{r}}_{\mu}) \quad (24b)$$

is reference frame indifferent. When the first term on the right-hand side (rhs) of (24a) vanishes, the force law reduces to that for conservative forces.

Now,

$$d[\partial(\Gamma + \Phi + E)/\partial \dot{\mathbf{r}}_{\mu}]/dt = \partial^2(\Gamma + \Phi + E)/\partial t \partial \dot{\mathbf{r}}_{\mu} + \dot{\mathbf{r}}_{\mu} \cdot \partial^2(\Gamma + \Phi + E)/\partial \mathbf{r}_{\mu} \partial \dot{\mathbf{r}}_{\mu} \quad (25)$$

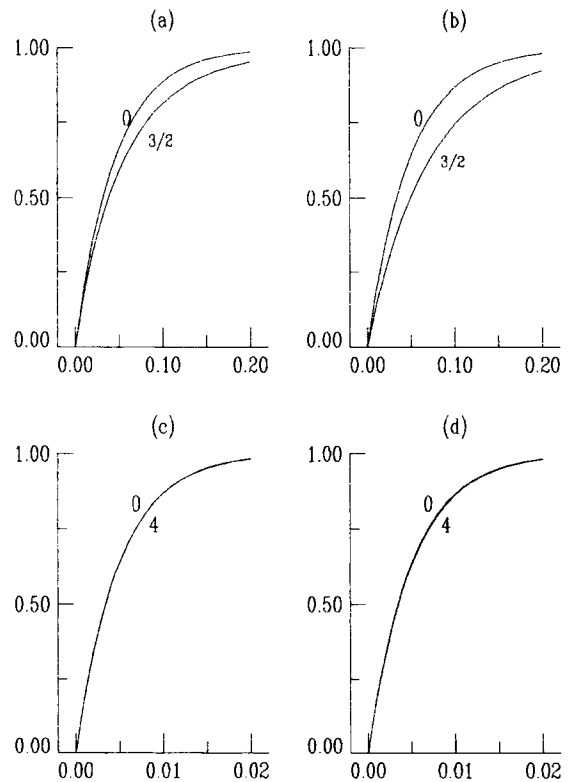


Figure 3 Dimensionless second normal stress difference responding to a unit step shear rate. Parts (a) and (b) are for a polymer chain composed of 10 beads; (c) and (d) are for 100 beads. Parts (a) and (c) are for $H_{33}/H = 0$; (b) and (d) are for $H_{33}/H = 1$. The ordinate of each graph is the stress difference normalized by its steady state value. The abscissa is dimensionless time: $tH/(m_p\dot{\gamma}_0)$. Each curve is marked by its value of the parameter H_{11}/H .

We assume that the molecular potentials do not depend explicitly upon time, i.e., they are scleronomic. Then the first term on the rhs of (25) vanishes. The equations of motion for the beads become

$$m_p \ddot{\mathbf{r}}_\mu = -\partial(\Gamma + \Phi + E)/\partial \mathbf{r}_\mu + \dot{\mathbf{r}}_\mu \cdot \times \partial^2(\Gamma + \Phi + E)/\partial \mathbf{r}_\mu / \partial \dot{\mathbf{r}}_\mu \quad (26)$$

From this point on, the analysis parallels that in Grisafi.²

The polymer phase space is conserved by

$$\partial f_p / \partial t = - \sum_{\mu=1}^{\alpha} [\partial / \partial \mathbf{r}_\mu \cdot (\dot{\mathbf{r}}_\mu f_p) + \partial / \partial \dot{\mathbf{r}}_\mu \cdot (\ddot{\mathbf{r}}_\mu f_p)] \quad (27)$$

where f_p is the polymer phase space distribution function. We define the peculiar velocity for a bead as

$$\mathbf{v}_\mu = \dot{\mathbf{r}}_\mu - \mathbf{u}(\mathbf{r}_\mu) \quad (28)$$

The substantial derivative for f_p is

$$Df_p / Dt = \partial f_p / \partial t + \sum_{\mu=1}^{\alpha} \mathbf{u}(\mathbf{r}_\mu) \cdot \partial f_p / \partial \mathbf{r}_\mu \quad (29)$$

We substitute the expression for the acceleration of a bead, found from eq. (26), into (27). Then, using the definitions of the peculiar velocity and the substantial derivative yields

$$Df_p / Dt = - \sum_{\mu=1}^{\alpha} [\partial / \partial \mathbf{r}_\mu \cdot (\mathbf{v}_\mu f_p) - 1/m_p \partial / \partial \dot{\mathbf{r}}_\mu \cdot \times f_p (\partial(\Gamma + \Phi + E) / \partial \mathbf{r}_\mu - \dot{\mathbf{r}}_\mu \cdot \partial^2(\Gamma + \Phi + E) / \partial \mathbf{r}_\mu / \partial \dot{\mathbf{r}}_\mu)] \quad (30)$$

Note that we have not assumed that the peculiar velocity is a solenoidal field as in Grisafi.²

We define the velocity space average of an arbitrary dynamic variable \mathbf{B} as

$$\langle \mathbf{B} \rangle = \prod_{\theta=1}^{\alpha} \int_{\Omega} d^3 \mathbf{v}_\theta f_p \mathbf{B} \quad (31)$$

where Ω signifies the velocity space domain. Using this average, the polymer configuration space distribution (CSD) function becomes

$$g_p = \langle 1 \rangle. \quad (32)$$

Taking the velocity space average of eq. (30) yields

$$m_p Dg_p / Dt = \sum_{\mu=1}^{\alpha} \prod_{\theta=1}^{\alpha} \int_{\Omega} d^3 \mathbf{v}_\theta \partial / \partial \mathbf{r}_\mu \cdot \times f_p (\partial(\Gamma + \Phi + E) / \partial \mathbf{r}_\mu - \dot{\mathbf{r}}_\mu \cdot \partial^2(\Gamma + \Phi + E) / \partial \mathbf{r}_\mu / \partial \dot{\mathbf{r}}_\mu) \quad (33)$$

where the average over the first rhs term of (30) vanishes by definition of the peculiar velocity.

We expand the divergence in the integral of (33) and apply chain rule differentiation. After some rearrangement it becomes

$$m_p Dg_p / Dt = \sum_{\mu=1}^{\alpha} [\langle \partial / \partial \mathbf{u}_\mu \cdot \partial(\Gamma + \Phi + E) / \partial \mathbf{r}_\mu \rangle - \langle \partial / \partial \mathbf{u}_\mu \cdot (\dot{\mathbf{r}}_\mu \cdot \partial^2(\Gamma + \Phi + E) / \partial \mathbf{r}_\mu / \partial \dot{\mathbf{r}}_\mu) \rangle + \sum_{\mu=1}^{\alpha} (\partial \mathbf{u} / \partial \mathbf{r}_\mu)^{-1} : \{ \partial \langle \partial(\Gamma + \Phi + E) / \partial \mathbf{r}_\mu \rangle / \partial \mathbf{r}_\mu - \langle \partial^2(\Gamma + \Phi + E) / \partial \mathbf{r}_\mu / \partial \mathbf{r}_\mu \rangle - \partial \langle \dot{\mathbf{r}}_\mu \cdot \partial^2(\Gamma + \Phi + E) / \partial \mathbf{r}_\mu / \partial \dot{\mathbf{r}}_\mu \rangle / \partial \mathbf{r}_\mu + \langle \partial(\dot{\mathbf{r}}_\mu \cdot \partial^2(\Gamma + \Phi + E) / \partial \mathbf{r}_\mu / \partial \dot{\mathbf{r}}_\mu) / \partial \mathbf{r}_\mu \rangle] \quad (34)$$

where \mathbf{u}_μ signifies $\mathbf{u}(r_\mu)$.

We transform from the set of bead coordinates, $\{\mathbf{r}_\mu\}$, to the center of mass coordinates, \mathbf{r}_c , and the set of spring coordinates, $\{\mathbf{Q}_i\}$, where $i = 1, 2, 3, \dots, \alpha - 1$. The transformation is accomplished by

$$\mathbf{Q}_i = \sum_{\mu=1}^{\alpha} B_{i\mu} \mathbf{r}_\mu \quad (35a)$$

and

$$\mathbf{r}_\mu = \mathbf{r}_c + \sum_{i=1}^{\alpha-1} B'_{\mu i} \mathbf{Q}_i \quad (35b)$$

where

$$B_{i\mu} = \delta_{(i+1)\mu} - \delta_{i\mu} \quad (35c)$$

and

$$B'_{\mu i} = (i - \mu) / \alpha \quad \text{for } \mu \leq i \\ = i / \alpha \quad \text{for } \mu > i \quad (35d)$$

We simplify the analysis by neglecting all concentration gradients. As noted in Grisafi,² the potential E must then vanish. Transforming variables in (34) yields

$$\begin{aligned}
 m_p Dg_p/Dt &= \sum_{\mu=1}^{\alpha} \sum_{i=1}^{\alpha-1} B_{i\mu} \langle \partial/\partial \mathbf{u}_{\mu} \cdot \partial(\Gamma + \Phi)/\partial \mathbf{Q}_i \rangle \\
 &- \sum_{\mu=1}^{\alpha} \sum_{i=1}^{\alpha-1} \sum_{j=1}^{\alpha-1} \sum_{k=1}^{\alpha-1} B_{i\mu} B_{j\mu} B'_{\mu k} \\
 &\times \langle \partial/\partial \mathbf{u}_{\mu} \cdot (\dot{\mathbf{Q}}_k \cdot \partial^2(\Gamma + \Phi)/\partial \mathbf{Q}_j / \partial \dot{\mathbf{Q}}_i) \rangle \\
 &+ \alpha (\partial \mathbf{u} / \partial \mathbf{r})^{-1} : \sum_{i=1}^{\alpha-1} \sum_{j=1}^{\alpha-1} A_{ij} [\partial \langle \partial(\Gamma + \Phi)/\partial \mathbf{Q}_i \rangle / \\
 &\partial \mathbf{Q}_j - \langle \partial^2(\Gamma + \Phi)/\partial \mathbf{Q}_j / \partial \mathbf{Q}_i \rangle] - \alpha (\partial \mathbf{u} / \partial \mathbf{r})^{-1} \\
 &: \sum_{i=1}^{\alpha-1} \sum_{j=1}^{\alpha-1} \sum_{k=1}^{\alpha-1} \sum_{l=1}^{\alpha-1} G_{ijkl} [\partial \langle \dot{\mathbf{Q}}_k \cdot \partial^2(\Gamma + \Phi)/\partial \mathbf{Q}_j / \partial \dot{\mathbf{Q}}_i \rangle / \\
 &\partial \mathbf{Q}_l - \langle \partial(\dot{\mathbf{Q}}_k \cdot \partial^2(\Gamma + \Phi)/\partial \mathbf{Q}_j / \partial \dot{\mathbf{Q}}_i) / \partial \mathbf{Q}_l \rangle] \quad (36)
 \end{aligned}$$

where \mathbf{r} is any position in the fluid,

$$A_{ij} = \sum_{\mu=1}^{\alpha} B_{i\mu} B_{j\mu} \quad (37a)$$

is the Rouse³ matrix, and

$$G_{ijkl} = \sum_{\mu=1}^{\alpha} B_{i\mu} B_{j\mu} B'_{\mu k} B_{\mu l} \quad (37b)$$

We now decouple the modes of vibration for the bead-spring chain with an orthogonal transformation. We transform the Rouse matrix with

$$A'_{ij} = \sum_{\mu=1}^{\alpha} B'_{\mu i} B'_{\mu j} \quad (38a)$$

expecting that this will also simplify G_{ijkl} to some extent. Transforming equation (36) yields

$$\begin{aligned}
 m_p Dg_p/Dt &= \sum_{\mu=1}^{\alpha} \sum_{i=1}^{\alpha-1} B'_{\mu i} \langle \partial/\partial \mathbf{u}_{\mu} \cdot \partial(\Gamma + \Phi)/\partial \mathbf{Q}'_i \rangle \\
 &- \sum_{\mu=1}^{\alpha} \sum_{i=1}^{\alpha-1} \sum_{j=1}^{\alpha-1} \sum_{k=1}^{\alpha-1} B_{k\mu} B'_{\mu j} B'_{\mu i} \\
 &\times \langle \partial/\partial \mathbf{u}_{\mu} \cdot (\dot{\mathbf{Q}}'_k \cdot \partial^2(\Gamma + \Phi)/\partial \mathbf{Q}'_j / \partial \dot{\mathbf{Q}}'_i) \rangle \\
 &+ (\partial \mathbf{u} / \partial \mathbf{r})^{-1} : \sum_{i=1}^{\alpha-1} a_i [\partial \langle \partial(\Gamma + \Phi)/\partial \mathbf{Q}'_i \rangle / \partial \mathbf{Q}'_i \\
 &- \langle \partial^2(\Gamma + \Phi)/\partial \mathbf{Q}'_i / \partial \mathbf{Q}'_i \rangle] \\
 &- \alpha (\partial \mathbf{u} / \partial \mathbf{r})^{-1} : \sum_{i=1}^{\alpha-1} \sum_{j=1}^{\alpha-1} \sum_{k=1}^{\alpha-1} \sum_{l=1}^{\alpha-1} G'_{ijkl}
 \end{aligned}$$

$$\begin{aligned}
 &\times [\partial \langle \dot{\mathbf{Q}}'_k \cdot \partial^2(\Gamma + \Phi)/\partial \mathbf{Q}'_j / \partial \dot{\mathbf{Q}}'_i \rangle / \partial \mathbf{Q}'_i \\
 &- \langle \partial(\dot{\mathbf{Q}}'_k \cdot \partial^2(\Gamma + \Phi)/\partial \mathbf{Q}'_j / \partial \dot{\mathbf{Q}}'_i) / \partial \mathbf{Q}'_i \rangle] \quad (39)
 \end{aligned}$$

where the \mathbf{Q}'_i are the eigenvectors of the Rouse³ matrix,

$$\mathbf{Q}'_i = \sum_{j=1}^{\alpha-1} A'_{ij} \mathbf{Q}_j \quad (40a)$$

and

$$G'_{ijkl} = \sum_{\mu=1}^{\alpha} B'_{\mu i} B'_{\mu j} B_{k\mu} B'_{\mu l} \quad (40b)$$

In the absence of all concentration gradients the solvent CSD is the constant solvent density. It is a mere formality to average eq. (39) over the solvent phase space. Doing so yields

$$\begin{aligned}
 m_p D \backslash g_p \backslash_s / Dt &= \sum_{\mu=1}^{\alpha} \sum_{i=1}^{\alpha-1} B'_{\mu i} \backslash \\
 &\langle \partial/\partial \mathbf{u}_{\mu} \cdot \partial(\Gamma + \Phi)/\partial \mathbf{Q}'_i \rangle \backslash_s \\
 &- \sum_{\mu=1}^{\alpha} \sum_{i=1}^{\alpha-1} \sum_{j=1}^{\alpha-1} \sum_{k=1}^{\alpha-1} B_{k\mu} B'_{\mu j} B'_{\mu i} \backslash \\
 &\langle \partial/\partial \mathbf{u}_{\mu} \cdot (\dot{\mathbf{Q}}'_k \cdot \partial^2(\Gamma + \Phi)/\partial \mathbf{Q}'_j / \partial \dot{\mathbf{Q}}'_i) \rangle \backslash_s \\
 &+ (\partial \mathbf{u} / \partial \mathbf{r})^{-1} : \sum_{i=1}^{\alpha-1} a_i \backslash \partial \langle \partial(\Gamma + \Phi)/\partial \mathbf{Q}'_i \rangle / \partial \mathbf{Q}'_i \\
 &- \langle \partial^2(\Gamma + \Phi)/\partial \mathbf{Q}'_i / \partial \mathbf{Q}'_i \rangle \backslash_s - \alpha (\partial \mathbf{u} / \partial \mathbf{r})^{-1} \\
 &: \sum_{i=1}^{\alpha-1} \sum_{j=1}^{\alpha-1} \sum_{k=1}^{\alpha-1} \sum_{l=1}^{\alpha-1} G'_{ijkl} \\
 &\times \backslash \partial \langle \dot{\mathbf{Q}}'_k \cdot \partial^2(\Gamma + \Phi)/\partial \mathbf{Q}'_j / \partial \dot{\mathbf{Q}}'_i \rangle / \partial \mathbf{Q}'_i \\
 &- \langle \partial(\dot{\mathbf{Q}}'_k \cdot \partial^2(\Gamma + \Phi)/\partial \mathbf{Q}'_j / \partial \dot{\mathbf{Q}}'_i) / \partial \mathbf{Q}'_i \rangle \backslash_s \quad (41)
 \end{aligned}$$

where each pair of backward slashes, with its subscript, denotes an average taken over the solvent phase space.

To form the governing equation for the intramolecular contribution to the total stress, we multiply eq. (41) by $\langle \mathbf{Q}'_m \dot{\mathbf{Q}}'_m \cdot \partial^2 \Phi / \partial \mathbf{Q}'_m / \partial \dot{\mathbf{Q}}'_m - \mathbf{Q}'_m \partial \Phi / \partial \mathbf{Q}'_m \rangle$ and then average over the polymer configuration space. Doing so and applying chain rule differentiation yields

$$\begin{aligned}
 m_p D \sigma_m / Dt &= \sum_{\mu=1}^{\alpha} \sum_{i=1}^{\alpha-1} B'_{\mu i} \backslash \langle \partial/\partial \mathbf{u}_{\mu} \cdot \partial(\Gamma + \Phi) / \\
 &\partial \mathbf{Q}'_i \rangle \langle \mathbf{Q}'_m \dot{\mathbf{Q}}'_m \cdot \partial^2 \Phi / \partial \mathbf{Q}'_m / \partial \dot{\mathbf{Q}}'_m
 \end{aligned}$$

$$\begin{aligned}
 & - \langle \mathbf{Q}'_m \partial \Phi / \partial \mathbf{Q}'_m \rangle \backslash \backslash - \sum_{\mu=1}^{\alpha} \sum_{i=1}^{\alpha-1} \sum_{j=1}^{\alpha-1} \sum_{k=1}^{\alpha-1} B_{k\mu} B'_{ij} B'_{\mu i} \\
 & \times \backslash \backslash \langle \partial / \partial \mathbf{u}_\mu \cdot (\dot{\mathbf{Q}}'_k \cdot \partial^2(\Gamma + \Phi) / \partial \mathbf{Q}'_j / \partial \dot{\mathbf{Q}}'_i) \rangle \\
 & \langle \mathbf{Q}'_m \dot{\mathbf{Q}}'_m \cdot \partial^2 \Phi / \partial \mathbf{Q}'_m / \partial \dot{\mathbf{Q}}'_m - \mathbf{Q}'_m \partial \Phi / \partial \mathbf{Q}'_m \rangle \backslash \backslash \\
 & - (\partial \mathbf{u} / \partial \mathbf{r})^{-1} : \sum_{i=1}^{\alpha-1} a_i \backslash \backslash \langle \partial(\Gamma + \Phi) / \partial \mathbf{Q}'_i \rangle \\
 & \times \partial \langle \mathbf{Q}'_m \dot{\mathbf{Q}}'_m \cdot \partial^2 \Phi / \partial \mathbf{Q}'_m / \partial \dot{\mathbf{Q}}'_m - \mathbf{Q}'_m \partial \Phi / \partial \mathbf{Q}'_m \rangle / \partial \mathbf{Q}'_i \\
 & + \langle \partial^2(\Gamma + \Phi) / \partial \mathbf{Q}'_i / \partial \mathbf{Q}'_i \rangle \\
 & \times \langle \mathbf{Q}'_m \dot{\mathbf{Q}}'_m \cdot \partial^2 \Phi / \partial \mathbf{Q}'_m / \partial \dot{\mathbf{Q}}'_m \\
 & - \mathbf{Q}'_m \partial \Phi / \partial \mathbf{Q}'_m \rangle \backslash \backslash + \alpha (\partial \mathbf{u} / \partial \mathbf{r})^{-1} : \sum_{i=1}^{\alpha-1} \sum_{j=1}^{\alpha-1} \sum_{k=1}^{\alpha-1} \sum_{l=1}^{\alpha-1} \\
 & \times G'_{ijkl} \backslash \backslash \langle \dot{\mathbf{Q}}'_k \cdot \partial^2(\Gamma + \Phi) / \partial \mathbf{Q}'_j / \partial \dot{\mathbf{Q}}'_i \rangle \\
 & \times \partial \langle \mathbf{Q}'_m \dot{\mathbf{Q}}'_m \cdot \partial^2 \Phi / \partial \mathbf{Q}'_m / \partial \dot{\mathbf{Q}}'_m - \mathbf{Q}'_m \partial \Phi / \partial \mathbf{Q}'_m \rangle / \\
 & \partial \mathbf{Q}'_i + \langle \partial(\dot{\mathbf{Q}}'_k \cdot \partial^2(\Gamma + \Phi) / \partial \mathbf{Q}'_j / \partial \dot{\mathbf{Q}}'_i) / \partial \mathbf{Q}'_i \rangle \\
 & \langle \mathbf{Q}'_m \dot{\mathbf{Q}}'_m \cdot \partial^2 \Phi / \partial \mathbf{Q}'_m / \partial \dot{\mathbf{Q}}'_m - \mathbf{Q}'_m \partial \Phi / \partial \mathbf{Q}'_m \rangle \backslash \backslash \quad (42)
 \end{aligned}$$

where

$$\begin{aligned}
 \sigma_m = \backslash \backslash \langle \mathbf{Q}'_m \dot{\mathbf{Q}}'_m \cdot \partial^2 \Phi / \partial \mathbf{Q}'_m / \partial \dot{\mathbf{Q}}'_m \\
 - \mathbf{Q}'_m \partial \Phi / \partial \mathbf{Q}'_m \rangle \backslash \backslash \quad (43)
 \end{aligned}$$

and the double pair of backward slashes, without subscripts, denotes the joint solvent-polymer average.

Equation (42) is the most general constitutive equation for this model when using scleronomic, monogenic, molecular forces. We may simplify this if we consider that the molecular potentials probably do not vary with the bulk flow velocity, or if they do, the variation is negligible over the size of a macromolecule. With this assumption, eq. (42) reduces to

$$\begin{aligned}
 m_p D\sigma_m / Dt + (\partial \mathbf{u} / \partial \mathbf{r})^{-1} : \sum_{i=1}^{\alpha-1} a_i \backslash \backslash \langle \partial(\Gamma + \Phi) / \\
 \partial \mathbf{Q}'_i \rangle \partial \langle \mathbf{Q}'_m \dot{\mathbf{Q}}'_m \cdot \partial^2 \Phi / \partial \mathbf{Q}'_m / \partial \dot{\mathbf{Q}}'_m - \mathbf{Q}'_m \partial \Phi / \partial \mathbf{Q}'_m \rangle / \\
 \partial \mathbf{Q}'_m + \langle \partial^2(\Gamma + \Phi) / \partial \mathbf{Q}'_i / \partial \mathbf{Q}'_i \rangle \\
 \times \langle \mathbf{Q}'_m \dot{\mathbf{Q}}'_m \cdot \partial^2 \Phi / \partial \mathbf{Q}'_m / \partial \dot{\mathbf{Q}}'_m - \mathbf{Q}'_m \partial \Phi / \partial \mathbf{Q}'_m \rangle \backslash \backslash \\
 = \alpha (\partial \mathbf{u} / \partial \mathbf{r})^{-1} : \sum_{i=1}^{\alpha-1} \sum_{j=1}^{\alpha-1} \sum_{k=1}^{\alpha-1} \sum_{l=1}^{\alpha-1} G'_{ijkl} \\
 \backslash \backslash \langle \dot{\mathbf{Q}}'_k \cdot \partial^2(\Gamma + \Phi) / \partial \mathbf{Q}'_j / \partial \dot{\mathbf{Q}}'_i \rangle \partial \langle \mathbf{Q}'_m \dot{\mathbf{Q}}'_m \cdot \partial^2 \Phi / \\
 \partial \mathbf{Q}'_m / \partial \dot{\mathbf{Q}}'_m - \mathbf{Q}'_m \partial \Phi / \partial \mathbf{Q}'_m \rangle / \partial \mathbf{Q}'_i
 \end{aligned}$$

$$\begin{aligned}
 & + \langle \partial(\dot{\mathbf{Q}}'_k \cdot \partial^2(\Gamma + \Phi) / \partial \mathbf{Q}'_j / \partial \dot{\mathbf{Q}}'_i) / \partial \mathbf{Q}'_i \rangle \\
 & \times \langle \mathbf{Q}'_m \dot{\mathbf{Q}}'_m \cdot \partial^2 \Phi / \partial \mathbf{Q}'_m / \partial \dot{\mathbf{Q}}'_m - \mathbf{Q}'_m \partial \Phi / \partial \mathbf{Q}'_m \rangle \backslash \backslash \quad (44)
 \end{aligned}$$

We may now consider specific forms for the molecular forces.

Linear Intramolecular Force

We proceed as we have done for the conservative force case. We consider a polymer solution at the theta temperature with an intramolecular potential such that

$$\partial \Phi / \partial \mathbf{Q}'_i = \mathbf{H} \cdot (\mathbf{Q}'_i - w \dot{\mathbf{Q}}'_i - \mathbf{d}) \quad (45)$$

where \mathbf{d} is the same intramolecular length scale as for the conservative force law and w is a time constant.

We define w such that

$$1/w \delta_{ij} \delta = \partial \dot{\mathbf{Q}}'_i / \partial \mathbf{Q}'_j \quad (46)$$

and so $w \neq 0$. Using the force law of eq. (45) in (44) and evaluating for a theta solvent yields

$$\begin{aligned}
 m_p D\sigma_m / Dt + [2(\alpha - 1) + \alpha^2 / 6(\alpha^2 - \alpha + 1)] \\
 \times (\partial \mathbf{u} / \partial \mathbf{r})^{-1} : \mathbf{H} \sigma_m \\
 = a_m (\partial \mathbf{u} / \partial \mathbf{r})^{-1} : \backslash \backslash \mathbf{H} \cdot (\mathbf{Q}'_m - w \langle \dot{\mathbf{Q}}'_m \rangle - \mathbf{d}) \\
 \times [\delta \mathbf{H} \cdot (\mathbf{Q}'_m - w \langle \dot{\mathbf{Q}}'_m \rangle - \mathbf{d}) + \mathbf{Q}'_m \mathbf{H} \\
 + \delta(w \langle \dot{\mathbf{Q}}'_m \rangle + \mathbf{Q}'_m) + \mathbf{Q}'_m \cdot \mathbf{H}] \backslash \backslash \\
 + \alpha w (\partial \mathbf{u} / \partial \mathbf{r})^{-1} : \sum_{k=1}^{\alpha-1} S_{km} \backslash \backslash \langle \dot{\mathbf{Q}}'_k \rangle \cdot \\
 \times \mathbf{H} [\delta \mathbf{H} \cdot (\mathbf{Q}'_m - w \langle \dot{\mathbf{Q}}'_m \rangle - \mathbf{d}) + \mathbf{Q}'_m \mathbf{H} \\
 + \delta(w \langle \dot{\mathbf{Q}}'_m \rangle + \mathbf{Q}'_m) \cdot \mathbf{H}] \backslash \backslash \quad (47)
 \end{aligned}$$

where

$$\begin{aligned}
 S_{km} = \sum_{i=1}^{\alpha-1} G'_{ikm} = (\alpha - m)(2k + 1 - 1/\alpha) \\
 \text{for } k \leq m \\
 = -2km/\alpha \text{ for } k > m \quad (48)
 \end{aligned}$$

We see from eq. (47) that we must also have equations for $\backslash \backslash \mathbf{Q}'_m \backslash \backslash$ and $\backslash \backslash \langle \dot{\mathbf{Q}}'_m \rangle \backslash \backslash$. To simplify the notation, we let $\mathbf{R}_m = \backslash \backslash \mathbf{Q}'_m \backslash \backslash$ and $\dot{\mathbf{R}} = \backslash \backslash \langle \dot{\mathbf{Q}}'_m \rangle \backslash \backslash$.

Governing Equation for \mathbf{R}_m

First, we derive the governing equation for \mathbf{R}_m . To do this, we may either return to eq. (41), multiply

it by \mathbf{Q}'_m and proceed in the same manner as before, or we may replace $\dot{\mathbf{Q}}'_m \cdot \partial^2 \Phi / \partial \mathbf{Q}'_m / \partial \dot{\mathbf{Q}}'_m - \partial \Phi / \partial \mathbf{Q}'_m$ in eq. (42) with scalar unity. Doing so either way yields

$$\begin{aligned} m_p D\mathbf{R}_m / Dt + [2(\alpha - 1) + \alpha^2 / 6(\alpha^2 - \alpha + 1)] \\ \times (\partial \mathbf{u} / \partial \mathbf{r})^{-1} : \mathbf{H} \mathbf{R}_m + a_m (\partial \mathbf{u} / \partial \mathbf{r})^{-1} : \mathbf{H} \cdot \mathbf{R} \delta \\ = a_m (\partial \mathbf{u} / \partial \mathbf{r})^{-1} : \mathbf{H} \cdot (w \dot{\mathbf{R}}_m - \mathbf{d}) \delta \\ - \alpha w (\partial \mathbf{u} / \partial \mathbf{r})^{-1} : \sum_{k=1}^{\alpha-1} S_{km} \dot{\mathbf{R}}_k \cdot \mathbf{H} \delta \quad (49) \end{aligned}$$

Equation (49) shows that \mathbf{R}_m , as well as σ_m , depends upon $\dot{\mathbf{R}}_m$. We now derive the governing equation for it.

Governing Equation for $\dot{\mathbf{R}}_m$

For the purpose of illustration, we return to the conservation equation for all of phase space to derive the governing equation for $\dot{\mathbf{R}}_m$. We return to eq. (30) and transform to the independent variables from $\{\mathbf{r}_\mu\}$ to \mathbf{r}_c and $\{\mathbf{Q}_i\}$. Then, neglecting all concentration gradients yields

$$\begin{aligned} m_p Df_p / Dt = \sum_{j=1}^{\alpha-1} \sum_{k=1}^{\alpha-1} A_{jk} \partial / \partial \dot{\mathbf{Q}}_j \cdot (f_p \partial(\Gamma + \Phi) / \partial \mathbf{Q}_k) \\ - \sum_{i=1}^{\alpha-1} \sum_{j=1}^{\alpha-1} \sum_{k=1}^{\alpha-1} \sum_{l=1}^{\alpha-1} G_{ijkl} \partial / \partial \dot{\mathbf{Q}}_i \cdot (f_p \dot{\mathbf{Q}}_j \cdot \\ \partial^2(\Gamma + \Phi) / \partial \mathbf{Q}_j / \partial \dot{\mathbf{Q}}_i) - m_p \sum_{\mu=1}^{\alpha} \sum_{i=1}^{\alpha-1} B_{i\mu} \partial / \partial \mathbf{Q}_i \cdot (f_p \mathbf{v}_\mu). \quad (50) \end{aligned}$$

We multiply equation (50) by $\dot{\mathbf{Q}}_m$ and then average over the polymer velocity space. Applying chain rule differentiation and simplifying yields

$$\begin{aligned} m_p D\langle \dot{\mathbf{Q}}_m \rangle / Dt + 3 \sum_{i=1}^{\alpha-1} \sum_{j=1}^{\alpha-1} \delta_{im} A_{ij} \langle \partial(\Gamma + \Phi) / \partial \mathbf{Q}_j \rangle \\ = 3 \sum_{j=1}^{\alpha-1} \sum_{k=1}^{\alpha-1} \sum_{l=1}^{\alpha-1} G_{mjkl} \langle \dot{\mathbf{Q}}_k \cdot \partial^2(\Gamma + \Phi) / \partial \mathbf{Q}_j / \partial \dot{\mathbf{Q}}_l \rangle \\ + m_p \sum_{\mu=1}^{\alpha} \sum_{i=1}^{\alpha-1} B_{i\mu} \langle \mathbf{v}_\mu \partial \dot{\mathbf{Q}}_m / \partial \mathbf{Q}_i \rangle : \delta. \quad (51) \end{aligned}$$

In the absence of all concentration gradients

$$\mathbf{v}_\mu = \dot{\mathbf{r}}_\mu - \mathbf{u}_\mu = \sum_{i=1}^{\alpha-1} B'_{\mu i} \dot{\mathbf{Q}}_i - \mathbf{u}_\mu \quad (52)$$

so equation (51) becomes

$$\begin{aligned} m_p D\langle \dot{\mathbf{Q}}_m \rangle / Dt + 3 \sum_{i=1}^{\alpha-1} \sum_{j=1}^{\alpha-1} \delta_{im} A_{ij} \langle \partial(\Gamma + \Phi) / \partial \mathbf{Q}_j \rangle \\ = 3 \sum_{j=1}^{\alpha-1} \sum_{k=1}^{\alpha-1} \sum_{l=1}^{\alpha-1} G_{mjkl} \langle \dot{\mathbf{Q}}_k \cdot \partial^2(\Gamma + \Phi) / \partial \mathbf{Q}_j / \partial \dot{\mathbf{Q}}_l \rangle \\ + \alpha m_p \sum_{i=1}^{\alpha-1} \langle \dot{\mathbf{Q}}_i \partial \dot{\mathbf{Q}}_m / \partial \mathbf{Q}_i \rangle : \delta \\ - m_p \sum_{\mu=1}^{\alpha} \sum_{i=1}^{\alpha-1} B_{i\mu} \mathbf{u}_\mu \langle \partial \dot{\mathbf{Q}}_m / \partial \mathbf{Q}_i \rangle : \delta. \quad (53) \end{aligned}$$

We now transform the independent variables with the same orthogonal transformation used before. Using the definition of the time constant w and after some rearrangement (53) reduces to

$$\begin{aligned} m_p D\langle \dot{\mathbf{Q}}'_m \rangle / Dt - 3\alpha m_p / w \langle \dot{\mathbf{Q}}'_m \rangle \\ = -3 \langle \partial(\Gamma + \Phi) / \partial \mathbf{Q}'_m \rangle - 3m_p / w \sum_{\mu=1}^{\alpha} B'_{\mu m} \mathbf{u}_\mu \quad (54) \end{aligned}$$

We simplify further by neglecting any variation of the bulk flow velocity over the size of a macromolecule. We expect that for all except very strong shear rates this assumption is valid. Doing so yields

$$\begin{aligned} m_p D\langle \dot{\mathbf{Q}}'_m \rangle / Dt - 3\alpha m_p / w \langle \dot{\mathbf{Q}}'_m \rangle \\ = -3 \langle \partial(\Gamma + \Phi) / \partial \mathbf{Q}'_m \rangle \quad (55) \end{aligned}$$

Averaging eq. (55) over the solvent and polymer configuration space yields the governing equation for $\dot{\mathbf{R}}_m$. We substitute the intramolecular force law of eq. (45) and evaluate at the theta temperature to find

$$\begin{aligned} D\dot{\mathbf{R}}_m / Dt - 3\alpha / w \dot{\mathbf{R}}_m \\ = -3 / m_p \mathbf{H} \cdot (\mathbf{R}_m - w \dot{\mathbf{R}}_m - \mathbf{d}) \quad (56) \end{aligned}$$

And so we see that eq. (56) closes the set of equations needed to solve for σ_m , \mathbf{R}_m , and $\dot{\mathbf{R}}_m$.

Assessment

Equations (47), (49), and (56) are a complete set needed to predict the intramolecular contribution to the total stress when using linear, nonconservative forces. They may be compared with eqs. (6) and (8), which use conservative, linear forces. Aside from being more complex, the nonconservative equations have an additional degree of freedom provided by the time constant w . Our purpose for con-

sidering nonconservative forces was not to add new parameters, but to see how the fundamental characteristics of the conservative, linear force predictions would change.

Comparing eqs. (47), (49), and (56) with (6) and (8) shows that the equations using nonconservative, linear forces are of the same form as those using conservative, linear forces. Hence, stress overshoot in a step response experiment is not predicted and the prediction for viscoplasticity remains. Thus, it appears that the conservative nature of the molecular forces is not responsible for these phenomena.

This leads us to consider what changes would have to be made to enable the model to predict stress overshoot and to remove the prediction for viscoplasticity. We note that, if the parameters \mathbf{H} or \mathbf{d} were to vary with the shear rate, the steady state stresses would have a shear rate dependence. Whether or not this would cause the model to predict stress overshoot remains to be seen because the transient equations would have to be resolved.

Giving either of the parameters \mathbf{H} or \mathbf{d} a shear rate dependence changes the linear intramolecular force law into a nonlinear one. This nonlinearity is with respect to $\dot{\mathbf{Q}}_i$ for homogeneous flow and with respect to both \mathbf{Q}_i and $\dot{\mathbf{Q}}_i$ for nonhomogeneous flows. Since neither thermodynamics nor statistical mechanics has identified a shear rate dependence for the intramolecular force within a polymer molecule, we are forced to resort to phenomenology and merely postulate one. If, for example, we were to assume that

$$\mathbf{d} = c \dot{\gamma}^n (\delta_1 + \delta_2 + \delta_3) \quad (57)$$

where c and n are arbitrary parameters, then the steady state stresses would vary in proportion to $\dot{\gamma}^{2n}$.

CONCLUSIONS

We have seen that this molecular model of a polymer solution predicts viscoplastic behavior unless the polymer's intramolecular force has a shear rate dependence. Not having a theoretical basis for such a force, we must resort to phenomenology and postulate one. Doing so removes the viscoplasticity prediction from the model, but it remains to be seen if this also causes the model to predict stress overshoot in response to a step change in shear rate.

The well-accepted notion of a symmetric stress tensor has led us to form a constraint upon the directionality of the intramolecular force. To obtain predictions of the first and second normal stress differences consistent with experiments, it is necessary that the flow (first) and indifferent (third) direction

normal components of the intramolecular Hooke's law constant be unequal. The second normal component of \mathbf{H} may be selected independently of the third, but it is constrained to the first by the symmetry of the stress tensor. This conclusion is based on the assumption that the intramolecular Hooke's law constant tensor is symmetric; an assumption adopted solely for convenience.

The concept of the theta temperature, or solvent, simplifies the analysis and at the same time shows that the intramolecular forces have greater bearing on the intramolecular contribution to the total stress than do the intermolecular forces. This may be an artifact of all models that use single molecule distributions instead of higher order distributions. Because we have used only single molecule distributions, our analysis predicts only the polymer's kinetic and intramolecular contributions to the total stress. Yet, the intramolecular forces are clearly of far greater magnitude than those between the polymer and the solvent, or even between polymer molecules, so we have reason to believe that the intramolecular contribution to the total stress dominates any intermolecular contributions. This would suggest that the use of single molecule distributions may be justified even when the polymer solution cannot be considered dilute. Based upon this belief, our model suggests that the feature of the solvent-polymer interaction most significant to rheology is to change the effective stress within a polymer molecule.

The need to use anisotropic, molecular forces in this analysis to predict results consistent with experiments probably results from the simplicity of the model. Using nonlinear functions for the molecular forces appears necessary for improving the agreement between this theory and experiments. Further complications to the molecular forces would be put to good use if their purpose is to identify the molecular phenomena of significance to rheology.

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