Inertially driven transient response in polymeric liquids

William W. Graessleya, Scott T. Milnerb,1

a Department of Chemical Engineering, Princeton University, Princeton, NJ 08544, United States
b ExxonMobil Research & Engineering Company, Annandale, NJ 08801, United States

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We report here a computational study, with inertial contributions included, of the time-dependent velocity and shear stress profiles following flow start-up from rest for a polymeric liquid. Earlier workers solved similar fluid-mechanical start-up problems with viscoelastic character represented by a single Maxwell element. They found significant oscillatory departures from the steady-state velocity profile that persist throughout the entire period of stress growth to steady state. Such results are unsettling since they imply that the usual assumptions about velocity fields for transient tests of polymeric liquids are seriously in error. It turns out, however, that such oscillations are rapidly suppressed when a broad distribution of relaxation times is employed, the physically appropriate situation for polymeric liquids. The initial shear wave oscillations decay quickly compared with the time to reach the stress steady state when realistic descriptions of their viscoelastic character are employed. We note that a combination of inertial contributions with sparse relaxation spectra in fluid-mechanical modeling can lead to spurious velocity and stress field predictions for polymeric liquid flows.

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1. Introduction

Stress growth following the onset from rest of steady shear flow is one of the experiments used to characterize the non-linear response of viscoelastic liquids. The experiments are typically conducted in the concentric cone-and-plate geometry, one boundary being set in motion at constant angular velocity while the other is held fixed. Stress components are typically calculated from measurements of total torque and axial thrust acting on the boundaries. Inertial effects are usually ignored in the data analysis. A steady-state velocity field is assumed to be established instantaneously, or at least within a time that is very short compared with the time required for the stress to reach steady state. A similar situation arises in large step strain experiments. Again inertial contributions are routinely ignored, yet the inertial contributions must certainly be large at least in the early time region.

Inertial effects in unsteady flows have attracted the interest of rheologists for many years [1–12]. Indeed, numerous studies have examined velocity profile development in viscoelastic liquids computationally, and quite naturally, viscoelastic character was introduced in the simplest possible manner. For example, Tanner [1] and Okeson and Emery [4] used the Oldroyd Model B to represent liquid response in steady shear rate start-up. Denn and Porteous [2] used an upper convected Maxwell model as did Kazakia and Rivlin [6]. Similar problems containing inertial terms are considered in Chapter 19 of Joseph’s book [8]. Oldroyd Model B is equivalent to the Lodge model [13] with a single relaxation time plus a Newtonian (solvent) contribution:

\[ \sigma(t) = -\Pi + \frac{\eta_0 - \eta_s}{\tau_1} \int_{-\infty}^{t} \exp \left( -\frac{t-t'}{\tau_1} \right) C^{-1}(t', t) \, dt' + \eta_s \dot{\gamma}(t). \] (1)

Thus, \( \sigma(t) \) is the extra stress tensor, \( C^{-1} (r, t) \) is the Finger strain tensor [14], \( \dot{\gamma}(t) \) is the rate of deformation tensor, \( \tau_1 \) is the relaxation time, \( \eta_s \) is the solvent viscosity, and \( \eta_0 \) is the zero shear viscosity of the liquid. The Maxwell model is equivalent to Eq. (1) with \( \eta_s \) set to zero.

All the hitherto analyses of simple shear start-up with appropriate inclusion of inertial contributions were based on models with a single relaxation time, and all yield strong oscillations in the velocity field. Moreover, the oscillations persist for times required to reach stress steady state for “negligible inertia”, i.e., in this case of the order the relaxation time. Here we show that, when more realistic relaxation time distributions are introduced—extending with contributions over the fully appropriate range for polymeric liquids—and nothing more, the oscillations subside quickly, and the velocity achieves a “negligible inertia” profile long before
the steady-state stress is approached. The effect of this proper filling out of the spectrum is illustrated computationally with distributions inferred from dynamic modulus data in the low frequency range as supplemented with predictions for higher frequencies with known behavior [15] and recent molecular theory [16]. The results are applied to data for sample C, an entangled polymer solution typical of those used in experimental start-up tests. We chose Laplace transform techniques to make the calculations [17] although Fourier transforms [18] would also have sufficed.

The characteristics of sample C are given in Section 2, the fluid mechanics problem is formulated in Section 3, an approximate solution applied to various sorts of discrete relaxation spectra is examined in Section 4, full solutions for both the velocity and stress profiles during start-up for sample C are presented in Section 5, and some broader implications are discussed in Section 6.

2. Test liquid and conditions

To implement the calculations for test sample C [19,20]—a 12 wt% solution (volume fraction $\phi = 0.14$, $\rho = 1.26 \times 103$ kg m$^{-3}$) of polystyrene ($M_w = 1.8 \times 10^6$, $M_w/M_n = 1.2$) in tricresyl phosphate ($\rho_s = 1.3 \times 10^3$ kg m$^{-3}$, $\eta_s = 0.07$ Pa s) at 25 $^\circ$C—we employ dynamic moduli data and values for its plateau modulus, entanglement molecular weight and various characteristic times. The dynamic moduli data and values for its plateau modulus, entanglement molecular weight and various characteristic times. The dynamic moduli for sample C are listed in Table 1. We obtain the plateau modulus from the value for undiluted polystyrene, $G_0^p = 2.0 \times 10^3$ Pa [21], and its concentration dependence, $G_0^p(\phi) = G_0^p(1)\phi^{2.3}$ [22]. Thus, $G_0^p = 2.2 \times 10^3$ Pa for sample C. We obtain the entanglement molecular weight for sample C from the polystyrene melt value, $M_c = 1.72 \times 10^4$ [21], and its concentration dependence, $M_c(\phi) = M_c(1)\phi^{-1.3}$ [22], leading to $M_c = 2.22 \times 10^5$. Hence with $M_w = 1.8 \times 10^6$ we have $E = M_w/M_c = 8.1$ entanglements per chain and $N_p = M_w/0.8 M_c = 10.1$ primitive path steps per chain [21].

We estimate the Rouse and Doi-Edwards path step relaxation times for sample C from their relationships to the path disengagement time $\tau_d$ [23,21], $\tau_x = \tau_d/(6N_p)$ and $\tau_\phi = \tau_d/\tau_x^2/(6N_p^2)$. Experimental values of viscosity and first normal stress coefficient at zero shear rate have been reported [20]: $\eta_0 = 6.6 \times 10^3$ Pa s and $\psi_{10} = 2.14 \times 10^5$ Pa s$^2$. We approximate the disengagement time with the weight-average relaxation time for the experimental spectrum [21],

$$\tau_y = \frac{\psi_{10}}{2\eta_0} = \eta_0 \bar{\rho},$$

(2)

giving $\tau_y \sim \tau_w = 16.2$ s and hence $\tau_y \sim 0.27$ s and $\tau_y \sim 0.26$ s.

The start-up data for sample C were gathered at 25 $^\circ$C using a cone-plate geometry (gap angle $8^\circ$, radius 2.5 cm), typical for such tests. As done in most other computational studies, we choose the shearing displacement of infinite parallel plates, planar Couette flow, to be the computational geometry, roughly matching the experiments by using a mean-square separation distance $D^2 = 10^{-5}$ m$^2$ ($D \sim 3$ mm). Many studies have shown [21] that the Lodge model predictions accurately describe start-up behavior for low-enough shear rates at all times and also over a wide range of higher shear rates ($0.06$ s$^{-1} \leq \dot{\gamma} \leq 20$ s$^{-1}$ for sample C) up to shear strains relative to rest of order unity [20]:

$$\sigma(\dot{\gamma}, t) = \int_0^t G(t - t')\dot{\gamma}(t') dt', \quad 0 \leq \dot{\gamma} t \leq \tau_y^{-1},$$

$$\sigma(\dot{\gamma}, t) = \int_0^t G(t - t')\dot{\gamma}(t') dt', \quad 0 \leq \dot{\gamma} t \leq 1, \quad \dot{\gamma} \geq \tau_y^{-1}.$$

No indication of oscillation was observed from 0.001 s to Lodge model breakdown (0.1–10 s, depending on $\dot{\gamma}$) [20].

3. Formulation

Consider a viscoelastic liquid with mass density $\rho$ initially at rest between infinite parallel plates that are separated in gradient direction $y$ by a fixed distance $D$. At $t = 0$, the upper plate (at $y = D$) is set in motion in displacement direction $x$ at a constant velocity $U_0$, while the lower plate (at $y = 0$) is held fixed. We assume that the other two components of velocity remain zero and that the $x$ component of velocity is a function $U$ of $y$ and $t$ alone. The $x$ component in the equation of motion [14] then reduces to

$$\frac{\partial \sigma}{\partial y} = \rho \frac{\partial U}{\partial t},$$

(4)

in which $\sigma(y, t)$ is the shear stress component $\sigma_{yx}$. The initial condition is

$$U(y, 0) = 0,$$

(5)

and boundary conditions are

$$U(0, t) = 0,$$

$$U(D, t) = U_0,$$

(6)

For the Lodge model [13], the shear stress for simple shear histories can be expressed as

$$\sigma(y, t) = \int_0^t G(t - t')\dot{\gamma}(y, t') dt',$$

(7)

in which $G(t)$ is the shear stress relaxation modulus of the liquid [15], and in this case $\dot{\gamma} = \partial U/\partial y$.

Eqs. (4) and (5) can be combined to give

$$\rho \frac{\partial U}{\partial t} = \int_0^t G(t - t')\frac{\partial^2 U}{\partial y^2} dt'.$$

(8)

Applying the Laplace transformation with respect to $t$ [17] to both sides of Eq. (8) converts it to a linear, ordinary differential equation:

$$\frac{d^2 \tilde{U}(y, s)}{dy^2} = \frac{s^2}{s (s^2)} \tilde{U}(y, s),$$

(9)
in which \( \hat{U}(y, s) \) and \( \hat{\zeta}(s) \) are the Laplace transforms of \( U(y, t) \) and \( \zeta(t) \). The boundary conditions given by Eq. (6) transform to

\[
\hat{U}(0, s) = 0, \quad \hat{U}(D, s) = \frac{U_0}{s}.
\]

Eq. (9) is readily solved to give

\[
\hat{U}(y, s) = \frac{U_0}{s} \sin h\left(\frac{y}{D}\right) \frac{\Gamma'(s)}{\sin h\left(\frac{y}{D}\right)},
\]

in which

\[
\Gamma'(s) = \left[\frac{\rho D^2}{\hat{\zeta}(s)}\right]^{1/2}.
\]

The velocity profile \( U(y, t) \) is the inverse transform of \( \hat{U}(y, s) \). If \( \hat{\zeta}(t) \) is given, \( \hat{\zeta}(s) \) can be calculated and Eq. (11) inverted by an appropriate complex plane integration [17].

For a discrete spectrum of \( N \) Maxwell modes the relaxation modulus can be written as

\[
\hat{G}(t) = \sum_{k=1}^{N} \frac{g_k}{\tau_k} e^{-t/\tau_k},
\]

in which \( g_k \) and \( \tau_k \) are the modulus contribution and relaxation time for the \( k \)th mode. The modes are labeled as usual [15], in decreasing order of relaxation time magnitude. Thus, \( \tau_1 \) is the longest relaxation time, etc. The transform of Eq. (13) with a Newtonian solvent contribution included is

\[
\hat{G}(s) = \sum_{k=1}^{N} \frac{g_k \tau_k}{1 + s \tau_k} + \eta_s,
\]

in which \( \eta_s \) is the solvent viscosity. Eq. (14) can be written as a ratio of polynomials in \( s \). Consequently, the singular points of Eq. (9) are poles, so Eq. (11) can be inverted by the Cauchy residue theorem [17]. Assuming the singular points are simple zeroes and hence that the poles are simple poles, the result is

\[
U(y, t) = U_0 \left[ \frac{y}{D} + 2 \sum_{n=1}^{\infty} \sum_{m=1}^{N} \frac{(-1)^n}{n} c_{mn} \sin \left( \frac{n \pi y}{D} \right) \exp(z_{mn} t) \right].
\]

The first term on the right is the steady-state velocity profile. The \( c_{mn} \) coefficients are given by

\[
c_{mn} = \frac{1}{1 - \alpha_n k_{mn}},
\]

in which

\[
k_{mn} = \sum_{k=1}^{N} \frac{g_k \tau_k}{(1 + z_{mn} \tau_k)^2},
\]

\[
\alpha_n = \frac{n^2 \pi^2}{\rho D^2},
\]

and the values of \( z_{mn} \) are the roots of the polynomial in \( s \):

\[
\frac{S}{\alpha_n} + \sum_{k=1}^{N} \frac{g_k \tau_k}{1 + s \tau_k} + \eta_s = 0.
\]

An expression for the shear stress relative to its steady-state value, \( \Delta\sigma(y, t) \), can be obtained with Eqs. (4) and (15). (The steady-state stress is independent of \( y \), and thus is a homogenous solution of Eq. (4).) With the spatial variable expressed as \( y = \xi D \),

\[
\Delta\sigma(\xi, t) = \frac{2U_0 \rho D}{\pi^2} \sum_{n=1}^{\infty} \sum_{m=1}^{N} \frac{(-1)^m}{n^2} c_{mn} z_{mn} \cos(n \pi \xi) \exp(z_{mn} t).
\]

With velocity also defined relative to steady-state values, \( U_0 \xi \), Eq. (15) yields

\[
\Delta U(\xi, t) = \frac{2U_0}{\pi} \sum_{n=1}^{\infty} \sum_{m=1}^{N} \frac{(-1)^m}{n} c_{mn} \sin(n \pi \xi \exp(z_{mn} t)).
\]

The two expressions for departures from steady state are related by

\[
\frac{\partial \Delta\sigma}{\partial \xi} = \rho D \frac{\partial \Delta U}{\partial t}.
\]

Eq. (15) reduces to the well-known solution for the velocity of a Newtonian fluid when all \( g_k \) are set equal to zero

\[
U(y, t) = U_0 \left[ \frac{y}{D} + 2 \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \sin \left( \frac{n \pi y}{D} \right) \exp(-\alpha_n n \eta_s t) \right].
\]

It also reduces to the Okeson–Emery [4] solution for \( N = 1 \), and to the Denn–Porteous [2] solution for \( N = 1 \) and \( \eta_s = 0 \).

4. An approximate analysis

Before embarking on detailed numerical computations of the velocity and shear stress transients, we introduce a simplified model in order to display clearly the essential physics of the problem. As above, the Laplace transform method is applied but now with a complex variable \( \omega \) in place of \( s \). This furnishes an immediate connection between the inertial contribution and the dynamic modulus of the liquid, leading finally to a damped harmonic oscillator formulation. In particular, we shall see that a single-mode Maxwell model gives a very poor account of the oscillatory transients for typical polymeric liquids and shear gaps because it greatly underestimates the decay rate of the inherently driven oscillations. We shall also see, on the other hand, that high frequency relaxation processes in the transition region—a universal feature of entangled flexible-chain polymeric liquids [15]—quench such oscillations in times much shorter than the time to reach stress steady state.

In the simplified model, we express velocity relative to the steady-state value as \( u(\xi, t) \),

\[
\Delta U(\xi, t) = \Delta U(\xi, t) = U_0 \xi \frac{\partial^2 U(\xi, t)}{\partial \xi^2} dt.
\]

The initial and boundary conditions are now the following:

\[
u(\xi, 0) = 0, \quad u(0, t) = 0, \quad u(1, t) = 0.
\]

The Laplace transformation of Eq. (24) with the substitution \( s = i\omega \), leads to

\[
\frac{\rho D^2 \partial u(\xi, \omega)}{\partial \xi^2} = \int_0^t \hat{G}(\tau - t') \frac{\partial^2 u(\xi, t')}{\partial \xi^2} dt'.
\]

The spatial dependence of velocity is of interest for purposes here only insofar as choosing a \( \gamma \)-coordinate position for which these oscillations are clearly displayed. Assuming no slip, liquid and wall at \( \xi = 0 \) and at \( \xi = 1 \) must move together, so time-dependent velocity oscillations must be zero at those positions. The midplane position, \( \xi = 1/2 \), is a natural choice. We also assume that the solution, like that in Eq. (15), consists of sums of separable terms in \( \xi \) and \( t (\omega t) \). Of the form \( \hat{U}(\xi, \omega) = \hat{U}(\xi) \hat{G}(\omega) \). We further assume that the longest-lived contribution to the transient at \( \xi = 1/2 \) is the lowest spatial mode that satisfies the zero boundary conditions at \( \xi = 0 \) and at \( \xi = 1 \). The lowest spatial mode in Eq. (21) suffices for the velocity oscillations—\( n = 1 \), corresponding to \( \hat{R}(\xi) = \sin \pi \xi \) is non-zero at
\[ \xi = 1/2. \] Substitution into Eqs. (24)–(26) and cancellations lead to
\[ \frac{-\iota \omega D^2}{\pi^2} = C_0(\omega). \] (27)

For the transformed stress relaxation modulus, we have
\[ \hat{C}_1(\omega) = \int_0^\infty G(t) \exp(-\iota \omega t) \, dt \]
\[ = \int_0^\infty G(t) \cos \omega t \, dt - i \int_0^\infty G(t) \sin \omega t \, dt. \] (28)

The second and third integrals in Eq. (28) are \( G'(\omega)/\omega \) and \( G''(\omega)/\omega \) respectively, \( G'(\omega) \) and \( G''(\omega) \) being the storage and loss moduli of the liquid [15]. Accordingly, Eq. (27) can be written as
\[ \frac{-\iota \omega^2}{\beta} = G'(\omega) - iG''(\omega), \] (29)
in which
\[ \beta = \frac{\pi^2}{\rho D^2}. \] (30)

Finally, with the loss modulus expressed in terms of dynamic viscosity, \( \eta'(\omega) = G'(\omega)/\omega \), we observe a resemblance to the characteristic equation for damped harmonic motion in particle mechanics [24], but with frequency-dependent coefficients, \( \eta'(\omega) \) and \( G'(\omega) \):
\[ \frac{\omega^2}{\beta} - i\eta'(\omega)\omega - G'(\omega) = 0. \] (31)

Denn and Porteous suggested a damped oscillator analogy many years ago [2]. In the standard analyses of damped harmonics the coefficients are constants, and such properties of interest as oscillation frequency and amplitude time dependence are readily obtainable [24]. Unfortunately, we have found no simple way to handle frequency-dependent coefficients rigorously without introducing awkward complexities. Instead, in the hope of finding some useful approximate formulas, we merely expect the constant coefficient equations but with circumsection, as described below.

We identify the real and imaginary parts of \( \omega \) satisfying Eq. (31) by writing \( \omega = \omega_{osc} + i\tau_{decay} \), whereupon the velocity perturbation in this simplified analysis (keeping only the lowest spatial mode) can be written:
\[ u(\xi, t) = A \sin \pi \xi \exp \left( -\frac{t}{\tau_{decay}} \right) \exp(i\omega_{osc}t). \] (32)

Note that since \( \omega \) is complex, \( \eta'(\omega) \) and \( G'(\omega) \) are complex as well, which complicates the usual analysis of Eq. (31) in terms of the oscillation frequency without damping \( \omega_0 \) and the quality factor \( Q \) [24]. However, if \( Q \) is not too small, \( \omega \) will be nearly real, and so \( \eta'(\omega) \) and \( G'(\omega) \) will also be nearly real, given by \( G'(\omega) \sim G'(\omega_{osc})/\omega \) and \( \eta'(\omega) \sim \eta'(\omega_{osc})/\omega \). Making this approximation, the resonant frequency is defined by setting the viscous term in Eq. (31) to zero, which yields
\[ \omega_0 = \sqrt{\beta G'(\omega_{osc})}/2. \] (33)

The quality factor \( Q \) is defined as the ratio of average stored elastic energy to the energy dissipated during one oscillation cycle [24]. For purposes here,
\[ Q = \frac{G'(\omega_{osc})}{2\omega_{osc}\eta'(\omega_{osc})} = \frac{G'(\omega_{osc})}{2G'(\omega_{osc})}, \] (34)

The oscillation frequency and decay time are then obtained:
\[ \omega_{osc} = (1 - 1/4Q^2)^{1/2} \omega_0, \] (35)
and
\[ \tau_{decay} = \frac{2Q}{\omega_0}. \] (36)

Eq. (35) together with Eqs. (33) and (34) give a (non-linear) equation for \( \omega_{osc} \), which then determines \( \omega_0 \) and \( Q \) (and \( \tau_{decay} \), by Eq. (36)).

From Eq. (35), a large quality \( Q \) thus corresponds to \( \omega_{osc} = \omega_0 \). As \( Q \) becomes smaller, \( \omega_{osc} \) decreases but only slowly until \( Q \) approaches unity, the departure being less than about 3% for all \( Q \geq 2 \). The response eventually approaches critical damping (\( Q = 1/2 \)), below which the system is overdamped, i.e., the oscillations disappear altogether. In addition, from Eq. (36), a large \( Q \) corresponds to large \( \omega_{osc} = \tau_{decay} \), i.e., a slow oscillation amplitude decay rate per cycle, i.e., weak damping.

A similar analysis can be made for the stress oscillations. From Eq. (20), the spatial modes for \( \Delta \sigma \) are given by \( \cos(n\pi \xi) \). The lowest mode, \( n = 1 \), corresponding to \( R(\xi) = \cos(2\pi \xi) \) is zero at \( \xi = 1/2 \), but the next mode, \( n = 2 \), corresponding to \( R(\xi) = \cos(2\pi \xi) \) is non-zero. Working that mode through in the manner applied to the velocity oscillations leads to \(-\iota \omega D^2/4\pi^2 = \hat{G}(\omega)\) and finally to \( \beta = 4\pi^2/\rho D^2 \). Thus, for weak damping, the oscillation frequency for stress is twice that for velocity (see Eqs. (30) and (33)).

\[ \omega_{osc,\sigma} = 2\omega_{osc}. \] (37)

Requiring self-consistency amongst Eqs. (33)–(36) can provide estimates of \( \omega_0 \) and \( Q \), and thus of \( \omega_{osc} \) and \( \tau_{decay} \) when \( Q \geq 2 \) from information on liquid properties and test geometry. Consider first the example of a liquid whose storage modulus rises from zero at low frequencies to an essentially constant plateau value, \( G^e = G_0^e \), for all frequencies beyond some range of the order of the terminal regime relaxation rate \( \tau_w \). Thus, from Eq. (33), \( \omega_0 = (\beta G_0^e)^{1/2} \) if \( \omega_0 >> \tau_w^{-1} \). For test sample C (see Section 2 for properties), the plateau modulus is about 2200 Pa, and \( D^2 = 0.0126 \text{ Pa}^{-1} \text{s}^2 \), yielding \( \beta \sim 780 \text{ Pa}^{-1} \text{s}^2 \) from Eq. (30) and thus \( \omega_0 \sim 1300 \text{s}^{-1} \). That frequency is more than four orders of magnitude larger than \( \tau_w^{-1} = 1/16.2 \text{s} = 0.06 \text{s}^{-1} \), thus very far indeed into the plateau regime for sample C.

We now estimate \( \omega \) under various assumptions as to the nature and frequency dependence of the loss modulus. For a single-mode Maxwell model, \( G'(\omega) \propto \omega^{-1} \) beyond the terminal relaxation peak, \( \omega_{max} \sim \tau_w^{-1} \). Hence in that region, \( G'(\omega) \sim G_0^e \omega^{-1} / (\omega \tau_w) \). The oscillation frequency, \( Q = \omega_{osc} \tau_w/2 \) from Eq. (34). With the sample C parameters and assuming \( Q \geq 2 \) so that \( \omega_{osc} = \omega_0 \) is a good approximation, we therefore expect \( Q \sim 800 \times 16/2 = 6400 \), corresponding to a very long-lived transient oscillation and confirming \( \omega_{osc} = \omega_0 \) to be a very good approximation. Thus, for the single-mode Maxwell model, Eq. (36) yields \( \tau_{decay} \sim 16 \text{s} \) compared to the time to reach stress steady state in a start-up experiment and accordingly consistent with the computations of Denn and Porteous [2].

More realistic descriptions of entangled polymer liquids with narrow molecular weight distributions have stronger viscous responses beyond \( \omega_{max} \sim \tau_w^{-1} \). Scaling as \( G'(\omega) \sim G_0^e / (\omega \tau_w)^{1/2} \) according to the Doi-Edwards model [23] and approximately as \( G'(\omega) \sim G_0^e / (\omega \tau_w)^{1/4} \) experimentally [21]. Together with \( G'(\omega) \sim G_0^e \), the quality factors at the oscillation frequency are now about \( Q = (\omega_{osc} \tau_w)^{1/2} = 2 \) and \( Q = (\omega_{osc} \tau_w)^{1/4} = 2/2 \), respectively. Hence with the sample C parameters and the \( \omega_{osc} = \omega_0 \) assumption, \( Q \sim 58 \) and \( Q \sim 5.3 \), are obtained (\( \tau_{decay} \sim 0.15 \text{s} \) and \( \sim 0.013 \text{s} \), respectively), both indicating much more rapid oscillation decay than the single-mode Maxwell model, though still consistent with the \( \omega_{osc} = \omega_0 \) approximation.

The plateau regime for entangled, flexible-chain polymer solutions and melts never extends out to arbitrarily high frequencies. At sufficiently high frequency the response leaves the plateau regime
and enters the transition regime [15]. The Rouse model provides a reasonable description in that regime, with the dynamic moduli given by $G'(\omega) \sim \frac{G_0''}{\omega \tau_p}$ for $\omega > \tau_p^{-1}$, in which $\tau_p$ is the path step relaxation time, 0.026 s for sample C. Accordingly, for $\omega_0 > \tau_p^{-1} = 38$ s, we have

$$\omega_0 = \left( \frac{G_0''}{\omega_0 \tau_p} \right)^{1/2} = 520 \omega_0^{1/4},$$

and

$$Q = \frac{1}{2}.$$  

Thus, $\omega_0 \approx 4200$ s$^{-1}$ by this simplified analysis, but more importantly, any system with resonant frequency in the transition regime is critically damped and would exhibit no oscillations in velocity at all. We interpret this to mean merely that damping by Rouse modes would be severe compared with the other models considered.

The estimates obtained above for various representative relaxation spectra are summarized in Table 3 for comparison with full solution calculations. In the following section we describe results of the full solution for velocity and stress start-up profiles of sample C.

5. Full solution

5.1. Fitting data with Maxwell and Rouse modes

To provide an analytical representation, experimental data for the dynamic moduli $G'(\omega)$ and $G''(\omega)$ are often fit to a sum of Maxwell modes. Commonly, the modulus scale and relaxation time of each mode, $\gamma_k$ and $\tau_k$, are allowed to vary and $\chi^2$, the sum of the least-square errors between the log of the measured $G'(\omega)$ or $G''(\omega)$ values and the calculated values is minimized. The number of modes $N$ is increased until the resulting decrease in $\chi^2$ upon adding one more mode does not justify the additional mode, i.e., until we are “fitting the noise”. Five modes sufficed for the Sample C data in Table 1. The resulting values of $\gamma_k$ and $\tau_k$ are given in Table 2. Of course, rheological data only cover a finite frequency range. A fit such as described above will have no Maxwell modes located outside the range of the data. At frequencies above the range of the data, the computed $G'(\omega)$ reaches a plateau value, and the computed $G''(\omega)$ falls like $1/\omega$. Such behavior is a spuriously result of the limited span of the fitted data, and not representative of how sample C would actually behave at such frequencies.

If we are dealing with entangled solutions or melts of linear polymers, we can make a reasonable estimate as to the behavior of $G'(\omega)$ and $G''(\omega)$ at frequencies above the typical extent of dynamical data. This estimate is based on the notion that the dynamics of entangled linear polymers are governed by confinement to tubes, and that within the tube the chain can undergo contour length fluctuations and stretching governed by the Rouse model [16]. We therefore assume, following this approach, that at high frequencies, the dynamic response of an entangled solution should be

$$G(t) \sim \frac{\rho g R_t}{M} \sum_{p=1}^{p_{max}} C_p \exp \left( -\frac{t^2}{\tau_p} \right),$$

in which $M$ is the molecular weight and $\tau_p$ the Rouse time. The factor $C_p$ is chosen to be $1/3$ for $p < M/M_c(\phi)$ and 1 for $p > M/M_c(\phi)$ since

![Fig. 1. Experimental dynamic response for sample C (points): fitted with (solid) and without (dotted) Rouse contribution. Also shown are Rouse contribution alone (dashed) and solvent viscosity alone (dot-dashed).](image)

only Rouse motion along the tube is permitted for Rouse modes below the entanglement length [16]. Having established what the Rouse-mode contribution to the rheological spectrum ought to be, we can fit the dynamical data to a sum of Maxwell modes plus the required Rouse-mode contribution. The latter is just another sum of Maxwell modes representing the Rouse response of our entangled polymer solution.

The results of this procedure are shown in Fig. 1. There the experimental $G'(\omega)$ and $G''(\omega)$ data are the points; the various spectra shown are the fit to Maxwell modes with and without a required Rouse contribution, the required Rouse contribution alone, and finally the total contribution to the dynamic response of the solvent viscosity, $G''(\omega) = \omega g \eta_s$. Note that the Rouse contribution, because of the condition on $C_p$ enforcing the absence of transverse modes corresponding to tube motion, has $G'(\omega)$ proportional to but not equal to $G''(\omega)$ above the Rouse time. Note also that the Rouse contribution only becomes comparable to the data near the very end of the frequency range of the data. Note further that the fit without the required Rouse contribution, when evaluated at frequencies well beyond the extent of the data, indeed has $G'(\omega)$ constant and $G''(\omega)$ decreasing as $1/\omega$.

Finally, note that the purely dissipative solvent contribution becomes larger than the $G'(\omega)$ fit without Rouse contributions at frequencies above $10^3$ s$^{-1}$, but is still negligible compared to the $G''(\omega)$ fit with Rouse contributions until much higher frequencies. It happens that typical frequencies for the transient oscillation on start-up of a rheometer are in the range of $10^3$ s$^{-1}$. To predict the transient response for sample C, we will need an accurate representation of $G'(\omega)$ and $G''(\omega)$ in this frequency range.

Evidently, the fit of rheological data without Rouse contributions gives an approximately correct elastic response (thus a proper estimate for the oscillation frequency) while markedly underestimating the damping (thus greatly overestimating the quality factor $Q$). Adding the solvent contribution to this fitted dynamic response will increase the damping of the transient oscillation somewhat, but still greatly overestimate the $Q$ factor. With the Rouse contributions included, since $G'(\omega)$ and $G''(\omega)$ are comparable in the frequency range of the oscillation, we shall find that the transient oscillation is strongly damped, with a $Q$ factor of order unity.

5.2. Root finding

To evaluate the velocity or stress transients using Eqs. (20) and (21), we need to find the roots of Eq. (19). Note that this equation has purely real coefficients, and that the denominators of the sum-

<table>
<thead>
<tr>
<th>$k$</th>
<th>log $t_0$ (s)</th>
<th>log $\gamma_k$ (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.76</td>
<td>0.37</td>
</tr>
<tr>
<td>2</td>
<td>1.61</td>
<td>2.06</td>
</tr>
<tr>
<td>3</td>
<td>0.67</td>
<td>2.78</td>
</tr>
<tr>
<td>4</td>
<td>-0.26</td>
<td>2.91</td>
</tr>
<tr>
<td>5</td>
<td>-1.39</td>
<td>3.12</td>
</tr>
</tbody>
</table>
mands vanish at \( z = -1/\tau_k \), meaning that the summand, and hence the left side of Eq. (19), approaches positive (negative) infinity as \( z \) approaches each value of \(-1/\tau_k\) from above (below). Continuity then implies that there is a value between every adjacent \(-1/\tau_i\) and \(-1/\tau_{i+1}\) at which the left side of Eq. (19) vanishes.

Hence there are \( N - 1 \) real roots \( z_{kn} \) such that

\[
-\frac{1}{\tau_k} < z_{kn} < -\frac{1}{\tau_{k+1}}. \tag{41}
\]

for \( k = 1, 2, \ldots, N - 1 \). These roots may easily be found numerically, e.g., by Newton’s method, given that we know each interval is guaranteed to contain one and only one real root.

Eq. (19) has \( N + 1 \) roots altogether, as can be seen by multiplying by the product of the denominators to yield a polynomial of degree \( N + 1 \). The remaining two roots, at least for values of \( n \) not too large, turn out to be a complex pair; corresponding to the transient oscillation. They can be found once the others are computed from the formulas for the sum and the sum of the roots of the polynomial of degree \( N + 1 \) with distinct roots \([25]\). Thus we use Eq. (19) to create a polynomial by multiplying by the product of the denominators and by \( a_n \). Identifying the sum and product of roots, we obtain

\[
\Sigma = \sum_{k=1}^{N+1} (-z_{kn}) = a_n \hat{\eta} + \sum_{k=1}^{N+1} \frac{1}{\tau_k}, \tag{42}
\]

\[
\Pi = \prod_{k=1}^{N+1} (-z_{kn}) = a_n \prod_{k=1}^{N+1} \left( \eta_i + \sum_{j=1}^{N+1} g_{ij} \right) \prod_{j=1}^{N+1} \left( \frac{1}{\tau_j} \right). \tag{43}
\]

Knowing the \( N - 1 \) real roots, we can compute the sum \( \Sigma^2 \) of the two remaining roots by subtracting the sum of the \( N - 1 \) real roots. Likewise we can compute the product \( \Pi^2 \) of the two remaining roots by dividing by the product of the \( N - 1 \) real roots. The final two roots can then be obtained by solving the quadratic equation

\[
z^2 + z\Sigma + \Pi = 0. \tag{44}
\]

When we carry out this numerical procedure to compute the roots of Eq. (19), we find (1) the values of the coefficients \( c_{mn} \) are all very small except for those corresponding to the complex pair of roots; (2) the real roots \( z_{mn} \) are nearly independent of \( n \); and (3) the ratio of real to imaginary part for the two complex roots is nearly independent of \( n \), while the magnitude of each is roughly proportional to \( n \). We use these numerical observations to assist the calculation of the transient response.

5.3. Results

We now present full solution results for velocity and shear stress at the midplane, \( U(1/2, t) \) and \( \Delta\sigma(1/2, t) \), for three cases: (1) dynamical spectrum corresponding to a fit of data for sample C alone, no transition region and no solvent contribution; (2) same, but with contribution from solvent viscosity included; and (3) dynamical spectrum corresponding to a fit of sample C data with the required transition contribution included. For each, we use the parameter values given in Section 2. Results for the three cases described above are presented in Figs. 2–4. The velocity transient is plotted in units of \( U_0 \). Examination of Eq. (4) shows that the characteristic scale of the stress perturbation is \( \sigma^* = \rho DU_0 \omega_{osc} \). We obtain \( \omega_{osc} \) as the imaginary part of the complex root \( z_{n1} \), for the lowest spatial mode. We scale time by the period corresponding to \( \omega_{osc} \).

\[
\tau = \frac{2\pi}{\omega_{osc}}. \tag{45}
\]

The dashed curves in Figs. 2–4 are the single-mode approximation to the various transients, computed by restricting the sums in Eqs. (20) and (21) to the lowest non-vanishing spatial mode \( n = 1 \) for the velocity, \( n = 2 \) for the stress) and keeping only the complex pair of roots. Evidently the single-mode approximation gives a quite accurate representation of the transients.

Values of the oscillation frequency \( \omega_{osc} \) graphically estimated from these results for both the velocity and stress are listed in Table 3. Also shown there are estimates of the corresponding amplitude decay times, defined in this case by

\[
\tau_{decay} = \frac{t_1 - t_2}{\ln(a_2/a_1)}. \tag{46}
\]

in which \( t_1 - t_2 \) is the time between successive peaks and \( a_2/a_1 \) is the ratio of peak heights.

As shown in Fig. 2 and confirmed by the results in Table 3, the transients computed with no contributions from either solvent viscosity or transition modes are long-lived, oscillating many times in the observable range before dissipating (see Section 2). Fig. 3 and corresponding Table 3 results show that adding the effects of solvent viscosity reduces the persistence of oscillation noticeably but not drastically. Only if we account appropriately for the response of
the polymer solution at high frequencies, as in Fig. 4, do the oscillations damp out quickly, i.e., well before the observable range is reached.

Also shown enclosed in parentheses in Table 3 are values of $\omega_{osc}$ and $\tau_{decay}$ as obtained with the simplified model embodied by Eqs. (30), (33), (34), (36) and (37). They turn out to agree rather well with the graphically determined values from the full model calculations in Figs. 2-4. Evidently, the simplified model, despite the apparent crudeness of its approximations, yields reasonable estimates of the full model predictions for solution C. Encouraged by this agreement, we offer some generalizations based on the simplified model about the relationship between molecular structure and the persistence of inertia-driven oscillations in the following section.

6. Discussion

The simplified model relates inertially driven oscillatory response following start-up, characterized by $\omega_{osc}$ and $\tau_{decay}$, to only the dynamic modulus of the liquid $G(\omega) = G(\omega) + iG'(\omega)$ and the parameter $\beta = \pi^2/\rho D^2$. Liquid density and testing geometry vary only slightly over any reasonable range of interest, such that for estimation purposes $\beta = 10^3/\text{Pa}^{-1}\text{s}^{-2}$ can be used for any system without serious error. Accordingly, within the limitations of the simplified model, oscillatory behavior and dynamic modulus are linked in an effectively universal way, and with modulus data available over an extended range, values of $\omega_{osc}$ and $\tau_{decay}$ can be estimated as explained in Section 4.

Table 3
Selected results from simplified model and full calculation responses for sample C.

<table>
<thead>
<tr>
<th>Calculation method</th>
<th>Spectrum</th>
<th>$\omega_{osc}$ (s$^{-1}$)</th>
<th>$\tau_{decay}$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Velocity</td>
<td>Stress</td>
</tr>
<tr>
<td>Simplified Maxwell</td>
<td>1300</td>
<td>2600</td>
<td>16</td>
</tr>
<tr>
<td>Simplified Doi-Edwards</td>
<td>1300</td>
<td>2600</td>
<td>0.15</td>
</tr>
<tr>
<td>Simplified Observed</td>
<td>1300</td>
<td>2600</td>
<td>0.013</td>
</tr>
<tr>
<td>Simplified Rouse</td>
<td>~4200</td>
<td>~8400</td>
<td>~0</td>
</tr>
<tr>
<td>Full Fig. 2 $G(\omega)$ fits alone</td>
<td>1675 (1400)*</td>
<td>3150 (2800)*</td>
<td>0.022 (0.045)*</td>
</tr>
<tr>
<td>Full Fig. 3 $G(\omega)$ + solvent</td>
<td>1695 (1400)</td>
<td>3140 (2800)</td>
<td>0.024 (0.028)</td>
</tr>
<tr>
<td>Full Fig. 4 $G(\omega)$ + Rouse</td>
<td>3140 (1980)</td>
<td>7220 (3960)</td>
<td>&lt;0.001 (0.0011)</td>
</tr>
</tbody>
</table>

* Values in parentheses calculated by the simplified method.
dispersions [33,34], the so-called ringing gels. Many demonstrate plateaus in $G'$ at high frequencies with much smaller and monotonically decreasing $G''$, and some of these are described with remarkable fidelity over the observed frequency range by the single-mode Maxwell model, showing no indication of transition region onsets [29,27,31,26]. Persistent oscillations following start-up, i.e., ringing gel behavior, might thus be expected although $\omega_{osc}$ would lie well above the experimental range and ringing has not been reported. Unfortunately, no viscoelastic data seem available for formulations that are reported to ring [33,34].

Finally, we note the possible dangers in representing polymeric liquids by single relaxation time models when inertial effects are to be included. Spurious velocity and stress fluctuations may be predicted which are absent, or at least strongly suppressed, in the real polymer liquid situation. Velocity fluctuations may be suppressed in single relaxation time modeling by arbitrarily increasing the Newtonian contribution, but that seems a dangerous expedient.

References