Rheologica Acta Rheol Acta 29:145–151 (1990)

A "zero-parameter" constitutive relation for simple shear viscoelasticity

J. C. Dyre

IMFUFA, Roskilde Universitetscenter, Denmark

Abstract: Based on the Cox-Merz rule and Eyring's expression for the nonlinear shear viscosity, a Wagner-type constitutive relation with no nontrivial adjustable parameters is proposed for simple shear viscoelasticity. The predictions for a number of non-steady shear flows are worked out analytically. It is shown that most features of shear viscoelasticity are reproduced by the model.

Key words: Shear flow; shear thinning; viscoelasticity; Cox-Merz rule

1. Introduction

After several years of research a number of useful constitutive relations are now available [1]. In order to reproduce experiments accurately these relations all contain a number of fitting parameters. In this paper the following question is asked: What is the simplest possible constitutive relation which still reproduces important features of viscoelasticity? To limit the discussion, only simple shear viscoelasticity is considered, and normal stresses are ignored all together. Starting from the Cox-Merz rule, a Wagner-type constitutive relation with no nontrivial adjustable parameters is arrived at. The nonlinear steady state shear viscosity is, by construction, close to that predicted by Eyring's phenomenological theory of liquid flow [2]. Various non-steady shear flows are then considered and worked out analytically. It is shown that the constitutive relation reproduces most qualitative features of shear viscoelasticity, with the notable exception of the overshoot usually observed in the shear stress growth upon inception of a steady shear flow.

2. The model

The well-known Cox-Merz rule [3] states that

$$\eta(\dot\gamma) = |\eta_0^*(\omega)|\Big|_{\omega=\dot\gamma} , \tag{1}$$

where $\eta(\dot\gamma)$ is the nonlinear shear viscosity as function of shear rate and $\eta_0^*(\omega)$ is the frequency-dependent viscosity in the linear response regime. The Cox-Merz rule is a useful empiricism obeyed by many polymeric liquids. The quantity $\eta_0^*(\omega)$ is obtained [1] from the equation

$$\eta_0^*(\omega) = \int_0^\infty dt' G(t') e^{-i\omega t'} , \tag{2}$$

where $G(t')$ is the shear relaxation modulus. By definition, $G(t')$ determines the stress τ in the linear limit from the shear rate history by means of

$$\tau(t) = \int_0^\infty dt' G(t') \dot\gamma(t-t') . \tag{3}$$

From Eqs. (1) and (2) one expects the Cox-Merz rule to be satisfied if

$$\eta(\dot\gamma) = \int_0^\infty dt' G(t') e^{-\dot\gamma t'} \quad (\dot\gamma > 0) . \tag{4}$$

A straightforward generalization of Eq. (3) to include Eq. (4) for the stationary case is the following constitutive relation

$$\tau(t) = \int_0^\infty dt' G(t') \dot\gamma(t-t') \cdot \exp\left\{ -\int_{t-t'}^{t} |\dot\gamma(t'')|\, dt'' \right\} . \tag{5}$$

Equation (5) is similar to Wagner's constitutive relation [1, 4]. The difference is that, in the "linear" part of the relation, γ in Wagner's model is here replaced by $\dot{\gamma}$. Also, the "damping function" is here $\exp\{-\int_{t-t'}^{t}|\dot{\gamma}|\}$ instead of Wagner's $\exp\{-|\int_{t-t'}^{t}\dot{\gamma}|\}$. The present choice of damping function is suggested because this damping function sums over all shear displacement taking place between time $t-t'$ and t, independent of the direction of the displacement.

Next, a specific form of $G(t')$ is chosen, namely $G(t')=E_1(t')$ where $E_1(t')$ is the exponential integral [5]

$$E_1(t')=\int_{t'}^{\infty}\frac{e^{-u}}{u}\,du\ . \tag{6}$$

For convenience we here and henceforth work with dimensionless time, stress, and viscosity, the latter quantity normalized so that $\eta_0^*(\omega=0)=1$. The final constitutive relation is

$$\tau(t)=\int_0^{\infty}dt'E_1(t')\dot{\gamma}(t-t')\cdot\exp\left\{-\int_{t-t'}^{t}|\dot{\gamma}(t'')|\,dt''\right\}\ . \tag{7}$$

The use of $E_1(t')$ as the relaxation modulus is motivated by the fact that this choice leads to a nonlinear viscosity which is close to that predicted by Eyring's phenomenological theory of liquid flow [2] which fits many experiments:

$$\eta(\dot{\gamma})=\frac{\sinh^{-1}(\dot{\gamma})}{\dot{\gamma}}\ . \tag{8}$$

To see this, note that the Laplace transform of E_1 is [5]

$$\tilde{E}_1(s)=\frac{\ln(1+s)}{s}\ , \tag{9}$$

so the nonlinear viscosity is given by

$$\eta(\dot{\gamma})=\frac{\ln(1+\dot{\gamma})}{\dot{\gamma}}\ . \tag{10}$$

From the identity $\sinh^{-1}(x)=\ln(x+\sqrt{1+x^2})$ it follows that Eyring's nonlinear shear viscosity for large $\dot{\gamma}$ is close to that predicted in Eq. (10). This is illustrated in Fig. 1. Note that the present model compared to Eyring's has a less sharp transition to nonlinear behavior. Figure 1 also shows that the Cox-Merz rule, as expected, is obeyed approximately by the constitutive relation. This observation is based on the fact that the frequency-dependent linear viscosity is given by

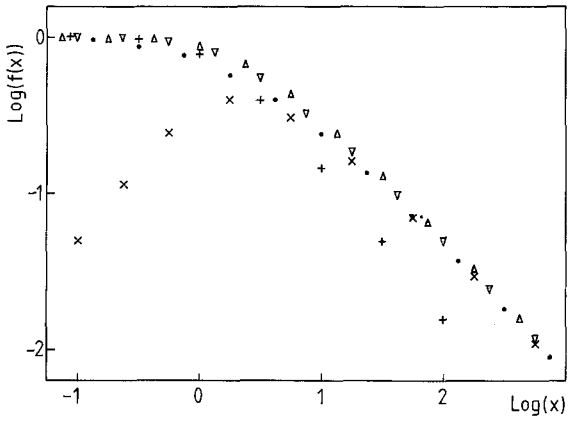

Fig. 1. Log-log plot of various quantities characterizing the model. In this figure, and throughout, dimensionless time, stress, and viscosity are used, the latter quantity normalized so that $\eta_0^*(\omega=0)=1$. The figure shows: (1) The predicted nonlinear viscosity as function of $x=\dot{\gamma}$ (●) [Eq. (10)], (2) Eyring's nonlinear viscosity as function of $x=\dot{\gamma}$ (△) [Eq. (8)], (3) $|\eta_0^*(\omega=x)|$ (▽) [Eq. (11)], and (4) the real (+) and the imaginary (×) part of $\eta_0^*(\omega=x)$ [Eq. (12)]. A comparison of the ● and △ points shows that Eyring's viscosity, which is known to give a good fit to many experiments, is reproduced reasonably well by the model. Comparing the ● and the ▽ points shows that the Cox-Merz rule is obeyed, though not quite accurately in the transition region. The real and imaginary parts of $\eta_0^*(\omega)$ looks much like in experiment

$$\eta_0^*(\omega)=\int_0^{\infty}dt'E_1(t')e^{-i\omega t'}=\frac{\ln(1+i\omega)}{i\omega}\ , \tag{11}$$

which implies for the real part and for the negative imaginary part

$$\eta'(\omega)=\mathrm{Arctan}(\omega)/\omega$$
$$\eta''(\omega)=\ln[\sqrt{1+\omega^2}]/\omega\ . \tag{12}$$

We now proceed to calculate the time-dependent nonlinear response in various situations (following Chapter 3.4 in [1]). Consider first the stress growth upon inception of a steady shear flow, i.e., the case when the shear rate is given by

$$\dot{\gamma}(t)=\begin{cases}0\ , & t<0\\ \dot{\gamma}_0\ , & t>0\ .\end{cases} \tag{13}$$

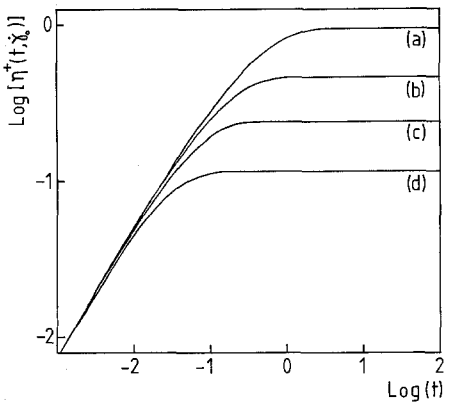

Fig. 2. Stress growth upon inception of a steady shear flow with shear rate $\dot{\gamma}_0$. The quantity $\eta^+(t,\dot{\gamma}_0)$, given by Eq. (16), is plotted as a function of time for: (a) $\dot{\gamma}_0 = 0.1$ (reflecting the linear limit), (b) $\dot{\gamma}_0 = 3$, (c) $\dot{\gamma}_0 = 10$, and (d) $\dot{\gamma}_0 = 30$. Like in experiment, $\eta^+(t,\dot{\gamma}_0)$ follows the linear $\eta^+(t)$ for short times while it stabilizes for large t at the nonlinear viscosity, a stabilization which takes place sooner the larger is $\dot{\gamma}_0$. The overshoot of $\eta^+(t,\dot{\gamma}_0)$ often seen in experiment is not reproduced by the model

In this case Eq. (7) implies for the stress τ^+:

$$\tau^+(t) = \dot{\gamma}_0 \int_0^t dt' E_1(t') e^{-\dot{\gamma}_0 t'} \tag{14}$$

or, for the quantity $\eta^+(t,\dot{\gamma}_0) = \tau^+(t)/\dot{\gamma}_0$,

$$\eta^+(t,\dot{\gamma}_0) = \int_0^t dt' E_1(t') e^{-\dot{\gamma}_0 t'} \ . \tag{15}$$

After a partial integration Eq. (15) reduces to

$$\eta^+(t,\dot{\gamma}_0) = \{E_1[(1+\dot{\gamma}_0)t] - E_1(t)e^{-\dot{\gamma}_0 t} + \ln(1+\dot{\gamma}_0)\}/\dot{\gamma}_0 \ , \tag{16}$$

where use has been made of the fact that $E_1(t)$ varies as $-\ln(t)$ for $t \to 0$. In Fig. 2 $\eta^+(t,\dot{\gamma}_0)$ is plotted in a logarithmic plot for different values of $\dot{\gamma}_0$. The figure shows that η^+ is always monotonously increasing. This is not quite like in experiment where there is usually a characteristic "overshoot" of η^+ as function of time before the steady state value is reached [1].

Consider now stress relaxation after cessation of a steady shear flow, i.e., when

$$\dot{\gamma}(t) = \begin{cases} \dot{\gamma}_0 \ , & t<0 \\ 0 \ , & t>0 \ . \end{cases} \tag{17}$$

Then Eq. (7) implies for the stress τ^-:

$$\tau^-(t) = \dot{\gamma}_0 \int_t^\infty dt' E_1(t') e^{-\dot{\gamma}_0(t'-t)} \ . \tag{18}$$

Equations (10), (15), and (18) imply

$$\eta^+(t,\dot{\gamma}_0) + e^{-\dot{\gamma}_0 t}\eta^-(t,\dot{\gamma}_0) = \frac{\ln(1+\dot{\gamma}_0)}{\dot{\gamma}_0} \ , \tag{19}$$

where $\eta^-(t,\dot{\gamma}_0) = \tau^-(t)/\dot{\gamma}_0$. By means of Eq. (16) we thus find

$$\eta^-(t,\dot{\gamma}_0) = \{E_1(t) - E_1[(1+\dot{\gamma}_0)t]e^{\dot{\gamma}_0 t}\}/\dot{\gamma}_0 \ . \tag{20}$$

Figure 3 shows η^- for various values of $\dot{\gamma}_0$. As in experiment, one finds that $\eta^-(t,\dot{\gamma}_0)$ is a monotonously decreasing function of time for all $\dot{\gamma}_0$, and that η^- reaches zero faster the larger is $\dot{\gamma}_0$.

We now turn to the calculation of stress relaxation after a sudden shearing displacement γ_0. The shear rate is given by $\dot{\gamma}(t) = \gamma_0 \delta(t)$. Substituted into Eq. (7), this gives

$$\tau(t) = (1 - e^{-\gamma_0}) E_1(t) \ , \tag{21}$$

which is easily shown by rewriting Eq. (7) as

$$\tau(t) = \int_0^\infty dt' E_1(t') \left[-\frac{d}{dt'}\right] e^{-\int_{t-t'}^t \dot{\gamma}(t'')dt''} \ , \tag{22}$$

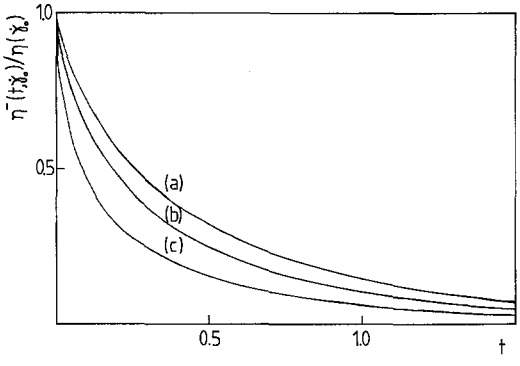

Fig. 3. Stress relaxation after cessation of a steady shear flow with shear rate $\dot{\gamma}_0$. The figure shows the quantity $\eta^-(t,\dot{\gamma}_0)/\eta(\dot{\gamma}_0)$ as a function of time, where η^- is given by Eq. (20), for: (a) $\dot{\gamma}_0 = 0.1$ (reflecting the linear limit), (b) $\dot{\gamma}_0 = 3$, and (c) $\dot{\gamma}_0 = 30$. As in experiment, $\eta^-(t,\dot{\gamma}_0)$ decreases to zero as $t \to \infty$ faster the larger is $\dot{\gamma}_0$

which is valid whenever $\dot{\gamma} \geq 0$. For the relaxation modulus $G(t, \gamma_0) = \tau(t)/\gamma_0$, one thus finds

$$G(t, \gamma_0) = E_1(t) \frac{1 - e^{-\gamma_0}}{\gamma_0} . \tag{23}$$

For $\gamma_0 \to 0$, $G(t, \gamma_0)$ reduces to the linear shear relaxation modulus $E_1(t)$. Equation (23) shows that $G(t, \gamma_0)$ factorizes into a function of time multiplied by a function of γ_0, as expected for a Wagner type model [1, 4].

Next we consider the calculation of the nonlinear creep compliance $J(t, \tau_0)$, defined as $\gamma(t)/\tau_0$, where $\gamma(t)$ is the total shear displacement in time t when a constant stress τ_0 is applied at $t = 0$. The calculation of J from a constitutive relation is usually complicated by the fact that $\gamma(t)$ is only given indirectly. For the present constitutive relation, however, $\gamma(t)$ may be found analytically in the following way. First, Eq. (7) is rewritten for the case under consideration as

$$\tau_0 e^{\gamma(t)} = \int_0^t dt' E_1(t') \dot{\gamma}(t - t') e^{\gamma(t - t')} \quad (t > 0) . \tag{24}$$

Equation (24) is linear in the variable $C(t) = \exp[\gamma(t)]$:

$$\tau_0 C(t) = \int_0^t dt' E_1(t') \dot{C}(t - t') . \tag{25}$$

This equation is now Laplace transformed into

$$\tau_0 \tilde{C}(s) = \tilde{E}_1(s) \tilde{\dot{C}}(s) \tag{26}$$

or

$$\tilde{C}(s) = \frac{\tau_0}{\ln(1 + s) - \tau_0} . \tag{27}$$

Here, use has been made of Eq. (9) and the identity $\tilde{\dot{C}}(s) = s\tilde{C}(s) - C(0) = s\tilde{C}(s) - 1$. $\tilde{C}(s)$ has a branch cut on the negative real axis from $s = -1$ to $s = -\infty$ and a pole at $s = \dot{\gamma}_0$, where

$$\dot{\gamma}_0 = e^{\tau_0} - 1 \tag{28}$$

is the steady state shear rate [Eq. (10)]. The Laplace inversion of Eq. (27) is performed by deforming the integration contour to run from $-\infty$ slightly below the negative real axis, rounding the pole at $s = \dot{\gamma}_0$, and returning to $-\infty$ above the negative real axis. After standard manipulations one thus finds

$$\dot{C}(t) = \tau_0 (1 + \dot{\gamma}_0) e^{\dot{\gamma}_0 t} + \tau_0 \int_1^\infty du e^{-ut} \frac{1}{[\ln(u - 1) - \tau_0]^2 + \pi^2} \tag{29}$$

or finally, by integration with respect to time,

$$e^{J(t, \tau_0)\tau_0} = 1 + \tau_0 \frac{1 + \dot{\gamma}_0}{\dot{\gamma}_0} (e^{\dot{\gamma}_0 t} - 1) + \tau_0 \int_1^\infty du \frac{1 - e^{-ut}}{u} \frac{1}{[\ln(u - 1) - \tau_0]^2 + \pi^2} . \tag{30}$$

In the linear limit Eq. (30) reduces to

$$J = t + \int_1^\infty du \frac{1 - e^{-ut}}{u} \frac{1}{\ln^2(u - 1) + \pi^2} . \tag{31}$$

The creep complicance $J(t, \tau_0)$ of Eq. (30) is plotted in Fig. 4 in a log-log plot for different values of $\dot{\gamma}_0$.

As a final example of the use of Eq. (7) consider the constrained recoil after a steady shear flow is interrupted at $t = 0$ by suddenly removing the shear stress. We wish to calculate the so-called recoverable shear γ_∞. Writing

$$\dot{\gamma}(t) = \begin{cases} \dot{\gamma}_0 , & t < 0 \\ -f(t) , & t > 0 , \end{cases} \tag{32}$$

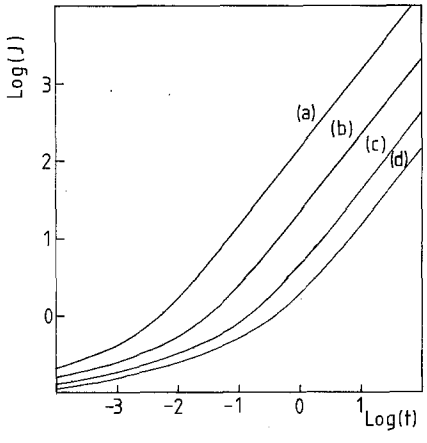

Fig. 4. Creep compliance $J = \gamma(t)/\tau_0$, where J is given by Eq. (30), plotted as function of time for: (a) $\dot{\gamma}_0 = 1000$, (b) $\dot{\gamma}_0 = 100$, (c) $\dot{\gamma}_0 = 10$, and (d) $\dot{\gamma}_0 = 1$, where $\dot{\gamma}_0$ is related to τ_0 by Eq. (28)

where $f(t)>0$, Eq. (7) implies for $t>0$

$$0 = -\int_0^t dt' E_1(t') f(t-t') e^{-\int_{t-t'}^t f(t'')dt''} + \int_t^\infty dt' E_1(t') \dot{\gamma}_0 e^{-\dot{\gamma}_0(t'-t)-\int_0^t f(t'')dt''} \quad (33)$$

or

$$\int_0^t dt' E_1(t') f(t-t') e^{\int_0^{t-t'} f(t'')dt''} = \dot{\gamma}_0 e^{\dot{\gamma}_0 t} \int_t^\infty dt' E_1(t') e^{-\dot{\gamma}_0 t'} . \quad (34)$$

Defining $F(t) = \exp\left(\int_0^t f(t'')dt''\right)$, Eq. (34) becomes

$$\int_0^t dt' E_1(t') \dot{F}(t-t') = \dot{\gamma}_0 e^{\dot{\gamma}_0 t} \int_t^\infty dt' E_1(t') e^{-\dot{\gamma}_0 t'} . \quad (35)$$

The Laplace transform of Eq. (35) is

$$\tilde{E}_1(s)[s\tilde{F}(s)-1] = \frac{\dot{\gamma}_0}{\dot{\gamma}_0 - s}[\tilde{E}_1(s) - \tilde{E}_1(\dot{\gamma}_0)] \quad (36)$$

or

$$\tilde{F}(s) = \frac{1}{s}\left[1 + \frac{\dot{\gamma}_0}{\dot{\gamma}_0 - s}\frac{\tilde{E}_1(s) - \tilde{E}_1(\dot{\gamma}_0)}{\tilde{E}_1(s)}\right] . \quad (37)$$

The recoverable shear is determined from $e^{\gamma_\infty} = \lim_{t\to\infty} F(t)$. This limit is given by the residue of the pole at $s=0$ of Eq. (37), and one finds $\gamma_\infty = \ln[2-\tilde{E}_1(\dot{\gamma}_0)]$, or

$$\gamma_\infty = \ln[2-\eta(\dot{\gamma}_0)] . \quad (38)$$

In the two limits one has

$$\gamma_\infty = \begin{cases} \frac{1}{2}\dot{\gamma}_0 , & \dot{\gamma}_0 \ll 1 \\ \ln 2 , & \dot{\gamma}_0 \gg 1 . \end{cases} \quad (39)$$

$\gamma_\infty(\dot{\gamma}_0)$ is monotonously increasing which is also the case in experiment. Also like in experiment, γ_∞ stabilizes on a recoverable shear of order one at high $\dot{\gamma}_0$.

3. Discussion

In this paper it has been argued that a simple constitutive relation exists which has no adjustable parameters (except the overall scaling of time and viscosity) and which gives a qualitatively correct picture of shear viscoelasticity. The relation Eq. (7) was arrived at by requiring the Cox-Merz rule to be satisfied and that Eyring's nonlinear viscosity Eq. (8) is to be reproduced approximately. This ensures a nonlinear viscosity and a frequency-dependent linear viscosity which are both close to those observed in many experiments. Figure 5 shows the nonlinear steady state viscosity of the model compared to experiments on four polymeric liquids. In Fig. 6 the absolute value of the complex frequency-dependent viscosity of the model is compared to experiments on three of the systems of Fig. 5. In both figures there is a qualitative agreement between model and experiment. From studies of the literature it is estimated that 25–50% of the published rheological data on polymeric systems may be fitted similarly by the model. A quantitatively satisfactory fit is only possible for few systems, however. To obtain this, one or more fitting parameters must be introduced into the model, which will not be attempted here.

The choice of the linear relaxation modulus to be $E_1(t')$ may be justified from the box model, i.e., the

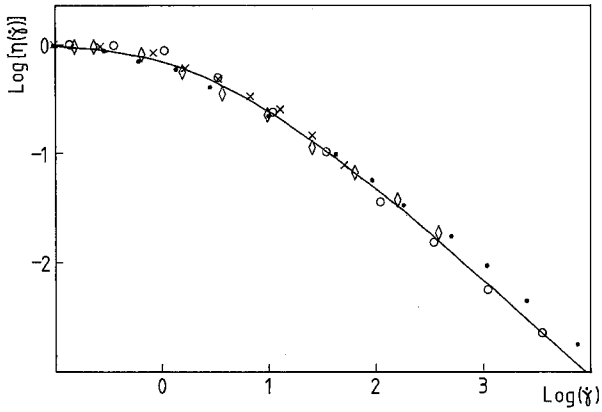

Fig. 5. Nonlinear viscosity of the model [full curve, Eq. (10)] compared to experiments on four different polymeric liquids. As throughout this work, both the viscosity and the shear rate are reported in dimensionless units, the scaling parameters being, respectively, the linear shear viscosity and $1/T$ where T is a characteristic time. The figure shows data for (a) linear, monodisperse polystyrene in 1-CN (○, Fig. 15 of [6]), (b) Poly-1-olefins (●, Fig. 1 of [7] based on data from [8]), (c) poly (methyl methacrylate) (×, Fig. 15a of [9]), and (d) 0.75% polyacrylamide (◇, Fig. 3 of [10] based on data from [11])

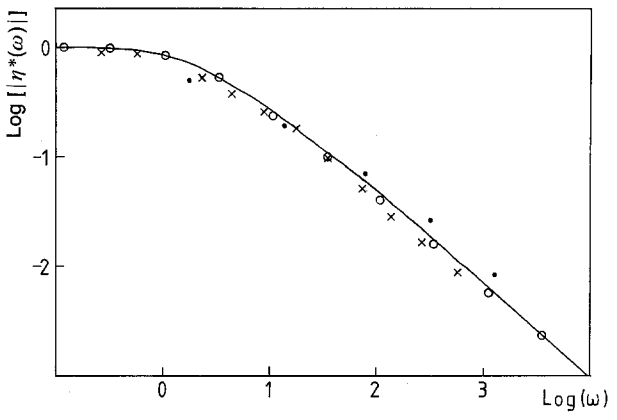

Fig. 6. Modulus of the complex linear frequency-dependent viscosity in the model [full curve, based on Eq. (12)] compared to experiments on three different polymeric liquids quoted in Fig. 5. For each set of data the dimensionless viscosity is shown as a function of the dimensionless frequency defined by the same characteristic time as used in Fig. 5. The figure shows data for (a) linear, monodisperse polystyrene in 1-CN (○), (b) poly-1-olefins (●), and (c) poly (methyl methacrylate) (×)

postulate of a uniform distribution of activation energies for microscopic motion. Consider the motion of a foreign microscopic particle in the liquid. Suppose the particle feels a spatially randomly varying potential energy, and that it moves by thermally activated hopping between the various potential energy minima. Then the linear mobility of the particle (the velocity divided by an external force acting on the particle), is to a good approximation given by [12]

$$\mu^*(\omega) = \mu(0)\,\frac{i\omega}{\ln(1+i\omega)}\ . \tag{40}$$

Assuming the Stokes law is valid for the particle, one has $\mu^* \propto 1/\eta^*$ which shows that the linear shear relaxation modulus of the liquid is $E_1(t')$ in this approximation.

Because the Cox-Merz rule is obeyed by the model it is not surprising that the Gleissele mirror relation [1] is also satisfied: The linear limit of η^+ from Eq. (16) is

$$\lim_{\dot\gamma_0 \to 0} \eta^+(t,\dot\gamma_0) = tE_1(t) - e^{-t} + 1\ . \tag{41}$$

Gleissele's mirror relation states that $\eta(\dot\gamma)$ is equal to this limit evaluated at $t = 1/\dot\gamma$, thus

$$\eta(\dot\gamma) = \begin{cases} 1\ , & \dot\gamma \ll 1 \\ (1 - C + \ln\dot\gamma)/\dot\gamma\ , & \dot\gamma \gg 1\ , \end{cases} \tag{42}$$

where $C = 0.577\ldots$ is Euler's constant. A comparison of Eqs. (10) and (42) shows that the mirror relation is indeed satisfied to a good approximation.

The constitutive relation Eq. (7) reproduces most qualitative features of shear viscoelasticity. (An exception is the overshoot usually observed in η^+ as a function of time, where the model predicts η^+ to increase monotonously to the steady state value.) The fact that qualitative features of experiment are generally reproduced is not surprising, given the similarity between the present model and the Wagner model, which is well-known to give a satisfactory description of experiment. However, it should be noted that the present model, despite the similarity to Wagner's model in the use of an exponential damping function, does not belong to the class of single integral constitutive relations of the Boltzmann-superposition-type involving a nonlinear strain measure. This is because, in Eq. (7), $\dot\gamma$ appears instead of γ. As shown by Booij et al. [13], for the former type of models the Cox-Merz rule may be accurately reproduced only if one uses a specific non-monotonous strain measure. This problem is avoided here because the analysis of Booij et al. does not apply to this model; however, it should be emphasized that the Cox-Merz rule is after all obeyed only approximately in the present model (Fig. 1).

The use of an exponential damping function in the present model is inspired by Wagner's work [4]. This damping function, in effect, cuts-off relaxation processes with rates less than the shearing rate, an idea discussed by several authors [14–18]. An important difference from Wagner's model is that his damping function is $\exp[-|\int_{t-t'}^{t}\dot\gamma|]$, whereas we here use $\exp[-\int_{t-t'}^{t}|\dot\gamma|]$. For a monotonously increasing or decreasing $\gamma(t)$ this does not make any difference. In more general flows there may be considerable differences between the two approaches. For instance, if the net shear displacement between time $t-t'$ and t is zero there is no damping at all in Wagner's approach. In contrast, all shear displacement taking place between time $t-t'$ and t contributes to the damping in the model of Eq. (7). Thereby an irreversibility related to the network rupture hypothesis of Tanner [14, 18] is incorporated into the model. The model may be regarded as expressing a continuous version of Tanner's idea that entanglements are lost irreversibly in the process of deformation as soon as a limiting strain is exceeded; here entanglements are lost continuously during any deformation. In passing we note that Wagner's model has been extended to incorporate irreversibility using a rather complicated functional of the strain history in the memory function [19]. This

gives better agreement with experiment than the original Wagner model.

A possible objection to the kind of damping term used here is that, for a periodic shear $\gamma = \gamma_0 \sin(\omega t)$, one might expect that the nonlinearity sets in at high frequencies, even at very small amplitudes (because the damping apparently is a function of $\gamma_0\omega$, and not of γ_0), in contradiction to experiment. This, however, is not correct: Suppose the worst possible case of the non-linearity, i.e., put the damping function equal to $\exp(-\omega\gamma_0 t')$ in Eq. (7). Then the response is

$$\tau(t) = \gamma_0\omega \int_0^\infty dt' E_1(t') \cos[\omega(t-t')] e^{-\omega\gamma_0 t'} = \gamma_0\omega[\cos(\omega t)\,\mathrm{Re}\,g - \sin(\omega t)\,\mathrm{Im}\,g] \,, \quad (43)$$

where

$$g = \int_0^\infty dt' E_1(t') e^{-(i\omega+\gamma_0\omega)t'} = \frac{\ln(1+x)}{x} \,, \quad x = i\omega + \gamma_0\omega \,. \quad (44)$$

At a fixed ω the onset of nonlinearity may be estimated from

$$\gamma_0\omega \simeq \left| \frac{g(x)}{g'(x)} \right|_{x=i\omega} \,, \quad (45)$$

which is the criterion for the first order term being equal to the zero-th order term in the Taylor expansion of g as function of γ_0. Equation (45) leads to

$$\gamma_0\omega \simeq \omega \left| \frac{\ln(1+i\omega)}{i\omega/(1+i\omega) - \ln(1+i\omega)} \right| \,. \quad (46)$$

It is now easy to see that whenever $\omega \geq 1$ the onset of nonlinearity takes place for γ_0 of order one. For $\omega \ll 1$, however, the onset of nonlinearity is at $\gamma_0 \simeq \omega^{-1}$, corresponding to a maximum shear rate of order one in the periodic variation.

Acknowledgement

The author wishes to thank O. Hassager for several helpful comments on an early draft of this manuscript. The work was supported by the Danish Natural Science Research Council.

References

1. Bird RB, Armstrong RC, Hassager O (1987) Dynamics of Polymeric Liquids, Second Edition. Wiley, New York
2. Kincaid JF, Eyring H, Stearn AE (1941) Chem Rev 28:301 – 365
3. Cox WP, Merz EH (1958) J Polym Sci 28:619 – 622
4. Wagner MH (1979) Rheol Acta 18:33 – 50
5. Abramowitz M, Stegun IA (eds) (1972) Handbook of Mathematical Functions. Dover Publications, New York
6. Yasuda K, Armstrong RC, Cohen RE (1981) Rheol Acta 20:163 – 178
7. Kulicke WM, Porter RS (1980) Rheol Acta 19:601 – 605
8. Wang JS, Knox JR, Porter RS (1978) J Polym Sci, Polym Phys Ed 16:1709 – 1719
9. Martinez CB, Williams MC (1980) J Rheol 24:421 – 450
10. Wagner MH (1977) Rheol Acta 16:43 – 50
11. Marsh BD (1967) (as cited by PJ Carreau, IF Macdonald, RB Bird (1968) Chem Eng Sci 23:901)
12. Dyre JC (1988) J Appl Phys 64:2456 – 2468
13. Booij HC, Leblans P, Palmen J, Tiemersma-Thoone G (1983) J Polym Sci, Polym Phys Ed 21:1703 – 1711
14. Tanner RI, Simmons JM (1967) Chem Eng Sci 22:1803 – 1815
15. Chen I-J, Bogue DC (1972) Trans Soc Rheol 16:59 – 78
16. Bersted BH (1976) J Appl Polym Sci 20:2705 – 2714
17. Thurston GB (1981) J Non-Newtonian Fluid Mech 9:57 – 68
18. Tanner RI (1969) AIChE J 15:177
19. Wagner MH, Stephenson SE (1979) J Rheol 23: 489 – 504

(Received September 12, 1989;
in revised form December 1, 1989)

Authors' address:

Dr. Jeppe C. Dyre
IMFUFA
Roskilde Universitetscenter
P.O. Box 260
4000-Roskilde, Denmark