Non-Newtonian Fluid Mechanics

(Part - X)

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The White-Metzner Model

White-Metzner Constitutive Equation

White-Metzner model has been presented based on the following modification of the upper-convected Maxwell (UCM) model:

$$\boldsymbol{\tau} + \frac{\eta(\dot{\gamma})}{G}\boldsymbol{\tau}_{(1)} = \eta(\dot{\gamma})\boldsymbol{\gamma}_{(1)} \qquad (1)$$

where $\dot{\gamma}$ is the generalized shear rate and G is a constant modulus.

$$\dot{\gamma} = \sqrt{\frac{1}{2}II(\boldsymbol{\gamma}_{(1)})} \qquad (2)$$

A few material functions for this model are summarized in the table. This model has the advantage of being relatively simple and yet still giving reasonable shapes for the shear-rate dependent viscosity and first normal stress coefficient. It can also be used in fast time-dependent motions, although its predictions are not completely realistic in these problems. This stems from its lack of a linear viscoelastic limit for small displacement gradients. In steady shear free flows, the model gives infinite elongational viscosities $\bar{\eta}_1$ and $\bar{\eta}_2$ in the same way as the convected Maxwell model; the exact value of elongation rate at which these viscosities become infinite depends on the particular form of $\eta(\dot{\gamma})$. The model has been found useful in exploratory hydrodynamic calculations aimed at assessing the interaction of shear thinning and memory on flow fields.

The White-Metzner Model

There are of course other ways in which invariants could be introduced into the model. There is no reason, other than for preserving simplicity, to include the invariant II of $\dot{\gamma}$ but not III in the model. Similarly, we could include invariants of stress. The molecularly based Phan-Thien-Tanner and the FENE-P models both include tr($\boldsymbol{\tau}$), with a certain amount of success.

Material Functions for the White–Metzner Model

Steady shear flow	$\eta = \eta(\dot{\gamma})$ $\Psi_1 = 2\eta(\dot{\gamma})\lambda(\dot{\gamma})$ $\Psi_2 = 0$	(A)
Small-amplitude oscillatory shearing	η', η'' not defined[b]	
Start-up of steady shear flow	$\eta^+(t, \dot{\gamma}) = \eta(\dot{\gamma})[1 - e^{-t/\lambda(\dot{\gamma})}]$ $\Psi_1^+(t, \dot{\gamma}) = 2\eta(\dot{\gamma})\lambda(\dot{\gamma})\left[1 - \left(1 + \frac{t}{\lambda(\dot{\gamma})}\right)e^{-t/\lambda(\dot{\gamma})}\right]$	(B)
Steady shearfree flow $\left(\dot{\gamma} \equiv \sqrt{\tfrac{1}{2}II} = \sqrt{(3 + b^2)}\,\lvert\dot{\varepsilon}\rvert\right)$	$\bar{\eta}_1 = \dfrac{(3 + b)\eta(\dot{\gamma})}{(1 + (1 + b)\lambda\dot{\varepsilon})(1 - 2\lambda\dot{\varepsilon})}$ $\bar{\eta}_2 = \dfrac{2b\eta(\dot{\gamma})}{(1 + (1 - b)\lambda\dot{\varepsilon})(1 + (1 + b)\lambda\dot{\varepsilon})}$	(C)

Oldroyd Models

The Eight-Constant Oldroyd Model:

It is an empirical expression that linear in the stress tensor, but contains all allowable terms quadratic in velocity gradients and all allowable products of stresses and velocity gradients. Since it can give qualitatively correct results in a wide variety of flow situations, it has been popular for developing the numerical techniques for non-Newtonian fluid dynamics.

$$\boldsymbol{\tau} + \lambda_1 \boldsymbol{\tau}_{(1)} + \frac{\lambda_3}{2}\left(\boldsymbol{\tau}\gamma_{(1)} + \gamma_{(1)}\boldsymbol{\tau}\right) + \frac{\lambda_5}{2}\left[tr\left(\boldsymbol{\tau}\right)\right]\gamma_{(1)} + \frac{\lambda_6}{2}\left[tr\left(\boldsymbol{\tau}\gamma_{(1)}\right)\right]\boldsymbol{I} = \eta_0\left(\gamma_{(1)} + \lambda_2\gamma_{(2)} + \lambda_4\gamma_{(1)}{}^2 + \frac{\lambda_7}{2}\left[tr\left(\gamma_{(1)}{}^2\right)\right]\boldsymbol{I}\right) \quad (3)$$

where $\boldsymbol{I}$ is identity tensor. The blue terms belong to the Oldroyd-B model. Several simplified versions of this model, in which special values are assigned to some of the constants, have been used extensively in the literature; these are summarized in next Table.

Oldroyd Models

Models Included in the Oldroyd 8-Constant Model

Name of Model	Number of Constants	Values of Time Constants							Steady-State Shear Flow Material Functions[a]
		λ_1	λ_2	λ_3	λ_4	λ_5	λ_6	λ_7	
Oldroyd 6-constant model	6						0	0	η depends on $\dot{\gamma}$ Ψ_1 depends on $\dot{\gamma}$ Ψ_2 not simply related to Ψ_1
Oldroyd 4-constant model	4			0	0		0	0	η depends on $\dot{\gamma}$ Ψ_1 depends on $\dot{\gamma}$ $\Psi_2 = 0$
Oldroyd fluid A	3			$2\lambda_1$	$2\lambda_2$	0	0	0	$\eta = \eta_0$ $\Psi_1 = 2\eta_0(\lambda_1 - \lambda_2)$ $\Psi_2 = -\Psi_1$
Oldroyd fluid B (Convected Jeffreys)	3			0	0	0	0	0	$\eta = \eta_0$ $\Psi_1 = 2\eta_0(\lambda_1 - \lambda_2)$ $\Psi_2 = 0$

Oldroyd Models

Name of Model	Number of Constants	Values of Time Constants							Steady-State Shear Flow Material Functions[a]
		λ_1	λ_2	λ_3	λ_4	λ_5	λ_6	λ_7	
Corotational Jeffreys model	3			λ_1	λ_2	0	0	0	η depends on $\dot{\gamma}$ Ψ_1 depends on $\dot{\gamma}$ $\Psi_2 = -\frac{1}{2}\Psi_1$
Second-order fluid[c]	3	0		0		0	0	0	$\eta = \eta_0$ $\Psi_1 = -2\eta_0\lambda_2$ $\Psi_2 = \eta_0\lambda_4$
Convected Maxwell model	2		0	0	0	0	0	0	$\eta = \eta_0$ $\Psi_1 = 2\eta_0\lambda_1$ $\Psi_2 = 0$
Gordon–Schowalter	3	$\frac{\eta_s\lambda_1}{\eta_0}$	$\xi\lambda_1$	$\frac{\xi\eta_s\lambda_1}{\eta_0}$	0	0	0	0	η depends on $\dot{\gamma}$ Ψ_1 depends on $\dot{\gamma}$ $\Psi_2 < 0$
Johnson–Segalman	3	$\frac{\eta_s\lambda_1}{\eta_0}$	$\xi\lambda_1$	$\frac{\xi\eta_s\lambda_1}{\eta_0}$	0	0	0	0	η depends on $\dot{\gamma}$ Ψ_1 depends on $\dot{\gamma}$ $\Psi_2 < 0$

Material Functions of Oldroyd Model

Material Functions for the Oldroyd 8-Constant Model

Steady shear flow:

$$\frac{\eta}{\eta_0} = \frac{1 + \sigma_2 \dot{\gamma}^2}{1 + \sigma_1 \dot{\gamma}^2} \tag{A}$$

$$\frac{\Psi_1}{2\eta_0 \lambda_1} = \frac{\eta(\dot{\gamma})}{\eta_0} - \frac{\lambda_2}{\lambda_1} \tag{B}$$

$$\frac{\Psi_2}{\eta_0 \lambda_1} = -\frac{\Psi_1}{2\eta_0 \lambda_1} + \frac{(\lambda_1 - \lambda_3)}{\lambda_1}\frac{\eta}{\eta_0} - \frac{(\lambda_2 - \lambda_4)}{\lambda_1} \tag{C}$$

where $\sigma_i = \lambda_i(\lambda_3 + \lambda_5) + \lambda_{i+2}(\lambda_1 - \lambda_3 - \lambda_5) + \lambda_{i+5}(\lambda_1 - \lambda_3 - \frac{3}{2}\lambda_5)$

Small-amplitude oscillatory shearing:

$$\frac{\eta'}{\eta_0} = \frac{1 + \lambda_1 \lambda_2 \omega^2}{1 + \lambda_1^2 \omega^2} \tag{D}$$

$$\frac{\eta''}{\omega \eta_0} = \frac{(\lambda_1 - \lambda_2)}{1 + \lambda_1^2 \omega^2} \tag{E}$$

Steady elongational flow:

$$\frac{\bar{\eta}}{3\eta_0} = \frac{1 - (\lambda_2 - \lambda_4)\dot{\varepsilon} + (\frac{3}{2}\lambda_5 - \lambda_1 + \lambda_3)(2\lambda_2 - 2\lambda_4 - 3\lambda_7)\dot{\varepsilon}^2}{1 - (\lambda_1 - \lambda_3)\dot{\varepsilon} + (\frac{3}{2}\lambda_5 - \lambda_1 + \lambda_3)(2\lambda_1 - 2\lambda_3 - 3\lambda_6)\dot{\varepsilon}^2} \tag{F}$$

Some Tips on Constants of Model

Some sample material functions for the Oldroyd 8-constant model are given in Table. In order that these material functions agree at least qualitatively with experimental data, there are some restrictions on the choice of the constants that have to be imposed:

1. Since η' is known to decrease with increasing ω, we must impose the requirement that $0 < \lambda_2 < \lambda_1$.
2. Since viscosity is generally a monotone decreasing function of $\dot{\gamma}$, we must require that $0 < \sigma_2 < \sigma_1$ [where $\sigma_i = \lambda_i(\lambda_3 + \lambda_5) + \lambda_{i+2}(\lambda_1 - \lambda_3 - \lambda_5) + \lambda_{i+5}(\lambda_1 - \lambda_3 - \frac{3}{2}\lambda_5)$, with $i = 1, 2$].
3. Since $|\tau_{xy}|$ is to be a monotone increasing function of $\dot{\gamma}$ for steady shear flow, we have to require that $\sigma_2 \geq \frac{1}{9}\sigma_1$.
4. When $\eta(\dot{\gamma})$ and $\eta'(\omega)$ are plotted on the same graph with $\dot{\gamma} = \omega$, the η-curve generally lies above the η'-curve. For this to be true in the region of moderate $\dot{\gamma}$ and ω, we must require that $\sigma_1 - \sigma_2 < \lambda_1(\lambda_1 - \lambda_2)$.
5. For the elongational viscosity to be bounded for positive and negative $\dot{\varepsilon}$ it is necessary for $\lambda_1 - \lambda_3$ to be between $\frac{2}{3}(\lambda_5 + \lambda_6) \pm \frac{1}{3}[4\lambda_6^2 - 11\lambda_5\lambda_6 + 4\lambda_5^2]^{1/2}$.

Response of 4-Constant Oldroyd Model

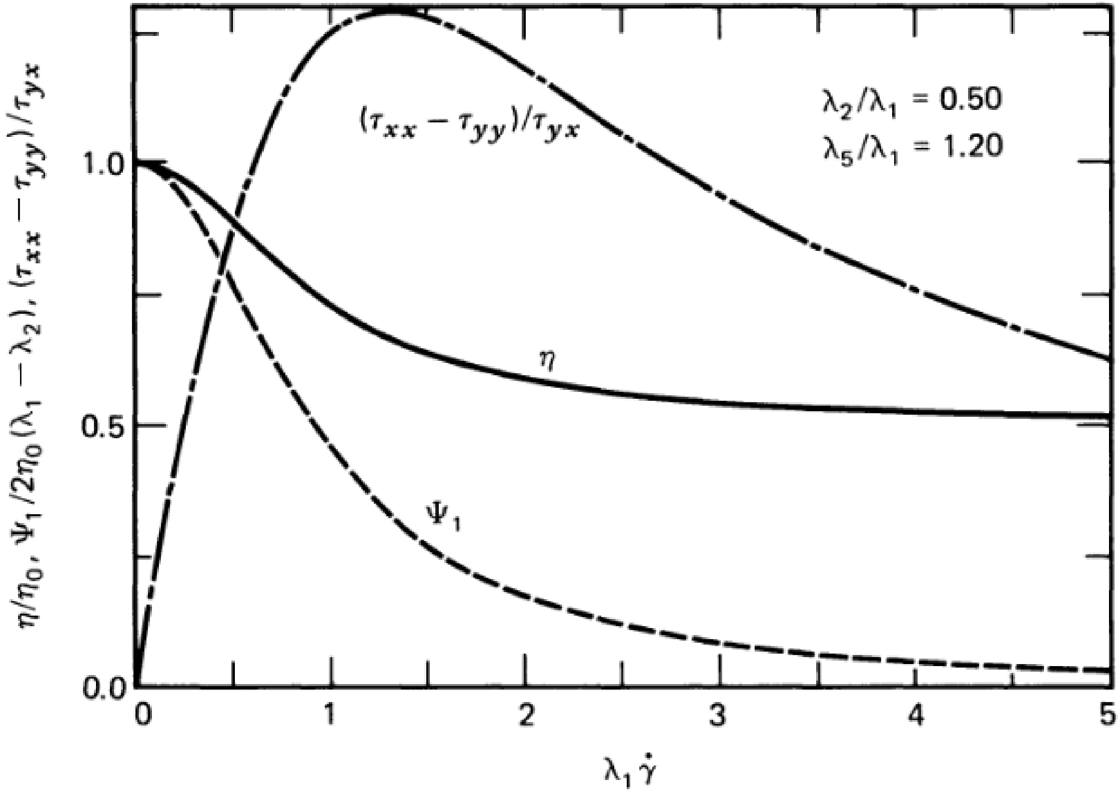
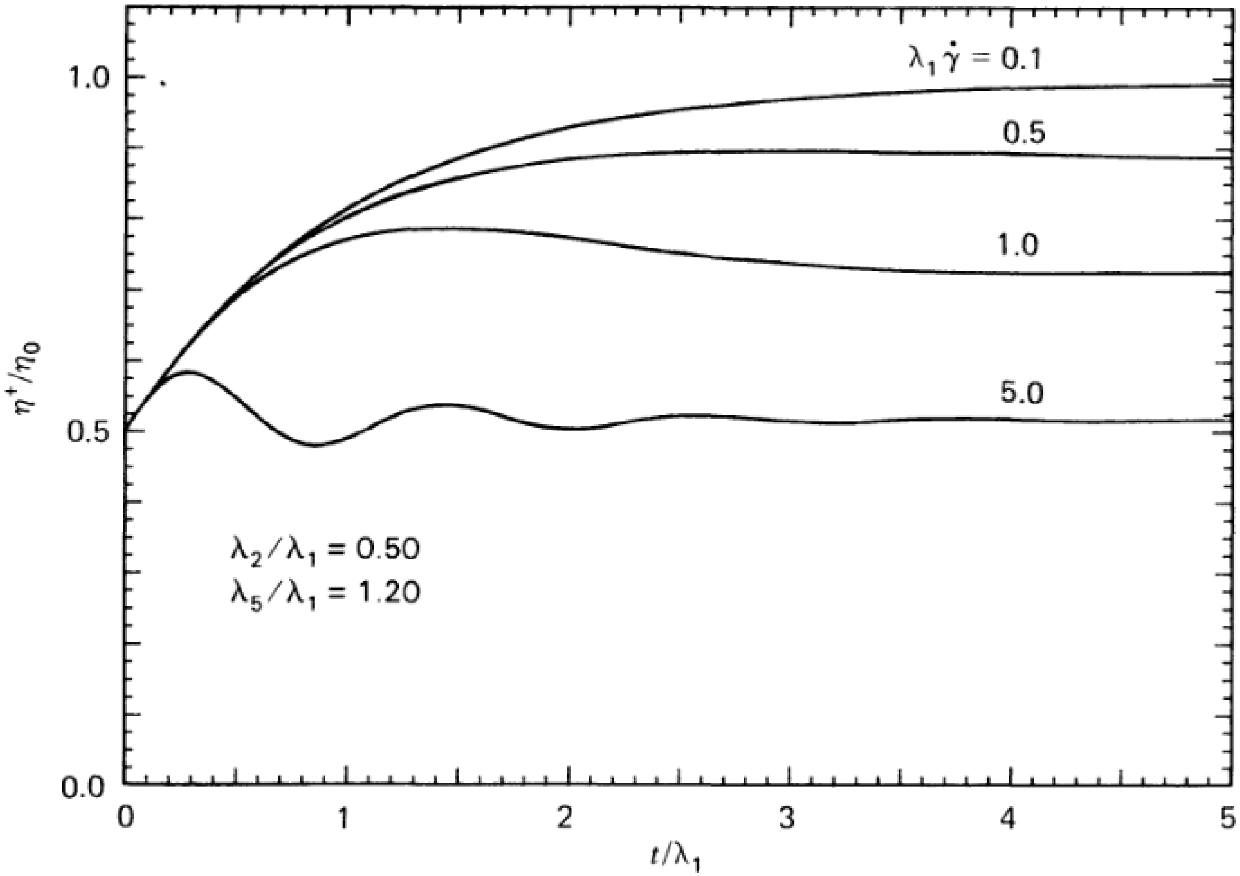


FIGURE 7.3-1. Dimensionless viscosity (——), first normal stress coefficient (- - - -), and stress ratio (— - —) as functions of dimensionless shear rate for the Oldroyd 4-constant model defined in Table 7.3-2. The second normal stress coefficient is zero. The shear thinning in η and Ψ_1 is in qualitative agreement with experimental observations, but experimental data show a monotone increasing stress ratio (cf. Fig. 3.3-8) in disagreement with the model predictions.

Response of 4-Constant Oldroyd Model



(a)

Response of 4-Constant Oldroyd Model

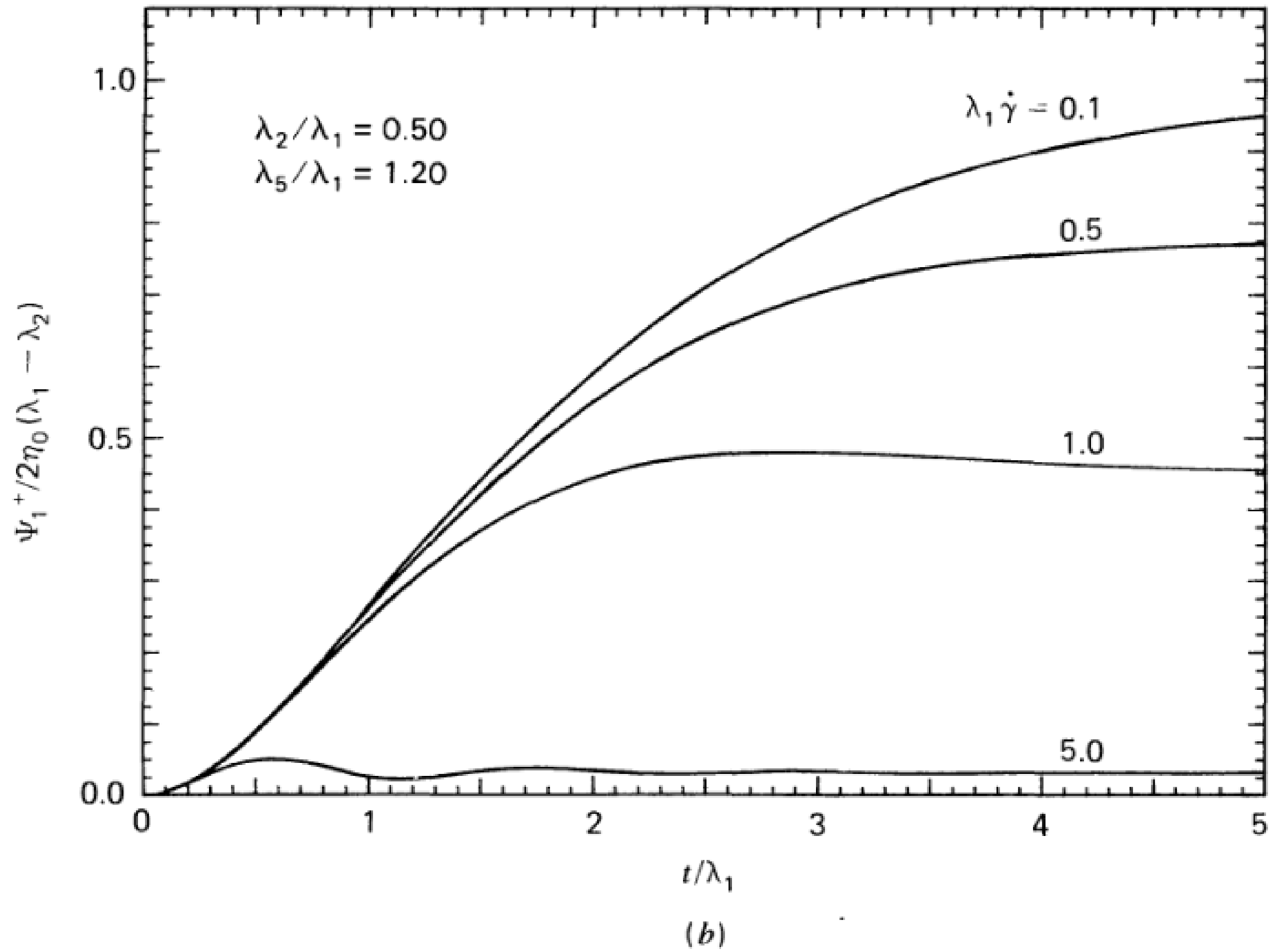
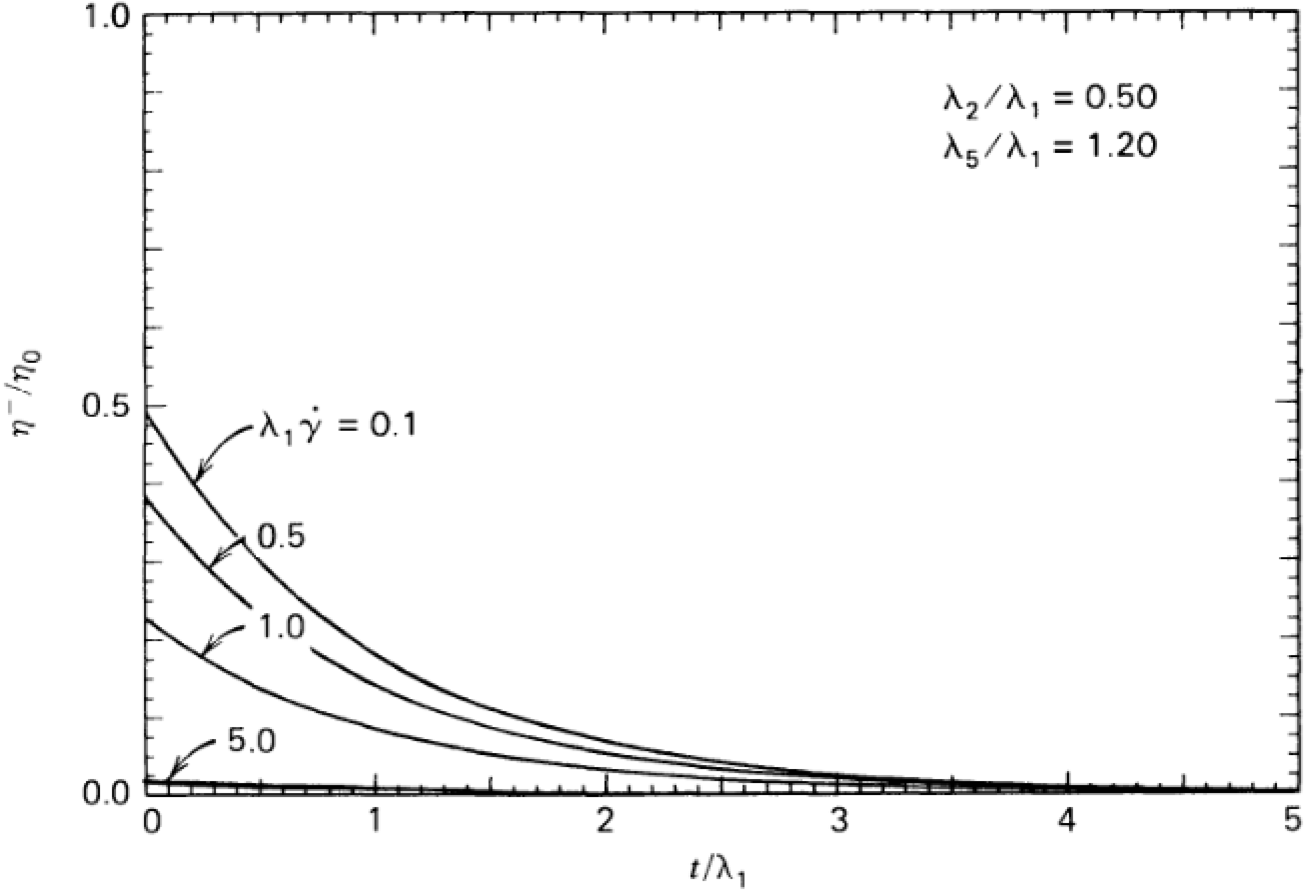


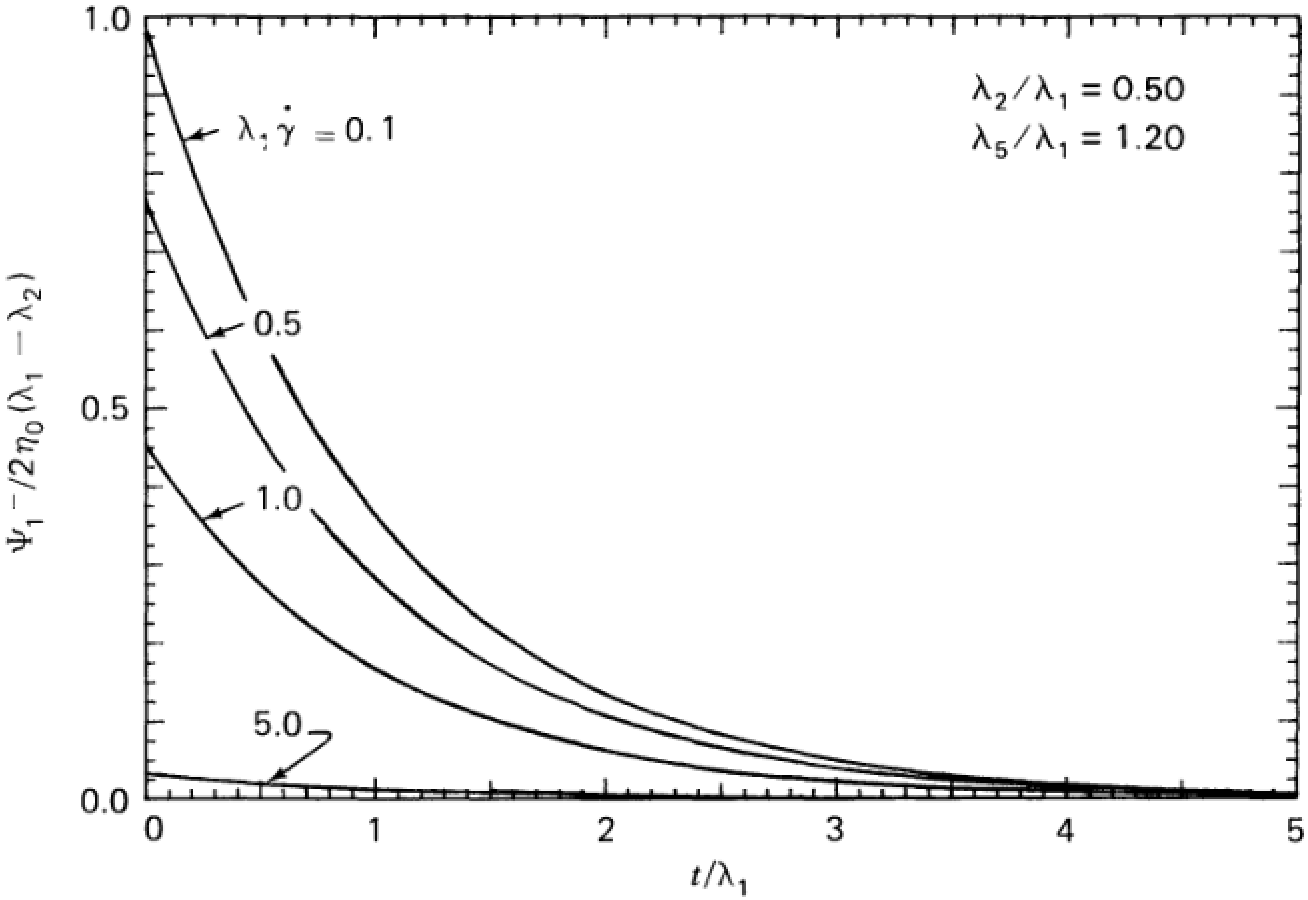
FIGURE 7.3-2. Stress growth material functions for start-up of steady shear flow for the Old 4-constant model defined in Table 7.3-2. These curves should be compared with the data in 3.4-7 through 3.4-10.

Response of 4-Constant Oldroyd Model



(a)

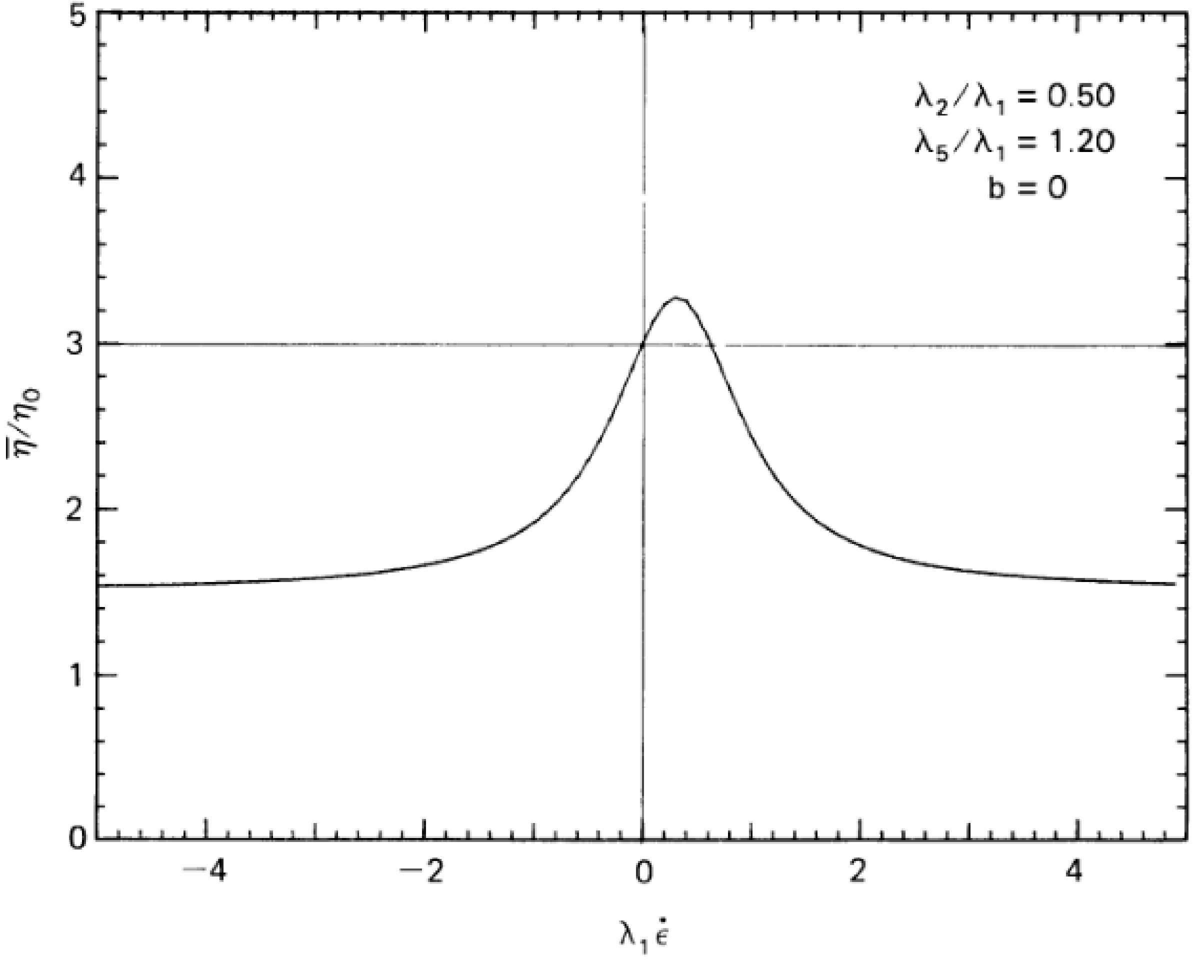
Response of 4-Constant Oldroyd Model



(*b*)

FIGURE 7.3-3. Stress relaxation material functions for cessation of steady shear flow of the Oldroyd 4-constant model defined in Table 7.3-2. These curves should be compared with the data in Figs. 3.4-11 through 3.4-13.

Response of 4-Constant Oldroyd Model



(a)

Response of 4-Constant Oldroyd Model

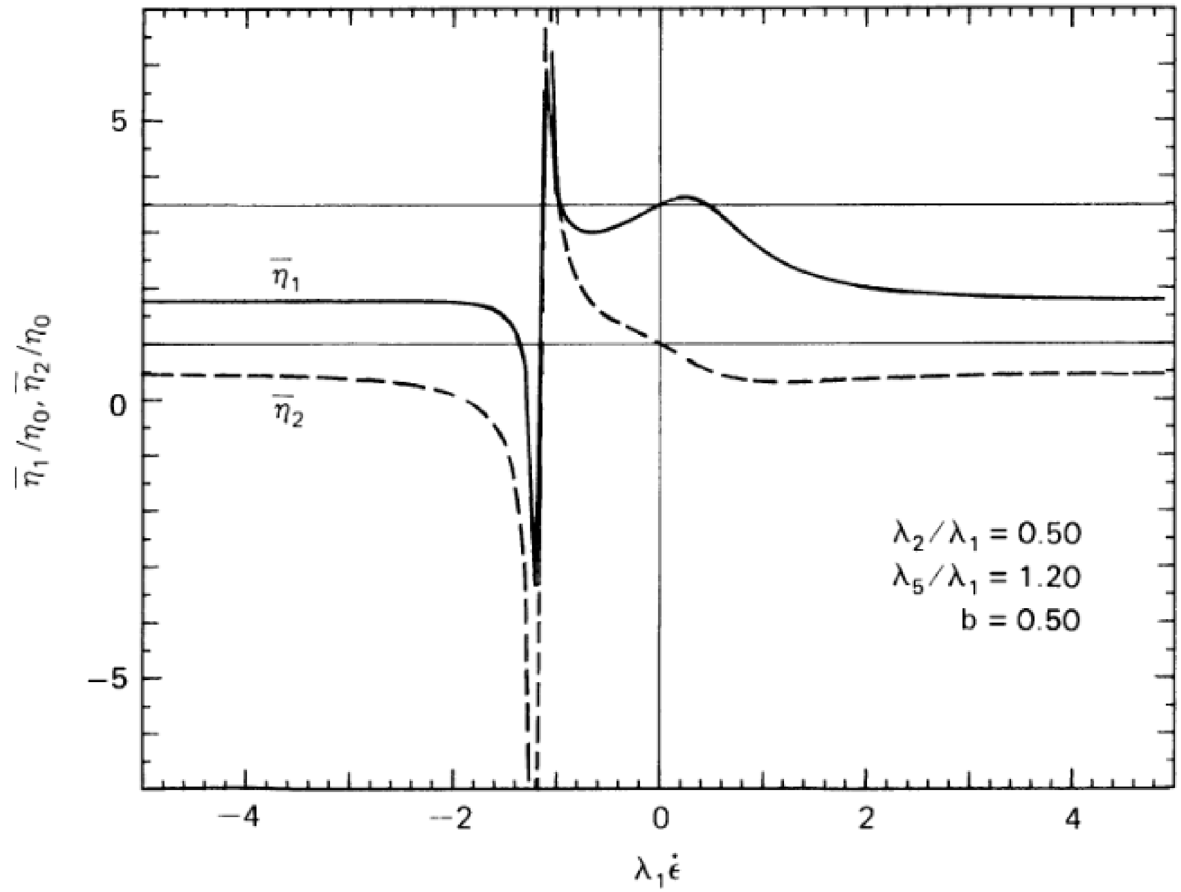


FIGURE 7.3-4. Steady shearfree flow material functions for the Oldroyd 4-constant model defined in Table 7.3-2 with $\lambda_2/\lambda_1 = 0.5$ and $\lambda_5/\lambda_1 = 1.2$ for several choices of the kinematic constant b: (*a*) $\bar{\eta}$ for elongational ($\dot{\varepsilon} > 0$) and biaxial stretching ($\dot{\varepsilon} < 0$) flow ($b = 0$); (*b*) $\bar{\eta}_1$ (——) and $\bar{\eta}_2$ (- - -) for $b = 0.5$. Note in part (*b*) that $\bar{\eta}_1$ and $\bar{\eta}_2$ are singular at a small negative value of $\dot{\varepsilon}$. Although there are no steady-state experimental data for $b = 0.5$, this singular behavior does not seem realistic.

The Giesekus Model

The Giesekus Constitutive Equation:

The Giesekus constitutive equation is a useful nonlinear model which is define as:

$$\boxed{\begin{aligned}&\boldsymbol{\tau} = \boldsymbol{\tau}_s + \boldsymbol{\tau}_p \\ &\boldsymbol{\tau}_s = \eta_s \boldsymbol{\gamma}_{(1)} \\ &\boldsymbol{\tau}_p + \lambda \boldsymbol{\tau}_{p(1)} + \left(\alpha \frac{\lambda}{\eta_p}\right)\left(\boldsymbol{\tau}_p \cdot \boldsymbol{\tau}_p\right) = \eta_p \boldsymbol{\gamma}_{(1)}\end{aligned}} \tag{4}$$

Here the model is written as a superposition of solvent and polymer contributions, $\boldsymbol{\tau}_s$ and $\boldsymbol{\tau}_p$, to the stress tensor, which is the form in which constitutive equations derived by kinetic theory arise naturally for polymer solutions. The Giesekus model contains four parameters: a relaxation time λ; the solvent and polymer contributions to the zero-shear-rate viscosity, η_s and η_p and the dimensionless "mobility factor" α. The origin of the term involving α can be associated with anisotropic Brownian motion and/or anisotropic hydrodynamic drag on the constituent polymer molecules. Equations (4) can be rewritten as a single constitutive equation by replacing $\boldsymbol{\tau}_p$ in

the last equation with $\boldsymbol{\tau} - \boldsymbol{\tau}_s = \boldsymbol{\tau} - \eta_s \boldsymbol{\gamma}_{(1)}$.

The Giesekus Model

This leads to

$$\boldsymbol{\tau} + \lambda_1 \boldsymbol{\tau} + a\frac{\lambda_1}{\eta_0}(\boldsymbol{\tau}.\boldsymbol{\tau}) - a\lambda_2\{\boldsymbol{\gamma}_{(1)}\cdot\boldsymbol{\tau} + \boldsymbol{\tau}\cdot\boldsymbol{\gamma}_{(1)}\} = \eta_0\left\{\boldsymbol{\gamma}_{(1)} + \lambda_2\boldsymbol{\gamma}_{(2)} - a\frac{\lambda_2^{\,2}}{\lambda_1}\left(\boldsymbol{\gamma}_{(1)}\cdot\boldsymbol{\gamma}_{(1)}\right)\right\} \qquad (5)$$

where the zero-shear-rate viscosity η_0, the retardation time λ_2, and the modified mobility parameter a, are given in terms of η_s, η_p, α and λ_1 (the relaxation time) as follows:

$$\eta_0 = \eta_s + \eta_p, \qquad \lambda_2 = \lambda_1\frac{\eta_s}{\eta_p} \qquad \& \qquad a = \frac{\alpha}{1-(\lambda_2/\lambda_1)} \qquad (6)$$

As given in Eq. (5), the Giesekus model is a special case of the Oldroyd 8-constant model to which a term involving $\boldsymbol{\tau}.\boldsymbol{\tau}$ is added. Note that if a = 0, the Oldroyd-B model is recovered; thus, the Oldroyd-B model can be written as the superposition in Eq. (4) with $\alpha = 0$. A number of equations used in the literature to which the Giesekus model can be reduced are listed in the next Table. Thus, considerable diversity in the rheological predictions of the model is possible.

The Giesekus Model

Models Included in the Giesekus Model

Name of Model	Values of Constants $\lambda_1 \geq 0$	λ_2	$0 \leq \alpha \leq 1$
Newtonian	$0, \lambda$	$0, \lambda$	0
Second-order fluid	0	$\lambda_2 < 0$	
Convected Maxwell		0	0
Convected Jeffreys		$\lambda_2 > 0$	0
"Leonov-like"		0	1/2
"Corotational Maxwell-like"		0	1

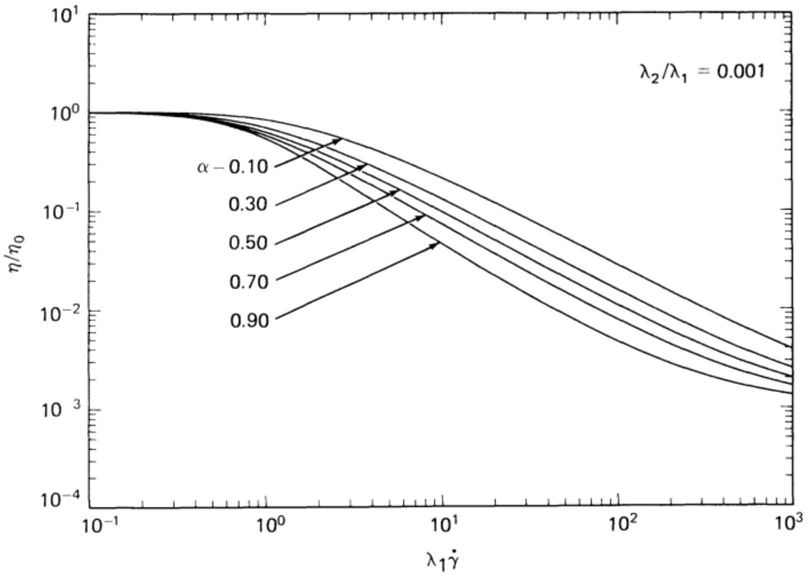
Some Points about the Giesekus Model

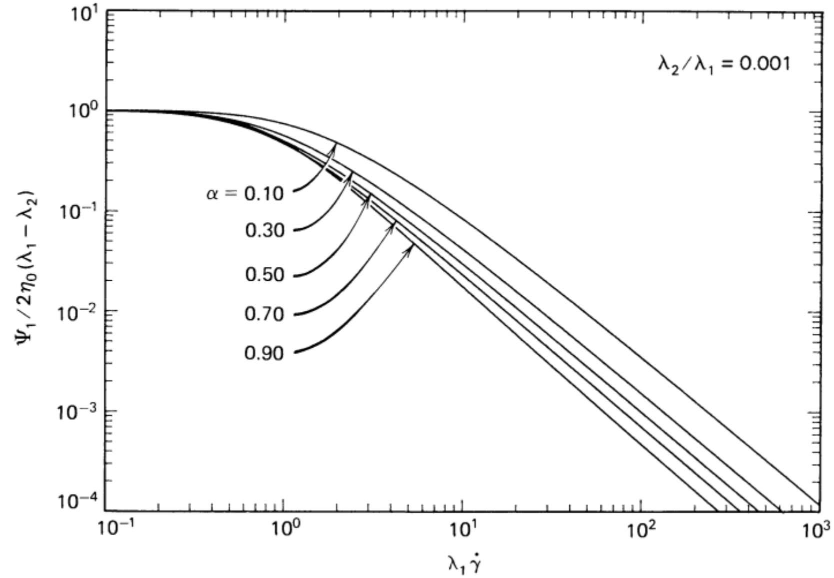
Some Points about the Giesekus Model:

The inclusion of the $\boldsymbol{\tau}.\boldsymbol{\tau}$ term in Giesekus model gives material functions that are much more realistic than those obtained for the Oldroyd 8-constant model. For example, large decreases in the viscosity and normal stress coefficients with increasing shear rate are possible. For all $\alpha \neq 0$ or 1 the power-law slope of the viscosity is -1 when λ_2 = 0; this is unrealistically steep. However, by adding a small retardation term (e.g., $\lambda_2 / \lambda_1 = 10^{-3}$), the value of d(log η)/d(log $\dot{\gamma}$) can be kept larger than -1 so that the magnitude of the shear stress is always increasing with increasing shear rate. The second normal stress coefficient is non-zero and can be varied in size relative to the first normal stress coefficient; for example, $\Psi_{2,0} = -(\alpha / 2)\Psi_{1,0}$. Provided $\alpha \neq 0$ the elongational viscosity is bounded and reaches a constant value at large strain rate. Graphs of several steady and transient, shear and shear-free flow material functions are shown in next figures through 8 for the special choice $\alpha = 1/3$. In general, we must require $0 < \alpha < 1/2$ for realistic properties.

This model has as gained prominence because it describes the power-law regions for viscosity and normal-stress coefficients; it also gives a reasonable description of the elongational viscosity and the complex viscosity.

Response of the Giesekus Model





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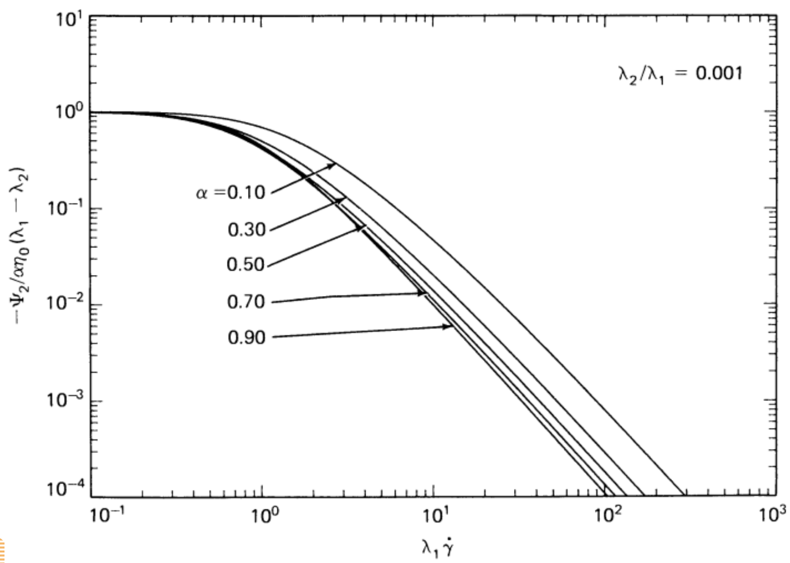
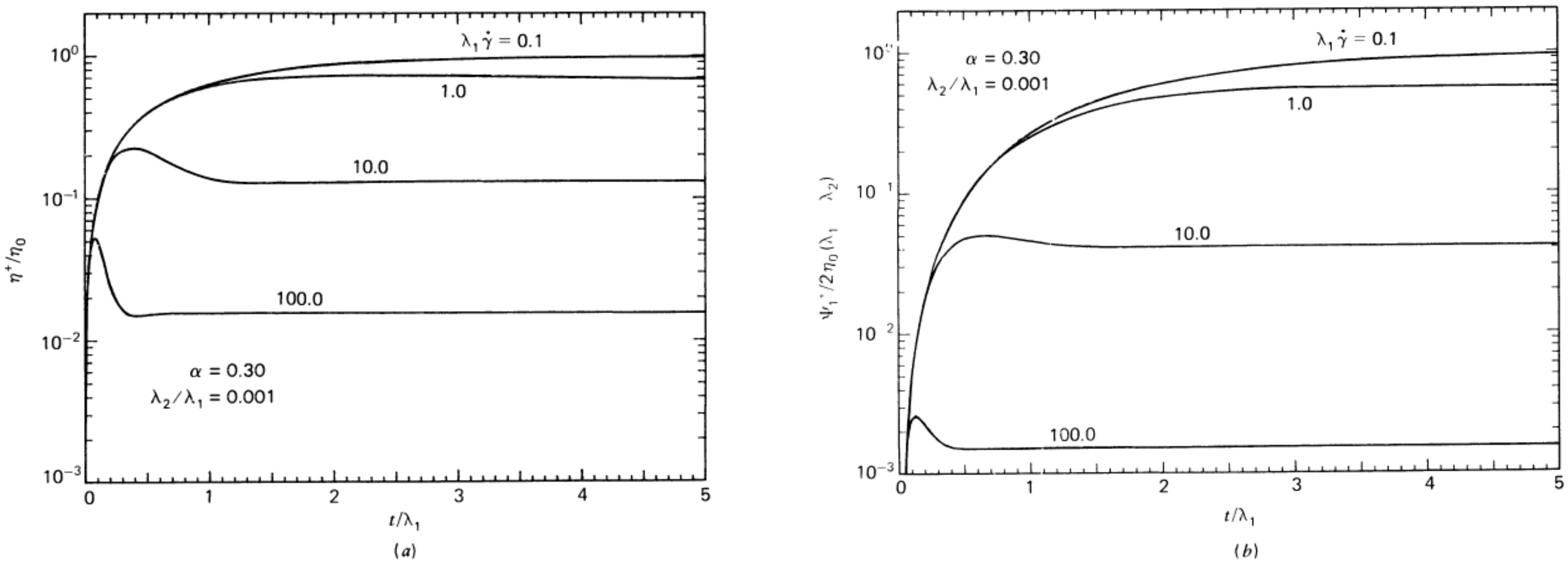


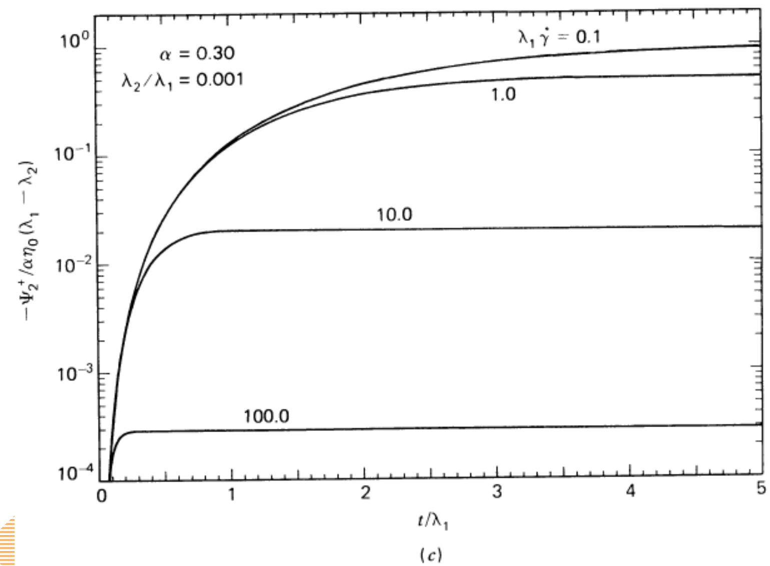
(c)

Dimensionless viscometric functions of steady shear flow of the Giesekus model for $\lambda_2/\lambda_1 = 10^{-3}$.

Response of the Giesekus Model



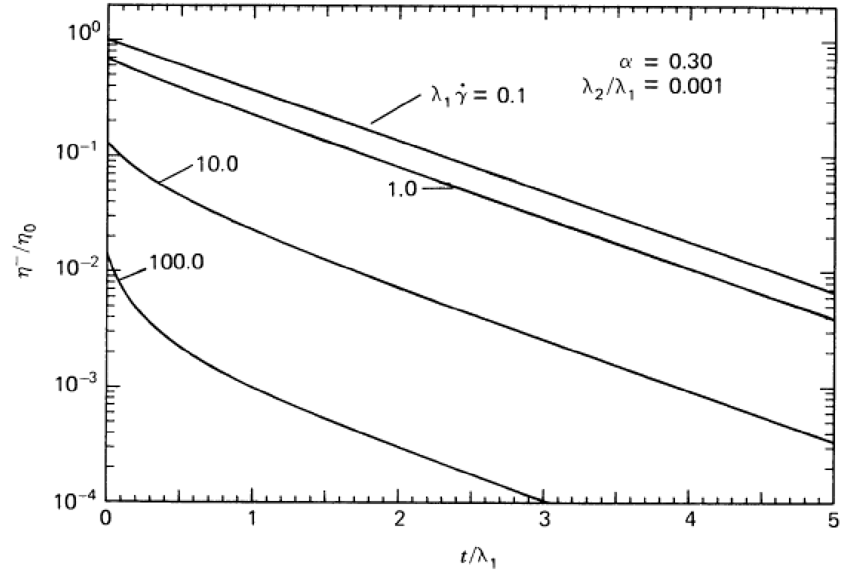
(a) (b)



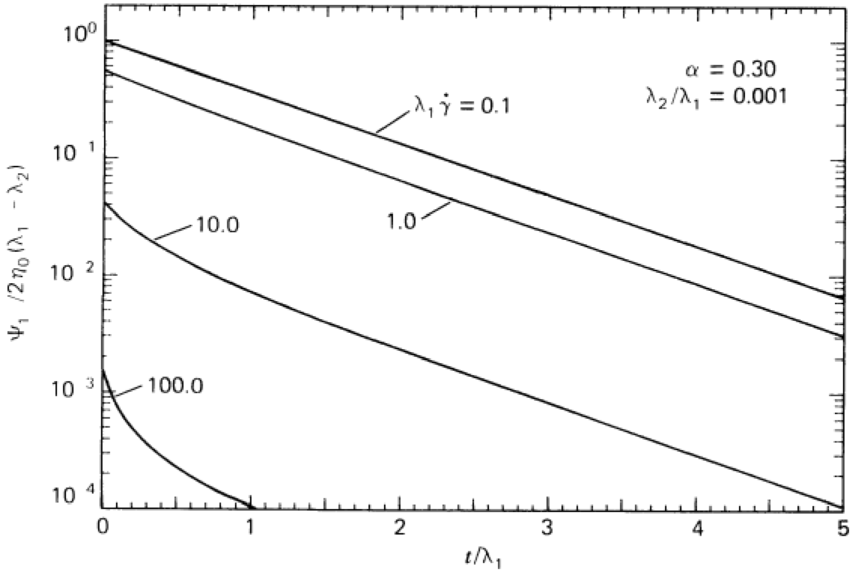
(c)

Dimensionless stress growth material functions for the Giesekus model for $\alpha = 0.3$ and $\lambda_2 / \lambda_1 = 10^{-3}$.

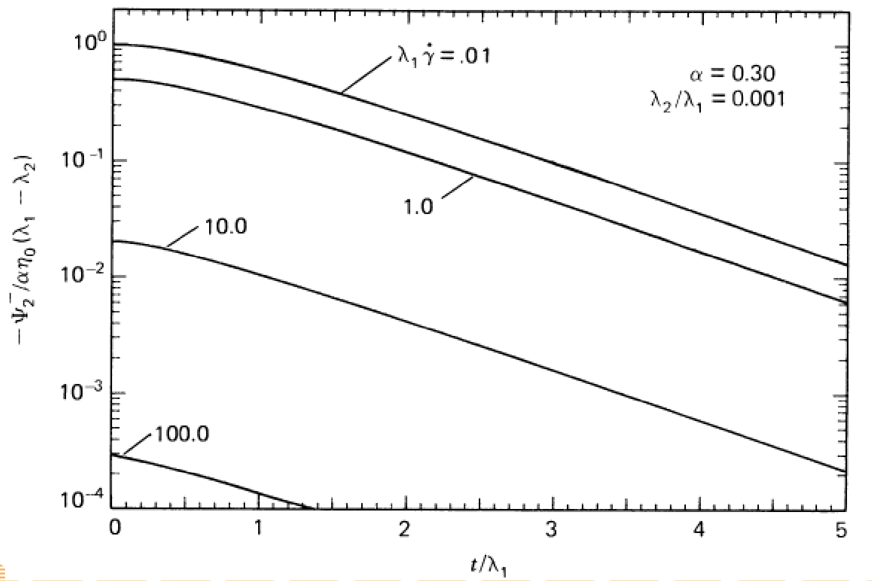
Response of the Giesekus Model



(a)



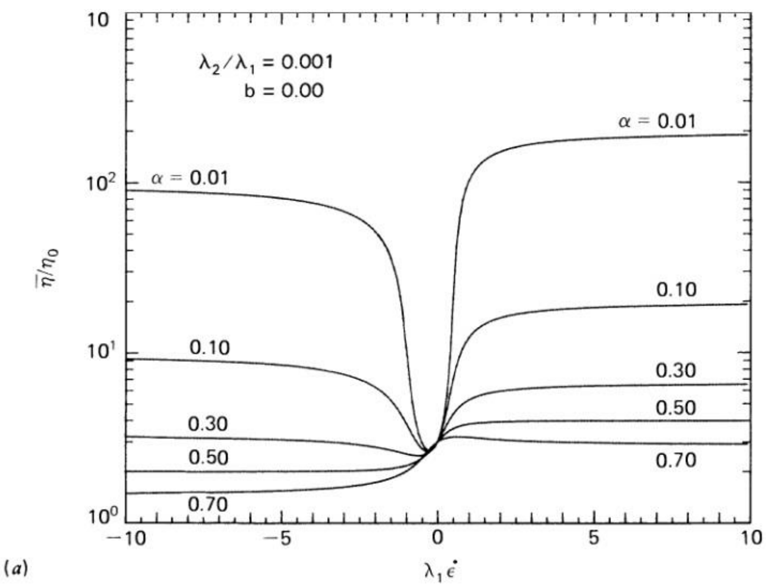
(b)

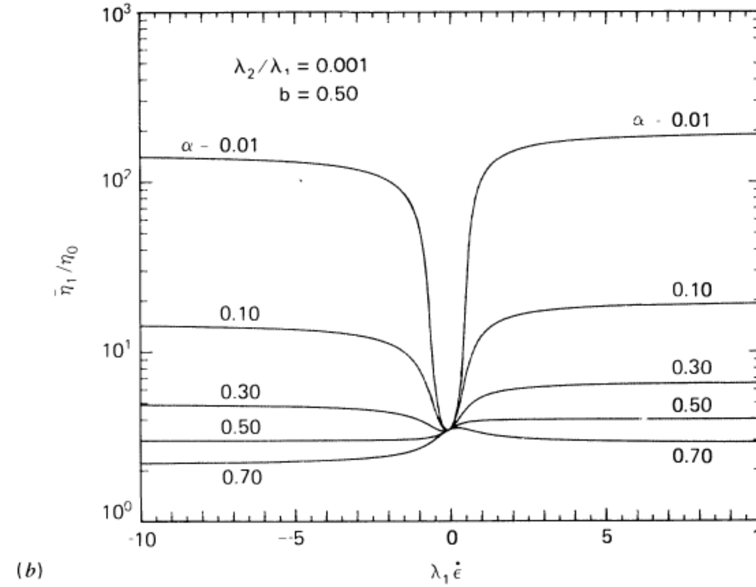


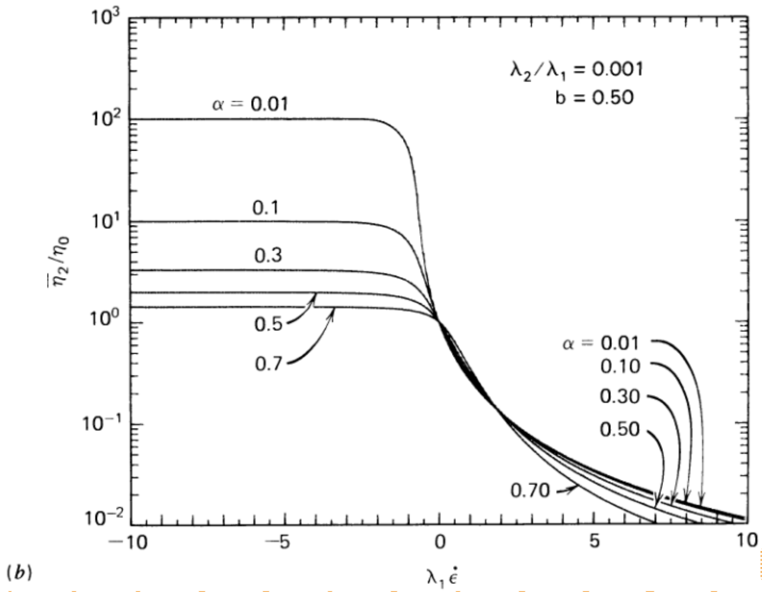
(c)

Dimensionless stress relaxation material functions for the Giesekus model for $\alpha = 0.3$ and $\lambda_2 / \lambda_1 = 10^{-3}$.

Response of the Giesekus Model







Dimensionless shear-free flow material functions for the Giesekus model with $\lambda_2/\lambda_1 = 10^{-3}$ and various values of α for several choices of the kinematic parameter b: (a) $\bar{\eta}$ for elongational ($\dot{\varepsilon} > 0$) and biaxial elongational ($\dot{\varepsilon} < 0$) flow for b=0 and (b) $\bar{\eta}_1$ and $\bar{\eta}_2$ for b=0.5.

FENE-P Model

The FENE (Finitely-Extensible-Nonlinear-Elastic) Dumbbell Model:

This constitutive equation results from a kinetic theory derivation using a nonlinear elastic dumbbell model to represent the polymer molecules in a dilute solution, where the solvent is a Newtonian fluid with viscosity η_s, and where the number of dumbbells per unit volume is n. Here, the following nonlinear spring force is used to derive the constitutive equation:

$$\mathbf{F} = \frac{H\mathbf{Q}}{\left[1-(Q/Q_0)^2\right]} \tag{7}$$

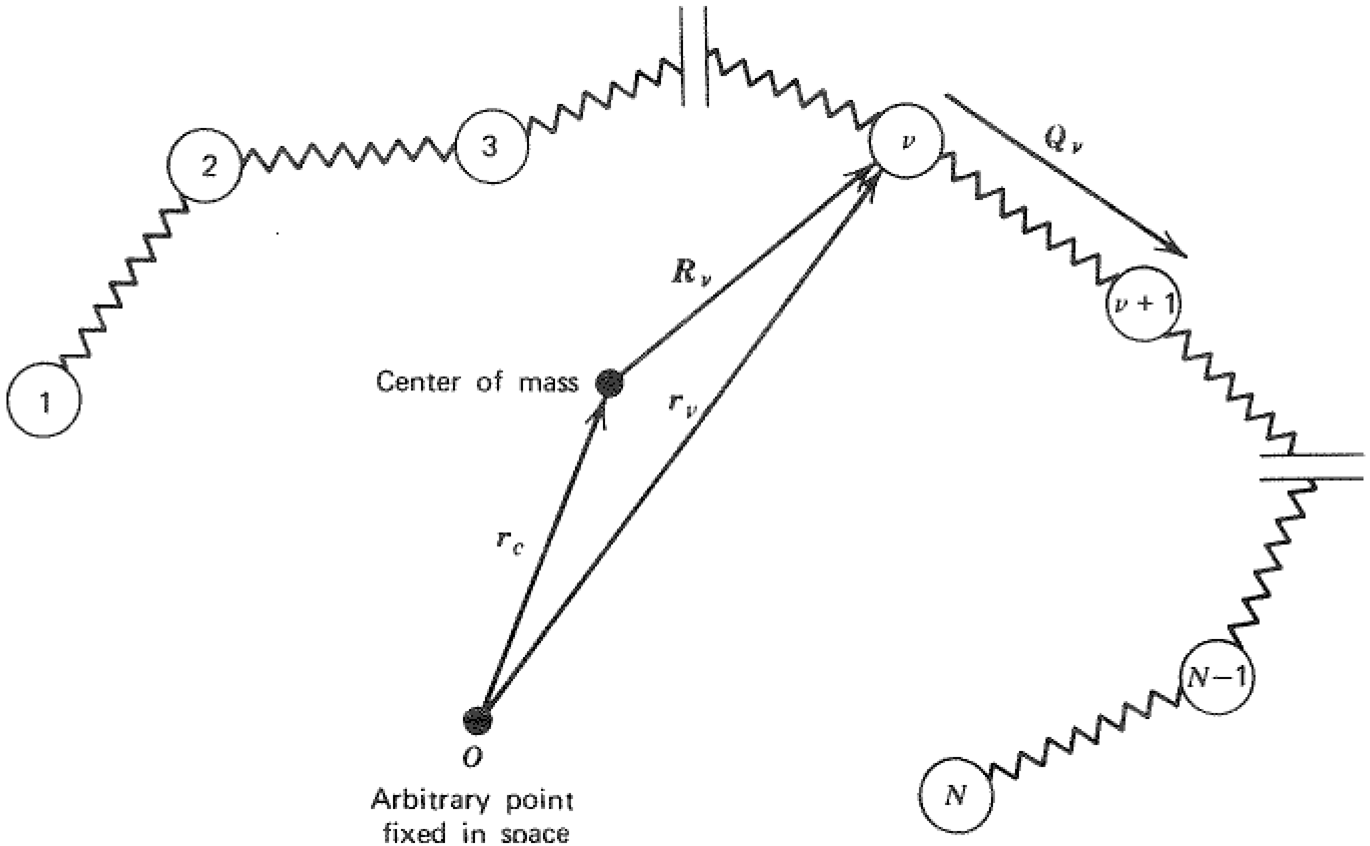
where H is spring constant, $\mathbf{Q}$ is the instantaneous length vector between the dumbbells, Q_0 is the maximum allowable length for the connectors. After making the Peterlin approximation (in the expression for the stress tensor, the average of a ratio is replaced by the ratio of the averages), to the following constitutive equation which is known as FENE-P model:

$$\boxed{\begin{aligned} &\boldsymbol{\tau} = \boldsymbol{\tau}_s + \boldsymbol{\tau}_p \\ &\boldsymbol{\tau}_s = \eta_s \boldsymbol{\gamma}_{(1)} \\ &Z\boldsymbol{\tau}_p + \lambda_H \boldsymbol{\tau}_{p(1)} - \lambda_H \left(\boldsymbol{\tau}_p + \frac{b}{b+2} nkT\mathbf{I}\right)\frac{D\ln Z}{Dt} = \frac{b}{b+2} nkT\lambda_H \boldsymbol{\gamma}_{(1)} \end{aligned}} \tag{8}$$

where λ_H is a time constant and Z is:

$$Z = 1 + \frac{3}{b}\left(\frac{b}{b+2} + \frac{\operatorname{tr}\boldsymbol{\tau}_p}{nkT}\right) \tag{9}$$

Material Functions of FENE-P Model



The freely jointed bead-spring chain model formed from N "beads" and N-1. The spring configurations are given by the connector vectors $\boldsymbol{Q}_{\nu}$ ($\nu = 1, 2, 3, ..., N$-1).

Some Tips on FENE-P Model

Some Tips on FENE-P Model:

This model contains a new dimensionless group called the *extensibility parameter* $b=HQ_0^2/kT$ which is generally between 30 to 300 and infinity in the Hookean spring limit. For infinite value of b, the FENE-P model is simplified to the Oldroyd-B model.

For simple shear flow at large enough shear rates, the viscosity of FENE-P model is:

$$\frac{\eta-\eta_s}{\eta_0-\eta_s}=\left(\frac{b+5}{b}\right)\left(\frac{b}{2}\right)^{1/3}\left(\frac{1}{\lambda_H\dot{\gamma}}\right)^{2/3} \tag{10}$$

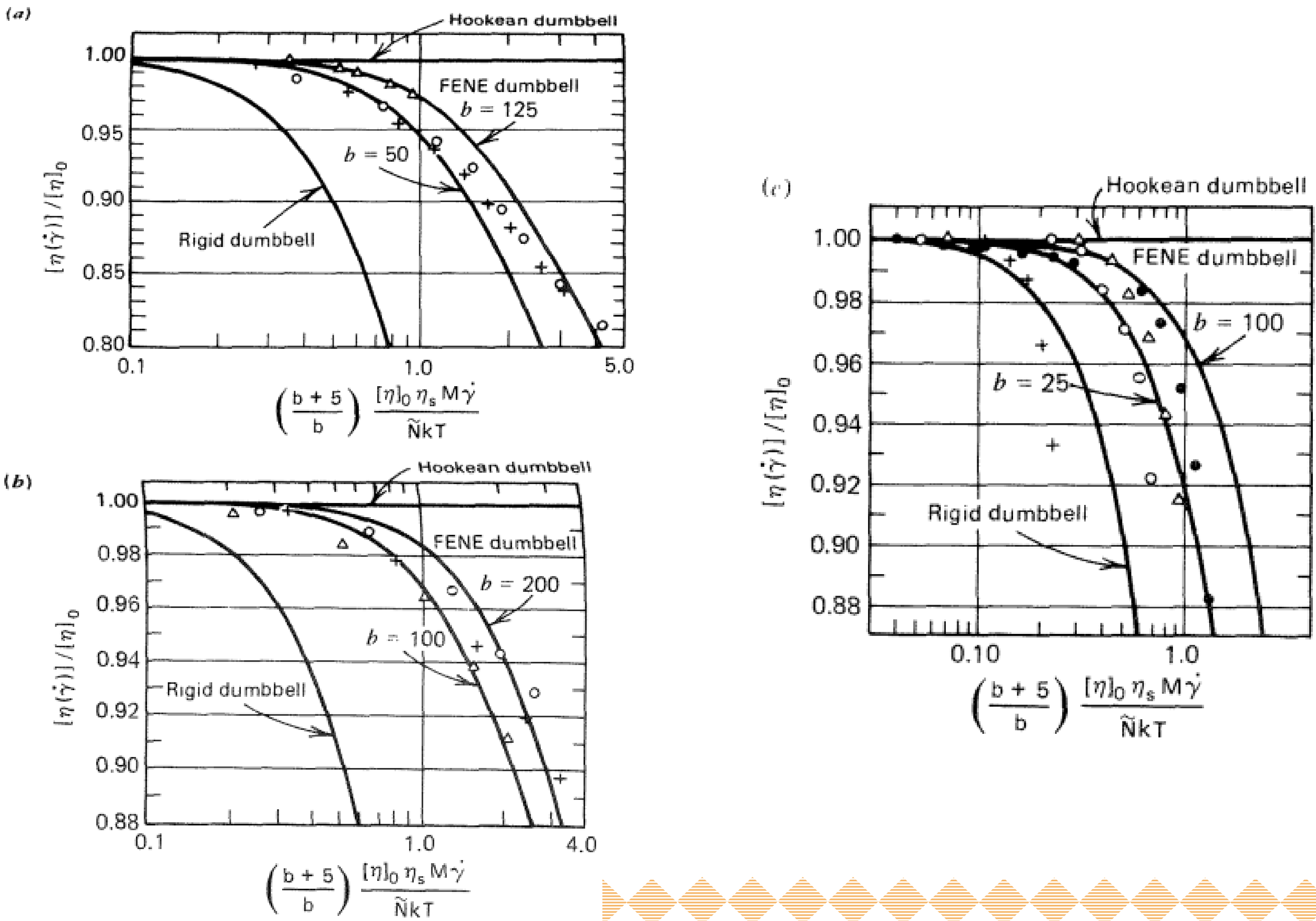
where $\eta_0=\eta_s+[b/(b+5)]nkT\lambda_H$ is the viscosity at zero shear rate. The viscosity is decreases with $\dot{\gamma}^{-2/3}$, agreeing with experimental observations. The model also gives Ψ_1 decreasing as $\dot{\gamma}^{-4/3}$, which seems to be appropriate. The second normal stress difference coefficient of this model is $\Psi_2=0$. Since Ψ_2 is too smaller than Ψ_1, we can see the results are not together unreasonable.

For elongational flow test, we have

$$\frac{\bar{\eta}(0)-3\eta_s}{\eta_0-\eta_s}=3;\quad \frac{\bar{\eta}(\infty)-3\eta_s}{\eta_0-\eta_s}=2(b+5);\quad \frac{\bar{\eta}(-\infty)-3\eta_s}{\eta_0-\eta_s}=\frac{1}{2}(b+5) \tag{11}$$

The slop of $\bar{\eta}(\dot{\varepsilon})$ at $\dot{\varepsilon}=0$ is positive. Thus, the model predicts a large elongational viscosity as the elongational rates increases, and a somewhat smaller increase as the elongational rate become negative (biaxial stretching).

Response of FENE-P Model



Response of FENE-P Model

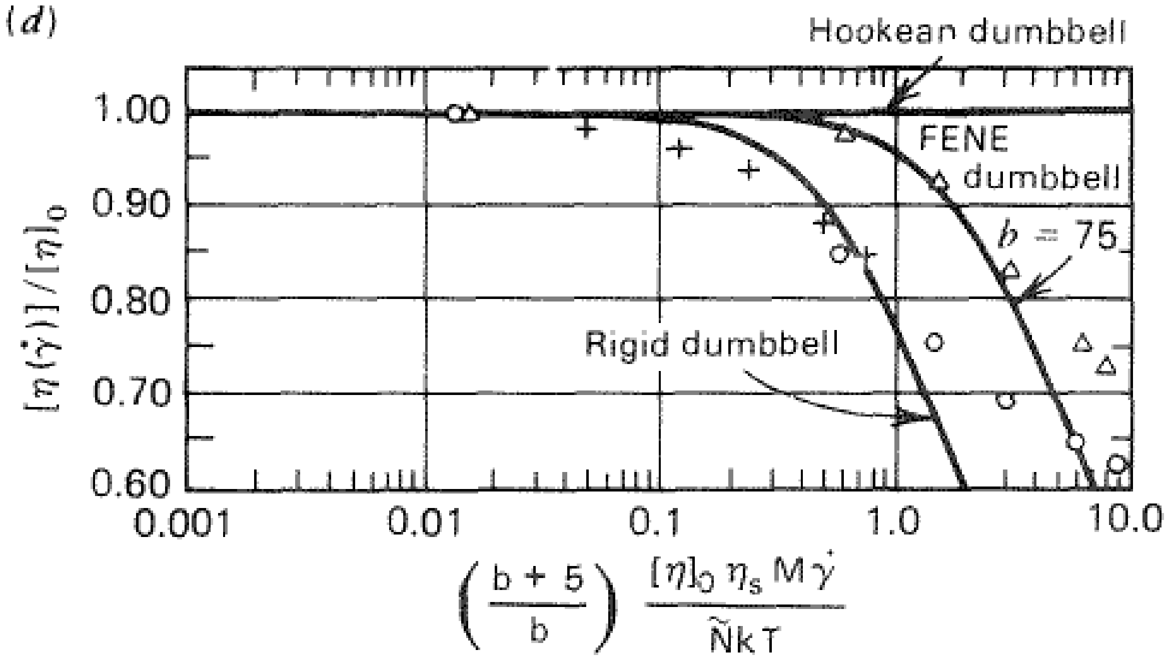


FIGURE 13.5-2. Comparison of experimental intrinsic viscosities and calculated curves from the FENE dumbbell model. (*a*) Polystyrene in benzene at 30°C for several molecular weights: 6×10^6 (+), 7.14×10^6 (○), 3.16×10^6 (△). Data of H. Suzuki, T. Kotaka, and H. Inagaki, *J. Chem. Phys.*, **51**, 1279–1285 (1969). (*b*) Polystyrene (molecular weight 10^7) in toluene for several temperatures: 20°C (+), 40°C (○), 60°C (△). Data of H. van Oene and L. H. Cragg, *J. Polym. Sci.*, **57**, 209–225 (1962). (*c*) Poly-α-methylstyrene in toluene at 25°C for several molecular weights: 0.696×10^6 (+), 1.24×10^6 (○), 1.46×10^6 (△), 1.82×10^6 (●). Data of I. Noda, Y. Yamada, and M. Nagasawa, *J. Phys. Chem.*, **72**, 2890–2898 (1968). (*d*) Cellulose in cadoxene at 25°C for several molecular weights: 0.330×10^6 (△), 0.109×10^6 (+), 0.429×10^6 (○). Data of E. Riande and J. M. Pereña, *Makromol. Chemie*, **175**, 2923–2938 (1974). Reprinted with permission from X. J. Fan, *J. Non-Newtonian Fluid Mech.*, **17**, 125–144 (1985).

The Phan-Thien Tanner (PTT) Model

The Phan-Thien & Tanner Model:

The five-constant model of Phan-Thien & Tanner (PTT) was derived from a network theory for polymer melts and is also nonlinear in the stresses:

$$\boxed{\begin{aligned} &\boldsymbol{\tau} = \boldsymbol{\tau}_s + \boldsymbol{\tau}_p \\ &\boldsymbol{\tau}_s = \eta_s \boldsymbol{\gamma}_{(1)} \\ &Y\boldsymbol{\tau}_p + \lambda \boldsymbol{\tau}_{p(1)} + \frac{1}{2}\xi\lambda\left(\boldsymbol{\gamma}_{(1)}.\boldsymbol{\tau}_p + \boldsymbol{\tau}_p.\boldsymbol{\gamma}_{(1)}\right) = \eta_p \boldsymbol{\gamma}_{(1)} \end{aligned}} \tag{12}$$

Here, Y is a function of the trace of the stress tensor:

$$Y = \exp\left[-\varepsilon\left(\lambda/\eta_0\right)\mathrm{tr}(\boldsymbol{\tau}_p)\right] \tag{13}$$

For small value of ε, the term Y can be estimated as:

$$Y \approx 1 - \varepsilon\left(\lambda/\eta_0\right)\mathrm{tr}(\boldsymbol{\tau}_p) \tag{14}$$

Using the above supposition, the model is called as the simplified Phan-Thien Tanner (SPTT) constitutive equation.

In fitting these parameters, it is found that the shear-flow properties are insensitive to ε and the shearfree flow properties are insensitive to ξ. Thus ξ and ε can be determined from separate sets of experiments. The fits are seen to be quite good, although it is not possible to fit exactly both η and Ψ_1 in the high shear rate region with the same value of ξ.

Response of PTT Model

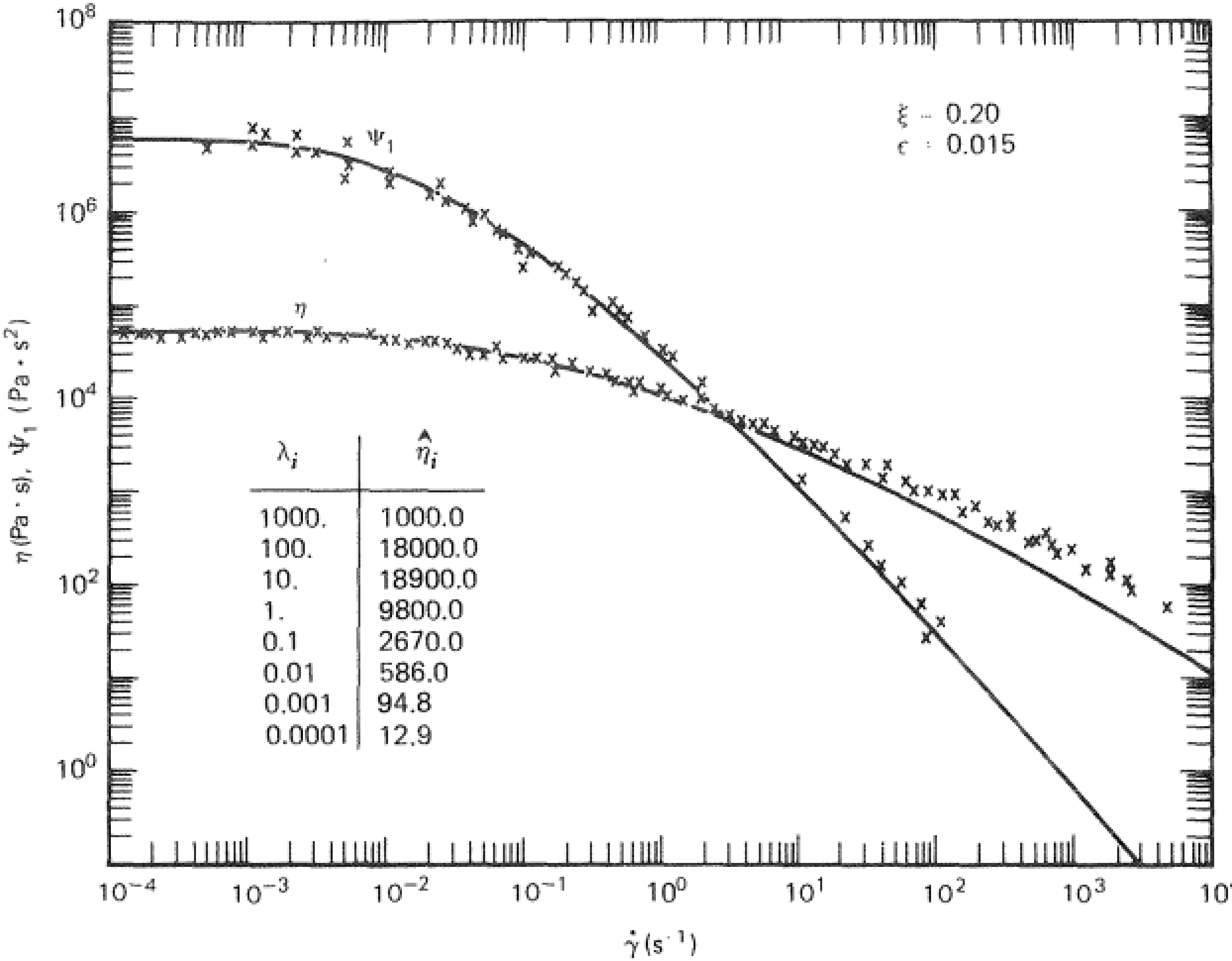
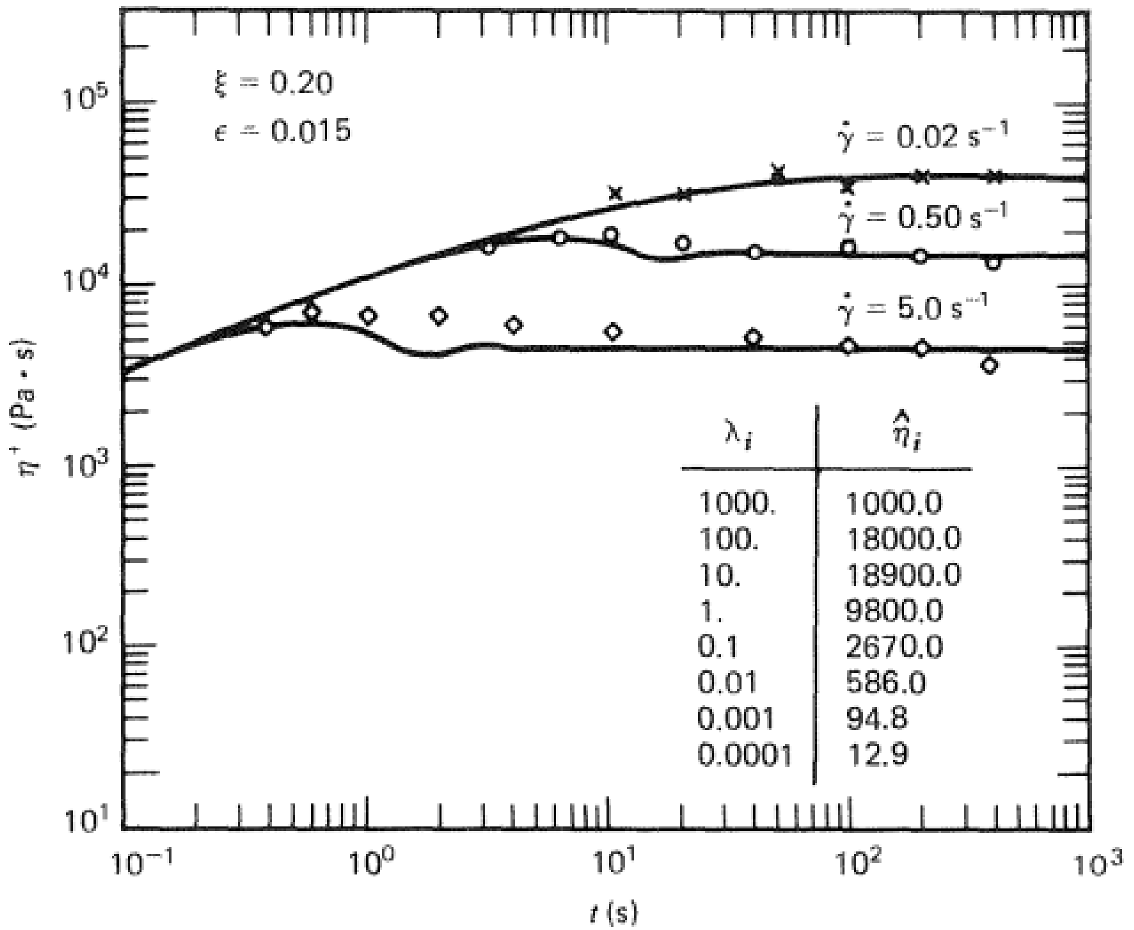


FIGURE 20.5-1. Comparison of predictions of the Phan-Thien-Tanner model, Eqs. 20.5-50, 51 and 52b, with η and Ψ_1 data for a low density polyethylene melt. The constants λ_{0j} and $\hat{\eta}_j$ were fit with linear viscoelastic data (cf. Example 5.3-7); the constants ξ and ε were chosen to be 0.2 and 0.015, respectively, in order to achieve a best fit of the data. Data from H. M. Laun, *Rheol. Acta*, **17**, 1-15

Response of PTT Model



λ_i	$\hat{\eta}_i$
1000.	1000.0
100.	18000.0
10.	18900.0
1.	9800.0
0.1	2670.0
0.01	586.0
0.001	94.8
0.0001	12.9

FIGURE 20.5-2. Comparison of the Phan-Thien-Tanner model predictions with low density polyethylene data for η^+ in the start-up of steady shear flow. The model parameters are the same as in Fig. 20.5-1. Data as reported by M. H. Wagner, *Rheol. Acta*, **15**, 136-142 (1976).

Response of PTT Model

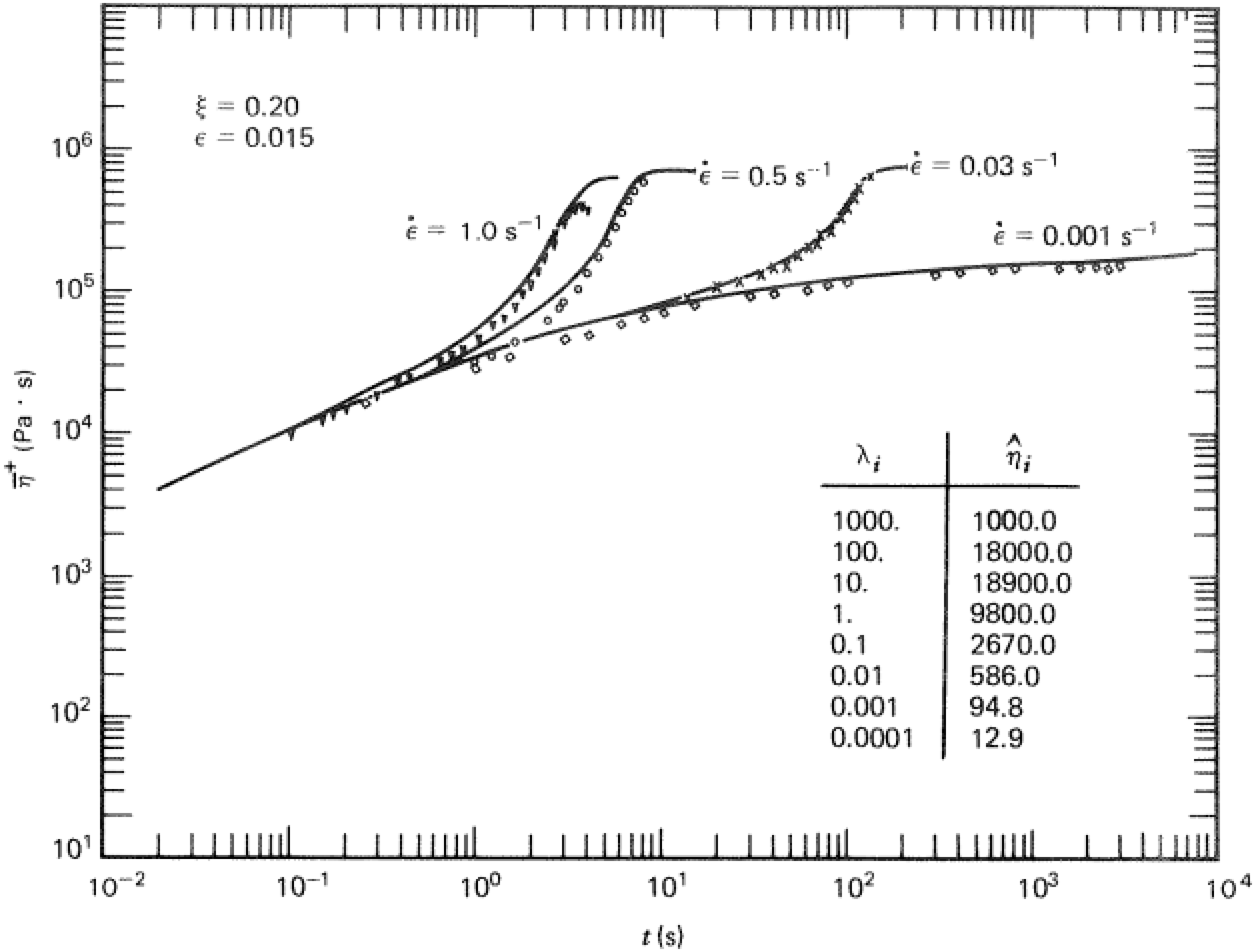


FIGURE 20.5-3. Comparison of the Phan-Thien-Tanner model predictions with low density polyethylene data for $\bar{\eta}^+$ in the start-up of steady elongational flow. The model parameters are the same as in Fig. 20.5-1. Data as reported by M. H. Wagner, *Rheol. Acta*, **18**, 39-50 (1979).

Integral Based Models

The Kaye-BKZ model:

The Kaye-BKZ model is a nonlinear generalization of the general linear viscoelastic model, and contains two unspecified functions:

$$\tau = -\int_{-\infty}^{t} M(t-t')\left[\frac{\partial W}{\partial I_1}\gamma_{[0]} + \frac{\partial W}{\partial I_2}\gamma^{[0]}\right]dt' \qquad (15)$$

Here, $M(t-t')$ is a "*memory function*" (a property of the material), and $W(I_1,I_2)$ is a "*potential function*" that depends on the two scalar invariants of the Finger strain tensor **B**. The two relative finite strain tensors are defined by: $\boldsymbol{\gamma}_{[0]} = \boldsymbol{\delta} - \mathbf{B}$ and $\boldsymbol{\gamma}^{[0]} = \mathbf{B}^{-1} - \boldsymbol{\delta}$. It is necessary to require that the potential function obeys the relation $\partial W / \partial I_1 + \partial W / \partial I_2 = 1$ at $I_1 = 3$, $I_2 = 3$ to guarantee that the model simplifies correctly in the linear limit.

Kaye proposed a modification of the Kaye-BKZ model in which the potential function is given in terms of the principal stretches. Specifically, he considers that W is the sum of the nth powers of the principal stresses. All the nonlinear rheological properties can then be computed from the relaxation spectrum of linear viscoelasticity and the power n.

Integral Based Models

The Curtiss-Bird Model:

The Curtiss-Bird constitutive equation was derived for a melt made up of a monodisperse set of freely jointed, interacting bead-rod chains, using a phase-space kinetic theory. The resulting equation is:

$$\boldsymbol{\tau} = NnkT\left\{\int_{-\infty}^{t}\mu(t-t')\mathbf{A}^{(2)}dt' + \frac{1}{2}\varepsilon\boldsymbol{\gamma}_{(1)} : \int_{-\infty}^{t}\nu(t-t')\mathbf{A}^{(4)}dt' - \frac{1}{3}\boldsymbol{\delta}\right\} \tag{16}$$

Here, N is the number of beads in the bead-rod chain, n is the number density of chains, μ and ν are memory functions containing a time constant λ, $\mathbf{A}^{(2)}$ is a second-order tensor function of the nonlinear strain tensor $\gamma^{[0]}$, and $\mathbf{A}^{(4)}$ is a fourth-order tensor function of $\gamma^{[0]}$. The parameter ε is called the link-tension coefficient; when ε is set equal to zero, the Doi-Edwards constitutive equation is obtained.

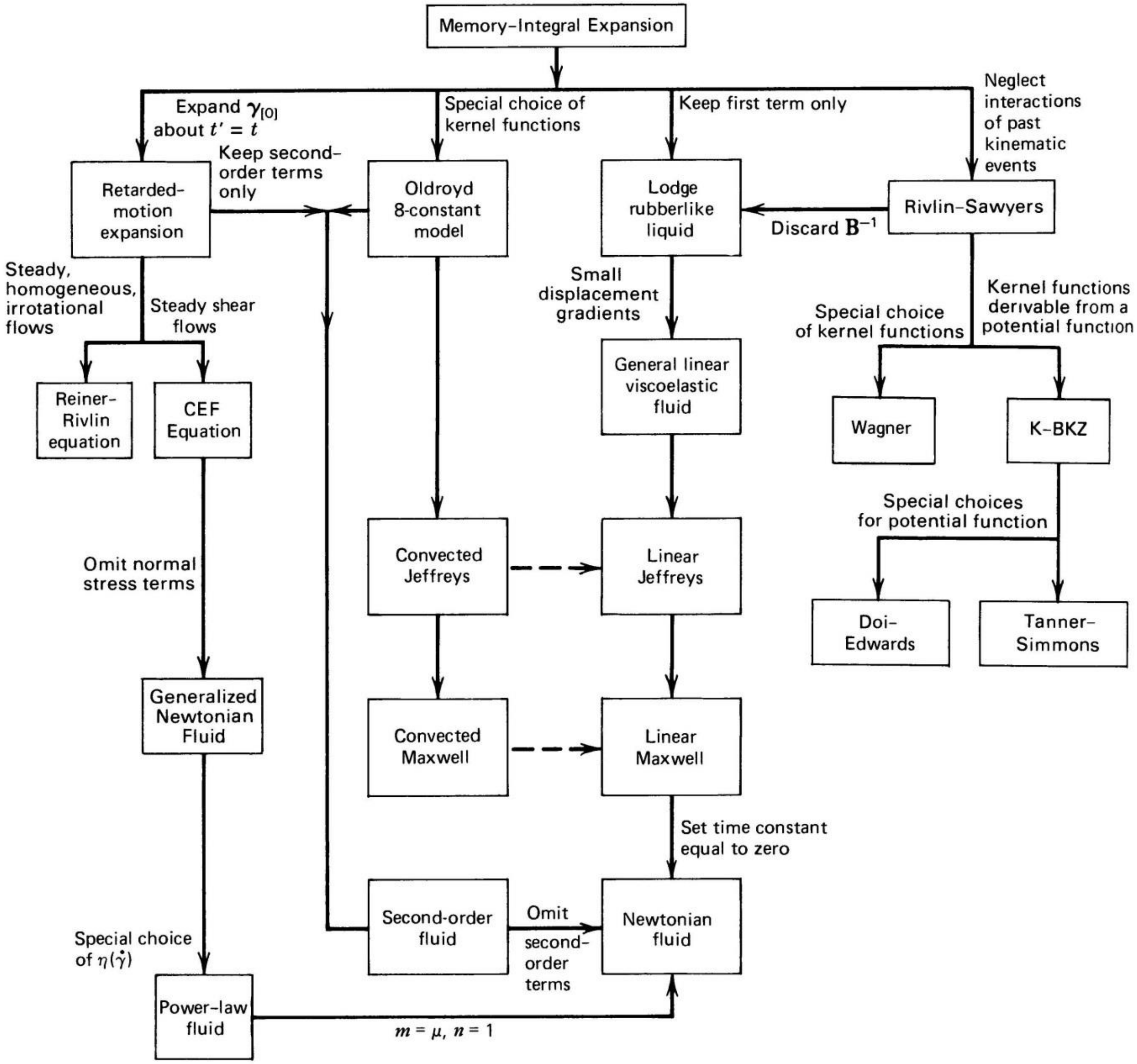
The Curtiss-Bird equation gives realistic shapes for the viscometric functions and the elongational viscosity. Some generalizations for this model (especially for polydisperse melts) have been represented in literature.

Constitutive Equations and Their Performance

Constitutive model	Small-strain	η	N_1	N_2	Steady elongation	Start/stop in shearing flow	Elongational start/recoil	Single shear step	Double-step shear	Remark
Newtonian, eqn (1.3)	P	P	U	U	P	P	U	U	U	Infinite stresses in step strains.
Generalized Newtonian, eqn (4.3)	P	E	U	U	P	P	U	U	U	Infinite stresses in step strains.
Reiner–Rivlin, eqn (4.1)	P	E	U	E	E	P	U	U	U	As above.
Second-order, eqn (4.14), η, ν_1, ν_2 constant	P	P	P	P	U	U	U	U	U	At high elongation rates η_T becomes negative.
Higher-order fluids	P	M	M	M	U-P	U	U	U	U	See Schowalter (1978), p. 182, for forms of equations.
Criminale, Ericksen, Filbey, eqn (4.14)	P	E	E	E	U-P	U	U	U	U	Useful for viscometric flows.
Linear viscoelastic, eqn (2.70)	E	P	U	U	P	P	P	P	P	No non-linear effects.
Oldroyd, eqn (4.4)	M	M	M	M	P	M	P	P	P	Limited viscosity variation.
Green–Rivlin, eqn (4.25)	E	P	P	P	P	P	P	P	P	Double integral is hard to use.
Lodge–Maxwell, eqns (5.57, 5.58)	E	P	P	U	P	P	P	P	P	Useful for illustrative purposes.
White–Metzner	M	E	M	U	P	P	P	P	P	See footnote 1.
Co-rotational	E	E	E	M	M	P	P	U	U	Oscillation in start of shearing. See footnote 2.
Bird–Carreau, Carreau	E	E	E	G	P	M	P	P	P	See Bird *et al.* (1977*a*, *b*) and Problem 5.9.
Phan-Thien, eqn (5.152)	E	E	E	E	G	M	G	M-U	M-U	Unsuitable for large step strains.
Acierno *et al.*, eqns (5.116–119)	E	E	E	G	G	G	M	M	M	Poor step strain response.
KBKZ, eqn (4.43)	E	E	G	G	G	G	M	E	G-M	
KBKZ (Wagner), eqn (5.157)	E	E	G	G	G	G	G	E	G	See footnote 3.
Eqn (5.114)	M	G	G	U	G	G	M	M-U	M-U	Dilute solution theory: unsuitable for large step strains.
Leonov	E	E	G	G	M	G	M	M	M	
Doi–Edwards	M	M	M	M	M	M	M	M	M	

E: Exact
G: Good
M: Moderate
P: Poor
U: Unable

Relation between Constitutive Equations



Thank You