Chapter 6.2 Formulation of Constitutive Equations

a) Material objectivity

The relationship between the stress and deformation and rates of deformation should be independent of any superposed rigid motion of the material relative to fixed coordinates, that is: independent of local position in space, local rigid rotation and translation.

b) Coordinate indifference

The rheological equation of state should be independent of the choice of the base vectors used to express the stress, deformation and rate-of-deformation tensors. In simpler terms, the results should not depend on the frame of reference (material objectivity).

By using embedded coordinates, condition (a) is automatically satisfied. By writing the equation in tensor form condition (b) is automatically satisfied.

c) Determinism

Oldroyd (1950): The stress response in a material element should be invariant to a change of the rheological history of neighboring fluid elements.

Coleman and Noll (1961): A simple fluid = incompressible and isotropic material for which the stress at any time (in embedded coordinates) is given by a functional of the strain tensor. That is:

$$\hat{\sigma}_{ij}(t) = -\overset{t}{\underset{-\infty}{\Phi}}\left\{(\hat{g}_{ij}(t')\right\} \qquad (6.2\text{-}1b)$$

$$\hat{\sigma}^{ij}(t) = -\overset{t}{\underset{-\infty}{\Phi}}\left\{(\hat{g}^{ij}(t')\right\} \qquad (6.2\text{-}1a)$$

$\overset{t}{\underset{-\infty}{\Phi}}$ *is a functional of the deformation history.*

6.2-2 Maxwell Convected Models

$$\text{Maxwell A} \Rightarrow \left(1+\lambda_0 \frac{\partial}{\partial t}\right)\sigma^{ij} = \eta_0 \frac{\partial \gamma^{ij}}{\partial t}$$

$$\text{Maxwell B} \Rightarrow \left(1+\lambda_0 \frac{\partial}{\partial t}\right)\sigma_{ij} = -\eta_0 \frac{\partial \gamma_{ij}}{\partial t}$$

Integrating from –infinity to *t*:

$$\text{Maxwell A}' \Rightarrow \sigma^{ij} = -\int_{-\infty}^{t} \frac{\eta_0}{\lambda_0^2} e^{-\frac{(t-t')}{\lambda_0}} \left\{\gamma^{ij}(t') - \gamma^{ij}(t)\right\} dt'$$

$$\text{Maxwell B}' \Rightarrow \sigma_{ij} = \int_{-\infty}^{t} \frac{\eta_0}{\lambda_0^2} e^{-\frac{(t-t')}{\lambda_0}} \left\{\gamma_{ij}(t') - \gamma_{ij}(t)\right\} dt'$$

In fixed coordinates (correspondence at *t'=t*):

$$\text{Maxwell A''} \Rightarrow \left(1+\lambda_0 \frac{\delta}{\delta t}\right)\sigma^{ij} = -\eta_0 \dot{\gamma}^{ij}$$

$$\text{Maxwell B''} \Rightarrow \left(1+\lambda_0 \frac{\delta}{\delta t}\right)\sigma_{ij} = -\eta_0 \dot{\gamma}_{ij}$$

$$\text{Maxwell A'''} \Rightarrow \sigma^{ij} = -\int_{-\infty}^{t} \frac{\eta_0}{\lambda_0^2} e^{-\frac{(t-t')}{\lambda_0}} \left\{C^{-1ij}(t') - g^{ij}(t)\right\} dt'$$

$$= -\int_{-\infty}^{t} \frac{\eta_0}{\lambda_0^2} e^{-\frac{(t-t')}{\lambda_0}} \Gamma^{-1ij}(t') dt'$$

where $\underline{\underline{\Gamma}}^{-1} = \underline{\underline{C}}^{-1} - \underline{\underline{\delta}}$ (relative strain Finger tensor)

Also:

$$\text{Maxwell B'''} \Rightarrow \sigma_{ij} = \int_{-\infty}^{t} \frac{\eta_0}{\lambda_0^2} e^{-\frac{(t-t')}{\lambda_0}} \left\{ C_{ij}(t') - g_{ij}(t) \right\} dt'$$

$$= \int_{-\infty}^{t} \frac{\eta_0}{\lambda_0^2} e^{-\frac{(t-t')}{\lambda_0}} \Gamma_{ij}(t') dt'$$

where $\underline{\underline{\Gamma}} = \underline{\underline{C}} - \underline{\underline{\delta}}$ (relative strain Cauchy-Green tensor)

Example 6.2-1 Steady Simple Shear functions for Convected Maxwell Models

The velocity gradient tensor components in Cartesian coordinates:

$$v^j_{,i} = v_{j,i} = \dot{\gamma}\begin{pmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

$$v^i_{,j} = v_{i,j} = \dot{\gamma}\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

Upper convected derivative

$$\frac{\delta}{\delta t}\sigma^{ij} = \underbrace{\frac{\partial}{\partial t}\sigma^{ij}}_{0} + \underbrace{v^k \sigma^{ij}_{,k}}_{0} - v^i_{,k}\sigma^{kj} - v^j_{,k}\sigma^{ik}$$

$$\frac{\delta}{\delta t}\sigma^{ij} = -v^{i}{}_{,k}\sigma^{kj} - v^{j}{}_{,k}\sigma^{ik} = -v_{i,k}\sigma_{kj} - v_{j,k}\sigma_{kj}$$

$$\ldots\ldots = \dot{\gamma}\begin{pmatrix} 2\sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{22} & 0 & 0 \\ \sigma_{23} & 0 & 0 \end{pmatrix}$$

The upper-convected Maxwell model becomes:

$$\begin{pmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{pmatrix} - \lambda_0\,\dot{\gamma}\begin{pmatrix} 2\sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{22} & 0 & 0 \\ \sigma_{23} & 0 & 0 \end{pmatrix} = -\eta_0\begin{pmatrix} 0 & \dot{\gamma} & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

$$\begin{pmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{pmatrix} - \lambda_0 \dot{\gamma} \begin{pmatrix} 2\sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{22} & 0 & 0 \\ \sigma_{23} & 0 & 0 \end{pmatrix} = -\eta_0 \begin{pmatrix} 0 & \dot{\gamma} & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

This leads to 9 equations:

$$\sigma_{11} - 2\lambda_0 \dot{\gamma} \sigma_{21} = 0$$

$$\sigma_{21} - \lambda_0 \dot{\gamma} \sigma_{22} = -\eta_0 \dot{\gamma}$$

$$\sigma_{22} = 0$$

$$\sigma_{23} = \sigma_{32} = 0$$

$$\sigma_{31} - \lambda_0 \dot{\gamma} \sigma_{23} = 0$$

$$\sigma_{33} = 0$$

$\Rightarrow$

$$\sigma_{21} = -\eta_0 \dot{\gamma}$$

$$\sigma_{22} = 0$$

$$\sigma_{11} = -2\lambda_0 \eta_0 \dot{\gamma}^2$$

$$\sigma_{21} = -\eta_0 \dot{\gamma}$$

$$\sigma_{22} = 0$$

$$\sigma_{11} = -2\lambda_0 \eta_0 \dot{\gamma}^2$$

$$\eta = \eta_0 \ \left(\text{a constant}\right)$$

$$\psi_1 = -\frac{\sigma_{11} - \sigma_{22}}{\dot{\gamma}^2} = 2\lambda_0 \eta_0 \ \left(\text{a constant}\right)$$

$$\psi_2 = -\frac{\sigma_{22} - \sigma_{33}}{\dot{\gamma}^2} = 0$$

For the lower-convected Maxwell model:

$$\frac{\delta}{\delta t}\sigma_{ij} = v^k{}_{,i}\sigma_{kj} + v^k{}_{,j}\sigma_{kj} \;\; = v_{k,i}\sigma_{kj} + v_{k,j}\sigma_{ik}$$

$$\ldots\ldots = \dot{\gamma}\begin{pmatrix} 0 & \sigma_{11} & 0 \\ \sigma_{11} & 2\sigma_{12} & \sigma_{13} \\ 0 & \sigma_{13} & 0 \end{pmatrix}$$

$$\eta = \eta_0 \;\; (\text{a constant})$$

$$\psi_1 = -\frac{\sigma_{11} - \sigma_{22}}{\dot{\gamma}^2} = 2\lambda_0\eta_0 \;\; (\text{a constant})$$

$$\psi_2 = -\frac{\sigma_{22} - \sigma_{33}}{\dot{\gamma}^2} = -2\lambda_0\eta_0 = -\psi_1 \;\; (\text{unrealistic!})$$

Example 6.2-2 Uniaxial Elongational Viscosity for Upper Convected Maxwell Model

$$\underline{\underline{\dot{\gamma}}} = \dot{\varepsilon}\begin{pmatrix} 2 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

$$\nabla \underline{v} = \nabla \underline{v}^{+} = \dot{\varepsilon}\begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & -\frac{1}{2} \end{pmatrix}$$

$$\frac{\delta}{\delta t}\sigma^{ij} = -v^{i}{}_{,k}\sigma^{kj} - v^{j}{}_{,k}\sigma^{ik} = -2v_{i,k}\sigma_{kj} = -2\dot{\varepsilon}\begin{pmatrix} \sigma_{11} & 0 & 0 \\ 0 & -\frac{\sigma_{22}}{2} & 0 \\ 0 & 0 & -\frac{\sigma_{33}}{2} \end{pmatrix}$$

The upper-convected Maxwell model reduces to:

$$\begin{pmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{pmatrix} - \lambda_0 \dot{\varepsilon} \begin{pmatrix} 2\sigma_{11} & 0 & 0 \\ 0 & -\sigma_{22} & 0 \\ 0 & 0 & -\sigma_{33} \end{pmatrix} = -\eta_0 \begin{pmatrix} 2\dot{\varepsilon} & 0 & 0 \\ 0 & -\dot{\varepsilon} & 0 \\ 0 & 0 & -\dot{\varepsilon} \end{pmatrix}$$

$$\sigma_{11} - 2\lambda_0 \dot{\varepsilon} \sigma_{11} = -\eta_0 \dot{\varepsilon}$$

$$\sigma_{22} + \lambda_0 \dot{\varepsilon} \sigma_{22} = \eta_0 \dot{\varepsilon}$$

$$\sigma_{33} + \lambda_0 \dot{\varepsilon} \sigma_{33} = \eta_0 \dot{\varepsilon}$$

$$\sigma_{12} = \sigma_{21} = \sigma_{23} = \sigma_{32} = \sigma_{13} = \sigma_{31} = 0$$

$$\sigma_{11} - 2\lambda_0 \dot{\varepsilon} \sigma_{11} = -\eta_0 \dot{\varepsilon}$$

$$\sigma_{22} + \lambda_0 \dot{\varepsilon} \sigma_{22} = \eta_0 \dot{\varepsilon}$$

$$\sigma_{33} + \lambda_0 \dot{\varepsilon} \sigma_{33} = \eta_0 \dot{\varepsilon}$$

$$\sigma_{12} = \sigma_{21} = \sigma_{23} = \sigma_{32} = \sigma_{13} = \sigma_{31} = 0$$

$$\eta_E = -\frac{\sigma_{11} - \sigma_{22}}{\dot{\varepsilon}} = \eta_0 \left[\frac{2}{1 - 2\lambda_0 \dot{\varepsilon}} + \frac{1}{1 + \lambda_0 \dot{\varepsilon}} \right]$$

$$\ldots = \frac{3\eta_0}{\left(1 - 2\lambda_0 \dot{\varepsilon}\right)\left(1 + \lambda_0 \dot{\varepsilon}\right)}$$

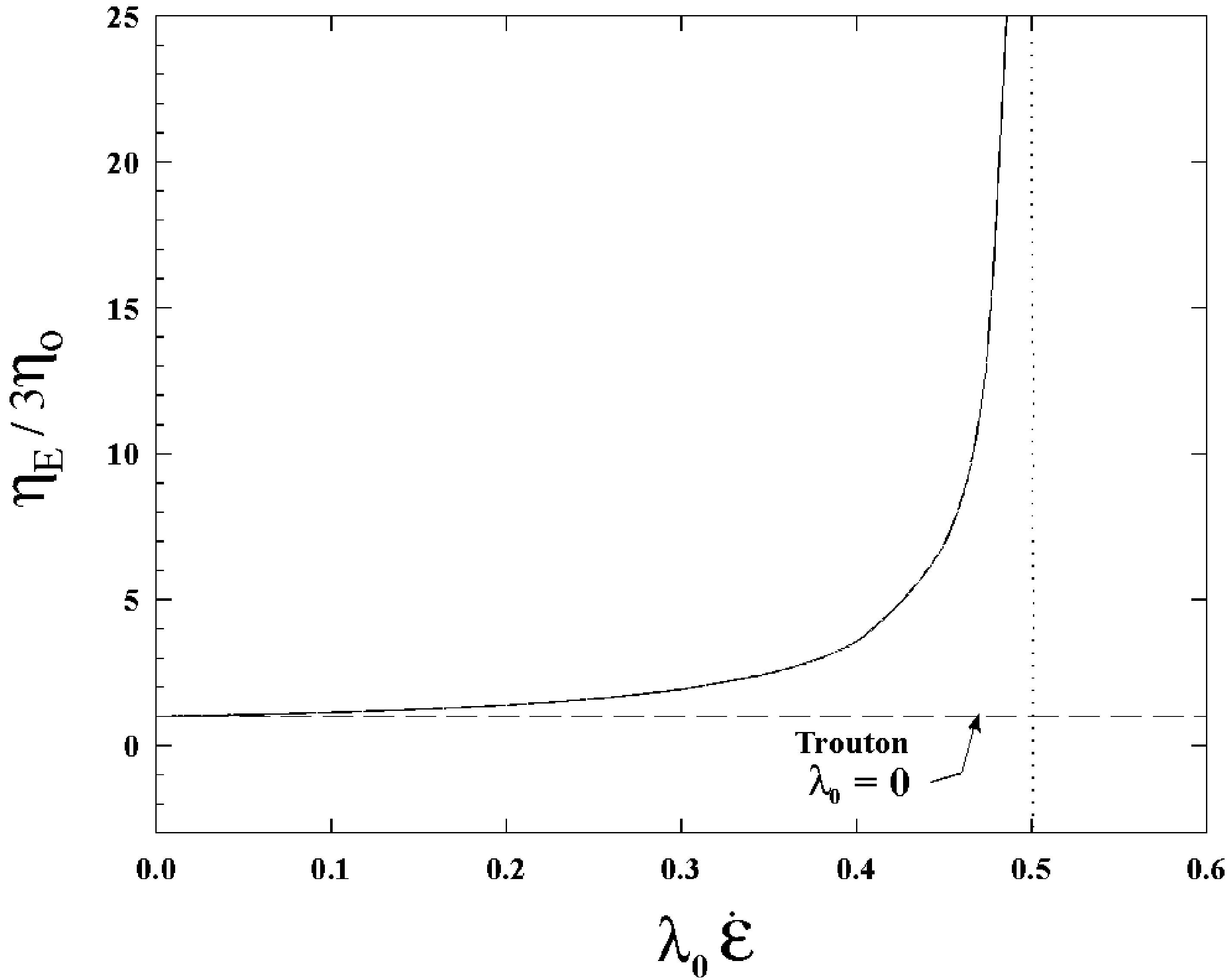

Fig.6.2-1 Steady uniaxial elongational viscosity for an upper-convected Maxwell fluid

6.3-2 Oldroyd-B Model

Oldroyd has proposed quite a few differential constitutive equations, the most useful being the Oldroyd-B (three constant) model:

$$\underline{\underline{\sigma}} + \lambda_1 \frac{\mathscr{D}\underline{\underline{\sigma}}}{\mathscr{D}t} - \frac{1}{2}\lambda_1 \left\{ \underline{\underline{\sigma}} \cdot \underline{\underline{\dot{\gamma}}} + \underline{\underline{\dot{\gamma}}} \cdot \underline{\underline{\sigma}} \right\} = -\eta_0 \left[\underline{\underline{\dot{\gamma}}} + \lambda_2 \frac{\mathscr{D}\underline{\underline{\dot{\gamma}}}}{\mathscr{D}t} - \lambda_2 \underline{\underline{\dot{\gamma}}}^2 \right]$$

For small amplitude oscillatory shear , this equation reduces to the Jeffrey model of section 5.2-3:

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

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

Reasonable predictions for Boger fluids!

6.3-3 White-Metzner Model

$$\left(1+\lambda(II_{\dot{\gamma}})\frac{\delta}{\delta t}\right)\sigma^{ij}=-\eta(II_{\dot{\gamma}})\dot{\gamma}^{ij}$$

where $II_{\dot{\gamma}}$ is the second invariant of the rate-of-strain tensor:

$$II_{\dot{\gamma}}=\underline{\underline{\dot{\gamma}}}:\underline{\underline{\dot{\gamma}}}=tr\,\underline{\underline{\dot{\gamma}}}^2$$

Example 6.3-1 Steady-State Properties of a White-Metzner Fluid

$$\lambda(II_{\dot{\gamma}})=\frac{\lambda_0}{1+a\lambda_0\sqrt{\frac{1}{2}II_{\dot{\gamma}}}}$$

$$\eta(II_{\dot{\gamma}})=G_0\lambda(II_{\dot{\gamma}})$$

For simple shear:

$$II_{\dot{\gamma}} = 2\dot{\gamma}^2 \Rightarrow \lambda(II_{\dot{\gamma}}) = \frac{\lambda_0}{1 + a\lambda_0 |\dot{\gamma}|}$$

$$\eta(\dot{\gamma}) = G_0 \frac{\lambda_0}{1 + a\lambda_0 |\dot{\gamma}|} = \frac{\eta_0}{1 + a\lambda_0 |\dot{\gamma}|}$$ (shear-thinning behavior with a power-law slope of -1). Also:

$$\psi_1 = \frac{2G_0\lambda_0^2}{\left(1 + a\lambda_0 |\dot{\gamma}|\right)^2} = \frac{\psi_{10}}{\left(1 + a\lambda_0 |\dot{\gamma}|\right)^2}$$

$$\psi_2 = 0$$

Example 6.3-2 Spinning of a Viscoelastic Fluid

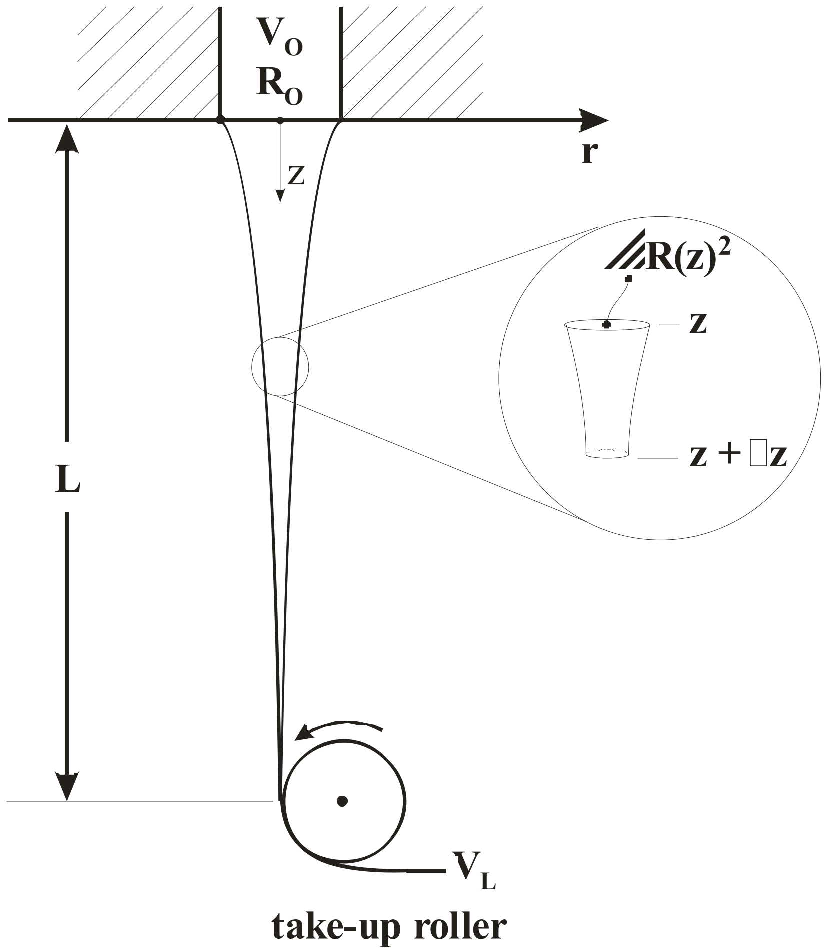

Fig.6.3-1 Fiber spinning

Mass balance:

$$\frac{v_z}{v_0} = \left(\frac{R_0}{R_z}\right)^2$$

Continuity eq.:

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r v_r\right) + \frac{dv_z}{dz} = 0$$

(assuming v_z is not a function of r)

Integrating :

$$v_r = -\frac{r}{2}\frac{dv_z}{dz} = 0$$

The velocity gradient tensor:

$$\nabla \underline{v} = \begin{pmatrix} -\frac{1}{2}\frac{dv_z}{dz} & 0 & 0 \\ 0 & -\frac{1}{2}\frac{dv_z}{dz} & 0 \\ -\frac{1}{2}r\frac{d^2v_z}{dz^2} & 0 & \frac{dv_z}{dz} \end{pmatrix}$$

The term $r\frac{d^2v_z}{dz^2}$ is of order of $\frac{v_L R_0}{L^2}$ (negligible for small $\frac{R_0}{L}$)

Hence, only two normal stress components have to be considered. The White-Metzner model yields:

$$\sigma_{rr} + \frac{\eta(\bar{\dot{\gamma}})}{G_0}\left[v_z \frac{d\sigma_{rr}}{dz} + \frac{dv_z}{dz}\sigma_{rr} \right] = \eta(\bar{\dot{\gamma}})\frac{dv_z}{dz} \qquad (6.3\text{-}18)$$

$$\sigma_{zz} + \frac{\eta(\bar{\dot{\gamma}})}{G_0}\left[v_z \frac{d\sigma_{zz}}{dz} - 2\frac{dv_z}{dz}\sigma_{zz} \right] = -2\eta(\bar{\dot{\gamma}})\frac{dv_z}{dz} \qquad (6.3\text{-}19)$$

where $\bar{\dot{\gamma}} = \sqrt{II_{\dot{\gamma}}/2} = \sqrt{3}dv_z/dz$ and $\eta(\bar{\dot{\gamma}}) = m\left|\bar{\dot{\gamma}}\right|^{n-1}$

A momentum balance on a control volume $\pi R^2(z)\Delta z$, neglecting gravitational, capillary and drag forces yields:

$$\left(\rho v_z v_z + P + \sigma_{zz}\right)\pi R^2\Big|_z - \left(\rho v_z v_z + P + \sigma_{zz}\right)\pi R^2\Big|_{z+\Delta z} = 0$$

Dividing by Δz and limit $\Delta z \longrightarrow 0$:

$$2\rho v_z v'_z + \frac{d}{dz}\left(P + \sigma_{zz}\right) = -\frac{2}{R}R'\left(\rho v_z v_z + P + \sigma_{zz}\right)$$

$$2\rho v_z v'_z + \frac{d}{dz}\left(P + \sigma_{zz}\right) = -\frac{2}{R} R'\left(\rho v_z v_z + P + \sigma_{zz}\right)$$

But: $$\frac{v_z}{v_0} = \left(\frac{R_0}{R_z}\right)^2 \quad \Rightarrow \quad \frac{dv_z}{dz} = v_z' = -\frac{2v_z}{R} R'$$

Combining:

$$\rho v_z v_z' + \frac{d}{dz}\left(P + \sigma_{zz}\right) = \frac{v_z'}{v_z}\left(P + \sigma_{zz}\right)$$

The pressure can be eliminated by noting that the radial normal component is constant, hence equal ot the atmospheric pressure:

$$P + \sigma_{rr} = \text{constant} = P_a = 0 \text{ (arbitrary)}$$

$$\rho v_z v_z' + \frac{d}{dz}\left(P + \sigma_{zz}\right) = \frac{v_z'}{v_z}\left(\sigma_{zz} - \sigma_{rr}\right) \qquad (6.3\text{-}25)$$

Eqs. 6.3-18, 19 and 25 have to be solved with the following boundary conditions:

$$\text{B.C.1: at } z = 0,\ v_z = v_0$$

$$\text{B.C.2: at } z = 0,\ \sigma_{zz} - \sigma_{rr} = -\frac{F}{\pi R_0^2}$$

$$\text{B.C.3: at } z = L,\ v_z = v_L$$

Dimensionless variables:

$$\varsigma = \frac{z}{L}, \ldots \phi = \frac{v_z}{v_0}, \ldots S_{ij} = \sigma_{ij} \frac{\pi R_0^2}{F}$$

The three equations become:

$$S_{rr} + De\phi'^{n-1}\left[\phi \frac{dS_{rr}}{d\varsigma} + \phi' S_{rr}\right] = N\phi'^{n}$$

$$S_{zz} + De\phi'^{n-1}\left[\phi \frac{dS_{zz}}{d\varsigma} - 2\phi' S_{zz}\right] = -2N\phi'^{n}$$

$$\frac{d}{d\varsigma}\left(S_{zz} - S_{rr}\right) = \frac{1}{\phi}\phi'\left(S_{zz} - S_{rr}\right)$$

The Deborah number is:

$$De = \frac{\lambda_{eff} v_0}{L} = 3^{(n-1)/2}\left(\frac{m}{G_0}\right)\left(\frac{v_0}{L}\right)^n$$

$$N = \frac{m\left(\sqrt{3}\,\frac{v_0}{L}\right)^{n-1}\left(\frac{v_0}{L}\right)}{F / \pi R_0^2}$$ …(ratio of viscous force over total force)

B.C.1: at $\varsigma = 0,\ \phi = 1$

B.C.2: at $\varsigma = 0,\ S_{zz} - S_{rr} = -1$

B.C.3: at $\varsigma = 1,\ \phi = \frac{v_L}{v_0} = DDR$ (draw-down ratio)

$$\frac{d}{d\varsigma}\left(S_{zz} - S_{rr}\right) = \frac{1}{\phi}\phi'\left(S_{zz} - S_{rr}\right) = \frac{1}{\phi}\frac{d\phi}{d\varsigma}\left(S_{zz} - S_{rr}\right)$$

Integrating: $S_{zz} - S_{rr} = C\phi = -\phi$ (using B.C. 2)

Combining:

$$\phi + \left(De\phi - 3N\right)\phi'^{n} - 2De^{2}\phi\phi'^{2n} - nDe\phi^{2}\phi''\phi'^{n-2} = 0$$

This second order non-linear equation has to be solved numerically, except for the two limiting cases:

a) Purely viscous fluids, *De* =0

$$\phi + \left(-3N\right)\phi'^{n} = 0$$

$$\Rightarrow \phi = \left[1 + (3N)^{-1/n}\left(\frac{n-1}{n}\right)\varsigma\right]^{\frac{n}{n-1}}$$

where *N* is obtained from B.C. 3.

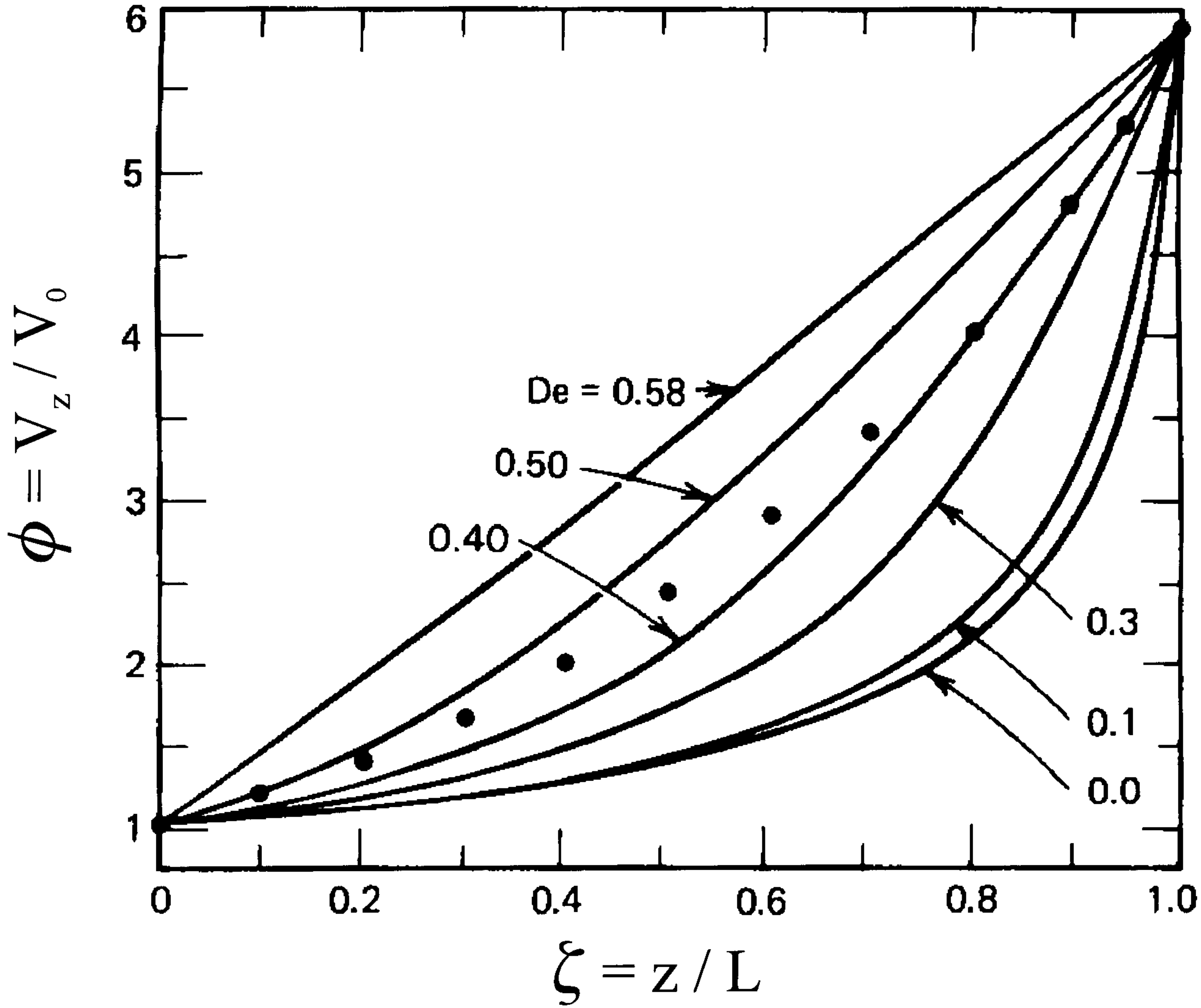

Fig. 6.3-2 Velocity profile in fiber spinning of a White-Metzner fluid compared to experimental data for a polystyrene melt at 170 °C, *n*=1/3, *DDR* = 5.85 (Fisher and Denn, 1976).

b) For large *De* numbers:

$$\frac{\phi}{De}+\left(\phi-\frac{3N}{De}\right)\phi'^{n}-2De\,\phi\phi'^{2n}-n\phi^{2}\phi''\phi'^{n-2}=0$$

$$\approx\phi\phi'^{n}-2De\,\phi\phi'^{2n}-n\phi^{2}\phi''\phi'^{n-2}=0$$

$$\Rightarrow 1-2De\phi'^{n}-n\phi\phi''\phi'^{-2}=0$$

The velocity profile becomes linear:

$$\phi=1+\frac{\varsigma}{De^{1/n}}$$

This result was verified numerically by Fisher and Denn (1976) for *De* = 0.58.

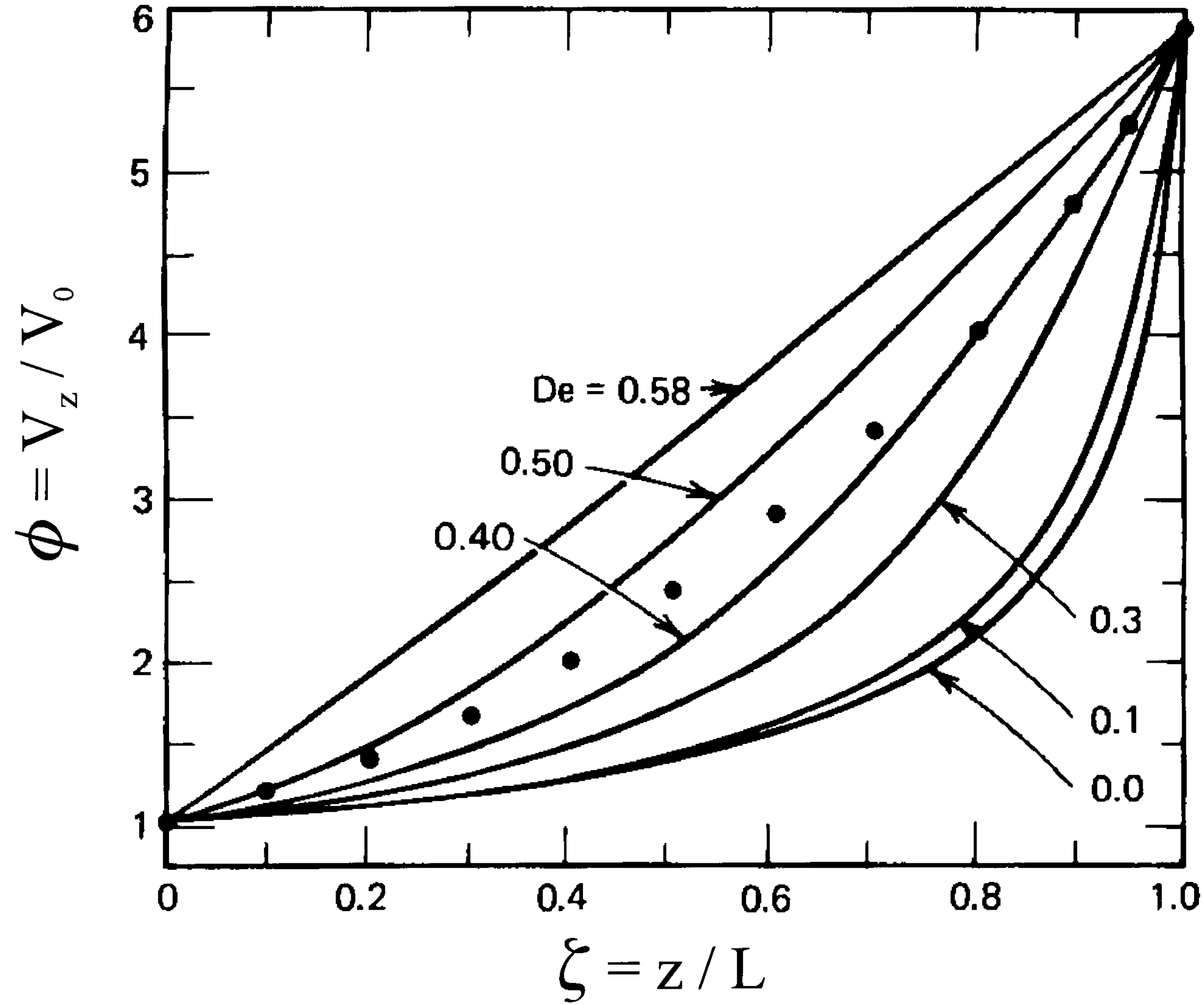

Fig. 6.3-2 Velocity profile in fiber spinning of a White-Metzner fluid compared to experimental data for a polystyrene melt at 170 °C, *n*=1/3, *DDR* = 5.85 (Fisher and Denn, 1976).

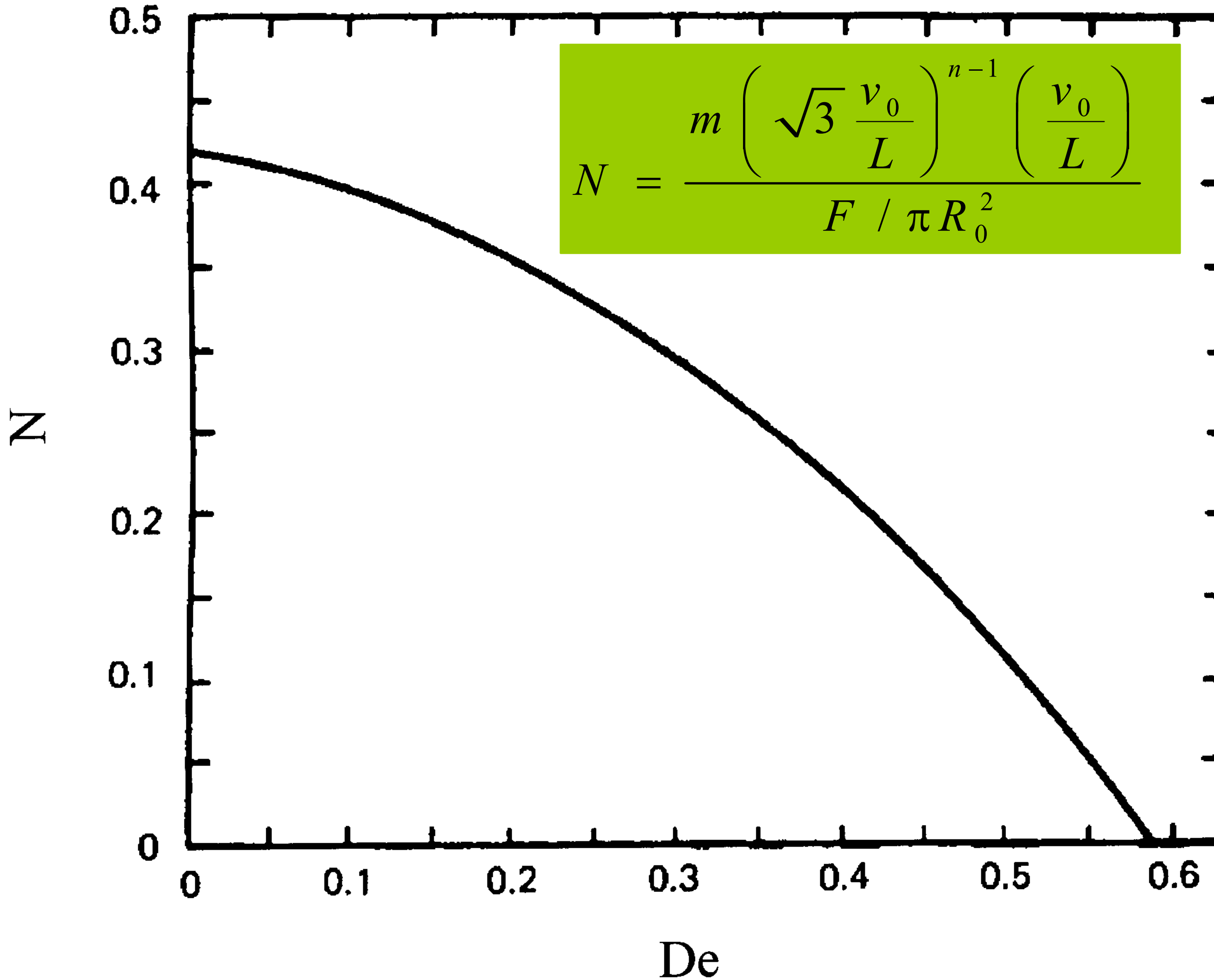

Fig. 6.3-3 Force ratio in fiber spinning of a White-Metzner fluid calculated for a polystyrene melt at 170 °C, n=1/3, DDR = 5.85, S_{zz} =-1 by Fisher and Denn (1976).

6.3-5 The Phan-Thien-Tanner Model

$$\sigma^{ij} = \sum_p \sigma^{ij}_{(p)}$$

$$\lambda_p \frac{\bar{\delta}}{\delta t}\sigma^{ij}_{(p)} + \sigma^{ij}_{(p)}\left(1 + \frac{a}{G_p} I_{\sigma(p)}\right) = -\frac{G_p \lambda_p}{1-\xi}\dot{\gamma}^{ij}$$

$$\text{where } \frac{\bar{\delta}}{\delta t}\underline{\underline{\sigma}} = \frac{D}{Dt}\underline{\underline{\sigma}} - \underline{\underline{L}}\cdot\underline{\underline{\sigma}} - \underline{\underline{\sigma}}\cdot\underline{\underline{L}}$$

$$\text{and } \underline{\underline{L}} = \nabla \underline{v} - \frac{\xi}{2}\underline{\underline{\dot{\gamma}}} \quad \text{(Gordon-Schowalter derivative)}$$

N.B. ξ is a slip parameter. For ξ = 0, affine deformation is predicted!

Predictions:

$$\frac{\psi_1}{\psi_2} = -\frac{\xi}{2} \Rightarrow \text{Secondary normal stress differences}$$

……………………related to the slip parameter

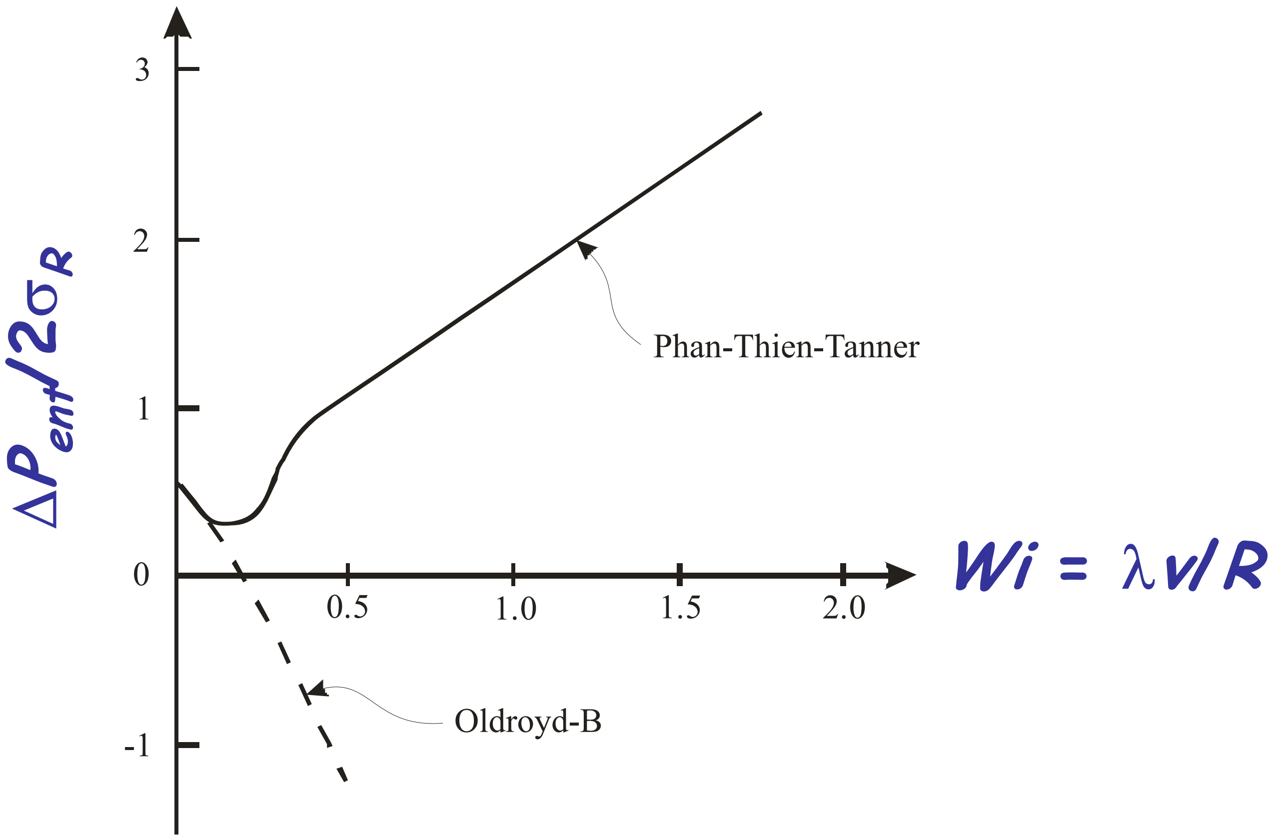

Fig. 6.3-6 Comparison of predictions for excess pressure drop at the entrance of a capillary. A single mode PTT model has been used with a =0.015 and $\xi = 0.1$ (Tanner, 1985)

6.4 Integral Constitutive Equations

6.4-1 The Lodge Model

From network theory, Lodge (1968) proposed the following equation:

$$\sigma^{ij} = -\int_{-\infty}^{t} m(t-t')\Gamma^{-1ij}(t')dt'$$

where $\underline{\underline{\Gamma}}^{-1} = \underline{\underline{C}}^{-1} - \underline{\underline{\delta}}$ (relative strain Finger tensor)

$$m(t-t') = \frac{\eta_0}{\lambda_0^2} e^{-\frac{(t-t')}{\lambda_0}} \quad \text{(memory function for a single mode)}$$

$$m(t-t') = \sum_{p=1}^{M} \frac{\eta_p}{\lambda_p^2} e^{-\frac{(t-t')}{\lambda_p}} \quad \text{(memory function for } M \text{ modes)}$$

Example 6.4-1 Elongational Stress Growth for a Lodge Rubber-Like Liquid.

For a start-up at constant elongational rate at t = 0, we have the following situations:

For $0 \le t' \le t$

$$\underline{\underline{C}}^{-1ij}(t') = \begin{pmatrix} \exp\left\{2\dot{\varepsilon}_\infty (t - t')\right\} & 0 & 0 \\ 0 & \exp\left\{\dot{\varepsilon}_\infty (t' - t)\right\} & 0 \\ 0 & 0 & \exp\left\{\dot{\varepsilon}_\infty (t' - t)\right\} \end{pmatrix}$$

For $t' \le 0 \le t$

$$\underline{\underline{C}}^{-1ij}(t') = \begin{pmatrix} \exp\left\{2\dot{\varepsilon}_\infty t\right\} & 0 & 0 \\ 0 & \exp\left\{-\dot{\varepsilon}_\infty t\right\} & 0 \\ 0 & 0 & \exp\left\{-\dot{\varepsilon}_\infty t\right\} \end{pmatrix}$$

For a multiple mode model:

$$\sigma_{11}(t) = -\sum_{p=1}^{M} \frac{\eta_p}{\lambda_p^2} \int_{-\infty}^{0} \exp\left\{-\frac{(t-t')}{\lambda_p}\right\} \left[\exp(2\dot{\varepsilon}_\infty t) - 1\right] dt'$$

$$\ldots\ldots\ldots \quad -\sum_{p=1}^{M} \frac{\eta_p}{\lambda_p^2} \int_{0}^{t} \exp\left\{-\frac{(t-t')}{\lambda_p}\right\} \left[\exp\left(2\dot{\varepsilon}_\infty (t-t')\right) - 1\right] dt'$$

$$\sigma_{22}(t) = \sigma_{33}(t) = -\sum_{p=1}^{M} \frac{\eta_p}{\lambda_p^2} \int_{-\infty}^{0} \exp\left\{-\frac{(t-t')}{\lambda_p}\right\} \left[\exp(-\dot{\varepsilon}_\infty t) - 1\right] dt'$$

$$\ldots\ldots\ldots \quad -\sum_{p=1}^{M} \frac{\eta_p}{\lambda_p^2} \int_{0}^{t} \exp\left\{-\frac{(t-t')}{\lambda_p}\right\} \left[\exp\left(\dot{\varepsilon}_\infty (t'-t)\right) - 1\right] dt'$$

The elongational viscosity is then :

$$\eta_E^+ = -\frac{\sigma_{11}(t)-\sigma_{22}(t)}{\dot{\varepsilon}_\infty} = \frac{1}{\dot{\varepsilon}_\infty}\sum_{p=1}^{M}\frac{\eta_p}{\lambda_p}\left[\begin{array}{l}\exp\left\{-\frac{t}{\lambda_p}(1-2\dot{\varepsilon}_\infty\lambda_p)\right\} \\ -\exp\left\{-\frac{t}{\lambda_p}(1+\dot{\varepsilon}_\infty\lambda_p)\right\}\end{array}\right]$$

$$\cdots\cdots\cdots + \frac{1}{\dot{\varepsilon}_\infty}\sum_{p=1}^{M}\frac{\eta_p}{\lambda_p}\left[\begin{array}{l}\frac{1}{1-2\dot{\varepsilon}_\infty\lambda_p}\exp\left\{-\frac{t}{\lambda_p}(1-2\dot{\varepsilon}_\infty\lambda_p)\right\} \\ -\frac{1}{1+\dot{\varepsilon}_\infty\lambda_p}\exp\left\{-\frac{t}{\lambda_p}(1+\dot{\varepsilon}_\infty\lambda_p)\right\}\end{array}\right]$$

The steady elongational viscosity is given by:

$$\eta_E = 3\sum_{p=1}^{M}\frac{\eta_p}{\left(1-2\dot{\varepsilon}_\infty\lambda_p\right)\left(1+\dot{\varepsilon}_\infty\lambda_p\right)}$$

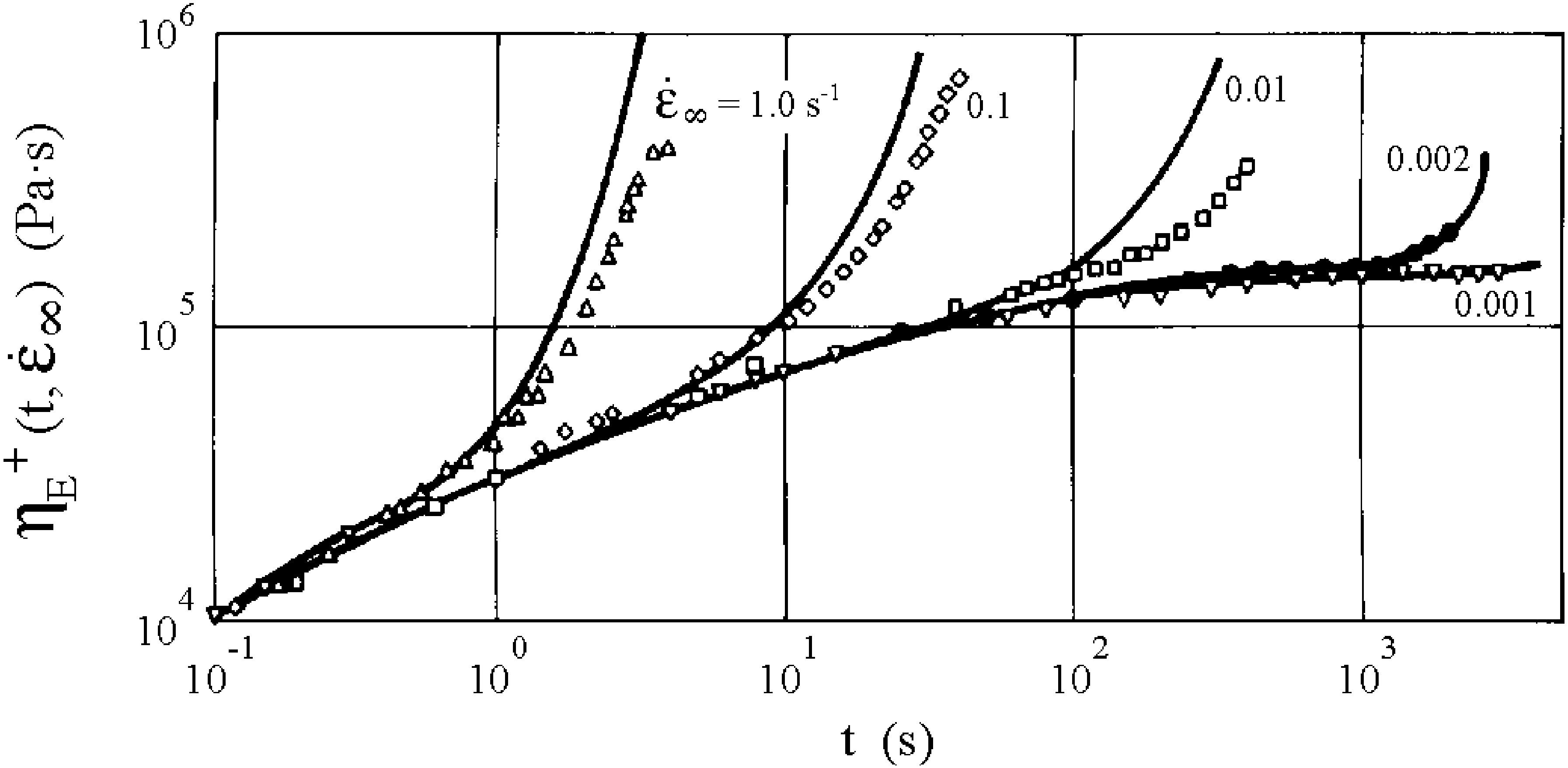

Fig. 6.4-1 Predictions of the Lodge model compared to the elongational stress growth data obtained by Meissner (1971) for a LDPE (Chang and Lodge, 1972). 5 modes were used to fit the data.

6.4-3 The K-BKZ Model

The Kaye-Berstein-Kearsley-Zapas model is an extension of the Lodge rubber-like elastic model:

$$\sigma^{ij} = -\int_{-\infty}^{t} m_1(t-t', I_{C^{-1}}, II_{C^{-1}})\Gamma^{-1ij}(t')$$

$$\cdots\cdots\cdots\cdots + m_2(t-t', I_{C^{-1}}, II_{C^{-1}})\Gamma^{ij}(t')dt'$$

where $m_1 = 2\dfrac{\partial u}{\partial I_{C^{-1}}}$

$$\cdots\cdots\cdots m_2 = -2\frac{\partial u}{\partial II_{C^{-1}}}$$

(memory functions dependent on the invariants of strain)

Special case of the Wagner model

Wagner (1976) assumed that the time and strain effects could be separable, hence the following simplified K-BKZ model has been proposed:

$$\sigma^{ij} = -\int_{-\infty}^{t} m_1(t-t')h(I_{C^{-1}}, II_{C^{-1}})\Gamma^{-1ij}(t')dt'$$

$$\text{where } h(I_{C^{-1}}, II_{C^{-1}}) = h(\gamma) = \exp\left\{-a\sqrt{\gamma^2}\right\}$$

……………………………………(in simple shear)

The damping function $h(\gamma)$ can be obtained from relaxation experiments such as those of Figure 6.4-2.

$$G(t) = -\frac{\sigma_{yx}(t)}{\gamma_0}$$

$$G_N(t) = -\frac{\sigma_{xx}(t) - \sigma_{yy}(t)}{\gamma_0^2}$$

The Lodge-Meissner relation:

$$G(t) = G_N(t)$$

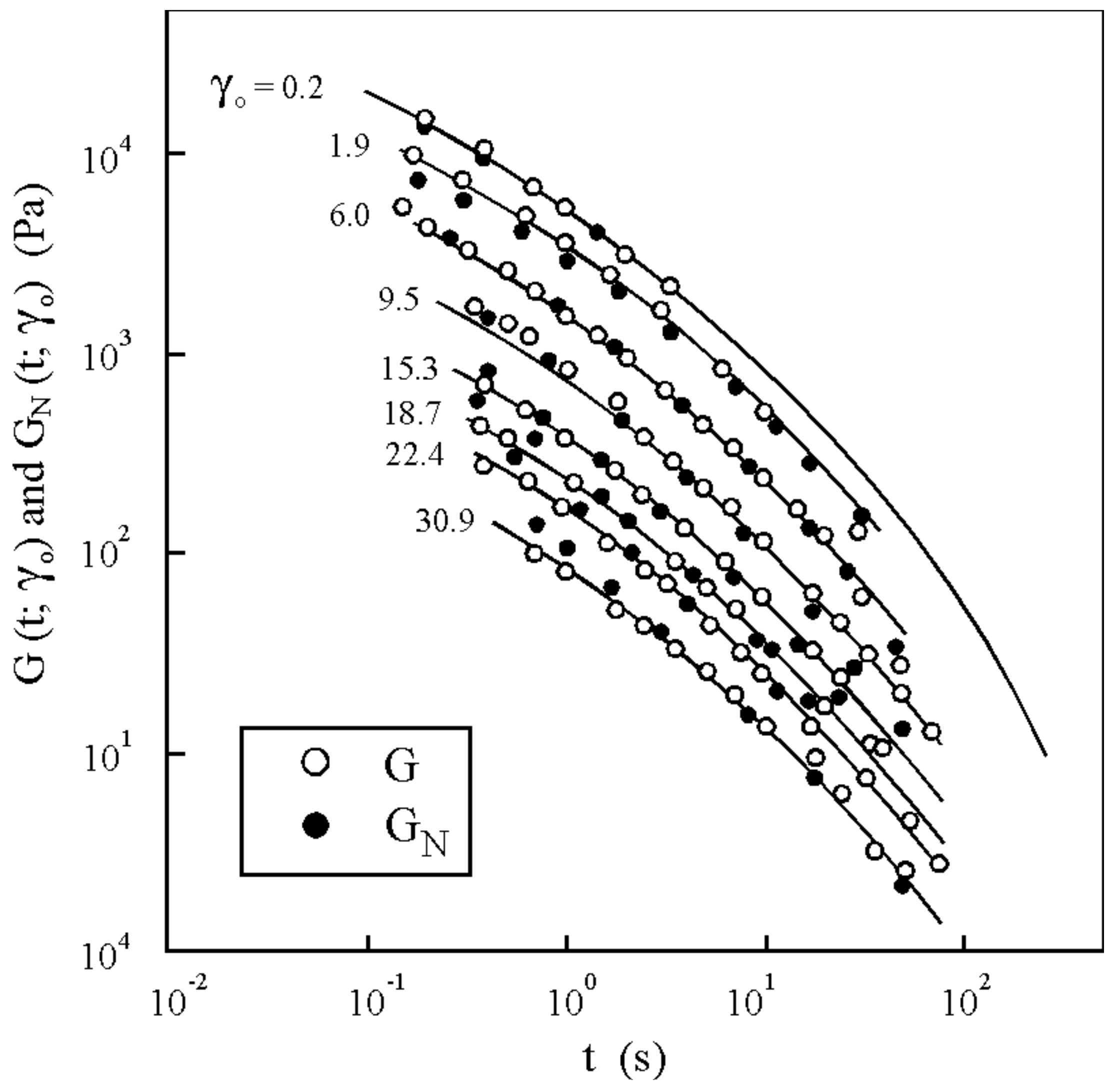

Fig. 6.4-2 Shear and normal stress relaxation moduli for a LDPE melt (data from Larson, 1988).