Lecture Notes for *CBE 5775 Rheology*

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CHAPTER 1

Elastic Solid

Lecture 1 **Date:** <YYYY-MM-DD>

Topic: Vector and tensor algebra; stress tensor; deformation tensor; Neo-Hookean solid; general elastic slid; equation of motion **Scribe:** Yang Han

1.1 Vector and Tensor Algebra

1.1.1 Vector in Rectangular Coordinates

$$\mathbf{v} = \mathbf{v}_x + \mathbf{v}_y + \mathbf{v}_z = v_x\hat{\mathbf{e}}_x + v_y\hat{\mathbf{e}}_y + v_z\hat{\mathbf{e}}_z = \sum_{i=1}^{3} v_i\hat{\mathbf{e}}_i \tag{1.1}$$

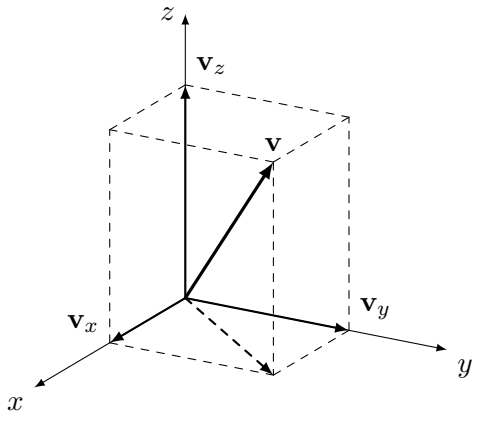


Figure 1.1: A vector in rectangular coordinates.

Here, $\hat{\mathbf{e}}_i$ are the base, unit vectors. A vector is called a first-order tensor. A scalar is a zero-order

tensor.

1.1.2 Tensor

A tensor is normally referred to as a second-order tensor:

$$\boldsymbol{\tau} = \sum_i \sum_j \tau_{ij}\, \hat{\mathbf{e}}_i \hat{\mathbf{e}}_j = \begin{bmatrix} \tau_{11} & \tau_{12} & \tau_{13} \\ \tau_{21} & \tau_{22} & \tau_{23} \\ \tau_{31} & \tau_{32} & \tau_{33} \end{bmatrix} \tag{1.2}$$

The transpose of the tensor is:

$$\boldsymbol{\tau}^T = \sum_i \sum_j \tau_{ji}\, \hat{\mathbf{e}}_i \hat{\mathbf{e}}_j = \begin{bmatrix} \tau_{11} & \tau_{21} & \tau_{31} \\ \tau_{12} & \tau_{22} & \tau_{32} \\ \tau_{13} & \tau_{23} & \tau_{33} \end{bmatrix} \tag{1.3}$$

If $\tau_{ij} = \tau_{ji}$, i.e., $\boldsymbol{\tau} = \boldsymbol{\tau}^T$, $\boldsymbol{\tau}$ is said to be symmetric. If $\tau_{ij} = \tau_{ji}$, $\boldsymbol{\tau}$ is antisymmetric.

$$\boldsymbol{\tau} = \frac{1}{2}(\boldsymbol{\tau} + \boldsymbol{\tau}^T) + \frac{1}{2}(\boldsymbol{\tau} - \boldsymbol{\tau}^T) = \frac{1}{2}\sum_i \sum_j (\tau_{ij} + \tau_{ji})\, \hat{\mathbf{e}}_i \hat{\mathbf{e}}_j + \frac{1}{2}\sum_i \sum_j (\tau_{ij} - \tau_{ji})\, \hat{\mathbf{e}}_i \hat{\mathbf{e}}_j \tag{1.4}$$

$$\boldsymbol{\tau} + \boldsymbol{\tau}^T = \begin{bmatrix} 2\tau_{11} & \tau_{12} + \tau_{21} & \tau_{13} + \tau_{31} \\ \tau_{21} + \tau_{12} & 2\tau_{22} & \tau_{23} + \tau_{32} \\ \tau_{31} + \tau_{13} & \tau_{32} + \tau_{23} & 2\tau_{33} \end{bmatrix} \tag{1.5}$$

This is a symmetric tensor.

$$\boldsymbol{\tau} - \boldsymbol{\tau}^T = \begin{bmatrix} 0 & \tau_{12} - \tau_{21} & \tau_{13} - \tau_{31} \\ \tau_{21} - \tau_{12} & 0 & \tau_{23} - \tau_{32} \\ \tau_{31} - \tau_{13} & \tau_{32} - \tau_{23} & 0 \end{bmatrix} \tag{1.6}$$

This is an antisymmetric tensor.

If $\boldsymbol{\tau}$ is symmetric, $\mathbf{a} \cdot \boldsymbol{\tau} = \boldsymbol{\tau} \cdot \mathbf{a}$. This is called commutative property:

$$\mathbf{a} \cdot \boldsymbol{\tau} = \sum_i \sum_j \sum_k a_k \tau_{ij}\, (\hat{\mathbf{e}}_k \cdot \hat{\mathbf{e}}_i \hat{\mathbf{e}}_j) = \sum_i \sum_j \sum_k a_k \tau_{ij}\, \delta_{ki} \hat{\mathbf{e}}_j = \sum_i \sum_j a_i \tau_{ij}\, \hat{\mathbf{e}}_j$$

$$\boldsymbol{\tau} \cdot \mathbf{a} = \sum_i \sum_j \sum_k \tau_{ij} a_k\, (\hat{\mathbf{e}}_i \hat{\mathbf{e}}_j \cdot \hat{\mathbf{e}}_k) = \sum_i \sum_j \sum_k a_k \tau_{ij}\, \delta_{jk} \hat{\mathbf{e}}_i = \sum_i \sum_j a_j \tau_{ij}\, \hat{\mathbf{e}}_i = \sum_i \sum_j a_i \tau_{ji}\, \hat{\mathbf{e}}_j$$

1.1.3 Operations

Addition (Subtraction) of Vectors

$$\mathbf{a}+\mathbf{b}=a_x\hat{\mathbf{e}}_x+a_y\hat{\mathbf{e}}_y+a_z\hat{\mathbf{e}}_z+b_x\hat{\mathbf{e}}_x+b_y\hat{\mathbf{e}}_y+b_z\hat{\mathbf{e}}_z=(a_x+b_x)\hat{\mathbf{e}}_x+(a_y+b_y)\hat{\mathbf{e}}_y+(a_z+b_z)\hat{\mathbf{e}}_z \quad (1.7)$$

Scalar (Dot) Product of Vectors

$$\mathbf{a}\cdot\mathbf{b}=ab\cos\theta_{ab} \quad (1.8)$$

Magnitude of a Vector

$$a=|\mathbf{a}|=(\mathbf{a}\cdot\mathbf{a})^{1/2}=(\sum_{i=1}a_i^2)^{1/2} \quad (1.9)$$

Products Involving Tensors

$$\hat{\mathbf{e}}_k\cdot\hat{\mathbf{e}}_i\hat{\mathbf{e}}_j=\delta_{ik}\hat{\mathbf{e}}_j \quad (1.10)$$

$$\hat{\mathbf{e}}_i\hat{\mathbf{e}}_j\cdot\hat{\mathbf{e}}_k=\delta_{jk}\hat{\mathbf{e}}_i \quad (1.11)$$

$$\hat{\mathbf{e}}_i\hat{\mathbf{e}}_j\cdot\hat{\mathbf{e}}_m\hat{\mathbf{e}}_n=\delta_{jm}\hat{\mathbf{e}}_i\hat{\mathbf{e}}_n \quad (1.12)$$

$$\hat{\mathbf{e}}_i\hat{\mathbf{e}}_j:\hat{\mathbf{e}}_m\hat{\mathbf{e}}_n=\delta_{jm}\delta_{in} \quad (1.13)$$

Here, the Kronecker delta is defined as

$$\delta_{ik}=\begin{cases}1 & \text{if } i=k\\ 0 & \text{if } i\neq k\end{cases} \quad (1.14)$$

Identity (Unit) Tensor

$$\mathbf{I}=\sum_i\sum_j I_{ij}\,\hat{\mathbf{e}}_i\hat{\mathbf{e}}_j=\sum_i I_{ij}\delta_{ij}\,\hat{\mathbf{e}}_i\hat{\mathbf{e}}_j=\sum_i I_{ii}\,\hat{\mathbf{e}}_i\hat{\mathbf{e}}_i=\begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix} \quad (1.15)$$

Obviously, $\mathbf{I}\cdot\mathbf{v}=\mathbf{v}\cdot\mathbf{I}=\mathbf{v}$ and $\mathbf{I}\cdot\boldsymbol{\tau}=\boldsymbol{\tau}\cdot\mathbf{I}=\boldsymbol{\tau}$.

Material or Substantial Derivative

$$\frac{\mathrm{D}}{\mathrm{D}t}=\frac{\partial}{\partial t}+\mathbf{v}\cdot\boldsymbol{\nabla}=\frac{\partial}{\partial t}+\sum_i v_i\frac{\partial}{\partial x_i} \quad (1.16)$$

Dyads

$$\boldsymbol{\nabla v} = \begin{bmatrix} \frac{\partial v_x}{\partial x} & \frac{\partial v_y}{\partial x} & \frac{\partial v_z}{\partial x} \\ \frac{\partial v_x}{\partial y} & \frac{\partial v_y}{\partial y} & \frac{\partial v_z}{\partial y} \\ \frac{\partial v_x}{\partial z} & \frac{\partial v_y}{\partial z} & \frac{\partial v_z}{\partial z} \end{bmatrix} \tag{1.17}$$

$$\mathbf{vv} = \sum_{i=1}^{3}\sum_{j=1}^{3} v_i \hat{\mathbf{e}}_i v_j \hat{\mathbf{e}}_j = \sum_{i=1}^{3}\sum_{j=1}^{3} v_i v_j \, \hat{\mathbf{e}}_i \hat{\mathbf{e}}_j = \begin{bmatrix} v_x v_x & v_x v_y & v_x v_z \\ v_y v_x & v_y v_y & v_y v_z \\ v_z v_x & v_z v_y & v_z v_z \end{bmatrix} \tag{1.18}$$

1.1.4 Coordinates

Cylindrical Coordinates

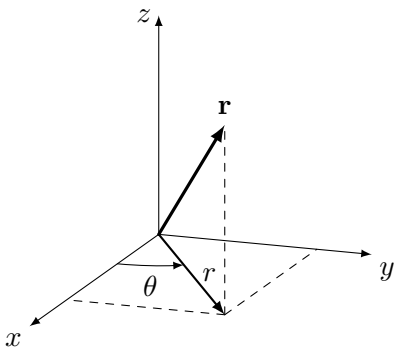


Figure 1.2: A vector in cylindrical coordinates.

$x = r\cos\theta,\ y = r\sin\theta,\ z = z$

$\mathbf{r} = r\cos\theta\,\hat{\mathbf{e}}_x + r\sin\theta\,\hat{\mathbf{e}}_y + z\,\hat{\mathbf{e}}_z$

$\mathrm{d}V = r\mathrm{d}r\mathrm{d}\theta\mathrm{d}z,\ \mathrm{d}S_r = r\mathrm{d}\theta\mathrm{d}z,\ \mathrm{d}S_\theta = \mathrm{d}r\mathrm{d}z,\ \mathrm{d}S_z = r\mathrm{d}r\mathrm{d}\theta$

Spherical Coordinates

$x = r\sin\theta\cos\phi,\ y = r\sin\theta\sin\phi,\ z = r\cos\theta$

$\mathbf{r} = r\sin\theta\cos\phi\,\hat{\mathbf{e}}_x + r\sin\theta\sin\phi\,\hat{\mathbf{e}}_y + r\cos\theta\,\hat{\mathbf{e}}_z$

$\mathrm{d}V = r^2\sin\theta\mathrm{d}r\mathrm{d}\theta\mathrm{d}\phi,\ \mathrm{d}S_r = r^2\sin\theta\mathrm{d}\theta\mathrm{d}\phi,\ \mathrm{d}S_\theta = r\sin\theta\mathrm{d}r\mathrm{d}\phi,\ \mathrm{d}S_z = r\mathrm{d}r\mathrm{d}\theta$

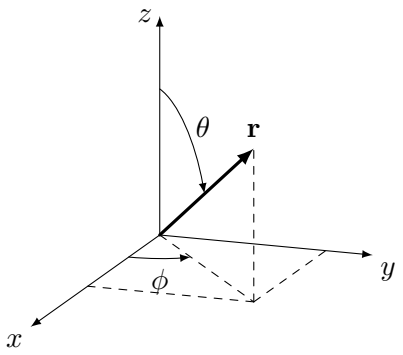


Figure 1.3: A vector in spherical coordinates.

1.2 Stress Tensor

1.2.1 Hook's Experiments

Extensional

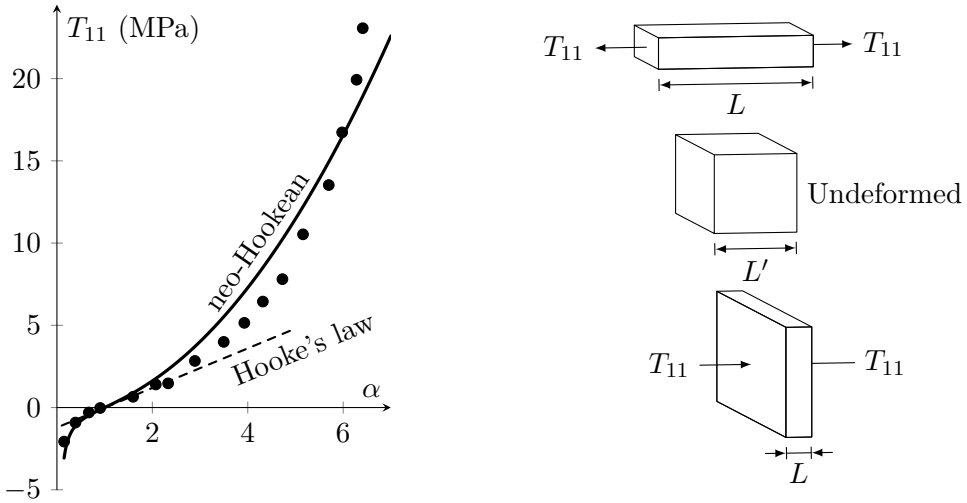


Figure 1.4: Uniaxial extension or compression.

A relation that fits the data reasonably well is

$$T_{11} = G(\alpha^2 - \frac{1}{\alpha}) \tag{1.19}$$

where T_{11} is the tensile force divided by the area a, which it acts upon

$$T_{11} = \frac{f}{a} \tag{1.20}$$

The G is the elastic modulus. $f \propto \Delta L$, where $\Delta L = L - L'$. $\alpha = L/L'$, where L' is the initial, undeformed length. We recognize that $\Delta L = f(\text{dimensions})$. Therefore, this equation can only work for a small deformation.

Shear

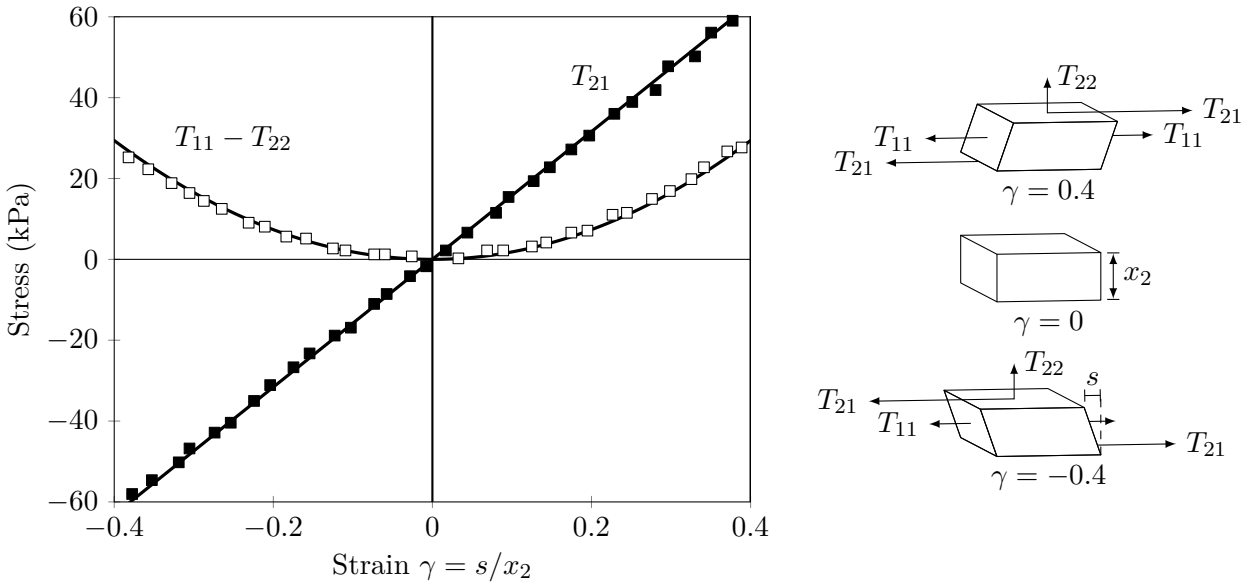


Figure 1.5: Simple shear.

Shear strain: $\gamma = s/x_2$, where s is the displacement of the top surface, and x_2 is the thickness.

Shear stress:

$$T_{12} = G\gamma \tag{1.21}$$

Normal stress difference

$$T_{11} - T_{22} = G\gamma^2 \tag{1.22}$$

1.2.2 Stress Tensor

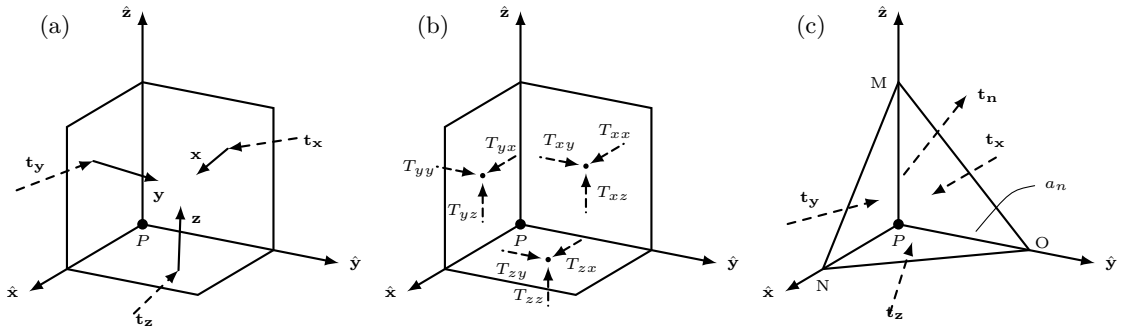


Figure 1.6: Stress tensor.

3 mutually perpendicular planes intersecting at Point P. The force balance on the tetrahedron:

$$a_n \mathbf{t_n} = a_x \mathbf{t_x} + a_y \mathbf{t_y} + a_z \mathbf{t_z} \tag{1.23}$$

We can find the 3 components as: $a_x = a_n \hat{\mathbf{n}} \cdot \hat{\mathbf{x}}$, $a_y = a_n \hat{\mathbf{n}} \cdot \hat{\mathbf{y}}$, $a_z = a_n \hat{\mathbf{n}} \cdot \hat{\mathbf{z}}$. We can then rewrite the above equation as:

$$a_n \mathbf{t_n} = (a_n \hat{\mathbf{n}} \cdot \hat{\mathbf{x}}) \mathbf{t_x} + (a_n \hat{\mathbf{n}} \cdot \hat{\mathbf{y}}) \mathbf{t_y} + (a_n \hat{\mathbf{n}} \cdot \hat{\mathbf{z}}) \mathbf{t_z} \tag{1.24}$$

$$\begin{aligned} \therefore \mathbf{t_n} &= \hat{\mathbf{n}} \cdot [\hat{\mathbf{x}} \mathbf{t_x} + \hat{\mathbf{y}} \mathbf{t_y} + \hat{\mathbf{z}} \mathbf{t_z}] \\ &= \hat{\mathbf{n}} \cdot [\hat{\mathbf{x}}\hat{\mathbf{x}} T_{xx} + \hat{\mathbf{x}}\hat{\mathbf{y}} T_{xy} + \hat{\mathbf{x}}\hat{\mathbf{z}} T_{xz} + \hat{\mathbf{y}}\hat{\mathbf{x}} T_{yx} + \hat{\mathbf{y}}\hat{\mathbf{y}} T_{yy} + \hat{\mathbf{y}}\hat{\mathbf{z}} T_{yz} + + \hat{\mathbf{z}}\hat{\mathbf{x}} T_{zx} + \hat{\mathbf{z}}\hat{\mathbf{y}} T_{zy} + \hat{\mathbf{z}}\hat{\mathbf{z}} T_{zz}] \end{aligned} \tag{1.25}$$

$$\mathbf{t_n} = \hat{\mathbf{n}} \cdot \begin{bmatrix} T_{xx} & T_{xy} & T_{xz} \\ T_{yx} & T_{yy} & T_{yz} \\ T_{zx} & T_{zy} & T_{zz} \end{bmatrix} = \hat{\mathbf{n}} \cdot \mathbf{T} \tag{1.26}$$

Example 1.2.1 - Stress on a Shear Plane in a Rod

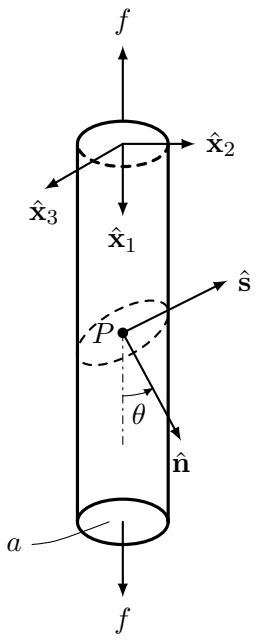


Figure 1.7: A shear plane in a rod.

(a) What is the state of the stress at Point P?

$\mathbf{T} = \hat{\mathbf{x}}_\mathbf{1} \mathbf{t_1} + \hat{\mathbf{x}}_\mathbf{2} \mathbf{t_2} + \hat{\mathbf{x}}_\mathbf{3} \mathbf{t_3}$

$\because \mathbf{t_1} = \hat{\mathbf{x}}_\mathbf{1}(f/a)$, $\mathbf{t_2} = 0$, $\mathbf{t_3} = 0$

$$\mathbf{T} = (f/a)\hat{\mathbf{x}}_\mathbf{1}\hat{\mathbf{x}}_\mathbf{1}, \text{ i.e., } \mathbf{T} = \begin{bmatrix} f/a & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

(b) What are the normal and shear stress on the cutting plane?

$\because \hat{\mathbf{n}} = \cos\theta\, \hat{\mathbf{x}}_\mathbf{1} + \sin\theta\, \hat{\mathbf{x}}_\mathbf{2}$

$$\therefore \mathbf{t_n} = \hat{\mathbf{n}} \cdot \mathbf{T} = \begin{bmatrix} \cos\theta & \sin\theta & 0 \end{bmatrix} \cdot \begin{bmatrix} f/a & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} = (f/a)\cos\theta\, \hat{\mathbf{x}}_\mathbf{1}$$

The normal stress on the $\hat{\mathbf{n}}$ plane:

$$T_{nn} = \mathbf{t_n} \cdot \hat{\mathbf{n}} = \begin{bmatrix} (f/a)\cos\theta & 0 & 0 \end{bmatrix} \cdot \begin{bmatrix} \cos\theta \\ \sin\theta \\ 0 \end{bmatrix} = (f/a)\cos^2\theta$$

$\because \mathbf{t_n} = T_{nn}\hat{\mathbf{n}} + T_{ns}\hat{\mathbf{s}}$

$$\begin{aligned} \therefore T_{ns}\hat{\mathbf{s}} &= \mathbf{t_n} - T_{nn}\hat{\mathbf{n}} \\ &= \begin{bmatrix} (f/a)\cos\theta & 0 & 0 \end{bmatrix} - \begin{bmatrix} (f/a)\cos^3\theta & (f/a)\cos^2\theta\, \sin\theta & 0 \end{bmatrix} \\ &= \begin{bmatrix} (f/a)\cos\theta\,(1-\cos^2\theta) & -(f/a)\cos^2\theta\, \sin\theta & 0 \end{bmatrix} \\ &= \begin{bmatrix} (f/a)\cos\theta\, \sin^2\theta & -(f/a)\cos^2\theta\, \sin\theta & 0 \end{bmatrix} \end{aligned}$$

$\because \hat{\mathbf{s}} = -\sin\theta\, \hat{\mathbf{x}}_\mathbf{1} + \cos\theta\, \hat{\mathbf{x}}_\mathbf{2}$

$\therefore T_{ns} = -(f/a)\cos\theta\, \sin\theta$

Example 1.2.2 - Stress on a Surface

Direction of vector normal to test surface	$\mathbf{t}_i$ (Pa)
$\hat{\mathbf{x}}_\mathbf{1}$	$\hat{\mathbf{x}}_\mathbf{1}$
$\hat{\mathbf{x}}_\mathbf{2}$	$3\hat{\mathbf{x}}_\mathbf{2} - \hat{\mathbf{x}}_\mathbf{3}$
$\hat{\mathbf{x}}_\mathbf{3}$	$-\hat{\mathbf{x}}_\mathbf{2} + 3\hat{\mathbf{x}}_\mathbf{3}$

(a) What is the state of the stress at point P?

$\mathbf{T} = \hat{\mathbf{x}}_\mathbf{1}\mathbf{t_1} + \hat{\mathbf{x}}_\mathbf{2}\mathbf{t_2} + \hat{\mathbf{x}}_\mathbf{3}\mathbf{t_3}$

$\therefore \mathbf{t_1} = \hat{\mathbf{x}}_\mathbf{1}$, $\mathbf{t_2} = 3\hat{\mathbf{x}}_\mathbf{2} - \hat{\mathbf{x}}_\mathbf{3}$, $\mathbf{t_3} = -\hat{\mathbf{x}}_\mathbf{2} + 3\hat{\mathbf{x}}_\mathbf{3}$

$$\mathbf{T} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 3 & -1 \\ 0 & -1 & 3 \end{bmatrix}$$

(b) Find the magnitude of the stress vector acting on a surface where the normal is $\hat{\mathbf{n}} = \frac{1}{\sqrt{2}}(\hat{\mathbf{x}}_\mathbf{1} + \hat{\mathbf{x}}_\mathbf{2})$.

$$\mathbf{t_n} = \hat{\mathbf{n}} \cdot \mathbf{T} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 1 & 0 \end{bmatrix} \cdot \begin{bmatrix} 1 & 0 & 0 \\ 0 & 3 & -1 \\ 0 & -1 & 3 \end{bmatrix} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ 3 \\ -1 \end{bmatrix} = \frac{1}{\sqrt{2}}(\hat{\mathbf{x}}_\mathbf{1} + 3\hat{\mathbf{x}}_\mathbf{2} - \hat{\mathbf{x}}_\mathbf{3})$$

$$|\mathbf{t_n}| = (\mathbf{t_n} \cdot \mathbf{t_n})^{1/2} = [\tfrac{1}{2}(1 \times 1 + 3 \times 3 + (-1) \times (-1))]^{1/2} = \sqrt{\tfrac{11}{2}}$$

(c) What is the normal stress acting on this surface?

$$T_{nn} = \hat{\mathbf{n}} \cdot \mathbf{t_n} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 1 & 0 \end{bmatrix} \cdot \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ 3 \\ -1 \end{bmatrix} = \tfrac{1}{2}(1 \times 1 + 1 \times 3 + 0 \times (-1)) = 2 \text{ Pa}$$

1.2.3 Pressure

Fluid at rest/equilibrium only supports normal stresses:

$$\mathbf{T} = \begin{bmatrix} -p & 0 & 0 \\ 0 & -p & 0 \\ 0 & 0 & -p \end{bmatrix} = -p \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = -p\,\mathbf{I} \tag{1.27}$$

For fluid not at rest/equilibrium, total stress = pressure + stress tensor due to flow/deformation

$$\mathbf{T} = -p\,\mathbf{I} + \boldsymbol{\tau} \tag{1.28}$$

We use normal stress differences to eliminate p:

$$T_{11} - T_{22} = \tau_{11} - \tau_{22} \tag{1.29}$$

$$T_{22} - T_{33} = \tau_{22} - \tau_{33} \tag{1.30}$$

For simple shear:

$$T_{11} - T_{22} = N_1 \text{ (first normal stress difference)} \tag{1.31}$$

$$T_{22} - T_{33} = N_2 \text{ (second normal stress difference)} \tag{1.32}$$

1.2.4 Invariants of Tensor

Invariants are independent of chosen coordinate system.

$$\mathbf{t_n} = \hat{\mathbf{n}} \cdot \mathbf{T} = \hat{\mathbf{n}} \cdot \begin{bmatrix} \sigma & 0 & 0 \\ 0 & \sigma & 0 \\ 0 & 0 & \sigma \end{bmatrix} = \begin{bmatrix} n_1 & n_2 & n_3 \end{bmatrix} \cdot \begin{bmatrix} \sigma & 0 & 0 \\ 0 & \sigma & 0 \\ 0 & 0 & \sigma \end{bmatrix} = \sigma \begin{bmatrix} n_1 \\ n_2 \\ n_3 \end{bmatrix} = \sigma\, \hat{\mathbf{n}} = \sigma\, \hat{\mathbf{n}} \cdot \mathbf{I} \tag{1.33}$$

$$\hat{\mathbf{n}} \cdot (\mathbf{T} - \sigma\, \mathbf{I}) = \mathbf{0} \tag{1.34}$$

$\because \hat{\mathbf{n}} \neq \mathbf{0}, \therefore \mathbf{T} - \sigma\mathbf{I} = \mathbf{0}$

$$\det(\mathbf{T} - \sigma\mathbf{I}) = \begin{vmatrix} T_{11} - \sigma & T_{12} & T_{13} \\ T_{21} & T_{22} - \sigma & T_{23} \\ T_{31} & T_{32} & T_{33} - \sigma \end{vmatrix} = 0 \tag{1.35}$$

Expanding the determinant yields the characteristic equation:

$$\sigma^3 - I_T\sigma^2 + II_T - III_T = 0 \tag{1.36}$$

The solution to this equation is:

$$I_T = \text{tr}\, \mathbf{T} = T_{11} + T_{22} + T_{33} = \sigma_1 + \sigma_2 + \sigma_3 \tag{1.37}$$

$$II_T = \frac{1}{2}[I_T^2 - \text{tr}\mathbf{T}^2] = T_{11}T_{22} + T_{11}T_{33} + T_{22}T_{33} - T_{12}T_{21} - T_{13}T_{31} - T_{23}T_{32} = \sigma_1\sigma_2 + \sigma_1\sigma_3 + \sigma_2\sigma_3 \tag{1.38}$$

$$III_T = \det \mathbf{T} = T_{11}T_{22}T_{33} + T_{12}T_{23}T_{31} + T_{13}T_{32}T_{21} - T_{11}T_{23}T_{32} - T_{21}T_{12}T_{33} - T_{31}T_{22}T_{13} = \sigma_1\sigma_2\sigma_3 \tag{1.39}$$

Example 1.3.1 - Invariant and Principal Stresses

From Example 1.2.1, the stress tensor in the rod is $\mathbf{T} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 3 & -1 \\ 0 & -1 & 3 \end{bmatrix}$. We aim to find the invariants and principle stresses.

$$\mathbf{T}^2 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 3 & -1 \\ 0 & -1 & 3 \end{bmatrix} \cdot \begin{bmatrix} 1 & 0 & 0 \\ 0 & 3 & -1 \\ 0 & -1 & 3 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 10 & -6 \\ 0 & -6 & 10 \end{bmatrix}$$

$I_T = \operatorname{tr} \mathbf{T} = 7$

$II_T = \frac{1}{2}(I_T^2 - \operatorname{tr} \mathbf{T}^2) = \frac{1}{2}[49 - (1 + 10 + 10)] = 14$

$$III_T = \det \mathbf{T} = \begin{vmatrix} 1 & 0 & 0 \\ 0 & 3 & -1 \\ 0 & -1 & 3 \end{vmatrix} = 8$$

$\therefore \sigma^3 - 7\sigma^2 + 14\sigma - 8 = 0$, $(\sigma - 1)(\sigma - 2)(\sigma - 4) = 0$, $\therefore \sigma_1 = 1$, $\sigma_2 = 2$, $\sigma_3 = 4$

Check the results: $I_T = \sigma_1 + \sigma_2 + \sigma_3 = 7$, $II_T = \sigma_1\sigma_2 + \sigma_1\sigma_3 + \sigma_2\sigma_3 = 14$, $III_T = \sigma_1\sigma_2\sigma_3 = 8$

Principle stresses:

$$\hat{\mathbf{n}}^{(i)} \cdot \mathbf{T} = \sigma_i \hat{\mathbf{n}}^{(i)} \implies \begin{bmatrix} n_1^{(i)} & n_2^{(i)} & n_3^{(i)} \end{bmatrix} \cdot \begin{bmatrix} 1 & 0 & 0 \\ 0 & 3 & -1 \\ 0 & -1 & 3 \end{bmatrix} = \sigma_i \begin{bmatrix} n_1^{(i)} \\ n_2^{(i)} \\ n_3^{(i)} \end{bmatrix}$$

$$\begin{bmatrix} n_1^{(i)} \\ 3n_2^{(i)} - n_3^{(i)} \\ -n_2^{(i)} + 3n_3^{(i)} \end{bmatrix} = \sigma_i \begin{bmatrix} n_1^{(i)} \\ n_2^{(i)} \\ n_3^{(i)} \end{bmatrix}$$

(1) For $i = 1$

$n_1^{(1)} = n_1^{(1)}$, $3n_1^{(1)} - n_3^{(1)} = n_2^{(1)}$, $-2n^{(1)} + 3n_3^{(1)} = n_3^{(1)} \implies n_2^{(1)} = n_3^{(1)} = 0 \implies n_1^{(1)} = \hat{\mathbf{x}}_\mathbf{1}$

(2) For $i = 2$

$n_1^{(2)} = 2n_1^{(2)}$, $3n_2^{(2)} - n_3^{(2)} = 2n_2^{(2)}$, $-n_2^{(2)} + 3n_3^{(2)} = 2n_3^{(2)} \implies n_1^{(2)} = 0, n_2^{(2)} = n_3^{(2)}$

$|\hat{\mathbf{n}}^{(2)}| = 2(n_2^{(2)})^2 = 1 \implies n_2^{(2)} = \frac{1}{\sqrt{2}} \implies \implies \hat{\mathbf{n}}^{(2)} = \frac{1}{\sqrt{2}}(\hat{\mathbf{x}}_\mathbf{2} + \hat{\mathbf{x}}_\mathbf{3})$

(3) For $i = 3$

$n_1^{(3)} = 4n_1^{(3)}$, $3n_1^{(3)} - n_3^{(3)} = 4n_2^{(3)}$, $-2n^{(3)} + 3n_3^{(3)} = 4n_3^{(3)} \implies n_1^{(3)} = 0, n_2^{(2)} = -n_3^{(2)}$

$|\hat{\mathbf{n}}^{(3)}| = 2(n_2^{(3)})^2 = 1 \implies n_2^{(3)} = \frac{1}{\sqrt{2}} \implies \implies \hat{\mathbf{n}}^{(3)} = \frac{1}{\sqrt{2}}(\hat{\mathbf{x}}_\mathbf{2} - \hat{\mathbf{x}}_\mathbf{3})$

1.3 Deformation Tensor (Deformation Gradient Tensor)

1.3.1 Definition

$\mathrm{d}\mathbf{x}'$ = rest of past time at t'

$\mathrm{d}\mathbf{x}$ = deformed or present state at t

$$\mathbf{F} = (\nabla' \mathbf{x})^T = \frac{\partial \mathbf{x}}{\partial \mathbf{x}'} = F_{ij}\hat{\mathbf{e}}_\mathbf{i}\hat{\mathbf{e}}_\mathbf{j} = \frac{\partial x_i}{\partial x'_j}\hat{\mathbf{e}}_\mathbf{i}\hat{\mathbf{e}}_\mathbf{j} = \begin{bmatrix} \frac{\partial x_1}{\partial x'_1} & \frac{\partial x_1}{\partial x'_2} & \frac{\partial x_1}{\partial x'_3} \\ \frac{\partial x_2}{\partial x'_1} & \frac{\partial x_2}{\partial x'_2} & \frac{\partial x_2}{\partial x'_3} \\ \frac{\partial x_3}{\partial x'_1} & \frac{\partial x_3}{\partial x'_2} & \frac{\partial x_3}{\partial x'_3} \end{bmatrix} \tag{1.40}$$

See Table A.1 for components of $\mathbf{F}$. Based on the definition:

$$\mathrm{d}x = \mathbf{F} \cdot \mathrm{d}\mathbf{x}' \tag{1.41}$$

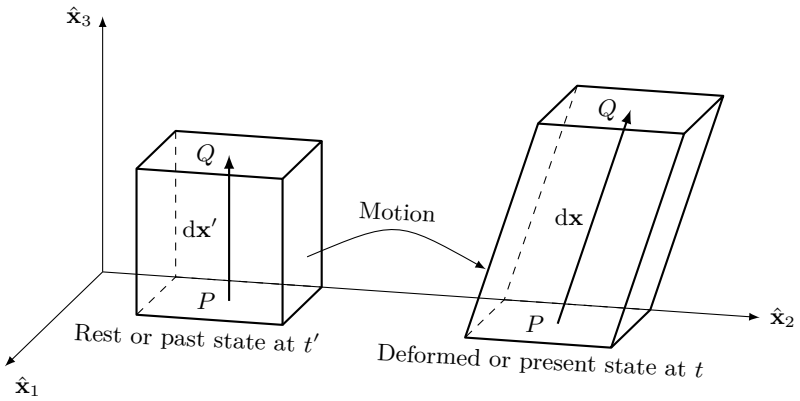


Figure 1.8: Solid at rest vs. a deformed one.

Example - Uniaxial Extension

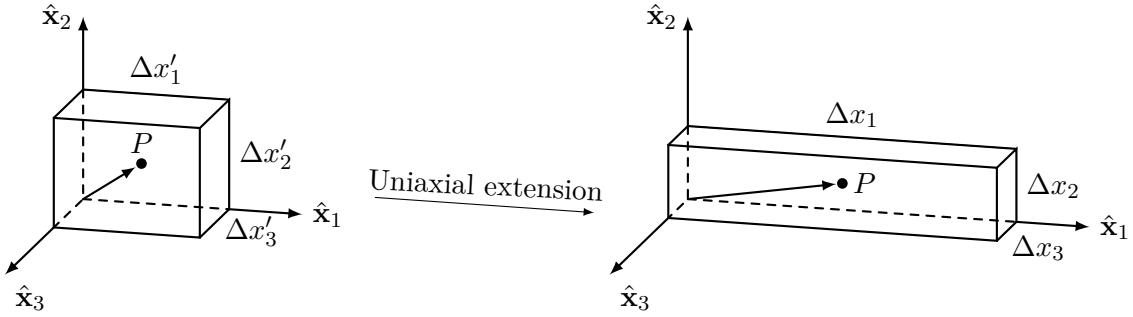


Figure 1.9: Uniaxial extension.

$x_1 = \frac{\Delta x_1}{\Delta x'_1} x'_1 = \alpha_1 x'_1$, $x_2 = \frac{\Delta x_2}{\Delta x'_2} x'_2 = \alpha_2 x'_2$, $x_3 = \frac{\Delta x_3}{\Delta x'_3} x'_3 = \alpha_3 x'_3$

$$\therefore \mathbf{F} = \begin{bmatrix} \alpha_1 & 0 & 0 \\ 0 & \alpha_2 & 0 \\ 0 & 0 & \alpha_3 \end{bmatrix}$$

Since uniaxial extension is symmetric about the $\hat{\mathbf{x}}_\mathbf{1}$ axis, $\alpha_2 = \alpha_3$. $V' = V$ for an incompressible material; therefore, $\Delta x_1' \Delta x_2' \Delta x_3' = \Delta x_1 \Delta x_2 \Delta x_3 \implies \alpha_1 \alpha_2 \alpha_3 = 1$.

$\alpha_1 \alpha_2^2 = 1$, $\alpha_2 = \frac{1}{\alpha_1^{1/2}}$

$$\therefore \mathbf{F} = \begin{bmatrix} \alpha_1 & 0 & 0 \\ 0 & \frac{1}{\alpha_1^{1/2}} & 0 \\ 0 & 0 & \frac{1}{\alpha_1^{1/2}} \end{bmatrix}$$

Example - Simple Shear

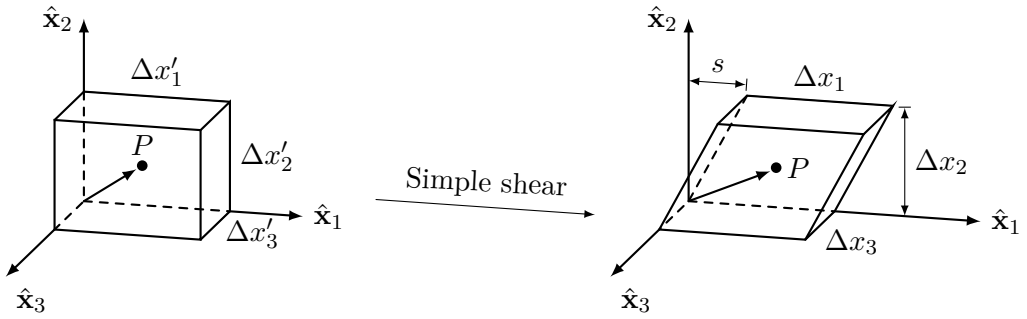


Figure 1.10: Simple shear.

$x_1 = x_1' + \frac{s}{\Delta x_2'} x_2' = x_1' + \gamma x_2', x_2 = x_2', x_3 = x_3'$

$$\therefore \mathbf{F} = \begin{bmatrix} 1 & \gamma & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \text{ (not symmetric)}$$

Example - Solid Body Rotation

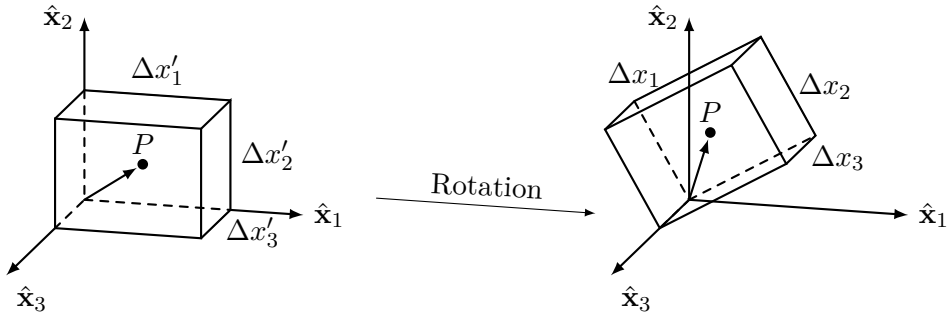


Figure 1.11: Solid body rotation.

$x_1 = x_1' \cos\theta - x_2' \sin\theta, x_2 = x_1' \sin\theta + x_2' \cos\theta, x_3 = x_3'$

$$\therefore \mathbf{F} = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

1.3.2 Elimination of Rotation

F describes deformation/shape change + rotation. For "frame indifference", we seek the elimination of rotation, so we can select the proper tensor forms in constitutive equations.

Finger deformation tensor (symmetric):

$$\mathbf{B} = \mathbf{F} \cdot \mathbf{F}^T \tag{1.42}$$

Cauchy-Green tensor:

$$\mathbf{C} = \mathbf{F}^T \cdot \mathbf{F} \tag{1.43}$$

For uniaxial extension:

$$\mathbf{B} = \mathbf{F} \cdot \mathbf{F}^T = \begin{bmatrix} \alpha_1 & 0 & 0 \\ 0 & \frac{1}{\alpha_1^{1/2}} & 0 \\ 0 & 0 & \frac{1}{\alpha_1^{1/2}} \end{bmatrix} \cdot \begin{bmatrix} \alpha_1 & 0 & 0 \\ 0 & \frac{1}{\alpha_1^{1/2}} & 0 \\ 0 & 0 & \frac{1}{\alpha_1^2 1/2} \end{bmatrix} = \begin{bmatrix} \alpha_1^2 & 0 & 0 \\ 0 & \frac{1}{\alpha_1} & 0 \\ 0 & 0 & \frac{1}{\alpha_1} \end{bmatrix} = \mathbf{C}$$

This is largely because **F** is symmetric, thereby $\mathbf{F} = \mathbf{F}^T$.

For simple shear:

$$\mathbf{B} = \mathbf{F} \cdot \mathbf{F}^T = \begin{bmatrix} 1 & \gamma & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \cdot \begin{bmatrix} 1 & \gamma & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} 1+\gamma^2 & \gamma & 0 \\ \gamma & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\mathbf{C} = \mathbf{F}^T \cdot \mathbf{F} = \begin{bmatrix} 1 & \gamma & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \cdot \begin{bmatrix} 1 & \gamma & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} 1 & \gamma & 0 \\ \gamma & 1+\gamma^2 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Both **B** and **C** are symmetric.

For solid body rotation:

$$\mathbf{B} = \mathbf{F} \cdot \mathbf{F}^T = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix} \cdot \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \mathbf{C} = \mathbf{I}$$

$\mathbf{B} = \mathbf{C} = \mathbf{I}$, and they are independent of θ, i.e., frame indifferent.

1.3.3 Inverse Deformation Tensor

$$\mathbf{F}^{-1} = (\nabla \mathbf{x}')^T = \frac{\partial \mathbf{x}'}{\partial \mathbf{x}} = F_{ij}^{-1} \hat{\mathbf{e}}_\mathbf{i} \hat{\mathbf{e}}_\mathbf{j} = \frac{\partial x_i'}{\partial x_j} \hat{\mathbf{e}}_\mathbf{i} \hat{\mathbf{e}}_\mathbf{j} = \begin{bmatrix} \frac{\partial x_1'}{\partial x_1} & \frac{\partial x_1'}{\partial x_2} & \frac{\partial x_1'}{\partial x_3} \\ \frac{\partial x_2'}{\partial x_1} & \frac{\partial x_2'}{\partial x_2} & \frac{\partial x_2'}{\partial x_3} \\ \frac{\partial x_3'}{\partial x_1} & \frac{\partial x_3'}{\partial x_2} & \frac{\partial x_3'}{\partial x_3} \end{bmatrix} \tag{1.44}$$

It is straightforward to show that $\mathrm{d}\mathbf{x}' = \mathbf{F}^{-1} \cdot \mathrm{d}\mathbf{x}$, $\mathbf{B}^{-1} = (\mathbf{F}^{-1})^T \cdot \mathbf{F}^{-1}$, and $\mathbf{C}^{-1} = \mathbf{F}^{-1} \cdot (\mathbf{F}^{-1})^T$.

For uniaxial extension:

$x_1' = 1/\alpha_1 \, x_1$, $x_2' = {\alpha_1}^{1/2} \, x_2$, $x_3' = {\alpha_1}^{1/2} \, x_3$

$$\therefore \mathbf{F}^{-1} = \begin{bmatrix} 1/\alpha_1 & 0 & 0 \\ 0 & {\alpha_1}^{1/2} & 0 \\ 0 & 0 & {\alpha_1}^{1/2} \end{bmatrix} = (\mathbf{F}^{-1})^T \text{ (symmetric tensor)}$$

$$\mathbf{B}^{-1} = (\mathbf{F}^{-1})^T \cdot \mathbf{F}^{-1} = \begin{bmatrix} 1/\alpha_1 & 0 & 0 \\ 0 & {\alpha_1}^{1/2} & 0 \\ 0 & 0 & {\alpha_1}^{1/2} \end{bmatrix} \cdot \begin{bmatrix} 1/\alpha_1 & 0 & 0 \\ 0 & {\alpha_1}^{1/2} & 0 \\ 0 & 0 & {\alpha_1}^{1/2} \end{bmatrix} = \begin{bmatrix} 1/\alpha_1^2 & 0 & 0 \\ 0 & \alpha_1 & 0 \\ 0 & 0 & \alpha_1 \end{bmatrix} = \mathbf{C}^{-1}$$

For simple shear:

$x_1' = x_1 - \gamma x_2' = x_1 - \gamma x_2$, $x_2' = x_2$, $x_3' = x_3$

$$\mathbf{F}^{-1} = \frac{\partial x_i'}{\partial x_j} \hat{\mathbf{e}}_\mathbf{i} \hat{\mathbf{e}}_\mathbf{j} = \begin{bmatrix} 1 & -\gamma & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \; (\mathbf{F}^{-1})^T = \begin{bmatrix} 1 & 0 & 0 \\ -\gamma & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\mathbf{B}^{-1} = (\mathbf{F}^{-1})^T \cdot \mathbf{F}^{-1} = \begin{bmatrix} 1 & 0 & 0 \\ -\gamma & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \cdot \begin{bmatrix} 1 & -\gamma & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} 1 & -\gamma & 0 \\ -\gamma & 1+\gamma^2 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\mathbf{C}^{-1} = \mathbf{F}^{-1} \cdot (\mathbf{F}^{-1})^T = \begin{bmatrix} 1 & -\gamma & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \cdot \begin{bmatrix} 1 & 0 & 0 \\ -\gamma & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} 1+\gamma^2 & -\gamma & 0 \\ -\gamma & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

For solid body rotation:

$\mathbf{B} = \mathbf{C} = \mathbf{I}$, hence $\mathbf{B}^{-1} = \mathbf{C}^{-1} = \mathbf{I}^{-1} = \mathbf{I}$.

1.4 Neo-Hookean Solid

We define a new parameter, G, as the elastic modulus. A neo-Hookean solid carries a constitutive equation as:

$$\mathbf{T} = -p\mathbf{I} + G\mathbf{B} \tag{1.45}$$

For uniaxial extension:

$$\mathbf{B} = \mathbf{F} \cdot \mathbf{F}^T = \begin{bmatrix} \alpha_1 & 0 & 0 \\ 0 & \frac{1}{\alpha_1^{1/2}} & 0 \\ 0 & 0 & \frac{1}{\alpha_1^{1/2}} \end{bmatrix} \cdot \begin{bmatrix} \alpha_1 & 0 & 0 \\ 0 & \frac{1}{\alpha_1^{1/2}} & 0 \\ 0 & 0 & \frac{1}{\alpha_1^2 1/2} \end{bmatrix} = \begin{bmatrix} \alpha_1^2 & 0 & 0 \\ 0 & \frac{1}{\alpha_1} & 0 \\ 0 & 0 & \frac{1}{\alpha_1} \end{bmatrix}$$

$\therefore T_{11} = -p + G\alpha_1^2$, $T_{22} = T_{33} = -p + \frac{G}{\alpha_1}$, $\frac{f_1}{a_1} = T_{11} = -p + G\alpha_1^2$

Assuming no tractions on the sides of the block, we have

$T_{22} = T_{33} = 0 \implies p = \frac{G}{\alpha_1}$

$\therefore \frac{f_1}{a_1} = T_{11} = G(\alpha_1^2 - \frac{1}{\alpha_1})$

$\because V$ is unchanged, $a_1 \Delta x_1 = a_1' \Delta x_1' \implies a_1 = \frac{a_1'}{\alpha_1}$

$\therefore \frac{f_1}{a_1'} = G(\alpha_1 - \frac{1}{\alpha_1^2})$

For simple shear:

$$\mathbf{B} = \mathbf{F} \cdot \mathbf{F}^T = \begin{bmatrix} 1 & \gamma & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \cdot \begin{bmatrix} 1 & \gamma & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} 1+\gamma^2 & \gamma & 0 \\ \gamma & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$\therefore T_{11} = -p + G(1+\gamma^2)$, $T_{12} = T_{21} = G\gamma$, $T_{22} = T_{22} = -p + G$

$T_{11} - T_{22} = G\gamma^2 = N_1$, $T_{22} - T_{33} = 0 = N_2$

1.5 General Elastic Solid

Assuming $\mathbf{T} = f(\mathbf{B})$, the constitutive equation of a general elastic solid is typically written in a form of a power series:

$$\mathbf{T} = f_0\mathbf{B}^0 + f_1\mathbf{B} + f_2\mathbf{B}^2 + f_3\mathbf{B}^3 + \cdots \tag{1.46}$$

Cauchy-Hamilton Theory

The characteristic equation:

$$\mathbf{B}^3 - I_B\mathbf{B}^2 + II_B\mathbf{B} - III_B\mathbf{I} = 0 \tag{1.47}$$

We rewrite the constitutive equation by only keeping the lower order terms:

$$\mathbf{T} = g_0\mathbf{I} + g_1\mathbf{B} + g_2\mathbf{B}^{-1} \tag{1.48}$$

For incompressible material, $g_0 = -p$ and $III_B = 1$ ($\because \alpha_1^2\alpha_2^2\alpha_3^2 = 1$). The above equation becomes:

$$\mathbf{T} = -p\mathbf{I} + g_1(I_B, II_B)\mathbf{B} + g_2(I_B, II_B)\mathbf{B}^{-1} \tag{1.49}$$

For neo-Hookean solid, $g_1 = G$ and $g_2 = 0$.

Mooney-Rivlin Equation

$$\mathbf{T} = -p\mathbf{I} + 2C_1\mathbf{B} - 2C_2\mathbf{B}^{-1} \tag{1.50}$$

Example - Uniaxial Extension

$$\mathbf{B} = \begin{bmatrix} \alpha_1^2 & 0 & 0 \\ 0 & \frac{1}{\alpha_1} & 0 \\ 0 & 0 & \frac{1}{\alpha_1} \end{bmatrix}, \mathbf{B}^{-1} = \begin{bmatrix} 1/\alpha_1^2 & 0 & 0 \\ 0 & \alpha_1 & 0 \\ 0 & 0 & \alpha_1 \end{bmatrix}$$

$\mathbf{T} = -p\mathbf{I} + g_1\mathbf{B} + g_2\mathbf{B}^{-1}$

$\therefore T_{11} = -p + g_1\alpha_1^2 + g_2/\alpha_1^2$, $T_{22} = T_{33} = -p + g_1/\alpha_1 + g_2\alpha_1$

$T_{11} - T_{22} = g_1(\alpha_1^2 - \frac{1}{\alpha_1}) - \frac{g_2}{\alpha_1}(\alpha_1^2 - \frac{1}{\alpha_1}) = (g_1 - \frac{g_2}{\alpha_1})(\alpha_1^2 - \frac{1}{\alpha_1})$

If $g_1 = 2C_1$ and $g_2 = -2C_2$, $T_{11} - T_{22} = (2C_1 + \frac{2C_2}{\alpha_1})(\alpha_1^2 - \frac{1}{\alpha_1})$

Example - Simple Shear

$$\mathbf{B} = \begin{bmatrix} \alpha_1^2 & 0 & 0 \\ 0 & \frac{1}{\alpha_1} & 0 \\ 0 & 0 & \frac{1}{\alpha_1} \end{bmatrix}, \mathbf{B}^{-1} = \begin{bmatrix} 1/\alpha_1^2 & 0 & 0 \\ 0 & \alpha_1 & 0 \\ 0 & 0 & \alpha_1 \end{bmatrix}$$

$$\mathbf{T} = -p\mathbf{I} + g_1\mathbf{B} + g_2\mathbf{B}^{-1}$$

$$\therefore T_{11} = -p + g_1(1+\gamma^2) + g_2,\ T_{22} = -p + g_1 + g_2(1+\gamma^2),\ T_{21} = g_1\gamma - g_2\gamma = (g_1 - g_2)\gamma$$

$$T_{11} - T_{22} = g_1\gamma^2 - g_2\gamma^2 = (g_1 - g_2)\gamma^2$$

1.6 Equation of Motion

1.6.1 Mass Balance

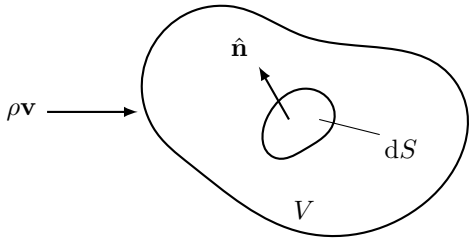


Figure 1.12: Control volume for mass balance.

$$m = \int_V \rho \,\mathrm{d}V \tag{1.51}$$

$$\frac{\mathrm{d}m}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t}\int_V \rho \,\mathrm{d}V \tag{1.52}$$

If mass is conserved, this should be equal to the mass flux across S:

$$\int_S (-\hat{\mathbf{n}}) \cdot \rho\mathbf{v} \,\mathrm{d}S = \frac{\mathrm{d}}{\mathrm{d}t}\int_V \rho \,\mathrm{d}V \tag{1.53}$$

Using the divergence theorem:

$$\int_S \hat{\mathbf{n}} \cdot \rho\mathbf{v} \,\mathrm{d}S = \int_V (\boldsymbol{\nabla} \cdot \rho\mathbf{v}) \,\mathrm{d}V \tag{1.54}$$

$$\therefore -\int_V (\boldsymbol{\nabla} \cdot \rho\mathbf{v}) \,\mathrm{d}V = \frac{\mathrm{d}}{\mathrm{d}t}\int_V \rho \,\mathrm{d}V \tag{1.55}$$

Using the Leibniz formula:

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_V \rho\,\mathrm{d}V = \int_V \frac{\partial\rho}{\partial t}\,\mathrm{d}V + \int_S \rho(\mathbf{v_s}\cdot\hat{\mathbf{n}})\,\mathrm{d}S \tag{1.56}$$

If the control volume is stationary, $\mathbf{v_s} = \mathbf{0}$

$$\therefore \int_V (\frac{\partial\rho}{\partial t} + \boldsymbol{\nabla}\cdot\rho\mathbf{v})\,\mathrm{d}V = 0 \tag{1.57}$$

Since the control volume is arbitrary, the integrand must be true everywhere:

$$\therefore \frac{\partial\rho}{\partial t} + \boldsymbol{\nabla}\cdot\rho\mathbf{v} = 0 \tag{1.58}$$

This is called the *Continuity Equation*.

Material Derivative by Definition

Rate of change as perceived by an observer moving with the fluid/material):

$$\begin{aligned}\frac{\mathrm{D}\rho}{\mathrm{D}t} &= \frac{\partial\rho}{\partial t} + \mathbf{v}\cdot\nabla\rho \\ &= -\nabla\cdot\rho\mathbf{v} + \mathbf{v}\cdot\nabla\rho \\ &= -(\nabla\rho)\cdot\mathbf{v} - \rho\nabla\cdot\mathbf{v} + \mathbf{v}\cdot\nabla\rho \\ &= -\rho\nabla\cdot\mathbf{v}\end{aligned} \tag{1.59}$$

For an incompressible material:

$$\boldsymbol{\nabla}\cdot\mathbf{v} = 0 \tag{1.60}$$

1.6.2 Momentum Balance

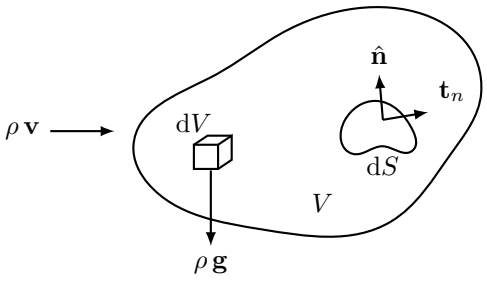


Figure 1.13: Control volume for momentum balance.

The momentum is defined as:

$$m\mathbf{v} = \int_V \rho\mathbf{v}\,\mathrm{d}V \tag{1.61}$$

The momentum balance in the control volume follows the statement below:

Rate of momentum change within V = rate of momentum addition across S due to flow + rate of momentum addition across S due to contact forces + rate of momentum addition in V due to body forces

This can be translated into a mathematical expression:

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_V \rho\mathbf{v}\,\mathrm{d}V = \int_S (-\hat{\mathbf{n}}\cdot\mathbf{v})\rho\mathbf{v}\,\mathrm{d}S + \int_S \hat{\mathbf{n}}\cdot\mathbf{T}\,\mathrm{d}S + \int_V \rho\mathbf{g}\,\mathrm{d}V \tag{1.62}$$

Using the divergence theorem:

$$\int_S (\hat{\mathbf{n}}\cdot\mathbf{v})\rho\mathbf{v}\,\mathrm{d}S = \int_V \boldsymbol{\nabla}\cdot\rho\mathbf{v}\mathbf{v}\,\mathrm{d}V \tag{1.63}$$

$$\int_S \hat{\mathbf{n}}\cdot\mathbf{T}\,\mathrm{d}S = \int_V \boldsymbol{\nabla}\cdot\mathbf{T}\,\mathrm{d}V \tag{1.64}$$

$$\therefore \frac{\mathrm{d}}{\mathrm{d}t}\int_V \rho\mathbf{v}\,\mathrm{d}V = -\int_V \boldsymbol{\nabla}\cdot\rho\mathbf{v}\mathbf{v}\,\mathrm{d}V + \int_V \boldsymbol{\nabla}\cdot\mathbf{T}\,\mathrm{d}V + \int_V \rho\mathbf{g}\,\mathrm{d}V \tag{1.65}$$

Using the Leibniz rule:

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_V \rho\mathbf{v}\,\mathrm{d}V = -\int_V \frac{\partial\rho\mathbf{v}}{\partial t}\,\mathrm{d}V + \int_S \rho\mathbf{v}(\mathbf{v_S}\cdot\hat{\mathbf{n}})\,\mathrm{d}S \tag{1.66}$$

For a stationary control volume, $\mathbf{v_S} = \mathbf{0}$

$$\therefore \int_V \frac{\partial\rho\mathbf{v}}{\partial t}\,\mathrm{d}V = -\int_V \boldsymbol{\nabla}\cdot\rho\mathbf{v}\mathbf{v}\,\mathrm{d}V + \int_V \boldsymbol{\nabla}\cdot\mathbf{T}\,\mathrm{d}V + \int_V \rho\mathbf{g}\,\mathrm{d}V \tag{1.67}$$

Similarly, the control volume is arbitrary, which leads to a differential form:

$$\frac{\partial\rho\mathbf{v}}{\partial t} = -\boldsymbol{\nabla}\cdot\rho\mathbf{v}\mathbf{v} + \boldsymbol{\nabla}\cdot\mathbf{T} + \rho\mathbf{g} \tag{1.68}$$

$$\because \frac{\partial\rho\mathbf{v}}{\partial t} = \mathbf{v}\frac{\partial\rho}{\partial t} + \rho\frac{\partial\mathbf{v}}{\partial t} \tag{1.69}$$

$$\boldsymbol{\nabla}\cdot\rho\mathbf{v}\mathbf{v} = \boldsymbol{\nabla}\cdot(\rho\mathbf{v})\mathbf{v} = \rho\mathbf{v}\cdot\boldsymbol{\nabla}\mathbf{v} + \mathbf{v}\boldsymbol{\nabla}\cdot(\rho\mathbf{v}) \tag{1.70}$$

$$\therefore \frac{\partial\rho\mathbf{v}}{\partial t} + \boldsymbol{\nabla}\cdot\rho\mathbf{v}\mathbf{v} = \rho\frac{\partial\mathbf{v}}{\partial t} + \rho\mathbf{v}\cdot\boldsymbol{\nabla}\mathbf{v} + \mathbf{v}(\frac{\partial\rho}{\partial t} + \boldsymbol{\nabla}\cdot(\rho\mathbf{v})) \tag{1.71}$$

Note that the last term in the parentheses is the continuity equation, which equals zero.

$$\therefore \rho(\frac{\partial\mathbf{v}}{\partial t} + \mathbf{v}\cdot\boldsymbol{\nabla}\mathbf{v}) = \frac{\mathrm{D}\mathbf{v}}{\mathrm{D}t} = \boldsymbol{\nabla}\cdot\mathbf{T} + \rho\mathbf{g} \tag{1.72}$$

The component forms of this equation is included in Table A.3. For solids, no flow and the body in

equilibrium with negligible gravity effects:

$$\boldsymbol{\nabla} \cdot \mathbf{T} = \mathbf{0} \tag{1.73}$$

Example 1.7.1 - Twisting of a Cylinder as neo-Hookean Solid

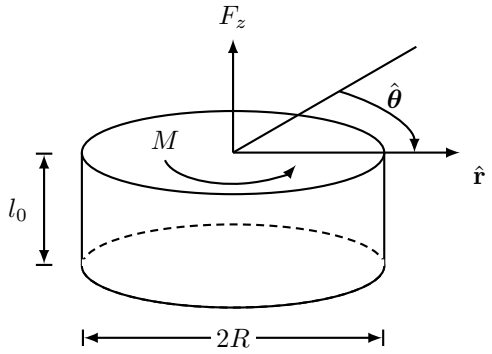


Figure 1.14: Twisting of a solid cylinder.

$r = r'$, $z = z'$, $\theta = \theta' + \frac{z'}{\ell_0}\theta_0 = \theta' + \alpha z'$

$$\mathbf{F} = \begin{bmatrix} \frac{\partial r}{\partial r'} & \frac{1}{r'}\frac{\partial r}{\partial \theta'} & \frac{\partial r}{\partial z'} \\ r\frac{\partial \theta}{\partial r'} & \frac{r}{r'}\frac{\partial \theta}{\partial \theta'} & r\frac{\partial \theta}{\partial z'} \\ \frac{\partial z}{\partial r'} & \frac{1}{r'}\frac{\partial z}{\partial \theta'} & \frac{\partial z}{\partial z'} \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & \alpha r \\ 0 & 0 & 1 \end{bmatrix}$$

$$\mathbf{F}^T = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & \alpha r & 1 \end{bmatrix}$$

$$\mathbf{B} = \mathbf{F} \cdot \mathbf{F}^T = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & \alpha r \\ 0 & 0 & 1 \end{bmatrix} \cdot \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & \alpha r & 1 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1+\alpha^2 r^2 & \alpha r \\ 0 & \alpha r & 1 \end{bmatrix}$$

$\mathbf{T} = -p\mathbf{I} + G\mathbf{B}$

$\therefore T_{rr} = -p + G$, $T_{\theta\theta} = -p + G(1+\alpha^2 r^2)$, $T_{\theta z} = T_{z\theta} = G\alpha r$, $T_{zz} = -p + G$

The torque on the cylinder:

$M = f(T_{z\theta}) = 2\pi \int_0^R T_{z\theta} r^2 \, \mathrm{d}r = 2\pi \int_0^R G\alpha r^3 \, \mathrm{d}r = \frac{1}{2}\pi G\alpha R^4$

The normal force:

$F_z = f(T_{zz})$

$\boldsymbol{\nabla} \cdot \mathbf{T} = \mathbf{0}$

The component form of this equation can be found in Table A.3:

r-component:

$\frac{1}{r}\frac{\partial}{\partial r}(rT_{rr}) + \frac{1}{r}\frac{\partial T_{\theta r}}{\partial \theta} - \frac{T_{\theta\theta}}{r} + \frac{\partial T_{zr}}{\partial z} = 0$

$\therefore T_{\theta\theta} = \frac{\partial}{\partial r}(rT_{rr}) = r\frac{\partial T_{rr}}{\partial r} + T_{rr}$

$-p + G(1 + \alpha^2 r^2) = -p + G + r\frac{\partial T_{rr}}{\partial r}$

$\therefore \frac{\partial T_{rr}}{\partial r} = G\alpha^2 r$

Assume no traction at $r = R \implies T_{rr}|_R = 0$

$\int_{T_{rr}}^{0} \mathrm{d}T_{rr} = \int_r^R G\alpha^2 r \,\mathrm{d}r$

$-T_{rr} = \frac{1}{2}G\alpha^2 r^2|_r^R = \frac{1}{2}G\alpha^2(R^2 - r^2)$

$T_{rr} = G\alpha^2(\frac{r^2}{2} - \frac{R^2}{2}) = T_{zz}$

$F_z = 2\pi \int_0^R rT_{zz} \,\mathrm{d}r = 2\pi \int_0^R G\alpha^2(\frac{r^2}{2} - \frac{R^2}{2})r \,\mathrm{d}r = -\frac{1}{4}\pi G\alpha^2 R^4$

$T_{12} = T_{\theta z}|_R = G\alpha R$

$\frac{2M}{\pi R^3} = \frac{2(\frac{1}{2}\pi G\alpha R^4)}{\pi R^3} = G\alpha R$

$\therefore T_{12} = T_{\theta z}|_R = \frac{2M}{\pi R^3}$

$T_{11} - T_{22} = T_{\theta\theta} - T_{zz} = -p + G(1 + \alpha^2 r^2) - (-p + G) = G\alpha^2 r^2$

$\therefore (T_{11} - T_{22})|_R = G\alpha^2 R^2$

$\frac{4F_z}{\pi R^2} = \frac{4(-\frac{1}{4}\pi G\alpha^2 R^4)}{\pi R^2} = -G\alpha^2 R^2$

$\therefore T_{11} - T_{22} = T_{\theta\theta} - T_{zz} = -\frac{4F_z}{\pi R^2}$

CHAPTER 2

Viscous Liquid

Lecture 2 **Date:** <YYYY-MM-DD>

Topic: Velocity gradient; rate of deformation tensor; Newtonian fluid; General viscous fluid; plastic behavior; balance equations **Scribe:** Yang Han

2.1 Velocity Gradient

An engineering student's first exposure to the concept of velocity gradient is typically with a shear flow of a Newtonian fluid (Sr. Newton, 1687):

$$\tau_{yx} = \eta \frac{\mathrm{d}v_x}{\mathrm{d}y} \tag{2.1}$$

$$\frac{\mathrm{d}v_x}{\mathrm{d}y} = \text{shear rate} = \dot{\gamma} \tag{2.2}$$

Here, the velocity gradient is typically expressed as:

$$\mathrm{d}\mathbf{v} = \frac{\partial \mathbf{v}}{\partial \mathbf{x}} \cdot \mathrm{d}\mathbf{x} \text{ or } \mathrm{d}\mathbf{v} = \mathbf{L} \cdot \mathrm{d}\mathbf{x} \tag{2.3}$$

$$\mathbf{L} = \begin{bmatrix} \frac{\partial v_x}{\partial x} & \frac{\partial v_x}{\partial y} & \frac{\partial v_x}{\partial z} \\ \frac{\partial v_y}{\partial x} & \frac{\partial v_y}{\partial y} & \frac{\partial v_y}{\partial z} \\ \frac{\partial v_z}{\partial x} & \frac{\partial v_z}{\partial y} & \frac{\partial v_z}{\partial z} \end{bmatrix} = \frac{\partial v_i}{\partial x_j} \hat{\mathbf{e}}_\mathbf{i} \hat{\mathbf{e}}_\mathbf{j} = (\boldsymbol{\nabla} \mathbf{v})^T \tag{2.4}$$

From Chapter 1, Eq. (1.41), we know $\mathrm{d}\mathbf{x} = \mathbf{F} \cdot \mathrm{d}\mathbf{x}'$. Noting that $\mathrm{d}\mathbf{x}'$ is fixed at t', we can express the time derivative of x as:

$$\frac{\partial \mathbf{x}}{\partial t} = \frac{\partial \mathbf{F}}{\partial t} \cdot \mathrm{d}\mathbf{x}' + \mathbf{F}\frac{\partial(\mathrm{d}\mathbf{x}')}{\partial t} = \frac{\partial \mathbf{F}}{\partial t} \cdot \mathrm{d}\mathbf{x}' \tag{2.5}$$

$$\therefore \frac{\partial \mathbf{x}}{\partial t} = \mathrm{d}\mathbf{v} = \dot{\mathbf{F}} \cdot \mathrm{d}\mathbf{x}' \tag{2.6}$$

$$\dot{\mathbf{F}} \cdot \mathrm{d}\mathbf{x}' = \mathbf{L} \cdot \mathrm{d}\mathbf{x} = \mathbf{L} \cdot \mathbf{F} \cdot \mathrm{d}\mathbf{x}' \tag{2.7}$$

$$\therefore \dot{\mathbf{F}} = \mathbf{L} \cdot \mathbf{F} \tag{2.8}$$

$$\because \lim_{\mathbf{x}' \to \mathbf{x}} \mathbf{F} = \mathbf{I} \tag{2.9}$$

$$\therefore \lim_{\mathbf{x}' \to \mathbf{x}} \dot{\mathbf{F}} = \mathbf{L} \tag{2.10}$$

See Table A.2 for $\mathbf{L}$ components.

Example - Uniaxial Extensional Flow

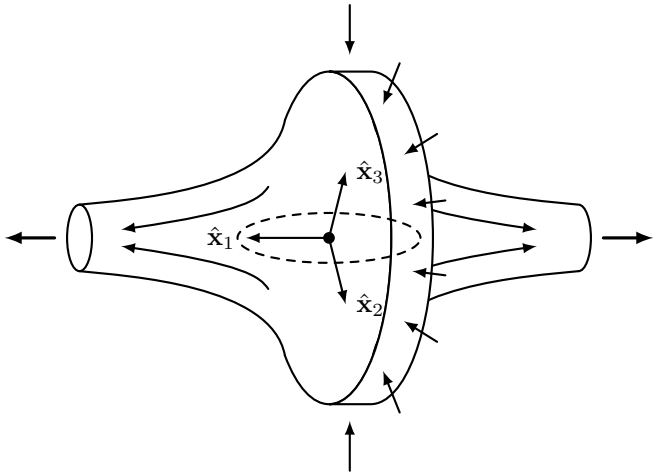


Figure 2.1: Uniaxial extensional flow.

$x_1 = \alpha_1 x_1'$

$v_1 = \frac{\mathrm{d}x_1}{\mathrm{d}t} = \lim_{x_1' \to x_1} \frac{\mathrm{d}\alpha_1}{\mathrm{d}t} x_1 = \dot{\alpha}_1 x_1$

Similarly, $v_2 = \dot{\alpha}_2 x_2$ and $v_2 = \dot{\alpha}_3 x_3$.

$$\mathbf{L} = \begin{bmatrix} \frac{\partial v_1}{\partial x_1} & \frac{\partial v_1}{\partial x_2} & \frac{\partial v_1}{\partial x_3} \\ \frac{\partial v_2}{\partial x_1} & \frac{\partial v_2}{\partial x_2} & \frac{\partial v_2}{\partial x_3} \\ \frac{\partial v_3}{\partial x_1} & \frac{\partial v_3}{\partial x_2} & \frac{\partial v_3}{\partial x_3} \end{bmatrix} = \begin{bmatrix} \dot{\alpha}_1 & 0 & 0 \\ 0 & \dot{\alpha}_2 & 0 \\ 0 & 0 & \dot{\alpha}_3 \end{bmatrix}$$

Since an uniaxial extension flow is symmetric, $v_2 = v_3$. For an incompressible fluid, $\boldsymbol{\nabla} \cdot \mathbf{v} = 0$.

$\therefore \dot{\alpha}_1 + \dot{\alpha}_2 + \dot{\alpha}_3 = 0$

$\dot{\alpha}_2 = \dot{\alpha}_3 = -\frac{1}{2}\dot{\alpha}_1$

$$\mathbf{L} = \begin{bmatrix} \dot{\alpha}_1 & 0 & 0 \\ 0 & -\dot{\alpha}_1/2 & 0 \\ 0 & 0 & -\dot{\alpha}_1/2 \end{bmatrix} = \begin{bmatrix} \dot{\epsilon}_1 & 0 & 0 \\ 0 & -\dot{\epsilon}_1/2 & 0 \\ 0 & 0 & -\dot{\epsilon}_1/2 \end{bmatrix} \text{ (symmetric)}$$

Example - Steady Simple Shear Flow

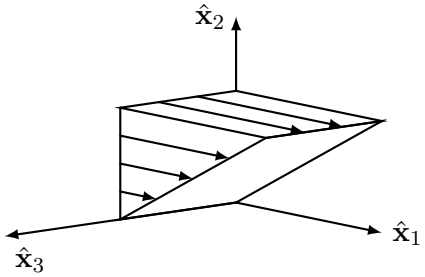


Figure 2.2: Simple shear flow.

$\frac{\mathrm{d}x_1}{\mathrm{d}t} = \frac{\mathrm{d}\gamma}{\mathrm{d}t}x_2 = \dot{\gamma}x_2 = v_1$, $v_2 = v_3 = 0$

$$\mathbf{L} = \begin{bmatrix} \frac{\partial v_1}{\partial x_1} & \frac{\partial v_1}{\partial x_2} & \frac{\partial v_1}{\partial x_3} \\ \frac{\partial v_2}{\partial x_1} & \frac{\partial v_2}{\partial x_2} & \frac{\partial v_2}{\partial x_3} \\ \frac{\partial v_3}{\partial x_1} & \frac{\partial v_3}{\partial x_2} & \frac{\partial v_3}{\partial x_3} \end{bmatrix} = \begin{bmatrix} 0 & \dot{\gamma} & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

Example - Solid Body Rotation

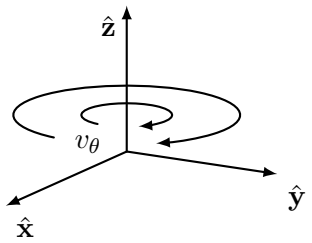


Figure 2.3: Rotational flow.

$v_\theta = \Omega r$, $v_r = v_z = 0$

From Table A.2:

$L_{rr} = \frac{\partial v_r}{\partial r} = 0$, $L_{r\theta} = \frac{1}{r}\frac{\partial v_r}{\partial \theta} - \frac{v_\theta}{r} = -\Omega$, $L_{rz} = \frac{\partial v_r}{\partial z} = 0$

$L_{\theta r} = \frac{\partial v_\theta}{\partial r} = \Omega$, $L_{\theta\theta} = \frac{1}{r}\frac{\partial v_\theta}{\partial \theta} + \frac{v_r}{r} = 0$, $L_{\theta z} = \frac{\partial v_\theta}{\partial z} = 0$

$L_{zr} = \frac{\partial v_z}{\partial r} = 0$, $L_{z\theta} = \frac{1}{r}\frac{\partial v_z}{\partial \theta} = 0$, $L_{zz} = \frac{\partial v_z}{\partial z} = 0$

$$\therefore \mathbf{L} = \begin{bmatrix} 0 & -\Omega & 0 \\ \Omega & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

2.2 Rate of Deformation Tensor

The rate of deformation tensor is defined as:

$$2\mathbf{D} = \mathbf{L} + \mathbf{L}^T = (\boldsymbol{\nabla}\mathbf{v})^T + \boldsymbol{\nabla}\mathbf{v} \tag{2.11}$$

Compared to $\mathbf{L}$, $2\mathbf{D}$ is a symmetric tensor.

We can also define an antisymmetric version, which represents the vorticity tensor:

$$2\mathbf{W} = \mathbf{L} - \mathbf{L}^T = (\boldsymbol{\nabla}\mathbf{v})^T - \boldsymbol{\nabla}\mathbf{v} \tag{2.12}$$

It is straightforward to note:

$$\mathbf{L} = \mathbf{D} + \mathbf{W} \tag{2.13}$$

Example - Uniaxial Extensional Flow

$$\mathbf{L} = \begin{bmatrix} \dot{\epsilon}_1 & 0 & 0 \\ 0 & -\dot{\epsilon}_1/2 & 0 \\ 0 & 0 & -\dot{\epsilon}_1/2 \end{bmatrix}, \mathbf{L}^T = \begin{bmatrix} \dot{\epsilon}_1 & 0 & 0 \\ 0 & -\dot{\epsilon}_1/2 & 0 \\ 0 & 0 & -\dot{\epsilon}_1/2 \end{bmatrix}$$

$$\therefore 2\mathbf{D} = \begin{bmatrix} 2\dot{\epsilon}_1 & 0 & 0 \\ 0 & -\dot{\epsilon}_1 & 0 \\ 0 & 0 & -\dot{\epsilon}_1 \end{bmatrix}, 2\mathbf{W} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \text{ (irrotational flow)}$$

Invariants:

$I_{2D} = \text{tr}(2\mathbf{D}) = 2\dot{\epsilon}_1 - \dot{\epsilon}_1 - \dot{\epsilon}_1 = 0$

$$(2\mathbf{D})^2 = \begin{bmatrix} 2\dot{\epsilon}_1 & 0 & 0 \\ 0 & -\dot{\epsilon}_1 & 0 \\ 0 & 0 & -\dot{\epsilon}_1 \end{bmatrix} \cdot \begin{bmatrix} 2\dot{\epsilon}_1 & 0 & 0 \\ 0 & -\dot{\epsilon}_1 & 0 \\ 0 & 0 & -\dot{\epsilon}_1 \end{bmatrix} = \begin{bmatrix} 4\dot{\epsilon}_1^2 & 0 & 0 \\ 0 & \dot{\epsilon}_1^2 & 0 \\ 0 & 0 & \dot{\epsilon}_1^2 \end{bmatrix}$$

$\therefore II_{2D} = \frac{1}{2}[(\text{tr}\, 2\mathbf{D}) - \text{tr}\,(2\mathbf{D})^2] = -3\dot{\epsilon}_1^2$

$III_{2D} = \det 2\mathbf{D} = 2\dot{\epsilon}_1(\dot{\epsilon}_1)(\dot{\epsilon}_1) = 2\dot{\epsilon}_1^3$

Simple Shear

$$\mathbf{L} = \begin{bmatrix} 0 & \dot{\gamma} & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \mathbf{L}^T = \begin{bmatrix} 0 & 0 & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$2\mathbf{D} = \begin{bmatrix} 0 & \dot{\gamma} & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, 2\mathbf{W} = \begin{bmatrix} 0 & \dot{\gamma} & 0 \\ -\dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

Invariants:

$I_{2D} = \text{tr}(2\mathbf{D}) = 0$

$$(2\mathbf{D})^2 = \begin{bmatrix} 0 & \dot{\gamma} & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \cdot \begin{bmatrix} 0 & \dot{\gamma} & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} = \begin{bmatrix} \dot{\gamma}^2 & 0 & 0 \\ 0 & \dot{\gamma}^2 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$\therefore II_{2D} = \frac{1}{2}[(\text{tr}\, 2\mathbf{D}) - \text{tr}\,(2\mathbf{D})^2] = -\dot{\gamma}^2$

$III_{2D} = 0$

Solid Body Rotation

$$\mathbf{L} = \begin{bmatrix} 0 & -\Omega & 0 \\ \Omega & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \mathbf{L}^T = \begin{bmatrix} 0 & \Omega & 0 \\ -\Omega & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$2\mathbf{D} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \; 2\mathbf{W} = \begin{bmatrix} 0 & -2\Omega & 0 \\ 2\Omega & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$(2\mathbf{W})^2 = \begin{bmatrix} -4\Omega^2 & 0 & 0 \\ 0 & -4\Omega^2 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$I_{2W} = \mathrm{tr}(2\mathbf{W}) = 0$

$II_{2W} = \frac{1}{2}[(\mathrm{tr}\, 2\mathbf{W}) - \mathrm{tr}\,(2\mathbf{W})^2] = 4\Omega^2$

$III_{2W} = \det 2\mathbf{W} = 0$

2.3 Newtonian Fluid

$$\boldsymbol{\tau} = \eta\, 2\mathbf{D} \tag{2.14}$$

$$\mathbf{T} = -p\mathbf{I} + \boldsymbol{\tau} = -p\mathbf{I} + \eta\, 2\mathbf{D} \tag{2.15}$$

Example - Simple Shear

$$2\mathbf{D} = \begin{bmatrix} 0 & \dot{\gamma} & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$\mathbf{T} = -p\mathbf{I} + \eta \begin{bmatrix} 0 & \dot{\gamma} & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} = \begin{bmatrix} -p & \eta\dot{\gamma} & 0 \\ \eta\dot{\gamma} & -p & 0 \\ 0 & 0 & -p \end{bmatrix}$$

$T_{12} = T_{21} = \eta\dot{\gamma}$

$T_{11} = T_{22} = T_{33} = -p$

$\tau_{12} = \tau_{21} = \eta\dot{\gamma}$

Uniaxial Extension

$$2\mathbf{D} = \begin{bmatrix} 2\dot{\epsilon} & 0 & 0 \\ 0 & -\dot{\epsilon} & 0 \\ 0 & 0 & -\dot{\epsilon} \end{bmatrix}$$

$$\mathbf{T} = -p\mathbf{I} + \eta \begin{bmatrix} 2\dot{\epsilon} & 0 & 0 \\ 0 & -\dot{\epsilon} & 0 \\ 0 & 0 & -\dot{\epsilon} \end{bmatrix} = \begin{bmatrix} -p + 2\eta\dot{\epsilon} & 0 & 0 \\ 0 & -p - \eta\dot{\epsilon} & 0 \\ 0 & 0 & -p - \eta\dot{\epsilon} \end{bmatrix}$$

$T_{11} = -p + 2\eta\dot{\epsilon}$

$T_{22} = T_{33} = -p - \eta\dot{\epsilon}$

Assuming no traction on the surface:

$T_{22} = T_{33} = 0 \implies -p = \eta\dot{\epsilon}$

$\therefore T_{11} = 3\eta\dot{\epsilon}$

$\eta_{ext} = \eta_e = \frac{T_{11} - T_{22}}{\dot{\epsilon}} = 3\eta$

Example - Cone and Plate Rheometer

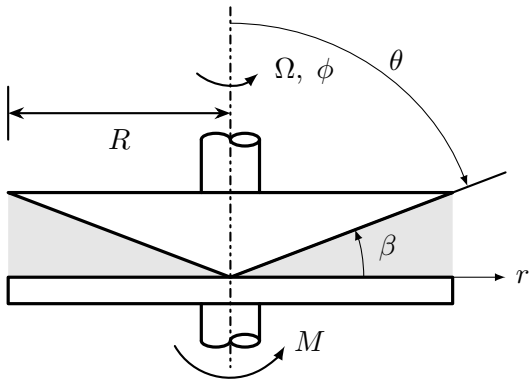


Figure 2.4: Cone-and-plate rheometer.

$v_r = v_\theta = 0,\ v_\phi = r\sin\theta\,\Omega$

From Table A.2:

$L_{rr} = \frac{\partial v_r}{\partial r} = 0,\ L_{r\theta} = \frac{1}{r}\frac{\partial v_r}{\partial \theta} - \frac{v_\theta}{r} = 0,\ L_{r\phi} = \frac{1}{r\sin\theta}\frac{\partial v_r}{\partial \phi} - \frac{v_\phi}{r} = -\frac{v_\phi}{r}$

$L_{\theta r} = \frac{\partial v_\theta}{\partial r} = 0,\ L_{\theta\theta} = \frac{1}{r}\frac{\partial v_\theta}{\partial \theta} + \frac{v_r}{r} = 0,\ L_{\theta\phi} = \frac{1}{r\sin\theta}\frac{\partial v_\theta}{\partial \phi} - \frac{v_\phi}{r}\cot\theta = -\frac{v_\phi}{r}\cot\theta$

$L_{\phi r} = \frac{\partial v_\phi}{\partial r}$, $L_{\phi\theta} = \frac{1}{r}\frac{\partial v_\phi}{\partial \theta}$, $L_{\phi\phi} = \frac{1}{r\sin\theta}\frac{\partial v_\phi}{\partial \phi} + \frac{v_r}{r} + \frac{v_\theta}{r}\cot\theta = 0$

$$\mathbf{L} = \begin{bmatrix} 0 & 0 & -\frac{v_\phi}{r} \\ 0 & 0 & -\frac{v_\phi}{r}\cot\theta \\ \frac{\partial v_\phi}{\partial r} & \frac{1}{r}\frac{\partial v_\phi}{\partial \theta} & 0 \end{bmatrix}$$

$$\mathbf{L}^T = \begin{bmatrix} 0 & 0 & \frac{\partial v_\phi}{\partial r} \\ 0 & 0 & \frac{1}{r}\frac{\partial v_\phi}{\partial \theta} \\ -\frac{v_\phi}{r} & -\frac{v_\phi}{r}\cot\theta & 0 \end{bmatrix}$$

$$2\mathbf{D} = \mathbf{L} + \mathbf{L}^T = \begin{bmatrix} 0 & 0 & \frac{\partial v_\phi}{\partial r} - \frac{v_\phi}{r} \\ 0 & 0 & \frac{1}{r}\frac{\partial v_\phi}{\partial \theta} - \frac{v_\phi}{r}\cot\theta \\ \frac{\partial v_\phi}{\partial r} - \frac{v_\phi}{r} & \frac{1}{r}\frac{\partial v_\phi}{\partial \theta} - \frac{v_\phi}{r}\cot\theta & 0 \end{bmatrix}$$

$\therefore 2D_{\theta\phi} = \frac{1}{r}\frac{\partial v_\phi}{\partial \theta} - \frac{v_\phi}{r}\cot\theta$

For a small $\beta < 0.1$, $\cot(\frac{\pi}{2} - 0.1) < 0.1 \implies \cot\theta = 0$

$\therefore 2D_{\theta\phi} = \frac{1}{r}\frac{\partial v_\phi}{\partial \theta} \cong \frac{1}{r}\frac{-\Delta v_\phi}{\Delta\theta} \cong -\frac{1}{r}\frac{v_\phi(\frac{\pi}{2}-\beta) - v_\phi(\frac{\pi}{2})}{(\frac{\pi}{2}-\beta)-\frac{\pi}{2}} = \frac{1}{r}\frac{v_\phi(\frac{\pi}{2}-\beta) - v_\phi(\frac{\pi}{2})}{\beta}$

$v_\phi(\frac{\pi}{2}) = 0$

$v_\phi(\frac{\pi}{2} - \beta) = \Omega r\sin(\frac{\pi}{2} - \beta) \cong \Omega r$

$\therefore \dot\gamma = 2D_{\theta\phi} \cong \frac{1}{r}\frac{\Omega r - 0}{\beta} = \frac{\Omega}{\beta}$

Now we estimate the torque to maintain the rotation. From Table A.3:

θ-component: $0 = -\frac{1}{r\sin\theta}\frac{\partial p}{\partial \phi} + \frac{1}{r^3}\frac{\partial}{\partial r}(r^3\tau_{r\phi}) + \frac{1}{r\sin\theta}\frac{\partial(\tau_{\theta\phi}\sin\theta)}{\partial\theta} + \frac{1}{r\sin\theta}\frac{\partial(\tau_{\phi\phi})}{\partial\phi} + \frac{\tau_{\phi r} - \tau_{r\phi} + 2\cot\theta\,\tau_{\theta\phi}}{r} + \rho g_\phi$

Noting that $\theta \to \frac{\pi}{2}$, $\sin\theta \to 1$

$\therefore 0 = \frac{1}{r}\frac{\partial \tau_{\theta\phi}}{\partial\theta} + \frac{2}{r}\cot\theta\,\tau_{\theta\phi}$

$\frac{\mathrm{d}\tau_{\theta\phi}}{\mathrm{d}\theta} + 2\cot\theta\,\tau_{\theta\phi} = 0$

$\frac{\mathrm{d}\tau_{\theta\phi}}{\tau_{\theta\phi}} = -2\cot\theta\,\mathrm{d}\theta$

$\ln\tau_{\theta\phi} = -2\int\frac{\cos\theta}{\sin\theta}\mathrm{d}\theta + C = -2\ln\sin\theta + C$

$\therefore \tau_{\theta\phi} = \frac{C_1}{\sin^2\theta} \cong const.$

$$
\begin{aligned}
M &= \int_0^{2\pi}\int_0^R r^2 \tau_{\theta\phi}|_{\pi/2}\,\mathrm{d}r\mathrm{d}\phi \\
&= \tau_{\theta\phi}|_{\pi/2}\int_0^{2\pi}\frac{1}{3}r^3|_0^R\,\mathrm{d}\phi \\
&= \tau_{\theta\phi}|_{\pi/2}\frac{2\pi}{3}R^3
\end{aligned}
$$

$\therefore \tau_{\theta\phi}|_{\pi/2} = \frac{3M}{2\pi R^3}$

2.4 General Viscous Fluid

$$\mathbf{T} = f(2\mathbf{D}) \tag{2.16}$$

$$\mathbf{T} = -p\mathbf{I} + \eta(II_{2D})\,2\mathbf{D} \text{ or } \boldsymbol{\tau} = \eta(II_{2D})\,2\mathbf{D} \tag{2.17}$$

Power Law

$$\eta(II_{2D}) = m|II_{2D}|^{(n-1)/2} \tag{2.18}$$

For simple shear, $II_{2D} = -\dot{\gamma}^2$, so that:

$$\eta(II_{2D}) = m|-\dot{\gamma}^2|^{(n-1)/2} = m\dot{\gamma}^{n-1} \tag{2.19}$$

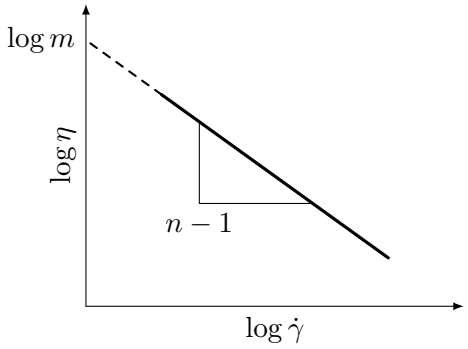


Figure 2.5: Power law model.

It is easy to notice that:

- $n = 1$, Newtonian
- $n < 1$, shear-thinning
- $n > 1$, shear-thickening

We can also write the shear stress for simple shear:

$$\tau_{12} = \tau_{21} = m\dot{\gamma}^n \tag{2.20}$$

Cross Model

This is a 4-parameter model: η_0, η_∞, K, n

$$\frac{\eta(II_{2D}) - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{1 + (K^2|II_{2D}|)^{(1-n)/2}} \tag{2.21}$$

For simple shear, $II_{2D} = -\dot{\gamma}^2$, so that:

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{1 + (K^2\dot{\gamma}^2)^{(1-n)/2}} = \frac{1}{1 + (K\dot{\gamma})^{(1-n)}} \tag{2.22}$$

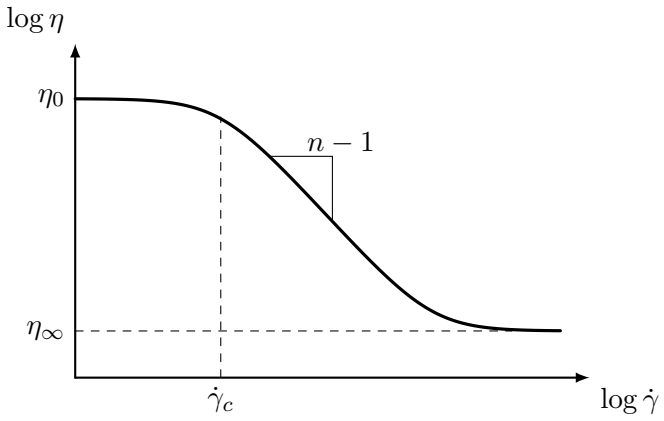


Figure 2.6: Cross model.

- For small $\dot{\gamma}$, $\eta = \eta_0$
- For intermediate $\dot{\gamma}$, $\eta - \eta_\infty \cong (\eta_0 - \eta_\infty)m\dot{\gamma}^{n-1}$, where $m = K^{n-1}$ and $K = 1/\dot{\gamma}_C$
- For large $\dot{\gamma}$, $\eta \to \eta_\infty$, Newtonian

Yasuda Model

This is a 5-parameter model: η_0, η_∞, λ, a, n

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{[1 + (\lambda|II_{2D}|^{1/2})^a]^{(1-n)/a}} \tag{2.23}$$

For simple shear:

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{[1 + (\lambda\dot{\gamma})^a]^{(1-n)/a}} \tag{2.24}$$

Carreau Model

This is a special case of the Yasuda model when $a = 2$:

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{[1 + (\lambda\dot{\gamma})^2]^{(1-n)/2}} \tag{2.25}$$

Ellis Model

This is a 3-parameter model: η_0, K, a

$$\frac{\eta(II_\tau)}{\eta_0} = \frac{1}{1 + (\frac{|II_\tau|}{K})^{a-1}} \tag{2.26}$$

For simple shear, $2\mathbf{D} = \begin{bmatrix} 0 & \dot{\gamma} & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$

$$\boldsymbol{\tau} = \eta(II_{2D})\, 2\mathbf{D} = \begin{bmatrix} 0 & \eta\dot{\gamma} & 0 \\ \eta\dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$\boldsymbol{\tau} \cdot \boldsymbol{\tau} = \begin{bmatrix} 0 & \eta\dot{\gamma} & 0 \\ \eta\dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \cdot \begin{bmatrix} 0 & \eta\dot{\gamma} & 0 \\ \eta\dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} = \begin{bmatrix} \eta^2\dot{\gamma}^2 & 0 & 0 \\ 0 & \eta^2\dot{\gamma}^2 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$\therefore II_\tau = \frac{1}{2}(I_\tau^2 - \mathrm{tr}(\boldsymbol{\tau}^2)) = \frac{1}{2}(0^2 - 2\eta^2\dot{\gamma}^2) = -\eta^2\dot{\gamma}^2$

We finally have:

$$\frac{\eta(II_\tau)}{\eta_0} = \frac{1}{1 + (\frac{\eta^2\dot{\gamma}^2}{K})^{a-1}} \tag{2.27}$$

Example - Flow of a Power Law Fluid in a Tube

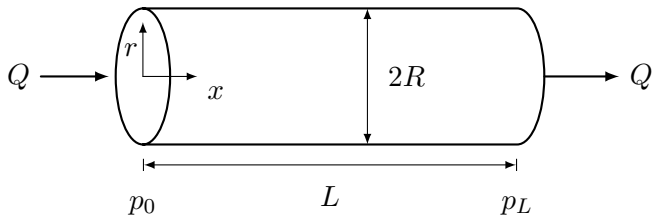


Figure 2.7: Pipe flow.

$v_x = v_x(r),\ v_\theta = 0,\ v_r = 0$

For the x-component (the one along the axial direction) in Table 1.7.1, p.48:

$0 = -\frac{\partial p}{\partial x} + \frac{1}{r}\frac{\partial}{\partial r}(r\tau_{rx}) = f(x) + g(r)$

$\therefore 0 = -\frac{\mathrm{d}p}{\mathrm{d}x} + \frac{1}{r}\frac{\mathrm{d}}{\mathrm{d}r}(r\tau_{rx})$

$\frac{\mathrm{d}p}{\mathrm{d}x} = C_1$, $\int_{p_0}^{p_L} \mathrm{d}p = C_1 \int_0^L \mathrm{d}x$, $C_1 = -\frac{p_0 - p_L}{L} = \frac{\mathrm{d}p}{\mathrm{d}x}$

$\frac{\mathrm{d}}{\mathrm{d}r}(r\tau_{rx}) = -\frac{p_0 - p_L}{L} r$

$r\tau_{rx} = -\frac{p_0 - p_L}{2L} r^2 + C_2$

$\tau_{rx} = -\frac{p_0 - p_L}{2L} r + \frac{C_2}{r}$

$\because \tau_{rx}$ cannot be infinite at $r = 0$, $C_2 = 0$

$\tau_{rx} = -\frac{p_0 - p_L}{2L} r$

$\tau_w = \tau_{rx}|_{r=R} = -\frac{p_0 - p_L}{2L} R$

Using τ_w, we can rewrite τ_{rx} as:

$\tau_{rx} = \tau_w(\frac{r}{R})$

For a power law fluid:

$\tau_{rx} = m|-\frac{\mathrm{d}v_x}{\mathrm{d}r}|^n = m(-\frac{\mathrm{d}v_x}{\mathrm{d}r})^n$

$m(-\frac{\mathrm{d}v_x}{\mathrm{d}r})^n = \tau_w(\frac{r}{R})$

$-\frac{\mathrm{d}v_x}{\mathrm{d}r} = (\frac{\tau_w}{m})^{1/n}(\frac{r}{R})^{1/n}$

$-\mathrm{d}v_x = (\frac{\tau_w}{m})^{1/n} R(\frac{r}{R})^{1/n}\,\mathrm{d}(\frac{r}{R})$

$-\int_0^{v_x} \mathrm{d}v_x = (\frac{\tau_w}{m})^{1/n} R \int_R^r (\frac{r}{R})^{1/n}\,\mathrm{d}(\frac{r}{R})$

$v_x = (\frac{\tau_w}{m})^{1/n} \frac{R}{1/n+1}[1 - (\frac{r}{R})^{1/n+1}]$

$Q = \int_0^{2\pi}\int_0^R v_x r\,\mathrm{d}r\mathrm{d}\theta = 2\pi R^2 \int_0^1 v_x(\frac{r}{R})\,\mathrm{d}(\frac{r}{R})$

$Q = 2\pi(\frac{\tau_w}{m})^{1/n}\frac{R^3}{1/n+1}\int_0^1[1-(\frac{r}{R})^{1/n+1}](\frac{r}{R})\,\mathrm{d}(\frac{r}{R})$

$Q = 2\pi R^3(\frac{\tau_w}{m})^{1/n}\frac{1}{1/n+1}[\frac{1}{2}(\frac{r}{R})^2-\frac{1}{1/n+3}(\frac{r}{R})^{1/n+3}]_0^1$

$Q = \frac{\pi R^3}{1/n+3}(\frac{\tau_w}{m})^{1/n} = \frac{\pi R^3}{1/n+3}[\frac{(p_0-p_L)R}{2mL}]^{1/n}$

2.5 Plastic Behavior

2.5.1 Bingham Model

1D Deformation

We can define a yielding stress τ_y:

$$\tau = G\gamma \text{ for } \tau < \tau_y \text{ (Hookean behavior)} \tag{2.28}$$

$$\tau = \eta\dot{\gamma} + \tau_y \text{ for } \tau \geq \tau_y \text{ (Newtonian behavior)} \tag{2.29}$$

Alternatively, we can write this as the Bingham plastic:

$$\dot{\gamma} = 0 \text{ for } \tau < \tau_y \tag{2.30}$$

$$\tau = \eta\dot{\gamma} + \tau_y \text{ for } \tau \geq \tau_y \tag{2.31}$$

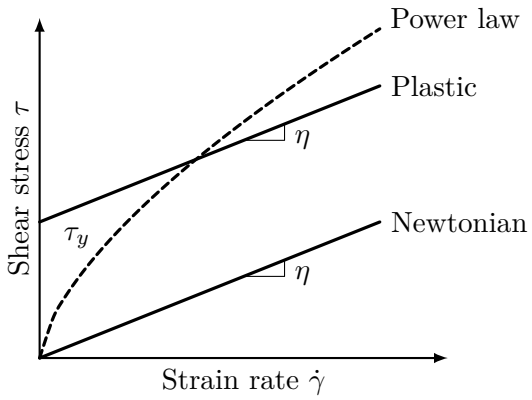


Figure 2.8: Bingham plastic.

3D Bingham Model

$$\boldsymbol{\tau} = G\mathbf{B} \text{ for } II_\tau < \tau_y^2 \tag{2.32}$$

$$\boldsymbol{\tau} = \Big[\eta_0 + \frac{\tau_y}{|II_{2D}|^{1/2}}\Big]2\mathbf{D} \text{ for } II_\tau \geq \tau_y^2 \tag{2.33}$$

Example - The Ketchup Bottle

$\tau_w(\pi DL) = p(\frac{\pi D^2}{4}) = \rho g H(\frac{\pi D^2}{4})$

$\tau_w = \frac{\rho g H D}{4L}$

Make a larger bottle neck diameter and a smaller bottle neck length will enable the ketchup to flow.

2.5.2 Other Useful Models

Casson Model

$$\dot{\gamma} = 0 \text{ for } \tau < \tau_y \tag{2.34}$$

$$\tau^{1/2} = \tau_y^{1/2} + (\eta\dot{\gamma})^{1/2} \text{ for } \tau \geq \tau_y \tag{2.35}$$

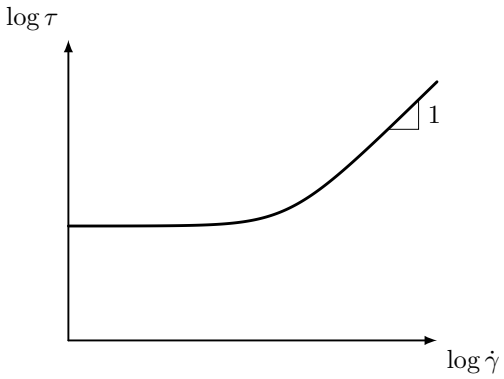


Figure 2.9: Casson model.

For the flow regime, we have $\frac{1}{2}\log\tau \sim \frac{1}{2}\log\eta + \frac{1}{2}\log\dot{\gamma}$. Therefore

$$\frac{\mathrm{d}\log\tau}{\mathrm{d}\log\dot{\gamma}} \sim 1 \tag{2.36}$$

Two-Viscosity Model: Herschel-Bulkley Model

For a lower Newtonian rather than a Hookean regime:

$$\boldsymbol{\tau} = 2\eta \mathbf{D} \text{ for } II_{2D}^{1/2} \leq \dot{\gamma}_C \tag{2.37}$$

$$\boldsymbol{\tau} = \Big[\frac{\tau_y}{|II_{2D}|^{1/2}} + m|II_{2D}|^{(n-1)/2}\Big] 2\mathbf{D} \text{ for } II_{2D}^{1/2} > \dot{\gamma}_C \tag{2.38}$$

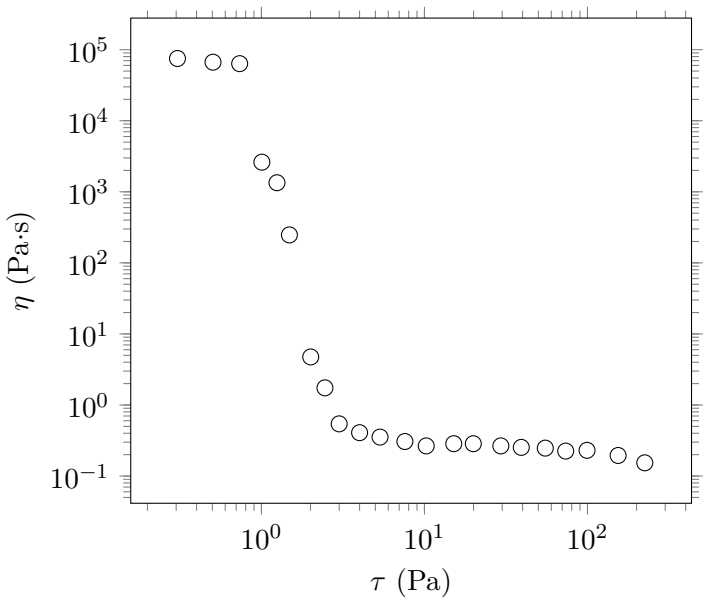


Figure 2.10: Herschel-Bulkley model.

The above example is a 6 wt.% iron oxide suspension. It shows extremely high shear viscosity at low $\dot{\gamma}$. At sufficiently high $\dot{\gamma}$, the suspension thins out based on the power law.

2.6 Balance Equation

Equation of Motion

$$\boldsymbol{\nabla} \cdot \mathbf{v} = 0 \text{ (Continuity eq.)} \tag{2.39}$$

$$\rho \frac{\mathrm{D}\mathbf{v}}{\mathrm{D}t} = \boldsymbol{\nabla} \cdot \mathbf{T} + \rho \mathbf{g} \text{ (Momentum eq.)} \tag{2.40}$$

Energy Equation

$$\rho \frac{\mathrm{D}T}{\mathrm{D}t} = k_T \nabla^2 T + \mathbf{T} : \mathbf{D} \tag{2.41}$$

Temperature and Pressure Dependence of Viscosity

$$\eta_0 = K_1 e^{bT} e^{ap} \tag{2.42}$$

For polymers: $b = -0.03$ to -0.1 K^{-1} and $a = 1 - 4$ kbar^{-1}.

Andrade-Eyring equation:

$$\eta_0 = K_1 e^{E_\eta/RT} \tag{2.43}$$

where E_η = flow activation energy. $E_\eta = 10 - 30$ kJ/mol for small molecules; $E_\eta = 25 - 85$ kJ/mol for polymers.

William-Landel-Ferry (WLF) equation

$$\log \frac{\eta T_r \rho_r}{\eta_r T \rho} = \frac{-C_1(T - T_r)}{C_2 + T - T_r} = \log a_T \tag{2.44}$$

a_T = shift factor of temperature; $C_1 = 17.44$ K and $C_2 = 51.6$ K for linear polymers in amorphous state.

Example - Viscous Dissipation in Shear Flow

$v_x = \frac{v_0}{B} y$, $v_x = v_0$ at $y = B$, the upper plate. For a steady temperature profile, the energy equation reads:

$\rho \hat{C}_p \frac{\mathrm{D}T}{\mathrm{D}t} = k_T \nabla^2 T + \mathbf{T} : \mathbf{D}$

At steady state:

$0 = k_T \frac{\mathrm{d}^2 T}{\mathrm{d}y^2} + \eta (\frac{\mathrm{d}v_x}{\mathrm{d}y})^2$

For a power law fluid, $\eta = m(\frac{\mathrm{d}v_x}{\mathrm{d}y})^{n-1}$, $\frac{\mathrm{d}v_x}{\mathrm{d}y} = \frac{v_0}{B}$

$\therefore 0 = k_T \frac{\mathrm{d}^2 T}{\mathrm{d}y^2} + m(\frac{v_0}{B})^{n-1}(\frac{v_0}{B})^2$

$\frac{\mathrm{d}^2 T}{\mathrm{d}y^2} = -\frac{m v_0^{n+1}}{k_T B^{n+1}}$, $\frac{\mathrm{d}T}{\mathrm{d}y} = -\frac{m v_0^{n+1}}{k_T B^n}(\frac{y}{B}) + C_1$

$T = -\frac{m v_0^{n+1}}{2 k_T B^{n-1}}(\frac{y}{B})^2 + C_1 y + C_2$

BC1: $T|_{y=0} = T_0$, $C_2 = T_0$

BC2: $T|_{y=B} = T_0$, $C_1 = \frac{m v_0^{n+1}}{2 k_T B^{n-1}}(\frac{1}{B})$

$\therefore T - T_0 = \frac{m v_0^{n+1}}{2 k_T B^{n-1}} \left[\frac{y}{B} - (\frac{y}{B})^2 \right]$

The maximum T occurs at $y = \frac{B}{2}$

$\therefore T_{max} - T_0 = \frac{m v_0^{n+1}}{8 k_T B^{n-1}} = \frac{1}{8} (\mathrm{Br} T_0)$

where Br $= \frac{m v_0^{n+1}}{k_T T_0}$ is the Brinkman number (heat generated by viscous dissipation vs. heat transported by molecular conduction).

CHAPTER 3

Linear Viscoelasticity

Lecture 3 **Date:** <YYYY-MM-DD>

Topic: Time-dependent properties; general linear viscoelastic model; small strain material functions; creeping; sinusoidal oscillation **Scribe:** Yang Han

3.1 Time-Dependent Properties

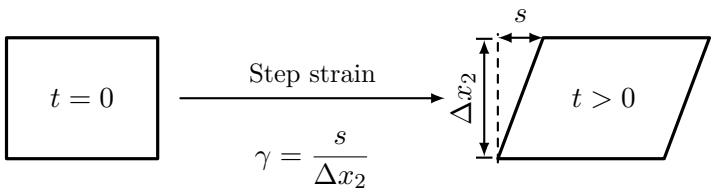


Figure 3.1: Transient behavior after step strain.

For simple shear:

$$G(t) = \frac{\tau_{21}(t)}{\gamma} \tag{3.1}$$

where G = relaxation modulus. If we keep the step strain on the top surface

- Hookean solid: no stress relaxation, τ = constant, $\tau(t) = G\gamma$, and constant G
- Newtonian fluid: τ relaxes instantly, no time effect
- Viscoelastic behavior:
  - Liquid: relaxes gradually to 0

– Solid: relaxes slowly to τ_e

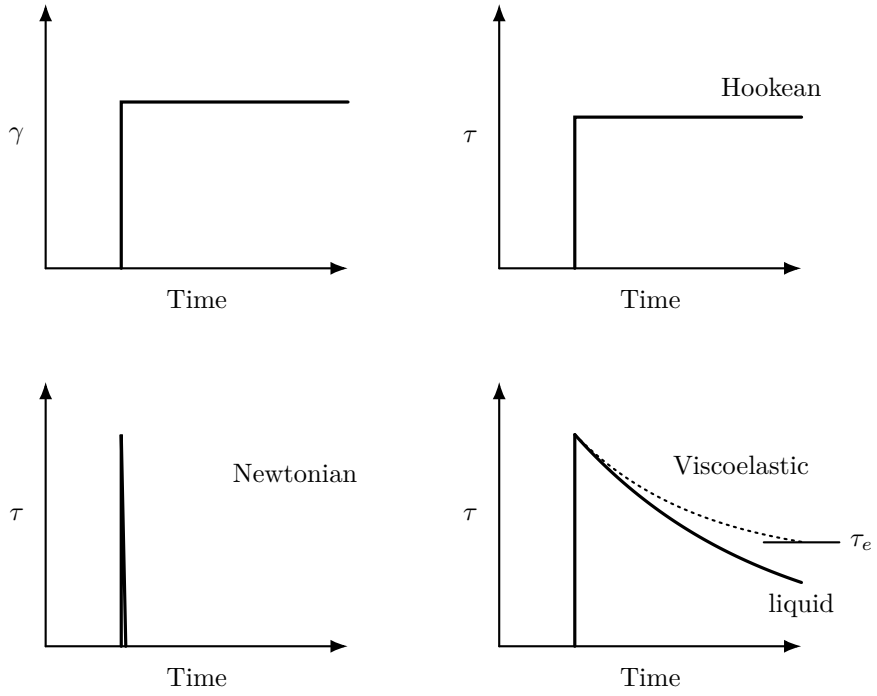


Figure 3.2: Transient response after step strain.

We can now define the viscoelasticity.

For nonlinear viscoelasticity:

$$G(t,\gamma) = \frac{\tau(t,\gamma)}{\gamma} \text{ for } \gamma > 1 \tag{3.2}$$

This case will be covered in Chapter 4.

For linear viscoelasticity:

$$G(t) = \frac{\tau(t)}{\gamma} \text{ for } \gamma < 1 \tag{3.3}$$

where τ varies linearly with strain γ.

3.2 General Linear Viscoelastic Model

Definitions

Since the stress changes linearly with the strain, we can express this linear relationship in a differential form:

$$\mathrm{d}\tau = G\mathrm{d}\gamma = G\frac{\mathrm{d}\gamma}{\mathrm{d}t}\mathrm{d}t = G\dot{\gamma}\mathrm{d}t \tag{3.4}$$

$$\tau(t) = \int_{-\infty}^{t} G(t-t')\dot{\gamma}(t')\,\mathrm{d}t' \tag{3.5}$$

where t' is the past time variable running from the infinite past $-\infty$ to the present time t.

Let $s = t = t'$, $t' = t - s$, $-\infty = t - s \implies s \to \infty$. These allow us to change the variable from t' to s as $\mathrm{d}t' = \mathrm{d}(t-s) = -\mathrm{d}s$:

$$\therefore \tau = \int_{0}^{\infty} G(s)\dot{\gamma}(t-s)\,\mathrm{d}s \tag{3.6}$$

Since we are trying to capture certain "relaxation" behavior of the viscoelasticity, we can define a decaying modulus as:

$$G(t) = G_0 e^{-t/\lambda} \tag{3.7}$$

where λ is the relaxation time. The linear viscoelasticity model then becomes:

$$\therefore \tau = \int_{-\infty}^{t} G_0 e^{-(t-t')/\lambda}\,\dot{\gamma}(t')\,\mathrm{d}t' \tag{3.8}$$

This is called a single exponential model, which typically does not fit experimental data well.

For improvement, we can try a multi-mode model:

$$G(t) = \sum_{k=1}^{N} G_k e^{-t/\lambda_k} \tag{3.9}$$

$$\therefore \tau = \int_{-\infty}^{t} \sum_{k=1}^{N} G_k e^{-(t-t')/\lambda_k}\,\dot{\gamma}(t')\,\mathrm{d}t' \tag{3.10}$$

For practical purposes, we typically choose the λ_k values and then fit for G_k.

A useful check for zero-shear viscosity:

$$\frac{\tau}{\dot{\gamma}} = \eta_0 = \int_{0}^{\infty} G(t)\,\mathrm{d}t = \text{ area under the relaxation curve} \tag{3.11}$$

Rouse Model

A popular approach to fit for G_k is the Rouse model:

$$G_k = G_0 \frac{\lambda_k}{\sum_k \lambda_k} \tag{3.12}$$

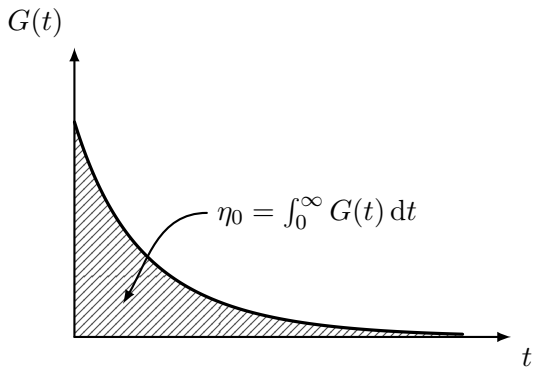


Figure 3.3: Relaxation modulus for simple shear.

where $\lambda_k = \frac{\lambda_0}{k^2}$. This model is good for dilute polymer solution or low MW systems.

Viscoelastic Solid

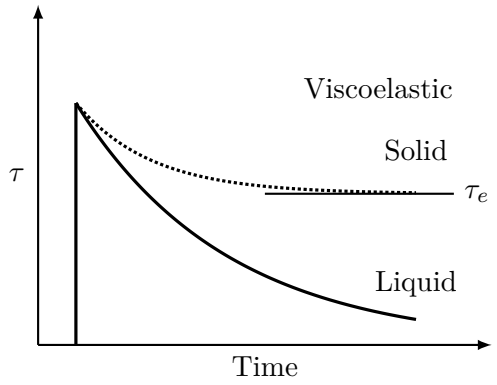


Figure 3.4: Viscoelastic solid vs. liquid.

If the material exhibit solid-like properties, an non-dissipating elastic modulus can be added:

$$\tau = \int_{-\infty}^{t} \left[\sum_{k=1}^{N} G_k e^{-(t-t')/\lambda_k} + G_e \right] \dot{\gamma}(t') \, \mathrm{d}t' \tag{3.13}$$

Relaxation Spectrum H

Sometimes, relaxation spectrum $H(\lambda)$ is used to reveal the underlying molecular or structural details. This is in contrast to G, which is a direct, macroscopic property. $H(\lambda)$ describes the distribution of relaxation times and their corresponding strengths within a material.

$$G(s) = \int_0^{\infty} \frac{H(\lambda)}{\lambda} e^{-s/\lambda} \, \mathrm{d}\lambda \tag{3.14}$$

For a narrow spacing of relaxation times, $s = t - t' \to 0 \implies e^{-s/\lambda} \to 1$.

$$\therefore G_k \cong H(\lambda_k) \int_{\lambda_{kH}}^{\lambda_k} (1) \frac{\mathrm{d}\lambda}{\lambda} \cong H(\lambda_k) \ln \frac{\lambda_k}{\lambda_{kH}} \tag{3.15}$$

Linear Viscoelasticity in 3D

$$\boldsymbol{\tau} = \int_{-\infty}^{t} G(t-t') 2\mathbf{D}(t') \, \mathrm{d}t' \tag{3.16}$$

For simple shear, $2\mathbf{D} = \begin{bmatrix} 0 & \dot{\gamma} & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$, $2D_{12} = 2D_{21} = \dot{\gamma}$.

Example - Stress Growth in Start-up of Steady Shear Flow

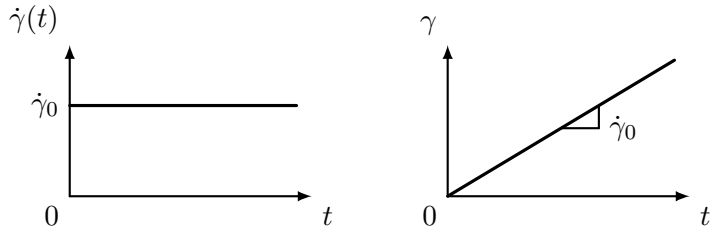


Figure 3.5: Start-up of steady shear flow.

$\gamma = \int_0^t \dot{\gamma}_0 \, \mathrm{d}t = \dot{\gamma}_0 t$

- $t < 0$, $\dot{\gamma} = 0$, $\tau_{12} = 0$
- $t \geq 0$, $t \geq 0$, $\dot{\gamma} = \dot{\gamma}_0$, $\tau_{12}(t) \implies \eta^+ = \frac{\tau_{12}(t)}{\dot{\gamma}_0}$

$\tau_{12} = \dot{\gamma}_0 \int_0^t G(t-t') \, \mathrm{d}t' = \dot{\gamma}_0 \int_0^t G(s) \, \mathrm{d}s$.

(a)

$$\begin{aligned} \eta^+(t) \equiv \frac{\tau_{12}(t)}{\dot{\gamma}_0} &= \int_0^t G(t-t') \, \mathrm{d}t' = \int_0^t G(s) \, \mathrm{d}s \\ &= \int_0^t \sum_{k=1}^{N} G_k e^{-s/\lambda_k} \, \mathrm{d}s \\ &= \sum_{k=1}^{N} G_k \lambda_k (1 - e^{-t/\lambda_k}) \end{aligned}$$

(b)

$$\eta_0 = \lim_{t \to \infty} \eta^+(t) = \sum_{k=1}^{N} G_k \lambda_k$$

Since G_k and λ_k are constant, η_0 is also a constant, which is equal to teh area under the $G(s)$ curve.

(c)

From Part (a), $\frac{\mathrm{d}\eta^+}{\mathrm{d}s} = G(s)$. Therefore, $G(s)$ can be calculated as the derivative of the $\eta^+(s)$ curve.

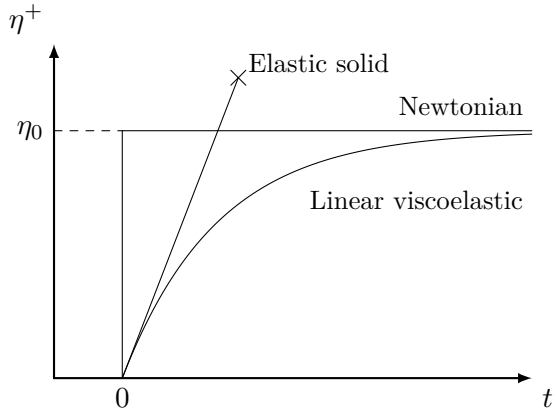


Figure 3.6: Time-dependent viscosity of start-up shear flow.

Differential Form

From the single exponential decay model $\tau = \int_{-\infty}^{t} G_0 e^{-(t-t')/\lambda}\,\dot{\gamma}(t')\,\mathrm{d}t'$, we can write a differential form:

$$\frac{\mathrm{d}\tau}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t}\int_{-\infty}^{t} G_0 e^{-(t-t')/\lambda}\,\dot{\gamma}(t')\,\mathrm{d}t' \tag{3.17}$$

We can apply the Leibniz' rule to bring the differentiation under the integral sign:

$$\frac{\mathrm{d}}{\mathrm{d}x}\int_{u(x)}^{v(x)} f(x,t)\,\mathrm{d}t = f(x,v(x))\frac{\mathrm{d}v}{\mathrm{d}x} - f(x,u(x))\frac{\mathrm{d}u}{\mathrm{d}x} + \int_{u(x)}^{v(x)} \frac{\partial f(x,t)}{\partial x}\,\mathrm{d}t \tag{3.18}$$

Here, $u(x) = -\infty$, $v(x) = t$, $t = t'$, $f(x,t) = f(t,t') = G_0 e^{-(t-t')/\lambda}\,\dot{\gamma}(t')$.

$$\begin{aligned} \therefore \frac{\mathrm{d}\tau}{\mathrm{d}t} &= G_0 e^{-(t-t)/\lambda}\,\dot{\gamma}(t)\frac{\mathrm{d}t}{\mathrm{d}t} - \frac{1}{\gamma}\int_{-\infty}^{t} G_0 e^{-(t-t')/\lambda}\,\dot{\gamma}(t')\,\mathrm{d}t' \\ &= G_0\dot{\gamma}(t) - \frac{1}{\gamma}\tau \end{aligned} \tag{3.19}$$

Or we can rearrange this equation as:

$$\therefore \tau + \lambda\frac{\mathrm{d}\tau}{\mathrm{d}t} = \lambda G_0\dot{\gamma} \tag{3.20}$$

Since $\eta_0 = \lim_{t\to\infty}\eta^+(t) = \sum_{k=1}^{N} G_k\lambda_k$, $\eta = G_0\lambda$ for single mode. Therefore, we can rewrite the differential form as:

$$\therefore \tau + \lambda \frac{\mathrm{d}\tau}{\mathrm{d}t} = \eta\dot{\gamma} \tag{3.21}$$

This equation was first proposed by James Clerk Maxwell (1867) for the viscosity of gas. Despite his initial misapplication of a good theory, rheologiests embrace it as the *Maxwell model*.

3.3 Small Strain Material Functions

3.3.1 Stress Relaxation

A stress relaxation experiment keeps the step strain and measure the evolution of the stress $\tau(t)$. The modulus is then calculated by $G(t) = \frac{\tau(t)}{\gamma_0}$.

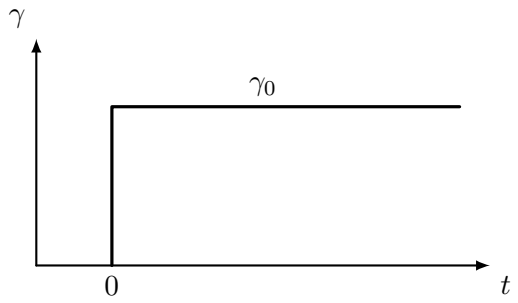


Figure 3.7: Stress relaxation.

A good example of stress relaxation is solutions with different degrees of intermolecular entanglement:

- Crosslinked rubbes show a short time relaxation followed by a constant modulus G
- Concentrated suspensions show a similar response but only at very small strain
- High MW polymeric liquids exhibit similar behavior at shorter times with a nearly constant modulus plateau G_0, eventually followed by flow at long times
- Dilute solution and suspensions have complete relaxation in short times

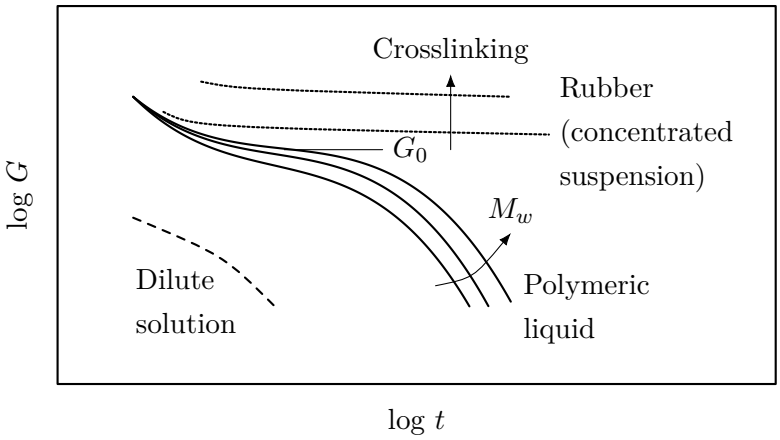


Figure 3.8: Stress relaxation of materials with different degrees of intermolecular entanglement.

3.3.2 Creep

Creeping experiment is useful for assessing the long-time end of the relaxation spectra. See Figure 3.9 for the experimental setup. Here are some key observations

- Rubber shows only short-term creep
- Polymeric liquid continues to deform, eventually reaching a steady state of a strain rate $\dot{\gamma}_\infty$

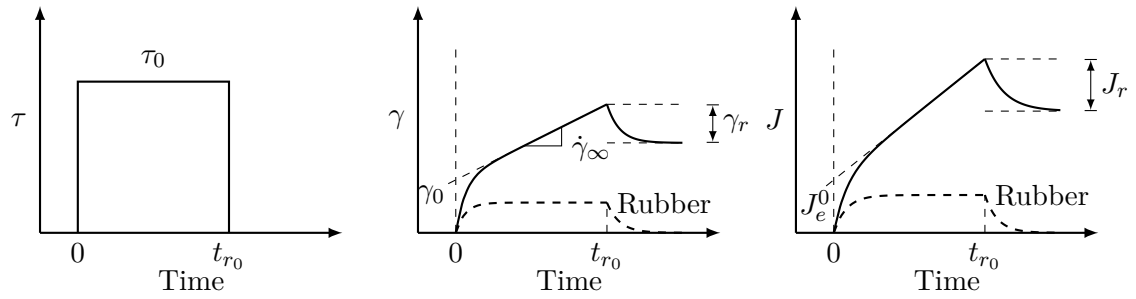


Figure 3.9: Key definitions of creeping curve.

Now we define the compliance $J(t)$:

$$J(t) = \frac{\gamma(t)}{\tau_0} \tag{3.22}$$

$$J(t) = J_e^0 + \frac{\dot{\gamma}_\infty t}{\tau_0} \tag{3.23}$$

Here $J_e^0 = \frac{\gamma_0}{\tau_0}$, $\tau_0 = \eta_0 \dot{\gamma}_\infty \implies J(t) = J_e^0 + \frac{t}{\eta_0}$.

For the single relaxation time model:

$$\eta_0 = \lim_{t\to\infty} \eta^+(t) = \sum_{k=1}^{N} G_k\lambda_k \implies \eta_0 = G_0\lambda \tag{3.24}$$

From definition:

$$G(t) = \frac{\tau(t)}{\gamma_0} \implies G_0 = \frac{\tau_0}{\gamma_0} \implies J_e^0 = \frac{1}{G_0} \tag{3.25}$$

Therefore, we have

$$J(t) = \frac{1}{G_0} + \frac{t}{\eta_0} = \frac{1}{G_0} + \frac{t}{\lambda G_0} \tag{3.26}$$

Let's now take a look how the relaxation modulus can be determined from a creep experiment. From the general linear viscoelastic model:

$$\tau_0 = \int_{-\infty}^{t} G(t-t')\dot{\gamma}(t')\,\mathrm{d}t' = \tau(t) = \int_{0}^{t} G(t-t')\dot{\gamma}(t')\,\mathrm{d}t' \tag{3.27}$$

It should be noted that τ_0 is applied at $t = 0$, hence the integration limits. From experiment, we know $\gamma(t) \implies \dot{\gamma}(t) = \frac{\mathrm{d}\gamma}{\mathrm{d}t}$. We can plug $\dot{\gamma}(t)$ into the integral and guess a form of $G(t)$. After performing the integration, we can check if the integral is equal to τ_0. This process might need to iterated. The steady state can be checked using creep recovery $J_r(t)$:

$$\lim_{t\to\infty} J_r(t) = J_e^0 \tag{3.28}$$

Example - Creeping after Imposing a Constant Shear Stress

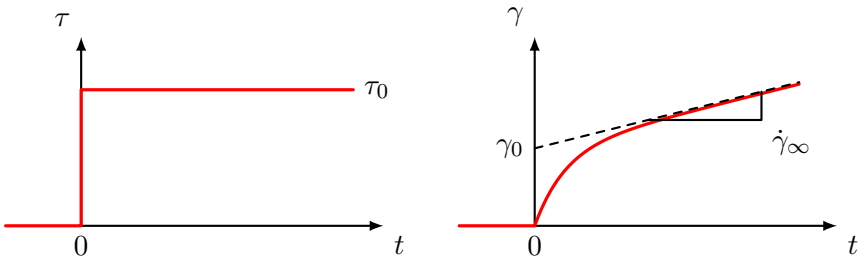


Figure 3.10: Transient behavior of stress and strain profiles of creeping experiment.

The goal is to derive a correlation between γ_0 and $\dot{\gamma}_\infty$. For a reference point at any present time t, the shear strain is:

$\gamma(t) = \int_0^t \dot{\gamma}(t')\,\mathrm{d}t'$

For very large time, the strain curve approaches the steady-state creeping:

$\lim_{t\to\infty} \gamma(t) = \gamma_0 + \dot{\gamma}_\infty t$

Again, for very large time, we can equate the two equaions above to obtain an expression of γ_0:

$\gamma_0 = \int_0^t \dot{\gamma}(t')\,\mathrm{d}t' - \dot{\gamma}_\infty t = \int_0^t \dot{\gamma}(t')\,\mathrm{d}t' - \int_0^t \dot{\gamma}_\infty\,\mathrm{d}t' = \int_0^t (\dot{\gamma}(t') - \dot{\gamma}_\infty)\,\mathrm{d}t'$

Hence, the goal is to formulate a term containing $\dot{\gamma} - \dot{\gamma}_\infty$ using the generalized linear viscoelastic model.

For the creeping experiment as shown, we have

$\tau_0 = \int_0^t G(t-t')\dot{\gamma}(t')\,\mathrm{d}t'$

Now, we focus only on the steady-state creeping region. Since the strain rate has reached a constant value of $\dot{\gamma}_\infty$, this region is equivalent to a steady-state shear flow with $\dot{\gamma} = \dot{\gamma}_\infty$ and $\tau = \tau_0$ as shown below:

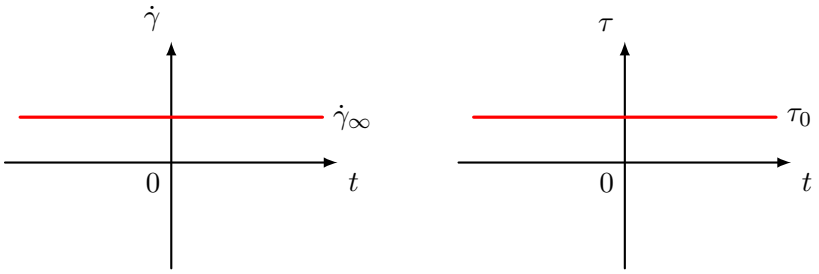


Figure 3.11: Shear rate and stress profiles of steady-state shear flow.

In this case, we have

$\tau_0 = \int_{-\infty}^t G(t-t')\dot{\gamma}_\infty\,\mathrm{d}t'$

It is important to note that this equation is not the limiting case of the creeping experiment as $t \to \infty$, as they represent distinct shear flow scenarios. The creeping case describes strain evolution under a step change to a constant shear stress, whereas the steady-state case describes a shear flow at a constant shear rate. For the same fluid (with identical G), both scenarios should converge to the same shear stress, τ_0.

We now equate the two shear stresses:

$\int_{-\infty}^t G(t-t')\dot{\gamma}_\infty\,\mathrm{d}t' = \int_0^t G(t-t')\dot{\gamma}(t')\,\mathrm{d}t'$

Letting the elapsed time be $s = t - t'$, the above equation can be written as:

$$\dot{\gamma}_\infty \int_0^\infty G(s)\,\mathrm{d}s = \int_0^t G(s)\dot{\gamma}(t-s)\,\mathrm{d}s$$

Since a term in the form of $\dot{\gamma} - \dot{\gamma}_\infty$ is desirable, we can split the limits of the integration of the LHS and rewrite the above equation as:

$$\dot{\gamma}_\infty \int_t^\infty G(s)\,\mathrm{d}s = \int_0^t G(s)[\dot{\gamma}(t-s) - \dot{\gamma}_\infty]\,\mathrm{d}s$$

We now integrate both sides of this equation over t for $t \in (0, \infty)$:

$$\dot{\gamma}_\infty \int_0^\infty \int_t^\infty G(s)\,\mathrm{d}s\,\mathrm{d}t = \int_0^\infty \int_0^t G(s)[\dot{\gamma}(t-s) - \dot{\gamma}_\infty]\,\mathrm{d}s\,\mathrm{d}t$$

This equation can be rearranged by interchanging the order of integration of s and t. For the LHS, the region of integration is shown in the left figure below:

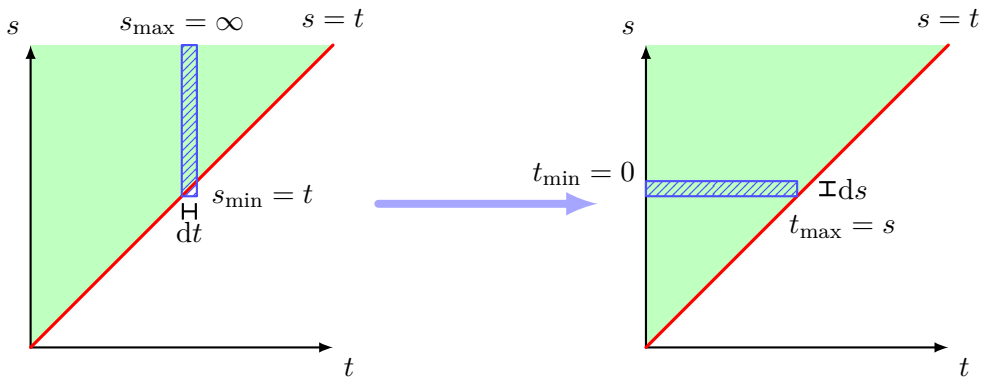


Figure 3.12: Integration region for the LHS.

Interchanging the integration order leads to $t \in (0, s)$ and $s \in (0, \infty)$, and we can obtain:

$$\text{LHS} = \dot{\gamma}_\infty \int_0^\infty \int_0^s G(s)\,\mathrm{d}t\,\mathrm{d}s = \dot{\gamma}_\infty \int_0^\infty G(s) \int_0^s \mathrm{d}t\,\mathrm{d}s = \dot{\gamma}_\infty \int_0^\infty sG(s)\,\mathrm{d}s$$

For the RHS, the region of integration is shown in the figure below:

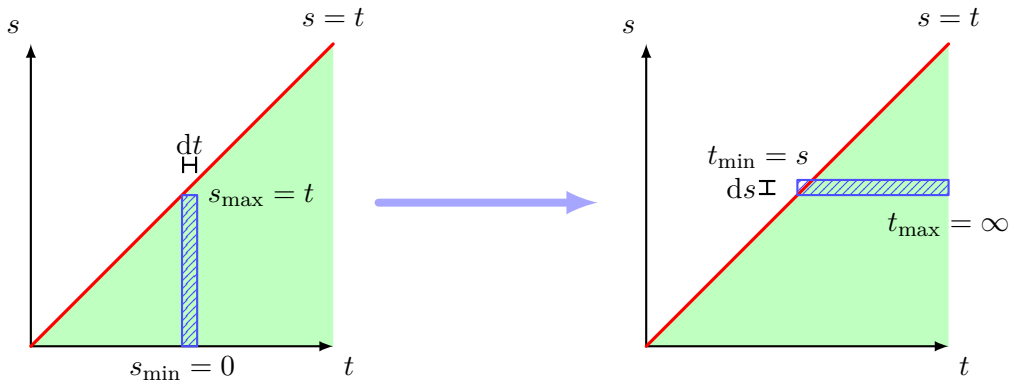


Figure 3.13: Integration region for the RHS.

Interchanging the integration order leads to $t \in (s, \infty)$ and $s \in (0, \infty)$, and we can obtain:

$$\text{RHS} = \int_0^\infty \int_s^\infty G(s)[\dot{\gamma}(t-s) - \dot{\gamma}_\infty]\,\mathrm{d}t\,\mathrm{d}s = \int_0^\infty G(s) \int_s^\infty [\dot{\gamma}(t-s) - \dot{\gamma}_\infty]\,\mathrm{d}t\,\mathrm{d}s$$

For the inner integral, we apply a change of variable $t' = t - s$, which results in $\mathrm{d}t' = \mathrm{d}t$ and we need to adjust the integration limits to $t' \in (0, \infty)$. Consequently, the RHS becomes:

$$\text{RHS} = \int_0^\infty G(s) \int_0^\infty [\dot{\gamma}(t') - \dot{\gamma}_\infty]\,\mathrm{d}t'\,\mathrm{d}s = \gamma_0 \int_0^\infty G(s)\,\mathrm{d}s$$

Equating LHS and RHS, we have

$$\frac{\gamma_0}{\dot{\gamma}_\infty} = \frac{\int_0^\infty sG(s)\,\mathrm{d}s}{\int_0^\infty G(s)\,\mathrm{d}s}$$

This equation is representative of a broad range of linear viscoelasticity experiments. In general, specific quantities measured across various shear experiments are expressed as the same of of integrals: $\int_0^\infty sG(s)\,\mathrm{d}s / \int_0^\infty G(s)\,\mathrm{d}s$. The specific measurable quantity depends on the type of shear experiment conducted. For the creeping experiment in this example, the measurable quantity is given by $\lim_{\tau_0 \to 0} \frac{\gamma_0}{\dot{\gamma}_\infty}$. Alternatively, we can use J_e^0 as the material function:

$$J_e^0 = \frac{\gamma_0}{\tau_0} = \frac{\gamma_0}{\int_{-\infty}^t G(t-t')\dot{\gamma}_\infty\,\mathrm{d}t'} = \frac{\gamma_0}{\dot{\gamma}_\infty} \frac{1}{\int_0^\infty G(s)\,\mathrm{d}s} = \frac{\int_0^\infty sG(s)\,\mathrm{d}s}{\left[\int_0^\infty G(s)\,\mathrm{d}s\right]^2}$$

3.3.3 Sinusoidal Oscillation

Definitions

This is a technique that is good for short time relaxations. We impose a strain

$$\gamma(t) = \gamma_0 \sin \omega t \tag{3.29}$$

In the linear viscoelasticity regime, we measure

$$\tau(t) = \tau_0 \sin(\omega t + \delta) \tag{3.30}$$

$\tau(t)$ can be decomposed into 2 phases: (1) a in-phase term with $\gamma(t)$ as $\tau_0' \sin \omega t$ and (2) an out-of-phase term as $\tau_0'' \cos \omega t$. With these, we can rewrite the stress as:

$$\tau = \tau_0' \sin \omega t + \tau_0'' \cos \omega t \tag{3.31}$$

Now, we define in-phase and out-of-phase modulI:

$$G' = \frac{\tau_0'}{\gamma_0} \text{ (elastic/storage modulus)} \tag{3.32}$$

$$G'' = \frac{\tau_0''}{\gamma_0} \text{ (viscous/loss modulus)} \tag{3.33}$$

The stress can then be expressed as:

$$\tau(t) = G'\gamma_0 \sin \omega t + G''\gamma_0 \cos \omega t \tag{3.34}$$

Experimentally, we measure $G'(\omega)$ and $G''(\omega)$ at different ω.

For elastic solid, $\tau(t) = G\gamma_0 \sin \omega t = G'\gamma_0 \sin \omega t + G''\gamma_0 \cos \omega t$, thus $G' = G,\ G'' = 0$. For viscous liquid, $\tau(t) = \eta\dot{\gamma}(t) = \eta\frac{\mathrm{d}\gamma}{\mathrm{d}t} = \eta\gamma_0 \cos \omega t = G'\gamma_0 \sin \omega t + G''\gamma_0 \cos \omega t$, thus $G' = 0, G'' = \eta\omega \implies \eta = \frac{G''}{\omega}$.

Now, we define the complex modulus G^*:

$$G^* = G' + iG'' \tag{3.35}$$

The magnitude of the complex modulus is

$$|G^*| = (G'^2 + G''^2)^{1/2} = \left[(\frac{\tau_0'}{\gamma_0})^2 + (\frac{\tau_0''}{\gamma_0})^2\right]^{1/2} = \frac{(\tau_0'^2 + \tau_0''^2)^{1/2}}{\gamma_0} \tag{3.36}$$

Since $\tau = \tau_0' \sin \omega t + \tau_0'' \cos \omega t$, it is easy to recognize that $\tau_0 = |G^*|\gamma_0 \implies |G^*| = \frac{\tau_0}{\gamma_0}$.

Often, a measure of material damping (i.e., loss factor) is reported in the literature:

$$\tan \delta = \frac{G''}{G'} \tag{3.37}$$

A material's ability to damp is a strong function of frequency and temperature. For instance, $\tan \delta$ values often show a peak at a material's glass transition temperature (T_g).

We can further define a dynamic viscosity:

$$\eta' = \frac{\tau_0''}{\dot{\gamma}_0} = \frac{G''\gamma_0}{\dot{\gamma}_0} = \frac{G''}{\omega} \tag{3.38}$$

In this equation, we need to use $\dot{\gamma}_0 = \gamma_0\omega$. Similarly, we can define an "elastic viscosity":

$$\eta'' = \frac{\tau_0'}{\dot{\gamma}_0} = \frac{G'}{\omega} \tag{3.39}$$

Therefore, a complex viscosity can be defined as:

$$|\eta^*| = (\eta'^2 + \eta''^2)^{1/2} = \left[(\frac{G''}{\omega})^2 + (\frac{G'}{\omega})^2\right]^{1/2} = \frac{1}{\omega}|G^*| \tag{3.40}$$

The imaginary part of the complex modulus, G'', is nothing physically imaginary. In fact, it is a measure of the energy dissipated per cycle of deformation per unit volume:

$$\begin{aligned}
\int_0^t \boldsymbol{\tau} : \mathbf{D}\,\mathrm{d}t &= \int_0^{2\pi/\omega} \tau\dot{\gamma}\,\mathrm{d}t \\
&= \int_0^{2\pi/\omega} (G'\gamma_0 \sin\omega t + G''\gamma_0\cos\omega t)(\omega\gamma_0\cos\omega t)\,\mathrm{d}t \\
&= \int_0^{2\pi/\omega} (\omega G'\gamma_0^2 \sin\omega t\cos\omega t + \omega G''\gamma_0^2\cos^2\omega t)\,\mathrm{d}t \\
&= \frac{1}{2}G'\gamma_0^2\sin^2\omega t|_0^{2\pi/\omega} + G''\gamma_0^2\int_0^{2\pi/\omega}\frac{1}{2}(1+\cos 2\omega t)\,\mathrm{d}\omega t \\
&= 0 + \frac{1}{2}G''\gamma_0^2(\omega t + \frac{1}{2}\sin 2\omega t)|_0^{2\pi/\omega} \\
&= \pi G''\gamma_0^2
\end{aligned} \tag{3.41}$$

Maxwell Model

Now, we want to apply the general viscoelastic model to the mathematical setup as introduced above. We know that $\tau(t) = \int_{-\infty}^t G(t-t')\dot{\gamma}(t')\,\mathrm{d}t'$. Plugging in $\dot{\gamma}(t) = \dot{\gamma}_0\cos\omega t$ and using $s = t - t'$, we have

$$\begin{aligned}
\tau &= \dot{\gamma}_0\int_0^\infty G(s)\cos\omega(t-s)\,\mathrm{d}s \\
&= \dot{\gamma}_0\int_0^\infty G(s)\cos\omega s\,\mathrm{d}s\cos\omega t + \dot{\gamma}_0\int_0^\infty G(s)\sin\omega s\,\mathrm{d}s\sin\omega t
\end{aligned} \tag{3.42}$$

Noting that $\dot{\gamma}_0 = \gamma_0\omega$, we have

$$\tau = \omega\gamma_0\int_0^\infty G(s)\cos\omega s\,\mathrm{d}s\cos\omega t + \omega\gamma_0\int_0^\infty G(s)\sin\omega s\,\mathrm{d}s\sin\omega t \tag{3.43}$$

Recall that $\tau(t) = G'\gamma_0\sin\omega t + G''\gamma_0\cos\omega t$, we can find the general expressions for the moduli:

$$G' = \omega\int_0^\infty G(s)\sin\omega s\,\mathrm{d}s \tag{3.44}$$

$$G'' = \omega \int_0^\infty G(s) \cos \omega s \, \mathrm{d}s \tag{3.45}$$

Now, let's try with the Maxwell model $G(s) = G_0 e^{-s/\lambda}$:

$$\begin{aligned}
G' &= \omega G_0 \int_0^\infty e^{-s/\lambda} \sin \omega s \, \mathrm{d}s \\
&= -\omega \lambda G_0 \int_0^\infty \sin \omega s \, \mathrm{d}e^{-s/\lambda} \\
&= -\omega \lambda G_0 \sin \omega s \, e^{-s/\lambda}|_0^\infty + \omega^2 \lambda G_0 \int_0^\infty e^{-s/\lambda} \cos \omega s \, \mathrm{d}s \\
&= \omega^2 \lambda G_0 \int_0^\infty e^{-s/\lambda} \cos \omega s \, \mathrm{d}s \\
&= -\omega^2 \lambda^2 G_0 \int_0^\infty \cos \omega s \, \mathrm{d}e^{-s/\lambda} \\
&= -\omega^2 \lambda^2 G_0 [\cos \omega s \, e^{-s/\lambda}|_0^\infty + \omega \int_0^\infty e^{-s/\lambda} \sin \omega s \, \mathrm{d}s] \\
&= \omega^2 \lambda^2 G_0 - \omega^2 \lambda^2 [G_0 \omega \int_0^\infty e^{-s/\lambda} \sin \omega s \, \mathrm{d}s] \\
&= \omega^2 \lambda^2 G_0 - \omega^2 \lambda^2 G'
\end{aligned} \tag{3.46}$$

$$\therefore G' = G_0 \frac{\omega^2 \lambda^2}{1 + \omega^2 \lambda^2} \tag{3.47}$$

Similarly, we can obtain:

$$G'' = G_0 \frac{\omega \lambda}{1 + \omega^2 \lambda^2} \tag{3.48}$$

With the multi-mode Maxwell model $G(t) = \sum_{k=1}^{N} G_k e^{-t/\lambda_k}$, we can perform the same manipulation for each term in the summation, which results in:

$$G'(\omega) = \sum_{k=1}^{N} G_k \frac{\omega^2 \lambda_k^2}{1 + \omega^2 \lambda_k^2} \tag{3.49}$$

$$G''(\omega) = \sum_{k=1}^{N} G_k \frac{\omega \lambda_k}{1 + \omega^2 \lambda_k^2} \tag{3.50}$$

These two moduli are measured by rheologists as a function of frequency for a wide range of viscoelastic fluids. A typical example is show in Figure 3.14. The inverse of the frequency where the two curves intersect, $\tau = 1/\omega_{\text{intersect}}$, is described as the typical relaxation time of the fluid.

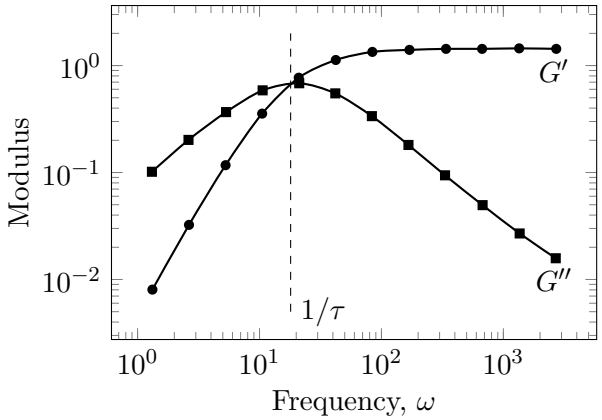


Figure 3.14: A typical plot of G' and G'' for a viscoelastic fluid.

An important note of linear viscoelasticity is that the material functions are directly related through mathematical transformations. Here we show an example of how η_0 and J_e^0 are related to G' and G''.

Recall that $\eta_0 = \int_0^\infty G(s)\,\mathrm{d}s$ and $J_e^0 = \frac{\int_0^\infty sG(s)\,\mathrm{d}s}{\left[\int_0^\infty G(s)\,\mathrm{d}s\right]^2}$. Expand Equations (3.44) and (3.45) in Taylor series around $\omega s = 0$

$G'' = \omega \int_0^\infty G(s)[1 - \frac{(\omega s)^2}{2} + \cdots]\,\mathrm{d}s$

$G' = \omega \int_0^\infty G(s)[\omega s - \frac{(\omega s)^3}{6} + \cdots]\,\mathrm{d}s$

Then in the limit as $\omega \to 0$

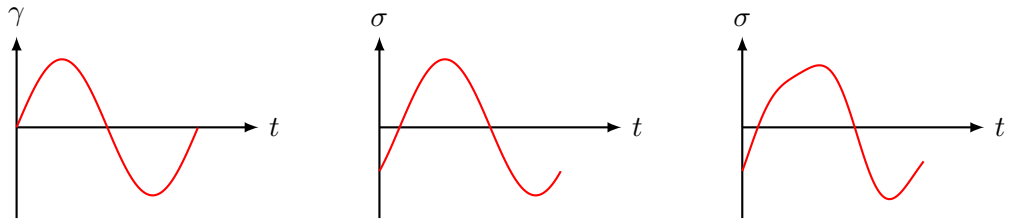
$$\lim_{\omega\to 0} G'' = \omega \int_0^\infty G(s)\,\mathrm{d}s \text{ and } \lim_{\omega\to 0} G' = \omega^2 \int_0^\infty sG(s)\,\mathrm{d}s$$

Thus

$$\eta_0 = \lim_{\omega\to 0} \frac{G''}{\omega} \text{ and } J_e^0 = \lim_{\omega\to 0} \frac{G'/\omega^2}{(G''/\omega)^2} = \lim_{\omega\to 0} \frac{G'}{G''^2}$$

Linear vs. Nonlinear Viscoelasticity

The derivation thus far is in the context of linear viscoelasticity. In rheology literature, this is often referred to as the small-amplitude oscillatory shear (SAOS). When the strain is large, the stress response of a fluid may no longer be sinusoidal. For large-amplitude oscillatory shear (LAOS), a typical nonlinear response is demonstrated in Figure 3.15.



Applied strain | Linear stress response | Nonlinear stress response

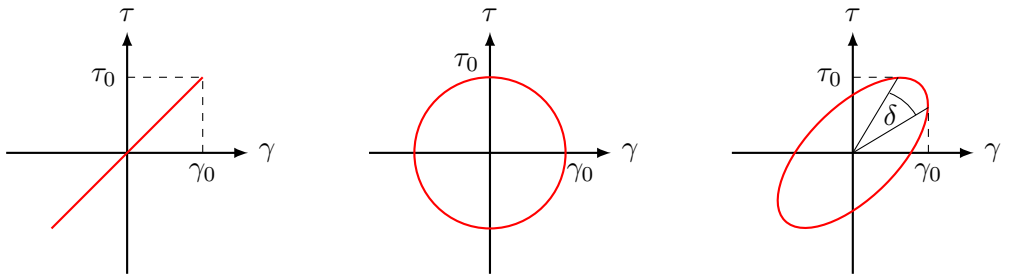
Figure 3.15: Linear vs. nonlinear response to an oscillatory shear.

Before we move forward, let's revisit the loss factor, $\tan\delta$. Based on Equations (3.30) and (3.37), we can rewrite the stress response as

$$\tau(t) = \tau_0 \sin\omega t \cos\delta + \tau_0 \cos\omega t \sin\delta \tag{3.51}$$

Compared to the applied strain $\gamma(t) = \gamma_0 \sin\omega t$, the phase shift, δ, can be easily measured by plotting $\tau(t)$ against $\gamma(t)$ in polar coordinates with ωt as the angular coordinate. These plots are *Lissajous curves*. A good example is shown in Figure 3.16. In a linearly elastic solid, $\tau = G_0\gamma$. This corresponds to a straight line. In a purely viscous fluid, $\tau = \eta\dot{\gamma} = \eta\gamma_0 \cos\omega t = \eta\gamma_0 \sin(\omega t + \frac{\pi}{2})$. This corresponds to an upright ellipse (or even a circle). Fluids that exhibit linear viscoelasticity have a slanted elliptical orbit somewhere in between these two extremes. This can be shown by the τ-γ trajectory equation of the Lissajous curve, which is obtained by eliminating ωt:

$$\frac{1}{G''^2\gamma_0^2}\tau^2 - \frac{2G'}{G''^2\gamma_0^2}\gamma\tau + \frac{G'^2 + G''^2}{G''^2\gamma_0^2}\gamma^2 = 1 \tag{3.52}$$



Linearly elastic | Purely viscous | Linearly viscoelastic

Figure 3.16: Lissajous curves for linear elastic, purely viscous, and viscoelastic fluids.

In a LAOS test, the Lissajous curve is not a pure sine function anymore, as demonstrated by Figure 3.17.

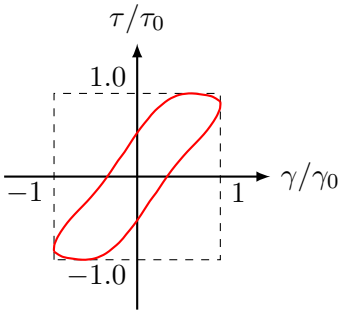


Figure 3.17: Lissajous curve for LAOS.

A consequence of the non-sinusoidal Lissajous curve is that the expressions for G' and G'' (i.e., Equations (3.49) and (3.49)) that we have derived for SAOS can not describe the nonlinear behaviors in a LAOS test. Instead, we need to find their LAOS analogues. We do so by presenting the stress response as a Fourier series:

$$\tau(t) = \sum_{\substack{n=1 \\ n \text{ odd}}}^{\infty} \tau_n \sin(n\omega t + \delta_n) \tag{3.53}$$

where the first term is exactly the response from linear viscoelasticity. We can split up this expression in the way we did before

$$\tau(t) = \gamma_0 \sum_{\substack{n=1 \\ n \text{ odd}}}^{\infty} [G'_n(\omega, \gamma_0) \sin(n\omega t) + G''_n(\omega, \gamma_0) \cos(n\omega t)] \tag{3.54}$$

Here, the moduli are not only functions of the frequency, ω, but also the strain γ_0. G'_n and G''_n can be calculated from the measured stress by taking its discrete Fourier transformation. This technique, however, is beyond the scope of this course. The transition from linear to nonlinear viscoelasticity is demonstrated in Figure 3.18.

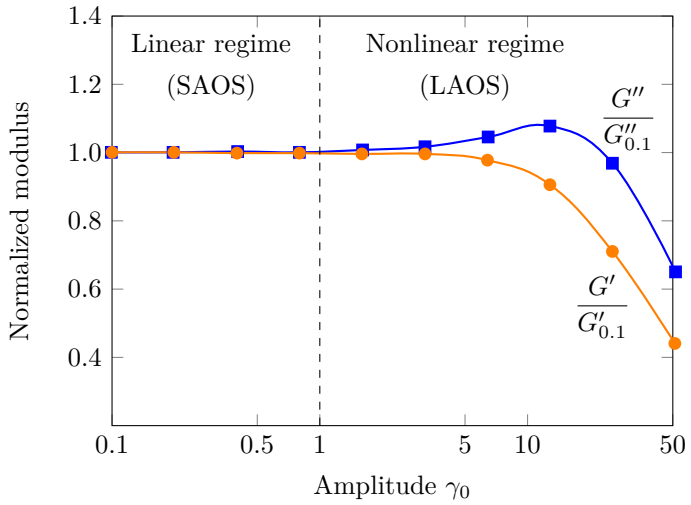


Figure 3.18: An amplitude sweep of G' and G''.

Generally, there are four types of behaviors for G' and G'' in a LAOS amplitude sweep, shown in Figure 3.19. These classes are:

- **Type I (strain thinning):** Both the elastic and viscous moduli decrease with increasing amplitude. This is commonly observed in polymer solutions. At low amplitudes, the polymer chains remain entangled, but at high amplitudes, the chains untangle as they are stretched, aligning with the flow direction, which decreases the local drag and thus the viscous modulus. As the chains extend, they reach their maximum length, reducing the elastic modulus. Most polymer solutions and melts display this behavior.
- **Type II (strain hardening):** Both moduli increase with increasing amplitude. Typically, certain segment interaction occurs as the amplitude increases, which resists the flow. For example, polymer chains can form microstructure which inhibits further deformation in the flow direction. Many biological gels (e.g., F-actin, fibrin, and collagen) exhibit this behavior.
- **Type III (weak strain overshoot):** Both moduli eventually decrease with increasing amplitude, but the viscous modulus initially increases. In this case, initial weak microstructure is formed which resists flow, but after a critical shear amplitude, the structure is destroyed and the chains align in the flow direction, aiding flow. This feature is common in soft, glassy materials, such as concentrated emulsions, suspensions, and pastes.
- **Type IV (strong strain overshoot):** Both moduli initially increase and eventually decrease with increasing amplitude. The mechanism here is the same as Type III, but with stronger intermolecular interaction (but not as strong as Type II). This behavior is seen in associative polymer solutions (e.g., phase-separating polymers).

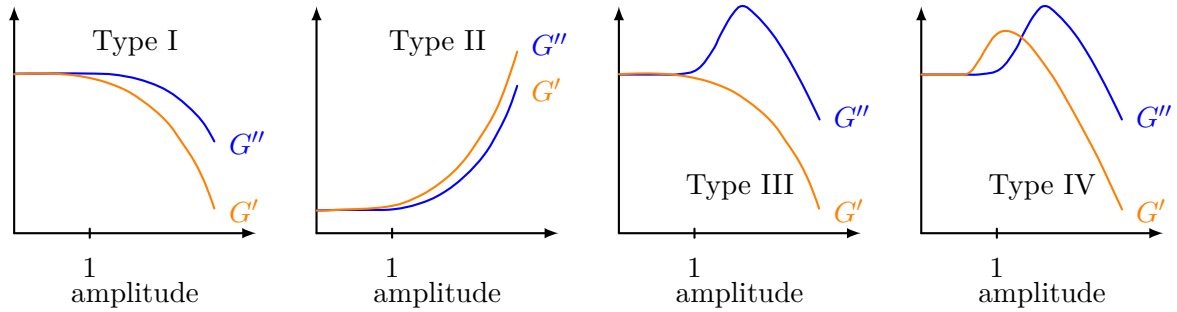


Figure 3.19: Types of behaviors for normalized G' and G'' in a LAOS amplitude sweep.

CHAPTER 4

Nonlinear Viscoelasticity

Lecture 4 **Date:** <YYYY-MM-DD>
Topic: Nonlinear viscoelastic behavior; second-order fluid model; upper-convected Maxwell model; more accurate constitutive models **Scribe:** Yang Han

4.1 Nonlinear Viscoelasticity Behaviors

4.1.1 Deborah Number

The Deborah number is defined as the ratio of the time it takes for a material to adjust to applied stresses or deformations, and the characteristic time scale of an experiment (or a computer simulation) probing the response of the material:

$$\mathrm{De} = \frac{\lambda}{t} \tag{4.1}$$

where λ represents the relaxation time of the material and t is the characteristic flow time. When $\mathrm{De} \ll 1$, the material exhibits viscous behavior; when $\mathrm{De} \gg 1$, the material exhibits elastic behavior. For an intermediate De, the material is considered to be viscoelastic. The linearity of the viscoelasticity depends on the magnitude of the strain:

- Small γ_0: linear viscoelasticity
- Large γ_0: nonlinear viscoelasticity

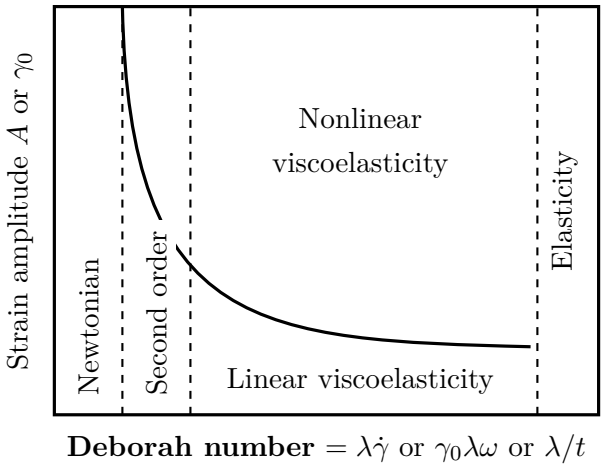


Figure 4.1: Classification of materials properties.

4.1.2 Nonlinear Phenomena

Normal Stress

For a simple shear "1" as the primary flow direction, we typically express the shear stress as $T_{21} = \eta\dot{\gamma} = \eta\frac{\mathrm{d}v_1}{\mathrm{d}x_2} = \eta\frac{\mathrm{d}v_x}{\mathrm{d}y} = T_{21}$.

The normal stress difference can be defined as $N_1 = T_{11} - T_{22}$ and $N_2 = T_{22} - T_{33}$. Here, we can further define the first and second normal stress coefficients:

$$\Psi_1 = \frac{T_{11} - T_{22}}{\dot{\gamma}^2} \tag{4.2}$$

$$\Psi_2 = \frac{T_{22} - T_{33}}{\dot{\gamma}^2} \tag{4.3}$$

See Figure 4.2 for LDPE melt as an exmpale. Ψ_1 and Ψ_2, as well as η, are nearly constant at low reduced shear rate. At higher shear rate, a clear shear-thinning behavior occurs.

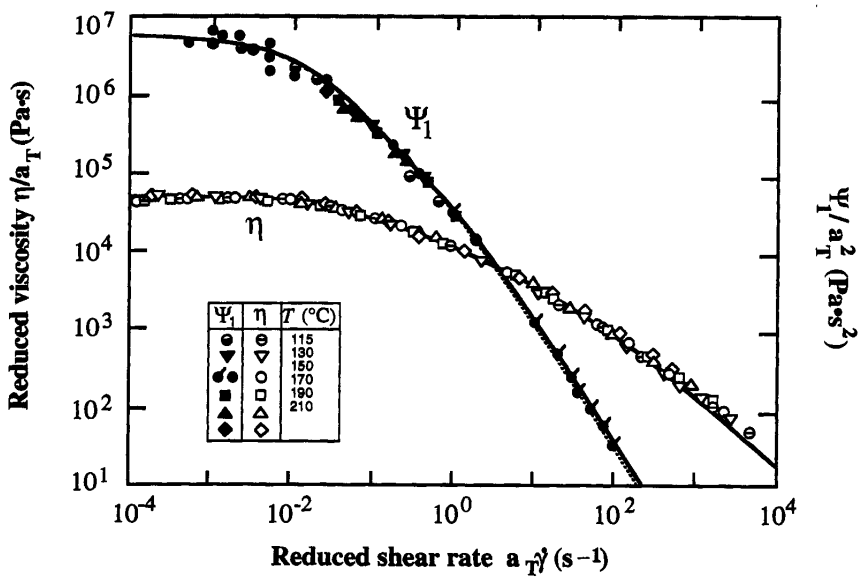


Figure 4.2: Steady state shear viscosity and primary normal stress coefficient for low density polyethylene.

4.1.3 Shear Thinning

For transient flow, we define a time-dependent viscosity as

$$\eta^+(t,\dot{\gamma}) \equiv \frac{T_{12}(t,\dot{\gamma})}{\dot{\gamma}} \tag{4.4}$$

See Figure 4.3 for 7.55% polybutadiene in HC oil:

- For a very low shear rate (0.0214 s^{-1}): linear viscoelasticity with η independent of $\dot{\gamma}$
- After going over a maximum η, overshoot, and η reduces
- At small t, η does not depart from linear viscoelastic behavior
- Nonlinear viscoelasticity occurs when both $\dot{\gamma}$ and γ are large

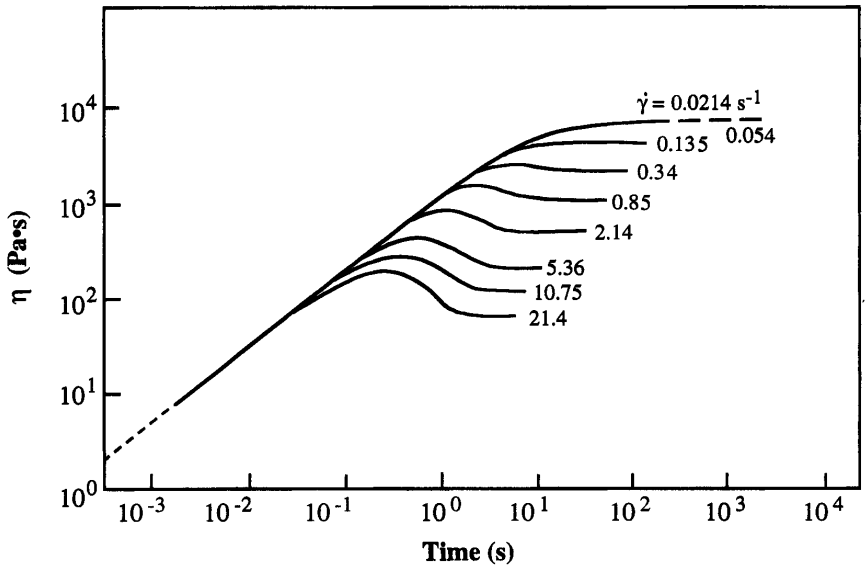


Figure 4.3: Time-dependent viscosity of polybutadiene in HC oil.

4.1.4 Extensional Thickening

Similarly, we can also define a time-dependent extensional viscosity as

$$\eta_u^+(t,\dot{\epsilon}) \equiv \frac{T_{11}(T,\dot{\epsilon}) - T_{22}(T,\dot{\epsilon})}{\dot{\epsilon}} \tag{4.5}$$

See Figure 4.4 as an example:

- Branched LDPEs show large extensional thickening, well above the linear viscoelasticity, even at small $\dot{\epsilon}$
- Melts without long side branches, PS and HDPE, exhibit much less extensional thickening

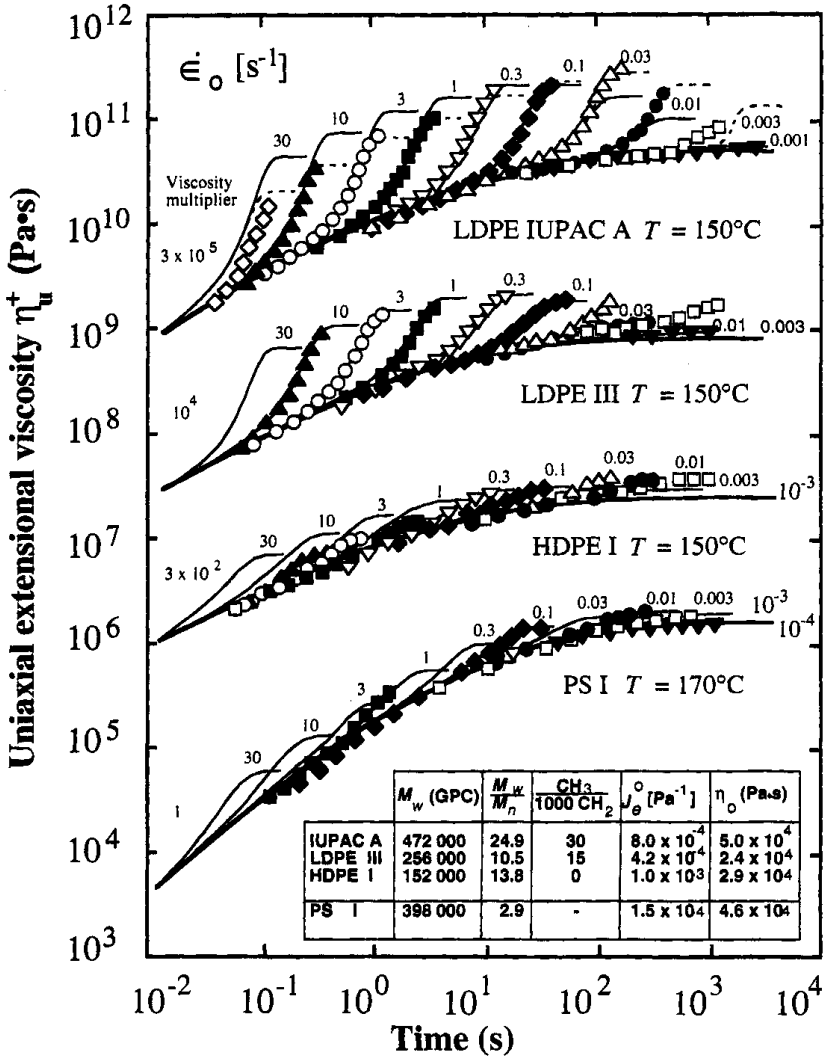


Figure 4.4: Time-dependent extensional viscosity of linear and branched polymer melts.

4.2 Second-Order Fluid Model

Definitions

The second order fluid is derived through a retarded motion expansion and is valid for slow, weak flows. The stress is Newtonian with small terms added:

$$\mathbf{T} = -p\mathbf{I} + \eta_0 2\mathbf{D} - \Psi_{1,0}\overset{\triangledown}{\mathbf{D}} + 4\Psi_{2,0}\mathbf{D}\cdot\mathbf{D} \tag{4.6}$$

$$\boldsymbol{\tau} = \eta_0 2\mathbf{D} - \Psi_{1,0}\overset{\triangledown}{\mathbf{D}} + 4\Psi_{2,0}\mathbf{D}\cdot\mathbf{D} \tag{4.7}$$

Here, the *upper-convected time derivative* is a special coordinate system whose base vectors stretch and rotate with material lines:

$$\overset{\triangledown}{\mathbf{D}} = \frac{\mathrm{D}\mathbf{D}}{\mathrm{D}t} - (\boldsymbol{\nabla}\mathbf{v})^T \cdot \mathbf{D} - \mathbf{D} \cdot \boldsymbol{\nabla}\mathbf{v} \tag{4.8}$$

The material derivative term $\frac{\mathrm{D}\mathbf{D}}{\mathrm{D}t}$ is

$$\frac{\mathrm{D}\mathbf{D}}{\mathrm{D}t} = \frac{\partial \mathbf{D}}{\partial t} + \mathbf{v} \cdot \boldsymbol{\nabla}\mathbf{D} \tag{4.9}$$

Here, the (covariant) derivative of $\mathbf{D}$ is a third-order tensor

$$\boldsymbol{\nabla}\mathbf{D} = (\sum_m \frac{\partial}{\partial x_m}\hat{\mathbf{e}}_\mathbf{m})(\sum_i \sum_j D_{ij}\hat{\mathbf{e}}_\mathbf{i}\hat{\mathbf{e}}_\mathbf{j}) = \sum_m \sum_i \sum_j \frac{\partial D_{ij}}{\partial x_m}\hat{\mathbf{e}}_\mathbf{m}\hat{\mathbf{e}}_\mathbf{i}\hat{\mathbf{e}}_\mathbf{j} \tag{4.10}$$

$$\begin{aligned}\mathbf{v} \cdot \boldsymbol{\nabla}\mathbf{D} &= \sum_m \sum_n \sum_i \sum_j v_n \frac{\partial D_{ij}}{\partial x_m}\hat{\mathbf{e}}_\mathbf{m} \cdot \hat{\mathbf{e}}_\mathbf{n}\hat{\mathbf{e}}_\mathbf{i}\hat{\mathbf{e}}_\mathbf{j} = \sum_m \sum_n \sum_i \sum_j v_n \frac{\partial D_{ij}}{\partial x_m}\delta_{mn}\hat{\mathbf{e}}_\mathbf{i}\hat{\mathbf{e}}_\mathbf{j} = \sum_i \sum_j v_m \frac{\partial D_{ij}}{\partial x_m}\hat{\mathbf{e}}_\mathbf{i}\hat{\mathbf{e}}_\mathbf{j} \\ &= \begin{bmatrix} v_1\frac{\partial D_{11}}{\partial x_1} + v_2\frac{\partial D_{11}}{\partial x_2} + v_3\frac{\partial D_{11}}{\partial x_3} & v_1\frac{\partial D_{12}}{\partial x_1} + v_2\frac{\partial D_{12}}{\partial x_2} + v_3\frac{\partial D_{12}}{\partial x_3} & v_1\frac{\partial D_{13}}{\partial x_1} + v_2\frac{\partial D_{13}}{\partial x_2} + v_3\frac{\partial D_{13}}{\partial x_3} \\ v_1\frac{\partial D_{21}}{\partial x_1} + v_2\frac{\partial D_{21}}{\partial x_2} + v_3\frac{\partial D_{21}}{\partial x_3} & v_1\frac{\partial D_{22}}{\partial x_1} + v_2\frac{\partial D_{22}}{\partial x_2} + v_3\frac{\partial D_{22}}{\partial x_3} & v_1\frac{\partial D_{23}}{\partial x_1} + v_2\frac{\partial D_{23}}{\partial x_2} + v_3\frac{\partial D_{23}}{\partial x_3} \\ v_1\frac{\partial D_{31}}{\partial x_1} + v_2\frac{\partial D_{31}}{\partial x_2} + v_3\frac{\partial D_{31}}{\partial x_3} & v_1\frac{\partial D_{32}}{\partial x_1} + v_2\frac{\partial D_{32}}{\partial x_2} + v_3\frac{\partial D_{32}}{\partial x_3} & v_1\frac{\partial D_{33}}{\partial x_1} + v_2\frac{\partial D_{33}}{\partial x_2} + v_3\frac{\partial D_{33}}{\partial x_3} \end{bmatrix}\end{aligned} \tag{4.11}$$

Example - Simple Shear

$$\mathbf{L} = \begin{bmatrix} 0 & \dot{\gamma} & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix},\ 2\mathbf{D} = \begin{bmatrix} 0 & \dot{\gamma} & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix},\ \mathbf{D} = \begin{bmatrix} 0 & \dot{\gamma}/2 & 0 \\ \dot{\gamma}/2 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$\mathbf{D} \cdot \mathbf{D} = \begin{bmatrix} 0 & \dot{\gamma}/2 & 0 \\ \dot{\gamma}/2 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \cdot \begin{bmatrix} 0 & \dot{\gamma}/2 & 0 \\ \dot{\gamma}/2 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} = \begin{bmatrix} \dot{\gamma}^2/4 & 0 & 0 \\ 0 & \dot{\gamma}^2/4 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$\begin{aligned}\overset{\triangledown}{\mathbf{D}} &= \frac{\mathrm{D}\mathbf{D}}{\mathrm{D}t} - (\boldsymbol{\nabla}\mathbf{v})^T \cdot \mathbf{D} - \mathbf{D} \cdot \boldsymbol{\nabla}\mathbf{v} \\ &= \frac{\partial \mathbf{D}}{\partial t} + \mathbf{v} \cdot \boldsymbol{\nabla}\mathbf{D} - (\boldsymbol{\nabla}\mathbf{v})^T \cdot \mathbf{D} - \mathbf{D} \cdot \boldsymbol{\nabla}\mathbf{v}\end{aligned}$$

$\frac{\partial \mathbf{D}}{\partial t} = \mathbf{0}$ (s.s.)

$\mathbf{v} \cdot \boldsymbol{\nabla}\mathbf{D} = \mathbf{0}$ (uniform deformation rate, no spatial distribution)

$$(\boldsymbol{\nabla}\mathbf{v})^T \cdot \mathbf{D} = \mathbf{L} \cdot \mathbf{D} = \tfrac{1}{2}\begin{bmatrix} 0 & \dot{\gamma} & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \cdot \begin{bmatrix} 0 & \dot{\gamma} & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} = \tfrac{1}{2}\begin{bmatrix} \dot{\gamma}^2 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$\mathbf{D}\cdot\boldsymbol{\nabla}\mathbf{v}=\mathbf{D}\cdot\mathbf{L}^T=\tfrac{1}{2}\begin{bmatrix}0&\dot\gamma&0\\\dot\gamma&0&0\\0&0&0\end{bmatrix}\cdot\begin{bmatrix}0&0&0\\\dot\gamma&0&0\\0&0&0\end{bmatrix}=\tfrac{1}{2}\begin{bmatrix}\dot\gamma^2&0&0\\0&0&0\\0&0&0\end{bmatrix}$$

$$\therefore\overset{\triangledown}{\mathbf{D}}=-\begin{bmatrix}\dot\gamma^2&0&0\\0&0&0\\0&0&0\end{bmatrix}$$

$$\begin{aligned}\boldsymbol{\tau}&=\eta_0 2\mathbf{D}-\Psi_{1,0}\overset{\triangledown}{\mathbf{D}}+4\Psi_{2,0}\mathbf{D}\cdot\mathbf{D}\\&=\eta_0\begin{bmatrix}0&\dot\gamma&0\\\dot\gamma&0&0\\0&0&0\end{bmatrix}+\Psi_{1,0}\begin{bmatrix}\dot\gamma^2&0&0\\0&0&0\\0&0&0\end{bmatrix}+\Psi_{2,0}\begin{bmatrix}\dot\gamma^2&0&0\\0&\dot\gamma^2&0\\0&0&0\end{bmatrix}\end{aligned}$$

By the definitions:

$\eta\equiv\frac{\tau_{12}}{\dot\gamma}=(\eta_0\dot\gamma+\Psi_{1,0}\cdot 0+\Psi_{2,0}\cdot 0)/\dot\gamma=\eta_0$ (cannot predict shear thinning)

$\Psi_1=\frac{\tau_{11}-\tau_{22}}{\dot\gamma^2}=[(\eta_0\cdot 0+\Psi_{1,0}\dot\gamma^2+\Psi_{2,0}\dot\gamma^2)-(\eta_0\cdot 0+\Psi_{1,0}\cdot 0+\Psi_{2,0}\dot\gamma^2)]/\dot\gamma^2=\Psi_{1,0}$ (can predict normal stress)

$\Psi_2=\frac{\tau_{22}-\tau_{33}}{\dot\gamma^2}=[(\eta_0\cdot 0+\Psi_{1,0}\cdot 0+\Psi_{2,0}\dot\gamma^2)-(\eta_0\cdot 0+\Psi_{1,0}\cdot 0+\Psi_{2,0}\cdot 0)]/\dot\gamma^2=\Psi_{2,0}$

Clearly, the second-order fluid model does not predict time-dependent properties.

Uniaxial Extension

$$\mathbf{L}=\begin{bmatrix}\dot\epsilon&0&0\\0&-\dot\epsilon/2&0\\0&0&-\dot\epsilon/2\end{bmatrix},\ 2\mathbf{D}=\mathbf{L}+\mathbf{L}^T=\begin{bmatrix}2\dot\epsilon&0&0\\0&-\dot\epsilon&0\\0&0&-\dot\epsilon\end{bmatrix},\ \mathbf{D}=\begin{bmatrix}\dot\epsilon&0&0\\0&-\dot\epsilon/2&0\\0&0&-\dot\epsilon/2\end{bmatrix}$$

$$\mathbf{D}\cdot\mathbf{D}=\begin{bmatrix}\dot\epsilon&0&0\\0&-\dot\epsilon/2&0\\0&0&-\dot\epsilon/2\end{bmatrix}\cdot\begin{bmatrix}\dot\epsilon&0&0\\0&-\dot\epsilon/2&0\\0&0&-\dot\epsilon/2\end{bmatrix}=\begin{bmatrix}\dot\epsilon^2&0&0\\0&\dot\epsilon^2/4&0\\0&0&\dot\epsilon^2/4\end{bmatrix}$$

$$\begin{aligned}\overset{\triangledown}{\mathbf{D}}&=\frac{\mathrm{D}\mathbf{D}}{\mathrm{D}t}-(\boldsymbol{\nabla}\mathbf{v})^T\cdot\mathbf{D}-\mathbf{D}\cdot\boldsymbol{\nabla}\mathbf{v}\\&=\frac{\partial\mathbf{D}}{\partial t}+\mathbf{v}\cdot\boldsymbol{\nabla}\mathbf{D}-(\boldsymbol{\nabla}\mathbf{v})^T\cdot\mathbf{D}-\mathbf{D}\cdot\boldsymbol{\nabla}\mathbf{v}\end{aligned}$$

$\frac{\partial \mathbf{D}}{\partial t} = \mathbf{0}$ (s.s.)

$\mathbf{v} \cdot \boldsymbol{\nabla}\mathbf{D} = \mathbf{0}$ (uniform deformation rate, no spatial distribution)

$$(\boldsymbol{\nabla}\mathbf{v})^T \cdot \mathbf{D} = \mathbf{L} \cdot \mathbf{D} = \frac{1}{2}\begin{bmatrix} \dot{\epsilon} & 0 & 0 \\ 0 & -\dot{\epsilon}/2 & 0 \\ 0 & 0 & -\dot{\epsilon}/2 \end{bmatrix} \cdot \begin{bmatrix} 2\dot{\epsilon} & 0 & 0 \\ 0 & -\dot{\epsilon} & 0 \\ 0 & 0 & -\dot{\epsilon} \end{bmatrix} = \frac{1}{2}\begin{bmatrix} 2\dot{\epsilon}^2 & 0 & 0 \\ 0 & \dot{\epsilon}^2/2 & 0 \\ 0 & 0 & \dot{\epsilon}^2/2 \end{bmatrix}$$

$$\mathbf{D} \cdot \boldsymbol{\nabla}\mathbf{v} = \mathbf{D} \cdot \mathbf{L}^T = \frac{1}{2}\begin{bmatrix} 2\dot{\epsilon} & 0 & 0 \\ 0 & -\dot{\epsilon} & 0 \\ 0 & 0 & -\dot{\epsilon} \end{bmatrix} \cdot \begin{bmatrix} \dot{\epsilon} & 0 & 0 \\ 0 & -\dot{\epsilon}/2 & 0 \\ 0 & 0 & -\dot{\epsilon}/2 \end{bmatrix} = \frac{1}{2}\begin{bmatrix} 2\dot{\epsilon}^2 & 0 & 0 \\ 0 & \dot{\epsilon}^2/2 & 0 \\ 0 & 0 & \dot{\epsilon}^2/2 \end{bmatrix}$$

$$\therefore \overset{\triangledown}{\mathbf{D}} = -\frac{1}{2}\begin{bmatrix} 4\dot{\epsilon}^2 & 0 & 0 \\ 0 & \dot{\epsilon}^2 & 0 \\ 0 & 0 & \dot{\epsilon}^2 \end{bmatrix}$$

$$\begin{aligned} \boldsymbol{\tau} &= \eta_0 2\mathbf{D} - \Psi_{1,0}\overset{\triangledown}{\mathbf{D}} + 4\Psi_{2,0}\mathbf{D} \cdot \mathbf{D} \\ &= \eta_0 \begin{bmatrix} 2\dot{\epsilon} & 0 & 0 \\ 0 & -\dot{\epsilon} & 0 \\ 0 & 0 & -\dot{\epsilon} \end{bmatrix} + \frac{1}{2}\Psi_{1,0}\begin{bmatrix} 4\dot{\epsilon}^2 & 0 & 0 \\ 0 & \dot{\epsilon}^2 & 0 \\ 0 & 0 & \dot{\epsilon}^2 \end{bmatrix} + \Psi_{2,0}\begin{bmatrix} 4\dot{\epsilon}^2 & 0 & 0 \\ 0 & \dot{\epsilon}^2 & 0 \\ 0 & 0 & \dot{\epsilon}^2 \end{bmatrix} \end{aligned}$$

$$\eta_u^+(t,\dot{\epsilon}) \equiv \frac{T_{11}-T_{22}}{\dot{\epsilon}} = [(2\eta_0\dot{\epsilon} + 2\Psi_{1,0}\dot{\epsilon}^2 + 4\Psi_{2,0}\dot{\epsilon}^2) - (-\eta_0\dot{\epsilon} + \tfrac{1}{2}\Psi_{1,0}\dot{\epsilon}^2 + \Psi_{2,0}\dot{\epsilon}^2)]/\dot{\epsilon} = 3\eta_0 + \tfrac{3}{2}(\Psi_{1,0} + 2\Psi_{2,0})\dot{\epsilon}$$

When $-\frac{\Psi_{2,0}}{\Psi_{1,0}} < 0.5$, $\eta_u^+ - 3\eta_0 > 0$:

- The first departure of η_u^+ from the Newtonian value will be positive
- The fluid will be extension thickening at low extension rates

4.3 Upper-Convected Maxwell Model

As demonstrated, the second-order fluid model does not predict time-dependent material functions. This is one of the main tasks of the upper-convected Maxwell (UCM) model. The idea is to incorporate nonlinearity into the simple Maxwell model. From the previous chapter, Equation (3.21):

$$\tau + \lambda\frac{\mathrm{d}\tau}{\mathrm{d}t} = \lambda G_0\dot{\gamma} = \eta\dot{\gamma} \tag{4.12}$$

We aim to replace the substantial time derivative (the red term above) with the upper-convected time derivative, as well as recasting the equation in a tensor form:

$$\boldsymbol{\tau} + \lambda \overset{\triangledown}{\boldsymbol{\tau}} = \eta_0 2\mathbf{D} \tag{4.13}$$

$$\boldsymbol{\tau} + \lambda \frac{\partial \boldsymbol{\tau}}{\partial t} + \lambda \mathbf{v} \cdot \boldsymbol{\nabla} \boldsymbol{\tau} - \lambda (\boldsymbol{\nabla} \mathbf{v})^T \cdot \boldsymbol{\tau} - \lambda \boldsymbol{\tau} \cdot \boldsymbol{\nabla} \mathbf{v} = \eta_0 2\mathbf{D} \tag{4.14}$$

Example - Start-up of Simple Shear

$$\mathbf{L} = \begin{bmatrix} 0 & \dot{\gamma} & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \; 2\mathbf{D} = \mathbf{L} + \mathbf{L}^T = \begin{bmatrix} 0 & \dot{\gamma} & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$\boldsymbol{\nabla} \boldsymbol{\tau} = \mathbf{0}$ (uniform rate of deformation)

Assume $\boldsymbol{\tau} = \begin{bmatrix} \tau_{11} & \tau_{12} & 0 \\ \tau_{21} & \tau_{22} & 0 \\ 0 & 0 & \tau_{33} \end{bmatrix}$ $(\tau_{12} = \tau_{21})$

$$(\boldsymbol{\nabla} \mathbf{v})^T \cdot \boldsymbol{\tau} = \mathbf{L} \cdot \boldsymbol{\tau} = \begin{bmatrix} 0 & \dot{\gamma} & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \cdot \begin{bmatrix} \tau_{11} & \tau_{12} & 0 \\ \tau_{21} & \tau_{22} & 0 \\ 0 & 0 & \tau_{33} \end{bmatrix} = \begin{bmatrix} \dot{\gamma}\tau_{21} & \dot{\gamma}\tau_{22} & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$\boldsymbol{\tau} \cdot \boldsymbol{\nabla} \mathbf{v} = \boldsymbol{\tau} \cdot \mathbf{L}^T = \begin{bmatrix} \tau_{11} & \tau_{12} & 0 \\ \tau_{21} & \tau_{22} & 0 \\ 0 & 0 & \tau_{33} \end{bmatrix} \cdot \begin{bmatrix} 0 & 0 & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} = \begin{bmatrix} \dot{\gamma}\tau_{12} & 0 & 0 \\ \dot{\gamma}\tau_{22} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$\boldsymbol{\tau} + \lambda \frac{\partial \boldsymbol{\tau}}{\partial t} - \lambda (\boldsymbol{\nabla} \mathbf{v})^T \cdot \boldsymbol{\tau} - \lambda \boldsymbol{\tau} \cdot \boldsymbol{\nabla} \mathbf{v} = \eta_0 2\mathbf{D}$

$$\begin{bmatrix} \tau_{11} & \tau_{12} & 0 \\ \tau_{21} & \tau_{22} & 0 \\ 0 & 0 & \tau_{33} \end{bmatrix} + \lambda \frac{\mathrm{d}}{\mathrm{d}t} \begin{bmatrix} \tau_{11} & \tau_{12} & 0 \\ \tau_{21} & \tau_{22} & 0 \\ 0 & 0 & \tau_{33} \end{bmatrix} - \lambda \begin{bmatrix} 2\dot{\gamma}\tau_{12} & \dot{\gamma}\tau_{22} & 0 \\ \dot{\gamma}\tau_{22} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} = \eta_0 \begin{bmatrix} 0 & \dot{\gamma} & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

For steady-state solution

$$\begin{bmatrix} \tau_{11} & \tau_{12} & 0 \\ \tau_{21} & \tau_{22} & 0 \\ 0 & 0 & \tau_{33} \end{bmatrix} - \lambda \begin{bmatrix} 2\dot{\gamma}\tau_{12} & \dot{\gamma}\tau_{22} & 0 \\ \dot{\gamma}\tau_{22} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} = \eta_0 \begin{bmatrix} 0 & \dot{\gamma} & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$\tau_{22} = 0 = \tau_{33}$

$\tau_{12} - \lambda\dot{\gamma}\tau_{22} = \eta_0\dot{\gamma} \implies \tau_{12} = \eta_0\dot{\gamma} \implies \eta_{s.s.} = \frac{\tau_{12}}{\dot{\gamma}} = \eta_0$

$\tau_{11} - 2\lambda\dot{\gamma}\tau_{12} = 0 \implies \tau_{11} = 2\lambda\dot{\gamma}\tau_{12} = 2\lambda\dot{\gamma}^2\eta_0$

$\therefore \Psi_1 = \frac{\tau_{11}-\tau_{22}}{\dot{\gamma}^2} = \frac{2\lambda\dot{\gamma}^2\eta_0-0}{\dot{\gamma}^2} = 2\eta_0\lambda$

$\Psi_2 = \frac{\tau_{11}-\tau_{22}}{\dot{\gamma}^2} = \frac{0-0}{\dot{\gamma}^2} = 0$

For transient solution

(1) $\tau_{22} + \lambda\frac{\mathrm{d}\tau_{22}}{\mathrm{d}t} = 0$, I.C.: $\tau_{22}|_{t=0} = 0$

$\tau_{22} = C_1 e^{-t/\lambda}$, $\tau_{22}|_{t=0} = 0 = C_1$

$\therefore \tau_{22} = 0$

Similarly, $\tau_{33} = 0$

(2) $\tau_{12} + \lambda\frac{\mathrm{d}\tau_{12}}{\mathrm{d}t} - \lambda\dot{\gamma}\tau_{22} = \eta_0\dot{\gamma} \implies \tau_{12} + \lambda\frac{\mathrm{d}\tau_{12}}{\mathrm{d}t} = \eta_0\dot{\gamma}$

$\frac{\mathrm{d}\tau_{12}}{\tau_{12}-\eta_0\dot{\gamma}} = -\mathrm{d}(\frac{t}{\lambda})$
$\ln(\tau_{12} - \eta_0\dot{\gamma})|_0^{\tau_{12}} = -\frac{t}{\lambda}|_0^t$

$\ln(\frac{\tau_{12}-\eta_0\dot{\gamma}}{-\eta_0\dot{\gamma}}) = -\frac{t}{\lambda}$

$\tau_{12} = \eta_0\dot{\gamma}(1 - e^{-t/\lambda})$

$\therefore \eta^+ = \frac{\tau_{12}}{\dot{\gamma}} = \eta_0(1 - e^{-t/\lambda})$

(3) $\tau_{11} + \lambda\frac{\mathrm{d}\tau_{11}}{\mathrm{d}t} - 2\lambda\dot{\gamma}\tau_{12} = 0$

$\frac{\mathrm{d}\tau_{11}}{\mathrm{d}t} + \frac{1}{\lambda}\tau_{11} = 2\dot{\gamma}^2\eta_0(1 - e^{-t/\lambda})$

$e^{t/\lambda}\frac{\mathrm{d}\tau_{11}}{\mathrm{d}t} + \frac{1}{\lambda}e^{t/\lambda}\tau_{11} = 2\dot{\gamma}^2\eta_0(e^{t/\lambda} - 1)$

$\frac{\mathrm{d}}{\mathrm{d}t}(e^{t/\lambda}\tau_{11}) = 2\dot{\gamma}^2\eta_0(e^{t/\lambda} - 1)$

$e^{t/\lambda}\tau_{11}|_0^{\tau_{11}} = 2\dot{\gamma}^2\eta_0(\lambda e^{t/\lambda} - t)|_0^t$

$e^{t/\lambda}\tau_{11} = 2\dot{\gamma}^2\eta_0(\lambda e^{t/\lambda} - t - \lambda + 0) = 2\dot{\gamma}^2\eta_0[\lambda e^{t/\lambda} - \lambda(1 + \frac{t}{\lambda})]$

$\tau_{11} = 2\dot{\gamma}^2\eta_0\lambda[1 - e^{-t/\lambda}(1 + \frac{t}{\lambda})]$

$\tau_{11} = 2\dot{\gamma}^2\eta_0\lambda[1 - e^{-t/\lambda}(1 + \frac{t}{\lambda})]$

$\Psi_1^+ = \frac{\tau_{11}-\tau_{22}}{\dot{\gamma}^2} = 2\eta_0\lambda[1 - e^{-t/\lambda}(1 + \frac{t}{\lambda})]$

See Figure 4.5 below:

- Newtonian: $\eta_{s.s.} = \eta_0$
- Second-order fluid: $\eta_{s.s.} = \eta_0$
- UCM/Lodge: $\eta^+ = \eta_0(1 - e^{-t/\lambda})$, same results as the linear viscoelastic model (LVE). Noth UCM and LVE predict a gradual rather than instantaneous growth in viscosity, but UCM is more realistic

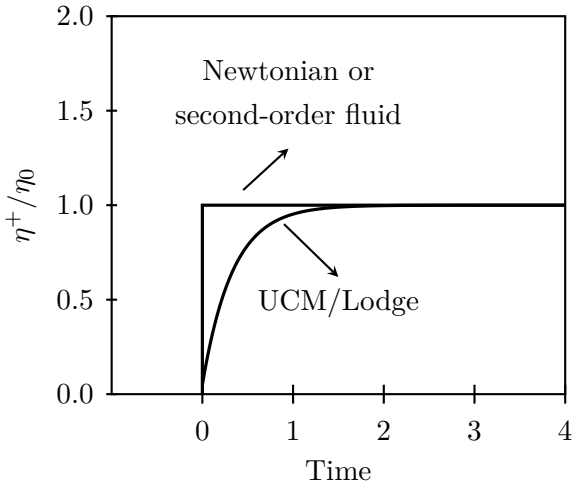


Figure 4.5: Shear viscosities predicted by different constitutive equations.

Example - Uniaxial Extension at Steady State

$$\mathbf{L} = \begin{bmatrix} \dot{\epsilon} & 0 & 0 \\ 0 & -\dot{\epsilon}/2 & 0 \\ 0 & 0 & -\dot{\epsilon}/2 \end{bmatrix}, \; 2\mathbf{D} = \mathbf{L} + \mathbf{L}^T = \begin{bmatrix} 2\dot{\epsilon} & 0 & 0 \\ 0 & -\dot{\epsilon} & 0 \\ 0 & 0 & -\dot{\epsilon} \end{bmatrix}$$

$\boldsymbol{\nabla\tau} = \mathbf{0}$ for uniform rate of deformation

$$(\boldsymbol{\nabla}\mathbf{v})^T \cdot \boldsymbol{\tau} = \mathbf{L} \cdot \boldsymbol{\tau} = \begin{bmatrix} \dot{\epsilon} & 0 & 0 \\ 0 & -\dot{\epsilon}/2 & 0 \\ 0 & 0 & -\dot{\epsilon}/2 \end{bmatrix} \cdot \begin{bmatrix} \tau_{11} & \tau_{12} & 0 \\ \tau_{21} & \tau_{22} & 0 \\ 0 & 0 & \tau_{33} \end{bmatrix} = \begin{bmatrix} \dot{\epsilon}\tau_{11} & \dot{\epsilon}\tau_{12} & 0 \\ -\frac{\dot{\epsilon}}{2}\tau_{21} & -\frac{\dot{\epsilon}}{2}\tau_{22} & 0 \\ 0 & 0 & -\frac{\dot{\epsilon}}{2}\tau_{33} \end{bmatrix}$$

$$\boldsymbol{\tau}\cdot\boldsymbol{\nabla}\mathbf{v}=\boldsymbol{\tau}\cdot\mathbf{L}^T=\begin{bmatrix}\tau_{11}&\tau_{12}&0\\\tau_{21}&\tau_{22}&0\\0&0&\tau_{33}\end{bmatrix}\cdot\begin{bmatrix}\dot\epsilon&0&0\\0&-\dot\epsilon/2&0\\0&0&-\dot\epsilon/2\end{bmatrix}=\begin{bmatrix}\dot\epsilon\tau_{11}&-\frac{\dot\epsilon}{2}\tau_{12}&0\\\dot\epsilon\tau_{21}&-\frac{\dot\epsilon}{2}\tau_{22}&0\\0&0&-\frac{\dot\epsilon}{2}\tau_{33}\end{bmatrix}$$

At steady-state

$$\begin{bmatrix}\tau_{11}&\tau_{12}&0\\\tau_{21}&\tau_{22}&0\\0&0&\tau_{33}\end{bmatrix}-\lambda\begin{bmatrix}2\dot\epsilon\tau_{11}&\frac{\dot\epsilon}{2}\tau_{12}&0\\\frac{\dot\epsilon}{2}\tau_{21}&-\dot\epsilon\tau_{22}&0\\0&0&-\dot\epsilon\tau_{33}\end{bmatrix}=\eta_0\begin{bmatrix}2\dot\epsilon&0&0\\0&-\dot\epsilon&0\\0&0&-\dot\epsilon\end{bmatrix}$$

$\tau_{11}-2\lambda\dot\epsilon\tau_{11}=2\eta_0\dot\epsilon \implies \tau_{11}=\frac{2\eta_0\dot\epsilon}{1-2\lambda\dot\epsilon}$

$\tau_{22}+\lambda\dot\epsilon\tau_{22}=-\eta_0\dot\epsilon \implies \tau_{22}=-\frac{\eta_0\dot\epsilon}{1+\lambda\dot\epsilon}$

$\tau_{33}+\lambda\dot\epsilon\tau_{33}=-\eta_0\dot\epsilon \implies \tau_{33}=-\frac{\eta_0\dot\epsilon}{1+\lambda\dot\epsilon}$

$\therefore \bar\eta_u=\frac{\tau_{11}-\tau_{22}}{\dot\epsilon}=\frac{2\eta_0}{1-2\lambda\dot\epsilon}+\frac{\eta_0}{1+\lambda\dot\epsilon}$

See Figure 4.6 below:

- UCM: $\bar\eta_u$ is extremely extension thickening; it rises to infinity as $\dot\epsilon\to\frac{1}{2\lambda}$
- Second-order fluid: $\bar\eta_u=3\eta_0+\frac{3}{2}(\Psi_{1,0}+2\Psi_{2,0})\dot\epsilon$; linear rise of viscosity with $\dot\epsilon$
- Newtonian: $\bar\eta_u=3\eta_0$, no dependence on $\dot\epsilon$

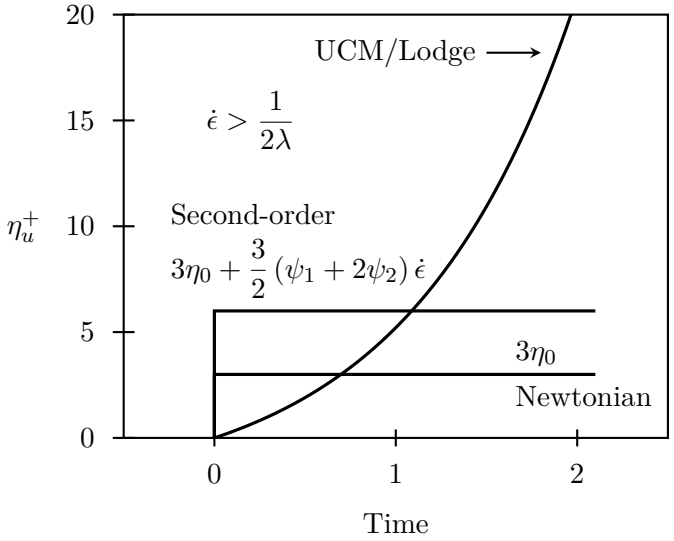


Figure 4.6: Extensional viscosities predicted by different constitutive equations.

Side-by-Side Comparison of Constitutive Models

Disadvantage of UCM model:

- It does not predict $\dot{\gamma}$-related material functions: $\eta^+ = \eta_0(1 - e^{-t/\lambda})$
- It does predict $\dot{\epsilon}$-related material functions: $\bar{\eta}_u = \frac{2\eta_0}{1-2\lambda\dot{\epsilon}} + \frac{\eta_0}{1+\lambda\dot{\epsilon}}$

Comparison among Newtonian, second-order, and UCM:

- Same prediction of $\dot{\gamma}$-related material functions
- Different prediction of $\dot{\epsilon}$-related material functions
- Usually, constitutive equations differe among themselves more strongly in their predictionof extensional viscosities than in their predictions of shear viscosities.

4.4 More Accurate Constitutive Models

4.4.1 Oldroyd-B Model

Assume a viscous dilute polymer solution, where the viscosity can be dissociated as the polymeric and solvent contributions:

$$\boldsymbol{\tau} = \boldsymbol{\tau}^p + \boldsymbol{\tau}^s \tag{4.15}$$

The polymeric contribution can be expressed by the UCM:

$$\boldsymbol{\tau}^p + \lambda_1 \overset{\triangledown}{\boldsymbol{\tau}^p} = \eta_p 2\mathbf{D} \tag{4.16}$$

The solvent contribution is usually just a Newtonian term:

$$\boldsymbol{\tau}^s = \eta_s 2\mathbf{D} \tag{4.17}$$

We can rewrite the total (deviatoric) stress as $\boldsymbol{\tau}^p = \boldsymbol{\tau} - 2\eta_s\mathbf{D}$. The UCM model then becomes:

$$\boldsymbol{\tau} - \eta_s 2\mathbf{D} + \lambda_1(\overset{\triangledown}{\boldsymbol{\tau}} - 2\eta_s\overset{\triangledown}{\mathbf{D}}) = 2\eta_p\mathbf{D} \tag{4.18}$$

$$\boldsymbol{\tau} + \lambda_1\overset{\triangledown}{\boldsymbol{\tau}} = 2(\eta_p + \eta_s)\mathbf{D} + 2\lambda_1\eta_s\overset{\triangledown}{\mathbf{D}} \tag{4.19}$$

We can define the total viscosity as $\eta_0 = \eta_p + \eta_s$. With it, we can rewrite the constitutive equation as:

$$\boldsymbol{\tau} + \lambda_1\overset{\triangledown}{\boldsymbol{\tau}} = 2\eta_0\mathbf{D} + 2\lambda_1\eta_s\overset{\triangledown}{\mathbf{D}} \tag{4.20}$$

For convenience, we can further define a retardation time $\lambda_2 = \frac{\eta_s}{\eta_0}\lambda_1$. We can finally arrive at the Oldroyd-B model:

$$\boldsymbol{\tau} + \lambda_1 \overset{\triangledown}{\boldsymbol{\tau}} = 2\eta_0(\mathbf{D} + \lambda_2 \overset{\triangledown}{\mathbf{D}}) \tag{4.21}$$

This constitutive equation is widely used in describing dilute polymeric liquids.

Example - Oldroyd-B Model

Transient Uniaxial Extensional Flow

(a) Assume that the stress tensor contains only three non-zero components: τ_{11}, τ_{22}, τ_{33}. Use the velocity gradient tensor for the startup of uniaxial extensional flow and substitute it into the Oldroyd-B constitutive equation to obtain the expanded form. Extract the τ_{11} and τ_{22} components from the expanded form and write these differential equations.

The Oldroyd-B model

$\boldsymbol{\tau} + \lambda_1 \overset{\triangledown}{\boldsymbol{\tau}} = \eta(2\mathbf{D} + 2\lambda_2 \overset{\triangledown}{\mathbf{D}})$

$\overset{\triangledown}{\boldsymbol{\tau}} = \frac{\partial \boldsymbol{\tau}}{\partial t} + \mathbf{v}\cdot\boldsymbol{\nabla}\boldsymbol{\tau} - (\boldsymbol{\nabla}\mathbf{v})^T\cdot\boldsymbol{\tau} - \boldsymbol{\tau}\cdot\boldsymbol{\nabla}\mathbf{v}$

- $\boldsymbol{\nabla}\boldsymbol{\tau} = \mathbf{0}$ (homogeneous flow)

$\overset{\triangledown}{\mathbf{D}} = \frac{\mathrm{D}\mathbf{D}}{\mathrm{D}t} - (\boldsymbol{\nabla}\mathbf{v})^T\cdot\mathbf{D} - \mathbf{D}\cdot\boldsymbol{\nabla}\mathbf{v}$

- $\frac{\mathrm{D}\mathbf{D}}{\mathrm{D}t} = 0$ (homogeneous flow)

For uniaxial extensional flow

$$\mathbf{L} = \mathbf{L}^T = \boldsymbol{\nabla}\mathbf{v} = (\boldsymbol{\nabla}\mathbf{v})^T = \begin{bmatrix} \dot{\epsilon} & 0 & 0 \\ 0 & -\dot{\epsilon}/2 & 0 \\ 0 & 0 & -\dot{\epsilon}/2 \end{bmatrix} = \mathbf{D}$$

$$\overset{\triangledown}{\boldsymbol{\tau}} = \begin{bmatrix} \frac{\partial \tau_{11}}{\partial t} & 0 & 0 \\ 0 & \frac{\partial \tau_{22}}{\partial t} & 0 \\ 0 & 0 & \frac{\partial \tau_{33}}{\partial t} \end{bmatrix} - \begin{bmatrix} 2\tau_{11}\dot{\epsilon} & 0 & 0 \\ 0 & -\tau_{22}\dot{\epsilon} & 0 \\ 0 & 0 & -\tau_{33}\dot{\epsilon} \end{bmatrix}$$

$$\overset{\triangledown}{\mathbf{D}} = -\begin{bmatrix} 2\dot{\epsilon}^2 & 0 & 0 \\ 0 & \dot{\epsilon}^2/2 & 0 \\ 0 & 0 & \dot{\epsilon}^2/2 \end{bmatrix}$$

The Oldroyd-B model then becomes

$$\begin{bmatrix} \tau_{11} & 0 & 0 \\ 0 & \tau_{22} & 0 \\ 0 & 0 & \tau_{33} \end{bmatrix} + \lambda_1 \begin{bmatrix} \frac{\partial \tau_{11}}{\partial t} & 0 & 0 \\ 0 & \frac{\partial \tau_{22}}{\partial t} & 0 \\ 0 & 0 & \frac{\partial \tau_{33}}{\partial t} \end{bmatrix} - \lambda_1 \begin{bmatrix} 2\tau_{11}\dot{\epsilon} & 0 & 0 \\ 0 & -\tau_{22}\dot{\epsilon} & 0 \\ 0 & 0 & -\tau_{33}\dot{\epsilon} \end{bmatrix}$$
$$= \eta \begin{bmatrix} 2\dot{\epsilon} & 0 & 0 \\ 0 & -\dot{\epsilon} & 0 \\ 0 & 0 & -\dot{\epsilon} \end{bmatrix} - 2\eta\lambda_2 \begin{bmatrix} 2\dot{\epsilon}^2 & 0 & 0 \\ 0 & \dot{\epsilon}^2/2 & 0 \\ 0 & 0 & \dot{\epsilon}^2/2 \end{bmatrix}$$

$\therefore \frac{\mathrm{d}\tau_{11}}{\mathrm{d}t} = -\left(\frac{1-2\lambda_1\dot{\epsilon}}{\lambda_1}\right)\left[\tau_{11} - \frac{2\eta\dot{\epsilon}(1-2\lambda_2\dot{\epsilon})}{(1-2\lambda_1\dot{\epsilon})}\right]$

$\frac{\mathrm{d}\tau_{22}}{\mathrm{d}t} = -\left(\frac{1+\lambda_1\dot{\epsilon}}{\lambda_1}\right)\left[\tau_{22} + \frac{\eta\dot{\epsilon}(1+\lambda_2\dot{\epsilon})}{(1+\lambda_1\dot{\epsilon})}\right]$

(b) Using the initial conditions that τ_{11} and τ_{22} are both zero at $t = 0$, solve the ordinary differential equations to obtain expressions for τ_{11} and τ_{22}.

$\int_0^{\tau_{11}} \frac{\mathrm{d}\tau_{11}}{\tau_{11} - \frac{2\eta\dot{\epsilon}(1-2\lambda_2\dot{\epsilon})}{(1-2\lambda_1\dot{\epsilon})}} = -\left(\frac{1-2\lambda_1\dot{\epsilon}}{\lambda_1}\right)\int_0^t \mathrm{d}t$

$\tau_{11} = 2\eta\dot{\epsilon}\left(\frac{1-2\lambda_2\dot{\epsilon}}{1-2\lambda_1\dot{\epsilon}}\right) - 2\eta\dot{\epsilon}\left(\frac{1-2\lambda_2\dot{\epsilon}}{1-2\lambda_1\dot{\epsilon}}\right)\exp\left[-\left(\frac{1-2\lambda_1\dot{\epsilon}}{\lambda_1}\right)t\right]$

Similarly,

$\tau_{22} = -\eta\dot{\epsilon}\left(\frac{1+\lambda_2\dot{\epsilon}}{1+\lambda_1\dot{\epsilon}}\right) + \eta\dot{\epsilon}\left(\frac{1+\lambda_2\dot{\epsilon}}{1+\lambda_1\dot{\epsilon}}\right)\exp\left[-\left(\frac{1+\lambda_1\dot{\epsilon}}{\lambda_1}\right)t\right]$

(c) Use the results from Part (b) along with the definition of uniaxial extensional viscosity to calculate the transient extensional viscosity of this fluid. Also find the expression for the steady-state extensional viscosity. What is the limitation of this equation in extensional flow?

$\eta_u^+ = \frac{\tau_{11}-\tau_{22}}{\dot{\epsilon}} = 3\eta\frac{(1-\lambda_2\dot{\epsilon}-2\lambda_1\lambda_2\dot{\epsilon}^2)}{(1-2\lambda_1\dot{\epsilon})(1+\lambda_1\dot{\epsilon})} - 2\eta\dot{\epsilon}\left(\frac{1-2\lambda_2\dot{\epsilon}}{1-2\lambda_1\dot{\epsilon}}\right)\exp\left[-\left(\frac{1-2\lambda_1\dot{\epsilon}}{\lambda_1}\right)t\right] - \eta\dot{\epsilon}\left(\frac{1+\lambda_2\dot{\epsilon}}{1+\lambda_1\dot{\epsilon}}\right)\exp\left[-\left(\frac{1+\lambda_1\dot{\epsilon}}{\lambda_1}\right)t\right]$

At steady state

$\eta_u = 3\eta\frac{(1-\lambda_2\dot{\epsilon}-2\lambda_1\lambda_2\dot{\epsilon}^2)}{(1-2\lambda_1\dot{\epsilon})(1+\lambda_1\dot{\epsilon})}$

$\dot{\epsilon} < 1/(2\lambda_1)$ is required for a positive η_u.

Steady Shear Flow

(d) Calculate the viscosity, first and second normal stress differences as a function of shear rate

predicted by the Oldroyd-B model in steady shear flow.

For steady shear flow

$$\mathbf{L} = (\boldsymbol{\nabla}\mathbf{v})^T = \begin{bmatrix} 0 & \dot{\gamma} & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \mathbf{L}^T = \boldsymbol{\nabla}\mathbf{v} = \begin{bmatrix} 0 & 0 & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, 2\mathbf{D} = \begin{bmatrix} 0 & \dot{\gamma} & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$(\boldsymbol{\nabla}\mathbf{v})^T \cdot \boldsymbol{\tau} = \begin{bmatrix} 0 & \dot{\gamma} & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \cdot \begin{bmatrix} \tau_{11} & \tau_{12} & \tau_{13} \\ \tau_{21} & \tau_{22} & \tau_{23} \\ \tau_{31} & \tau_{32} & \tau_{33} \end{bmatrix} = \begin{bmatrix} \dot{\gamma}\tau_{21} & \dot{\gamma}\tau_{22} & \dot{\gamma}\tau_{23} \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$\boldsymbol{\tau} \cdot \boldsymbol{\nabla}\mathbf{v} = \begin{bmatrix} \tau_{11} & \tau_{12} & \tau_{13} \\ \tau_{21} & \tau_{22} & \tau_{23} \\ \tau_{31} & \tau_{32} & \tau_{33} \end{bmatrix} \cdot \begin{bmatrix} 0 & 0 & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} = \begin{bmatrix} \dot{\gamma}\tau_{12} & 0 & 0 \\ \dot{\gamma}\tau_{22} & 0 & 0 \\ \dot{\gamma}\tau_{32} & 0 & 0 \end{bmatrix}$$

$$\therefore \overset{\triangledown}{\boldsymbol{\tau}} = -\begin{bmatrix} 2\dot{\gamma}\tau_{12} & \dot{\gamma}\tau_{22} & \dot{\gamma}\tau_{23} \\ \dot{\gamma}\tau_{22} & 0 & 0 \\ \dot{\gamma}\tau_{32} & 0 & 0 \end{bmatrix} \ (\tau_{12} = \tau_{21} \text{ and } \tau_{23} = \tau_{32})$$

$$(\boldsymbol{\nabla}\mathbf{v})^T \cdot \mathbf{D} = \begin{bmatrix} 0 & \dot{\gamma} & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \cdot \begin{bmatrix} 0 & \dot{\gamma}/2 & 0 \\ \dot{\gamma}/2 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} = \begin{bmatrix} \dot{\gamma}^2/2 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$\mathbf{D} \cdot \boldsymbol{\nabla}\mathbf{v} = \begin{bmatrix} 0 & \dot{\gamma}/2 & 0 \\ \dot{\gamma}/2 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \cdot \begin{bmatrix} 0 & 0 & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} = \begin{bmatrix} \dot{\gamma}^2/2 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$\therefore \overset{\triangledown}{\mathbf{D}} = -\begin{bmatrix} \dot{\gamma}^2 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

The Oldroyd-B model then becomes

$$\begin{bmatrix} \tau_{11} & \tau_{12} & \tau_{13} \\ \tau_{21} & \tau_{22} & \tau_{23} \\ \tau_{31} & \tau_{32} & \tau_{33} \end{bmatrix} - \lambda_1 \begin{bmatrix} 2\dot{\gamma}\tau_{12} & \dot{\gamma}\tau_{22} & \dot{\gamma}\tau_{23} \\ \dot{\gamma}\tau_{22} & 0 & 0 \\ \dot{\gamma}\tau_{32} & 0 & 0 \end{bmatrix} = \eta \begin{bmatrix} 0 & \dot{\gamma} & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} - 2\eta\lambda_2 \begin{bmatrix} \dot{\gamma}^2 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$\tau_{22} = \tau_{33} = \tau_{23} = \tau_{13} = 0$

$\tau_{12} - \lambda_1\dot{\gamma}\tau_{22} = \eta\dot{\gamma} \implies \tau_{12} = \eta\dot{\gamma}$

$\tau_{11} - 2\lambda_1\dot{\gamma}\tau_{12} = -2\eta\lambda_2\dot{\gamma}^2 \implies \tau_{11} = 2(\lambda_1 - \lambda_2)\eta\dot{\gamma}^2$

$\therefore \eta_{s.s.} = \frac{\tau_{12}}{\dot{\gamma}} = \eta$

$\Psi_{1,s.s.} = \frac{\tau_{11}-\tau_{22}}{\dot{\gamma}^2} = 2(\lambda_1 - \lambda_2)\eta$

$\Psi_{2,s.s.} = \frac{\tau_{22}-\tau_{33}}{\dot{\gamma}^2} = 0$

(e) What are the limitations of this equation in shear flow?

In the steady shear flow, the model predicts that the viscosity is not a function of $\dot{\gamma}$, essentially predicting only linear viscoelastic behavior. In addition, this model predicts that $\tau_{22} = \tau_{33} = 0$, showing that N_1 is only a function of τ_{11} and N_2 is always zero.

4.4.2 Other Maxwell Type Models

Most of the Maxwell-type models take the form

$$\overset{\triangledown}{\boldsymbol{\tau}} + f_c(\boldsymbol{\tau}, \mathbf{D}) + \frac{1}{\lambda}\boldsymbol{\tau} + f_d(\boldsymbol{\tau}) = 2G\mathbf{D} \tag{4.22}$$

where λ and G are the linear viscoelastic parameters ($G = \lambda\eta_0$)

- If $f_c = f_d = 0$, UCM
- If $f_c = \xi(\mathbf{D}\cdot\boldsymbol{\tau} + \boldsymbol{\tau}\cdot\mathbf{D})$ and $f_d = 0$, Johnson & Segalman
- If $f_c = a(2\mathbf{D}:\mathbf{D})^{1/2}$ and $f_d = 0$, White & Metzner
- $f_c = \frac{2\alpha}{3G}\mathbf{D}:\boldsymbol{\tau}(\boldsymbol{\tau} + G\mathbf{I})$ and $f_d = 0$, Larson
- If $f_c = 0$ and $f_d = \frac{\alpha}{\lambda G}\boldsymbol{\tau}\cdot\boldsymbol{\tau}$, Giesekus (Excellent fits in shearing flows; not the best for extensional flows)

CHAPTER 5

Shear Rheometry: Drag Flows

Lecture 5 **Date:** <YYYY-MM-DD>

Topic: Less sophisticated rheometers; Couette or concentric cylinder rheometer; cone and plate rheometer; parallel disk rheometer **Scribe:** Yang Han

5.1 Less Sophisticated Rheometers

Sliding Plate Rheometer

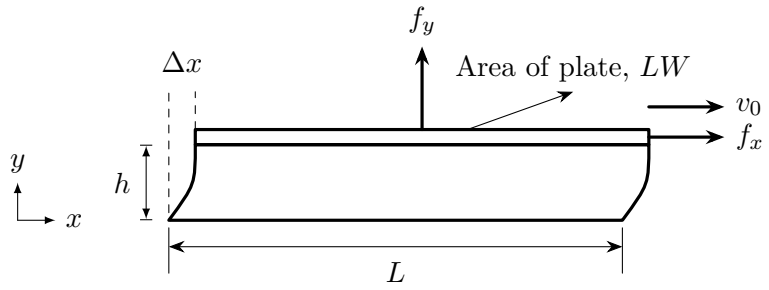


Figure 5.1: Sliding plate rheometer.

$v_x = (\frac{v_0}{h})y,\ v_y = v_z = 0$

$$\mathbf{L} = \begin{bmatrix} \frac{\partial v_x}{\partial x} & \frac{\partial v_x}{\partial y} & \frac{\partial v_x}{\partial z} \\ \frac{\partial v_y}{\partial x} & \frac{\partial v_y}{\partial y} & \frac{\partial v_y}{\partial z} \\ \frac{\partial v_z}{\partial x} & \frac{\partial v_z}{\partial y} & \frac{\partial v_z}{\partial z} \end{bmatrix} = \begin{bmatrix} 0 & \frac{v_0}{h} & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$\mathbf{L}^T = \begin{bmatrix} 0 & 0 & 0 \\ \frac{v_0}{h} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \; 2\mathbf{D} = \begin{bmatrix} 0 & \frac{v_0}{h} & 0 \\ \frac{v_0}{h} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$\dot{\gamma} = 2D_{xy} = \frac{\mathrm{d}v_x}{\mathrm{d}y} = \frac{v_0}{h}$

$\tau_{xy} = \frac{f_x}{LW}$

$\eta = \frac{\tau_{xy}}{\dot{\gamma}} = \frac{f_x h}{v_0 LW}$

Limitations: It can only be operated for a short time or small $\dot{\gamma}$; also, it is challenging to reach steady state.

Falling Ball Rheometer

Assume Newtonian and apply Stokes' law:

$\eta = \frac{2(\rho_b - \rho_f) g R^2}{9 v_\infty}$

Here, η is the apparent viscosity and v_∞ is the terminal velocity.

5.2 Couette or Concentric Cylinder Rheometer

Couette Rheometry

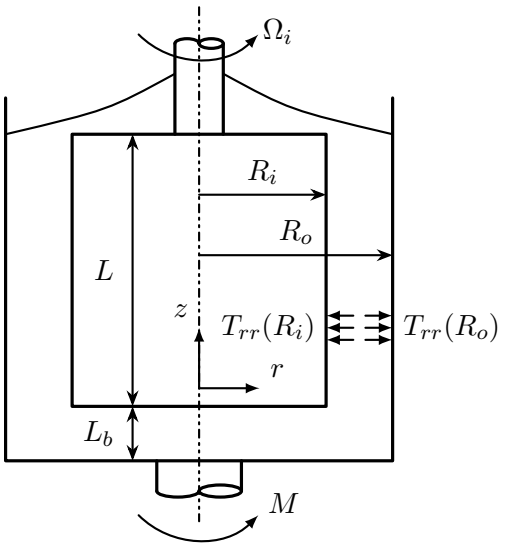


Figure 5.2: Couette rheometry.

If we rotate the inner cylinder for low viscosity materials, vortex occurs at $\mathrm{Re} \gg 1$. If we rotate the outer cylinder for low viscosity materials, vortex typically does not occur.

Assuming steady, laminar, isothermal flow, negligible gravity and end effects, and symmetry ($\frac{\partial}{\partial \theta} = 0$):

$$v_\theta = r\Omega,\ v_r = v_z = 0 \tag{5.1}$$

The equation of motion in cylindrical coordinates:

$$-\rho \frac{v_\theta^2}{r} = \frac{1}{r}\frac{\partial (r\tau_{rr})}{\partial r} - \frac{\tau_{\theta\theta}}{r}\ (r\text{-component}) \tag{5.2}$$

$$0 = \frac{\partial (r^2 \tau_{r\theta})}{\partial r}\ (\theta\text{-component}) \tag{5.3}$$

$$0 = -\frac{\partial p}{\partial z} + \rho g_z\ (z\text{-component}) \tag{5.4}$$

The boundary conditions are:

$$v_\theta = \Omega_i R_i \text{ at } r = R_i \tag{5.5}$$

$$v_\theta = 0 \text{ at } r = R_0 \tag{5.6}$$

$$v_\theta = \Omega_0 R_0 \text{ at } r = R_0 \text{ when both cylinders rotate} \tag{5.7}$$

Shear Stress

$$0 = \frac{\partial (r^2 \tau_{r\theta})}{\partial r} \tag{5.8}$$

$$r^2 \tau_{r\theta} = C_1 \tag{5.9}$$

$$\tau_{r\theta} = \frac{C_1}{r^2} \tag{5.10}$$

The torque exerted on the inner cylinder to maintain the flow is:

$$M_i = 2\pi R_i L \tau_{r\theta}|_{R_i} \cdot R_i = 2\pi R_i^2 L \tau_{r\theta}|_{R_i} \tag{5.11}$$

Therefore

$$\tau_{r\theta}|_{R_i} = \frac{M_i}{2\pi R_i^2 L} \tag{5.12}$$

Similarly, we have

$$\tau_{r\theta}|_{R_0} = \frac{M_i}{2\pi R_0^2 L} \tag{5.13}$$

Shear Rate

$$\mathbf{L} = \begin{bmatrix} \frac{\partial v_r}{\partial r} & \frac{1}{r}\frac{\partial v_r}{\partial \theta} - \frac{v_\theta}{r} & \frac{\partial v_r}{\partial z} \\ \frac{\partial v_\theta}{\partial r} & \frac{1}{r}\frac{\partial v_\theta}{\partial \theta} + \frac{v_r}{r} & \frac{\partial v_\theta}{\partial z} \\ \frac{\partial v_z}{\partial r} & \frac{1}{r}\frac{\partial v_z}{\partial \theta} & \frac{\partial v_z}{\partial z} \end{bmatrix} = \begin{bmatrix} 0 & -\frac{v_\theta}{r} & 0 \\ \frac{\partial v_\theta}{\partial r} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{5.14}$$

$$\mathbf{L}^T = \begin{bmatrix} 0 & \frac{\partial v_\theta}{\partial r} & 0 \\ -\frac{v_\theta}{r} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{5.15}$$

$$2\mathbf{D} = \begin{bmatrix} 0 & \frac{\partial v_\theta}{\partial r} - \frac{v_\theta}{r} & 0 \\ \frac{\partial v_\theta}{\partial r} - \frac{v_\theta}{r} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{5.16}$$

$$\therefore |2D_{r\theta}| = \dot{\gamma} = \frac{\partial v_\theta}{\partial r} - \frac{v_\theta}{r} = r\frac{\partial}{\partial r}(\frac{v_\theta}{r}) = r\frac{\partial \Omega}{\partial r} \tag{5.17}$$

For a small gap, the shear rate is nearly constant:

$$\dot{\gamma} \cong \frac{\Delta v_\theta}{\Delta r} - \Omega = \frac{\Omega_i \bar{R}}{R_0 - R_i} - \Omega_i = \frac{\Omega_i \bar{R}}{R_0 - R_i} \tag{5.18}$$

where $\bar{R} = \frac{R_0 + R_i}{2}$.

For a large gap:

$$\tau_{\theta r} = \frac{C_1}{r^2},\ \mathrm{d}\tau_{\theta r} = -C_1 r^{-3}\mathrm{d}r,\ \text{or } \mathrm{d}r = -\frac{1}{C_1} r^3 \mathrm{d}\tau_{\theta r} \tag{5.19}$$

$$\dot{\gamma} = |r\frac{\mathrm{d}\Omega}{\mathrm{d}r}| = |f\frac{\mathrm{d}\Omega}{-\frac{1}{C_1}r^3\mathrm{d}\tau_{\theta r}}| = \frac{2\frac{C_1}{r^2}\mathrm{d}\Omega}{\mathrm{d}\tau_{\theta r}} = 2\tau_{\theta r}\frac{\mathrm{d}\Omega}{\mathrm{d}\tau_{\theta r}} \tag{5.20}$$

$$\therefore \dot{\gamma}(\tau) = 2\tau\frac{\mathrm{d}\Omega}{\mathrm{d}\tau} \tag{5.21}$$

$$\int_0^{\Omega_i} \mathrm{d}\Omega = \Omega_i = \int_{\tau_{R_0}}^{\tau_{R_i}} \frac{\dot{\gamma}(\tau)}{2\tau}\,\mathrm{d}\tau \tag{5.22}$$

We can now use the Leibniz rule to differentiate Ω_i:

$$\frac{\mathrm{d}\Omega_i}{\mathrm{d}\tau_{R_i}} = 0 + \frac{\dot{\gamma}(\tau)}{2\tau}|_{\tau_{R_i}} \frac{\mathrm{d}\tau_{R_i}}{\mathrm{d}\tau_{R_i}} - \frac{\dot{\gamma}(\tau)}{2\tau}|_{\tau_{R_0}} \frac{\mathrm{d}\tau_{R_0}}{\mathrm{d}\tau_{R_i}} = \frac{1}{2}[\frac{\dot{\gamma}(\tau_{R_i})}{\tau_{R_i}} - \frac{\dot{\gamma}(\tau_{R_0})}{\tau_{R_0}} \frac{\mathrm{d}\tau_{R_0}}{\mathrm{d}\tau_{R_i}}] \tag{5.23}$$

From the θ-component of the equation of motion:

$$0 = \frac{\partial(r^2\tau_{r\theta})}{\partial r} \implies r^2\tau = const. \tag{5.24}$$

This leads to $R_i^2\tau_{R_i} = R_0^2\tau_{R_0}$, $\tau_{R_0} = (\frac{R_i}{R_0})^2\tau_{R_i}$, and thus $\frac{\mathrm{d}\tau_{R_0}}{\mathrm{d}\tau_{R_i}} = (\frac{R_i}{R_0})^2$. Therefore

$$\frac{\mathrm{d}\Omega_i}{\mathrm{d}\tau_{R_i}} = \frac{1}{2}\left[\frac{\dot{\gamma}(\tau_{R_i})}{\tau_{R_i}} - \frac{\dot{\gamma}(\tau_{R_0})}{\tau_{R_i}}\right] \tag{5.25}$$

$$2\tau_{R_i}\frac{\mathrm{d}\Omega_i}{\mathrm{d}\tau_{R_i}} = \dot{\gamma}(\tau_{R_i}) - \dot{\gamma}(\tau_{R_0}) \tag{5.26}$$

For a large gap, $\kappa = R_i/R_0 < 0.1$

$$\tau_{R_0} = (\frac{R_i}{R_0})^2\tau_{R_i} = (< 0.1)^2\tau_{R_i} \tag{5.27}$$

$$\therefore \dot{\gamma}(\tau_{R_0}) \ll \dot{\gamma}(\tau_{R_i}) \tag{5.28}$$

For power law fluid, $\tau_{R_0} = m[\dot{\gamma}(\tau_{R_0})]^n$, $\tau_{R_i} = m[\dot{\gamma}(\tau_{R_i})]^n$

$$\therefore \frac{\dot{\gamma}(\tau_{R_0})}{\dot{\gamma}(\tau_{R_i})} = (\frac{\tau_{R_0}}{\tau_{R_i}})^{1/n} = (\frac{R_i}{R_0})^{2/n} = \kappa^{2/n} \tag{5.29}$$

For $n = \frac{1}{3}$ and $\kappa = 0.1$, $\frac{\dot{\gamma}(\tau_{R_0})}{\dot{\gamma}(\tau_{R_i})} = 10^{-6}$. Since $\dot{\gamma}(\tau_{R_0})$ is negligible

$$2\tau_{R_i}\frac{\mathrm{d}\Omega_i}{\mathrm{d}\tau_{R_i}} = \dot{\gamma}(\tau_{R_i}) \tag{5.30}$$

From previously, we know $\tau_{R_i} = \frac{M_i}{2\pi R_i^2 L}$, and thus $\mathrm{d}\tau_{R_i} = \frac{\mathrm{d}M_i}{2\pi R_i^2 L}$. Therefore

$$\dot{\gamma}(\tau_{R_i}) = 2\frac{M_i}{2\pi R_i^2 L}\frac{\Omega_i \mathrm{d}\ln\Omega_i}{\frac{\mathrm{d}M_i}{2\pi R_i^2 L}} = 2\Omega_i\frac{\mathrm{d}\ln\Omega_i}{\mathrm{d}\ln M_i} \tag{5.31}$$

Again, for a power law fluid, $n = \frac{\mathrm{d}\ln M_i}{\mathrm{d}\ln\Omega_i}$. Taking the neglected, small term $\frac{\dot{\gamma}(\tau_{R_0})}{\dot{\gamma}(\tau_{R_i})}$ into account:

$$\dot{\gamma}(\tau_{R_i}) = \frac{2\Omega_i}{n(1-\kappa^{2/n})} \tag{5.32}$$

Similarly, we have

$$\dot{\gamma}(\tau_{R_0}) = -\frac{2\Omega_i}{n(1-\kappa^{-2/n})} \tag{5.33}$$

Normal Stress

Now, we focus on the r-component of the equation of motion

$$-\rho\frac{v_\theta^2}{r} = \frac{1}{r}\frac{\partial(r\tau_{rr})}{\partial r} - \frac{\tau_{\theta\theta}}{r} \tag{5.34}$$

The $\frac{v_\theta^2}{r}$ term is usually negligible

$$\therefore \frac{\mathrm{d}(r\tau_{rr})}{\mathrm{d}r} - \tau_{\theta\theta} = 0 \tag{5.35}$$

$$r\frac{\mathrm{d}(\tau_{rr})}{\mathrm{d}r} + \tau_{rr} - \tau_{\theta\theta} = 0 \tag{5.36}$$

$$\tau_{\theta\theta} - \tau_{rr} = r\frac{\mathrm{d}(\tau_{rr})}{\mathrm{d}r} \cong \frac{\tau_{rr}(R_i) - \tau_{rr}(R_0)\bar{R}}{R_0 - R_i} \tag{5.37}$$

$$\therefore T_{11} - T_{22} = \tau_{\theta\theta} - \tau_{rr} \cong \frac{\tau_{rr}(R_i) - \tau_{rr}(R_0)\bar{R}}{R_0 - R_i} \tag{5.38}$$

5.3 Cone and Plate Rheometer

Rheometry

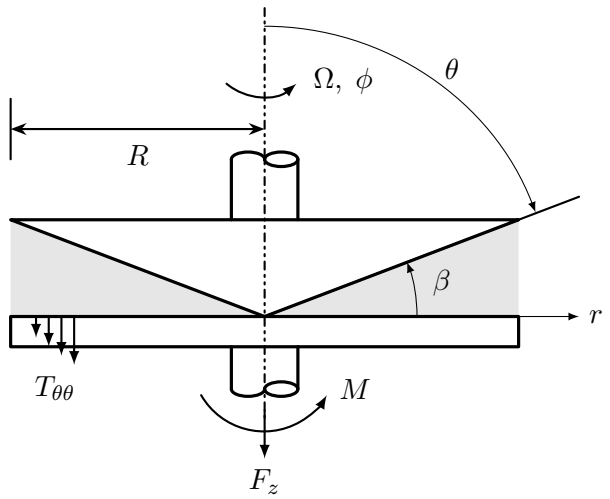


Figure 5.3: Cone and plate rheometry.

Assume steady, laminar, isothermal flow, negligible body forces, and spherical liquid boundary.

$$v_\phi(r,\theta) = \Omega r\sin\theta,\ v_r = v_\theta = 0 \tag{5.39}$$

The equation of motion in spherical coordinates:

$$-\rho\frac{v_\phi^2}{r} = \frac{1}{r^2}\frac{\partial}{\partial r}(r^2\tau_{rr}) - \frac{\tau_{\theta\theta}+\tau_{\phi\phi}}{r} \text{ (r-component)} \tag{5.40}$$

$$0 = \frac{1}{r\sin\theta}\frac{\partial(\tau_{\theta\theta}\sin\theta)}{\partial\theta} - \frac{\cot\theta\tau_{\phi\phi}}{r} \text{ (θ-component)} \tag{5.41}$$

$$0 = \frac{1}{r}\frac{\partial\tau_{\theta\phi}}{\partial\theta} + \frac{2}{r}\cot\theta\tau_{\theta\phi} \text{ (ϕ-component)} \tag{5.42}$$

The boundary conditions are:

$$v_\phi(\frac{\pi}{2}) = 0 \tag{5.43}$$

$$v_\phi(\frac{\pi}{2}-\beta) = \Omega r\sin(\frac{\pi}{2}-\beta) \cong \Omega r \tag{5.44}$$

Shear Stress

The ϕ-component of the equation of motion:

$$0 = \frac{1}{r}\frac{\partial\tau_{\theta\phi}}{\partial\theta} + \frac{2}{r}\cot\theta\tau_{\theta\phi} \tag{5.45}$$

$$\frac{\mathrm{d}\tau_{\theta\phi}}{\tau_{\theta\phi}} = -2\frac{\mathrm{d}\sin\theta}{\sin\theta} \tag{5.46}$$

$$\ln\tau_{\theta\phi} = -2\ln\sin\theta + C \tag{5.47}$$

$$\tau_{\theta\phi} = \frac{C_1}{\sin^2\theta} \implies \tau_{\theta\phi}|_{\pi/2} = C_1 \tag{5.48}$$

$$M = \int_0^{2\pi}\int_0^R r\tau_{\theta\phi}|_{\pi/2}\, r\,\mathrm{d}r\,\mathrm{d}\phi = \frac{2\pi R^3}{3}\tau_{\theta\phi}|_{\pi/2} \tag{5.49}$$

$$\therefore \tau_{\theta\phi}|_{\pi/2} = \frac{3M}{2\pi R^3} = \tau_{\theta\phi}\sin^2\theta \tag{5.50}$$

$$\tau_{\theta\phi} = \frac{3M}{2\pi R^3\sin^2\theta} \tag{5.51}$$

For $\theta \to \pi/2$:

$$\tau_{12} = \tau_{\theta\phi} = \frac{3M}{2\pi R^3} \tag{5.52}$$

Shear Rate

We have derived $\mathbf{L}$ in Chapter 2:

$$\mathbf{L} = \begin{bmatrix} 0 & 0 & \frac{\partial v_\phi}{\partial r} - \frac{v_\phi}{r} \\ 0 & 0 & \frac{1}{r}\frac{\partial v_\phi}{\partial \theta} - \frac{v_\phi}{r}\cot\theta \\ \frac{\partial v_\phi}{\partial r} - \frac{v_\phi}{r} & \frac{1}{r}\frac{\partial v_\phi}{\partial \theta} - \frac{v_\phi}{r}\cot\theta & 0 \end{bmatrix} \tag{5.53}$$

$$|2D_{\theta\phi}| = |2D_{\phi\theta}| = |\frac{1}{r}\frac{\partial v_\phi}{\partial \theta} - \frac{v_\phi}{r}\cot\theta| = \dot\gamma_{\theta\phi} = \dot\gamma_{\phi\theta} \tag{5.54}$$

$$\begin{aligned} \therefore \dot\gamma_{\theta\phi} = \dot\gamma_{\phi\theta} &= |\frac{1}{r}\frac{\partial v_\phi}{\partial \theta} - \frac{v_\phi}{r}\cot\theta| \cong |\frac{1}{r}\frac{\partial v_\phi}{\partial \theta}| \\ &\cong |\frac{1}{r}v_\phi(\frac{\pi}{2} - \beta) - v_\phi(\frac{\pi}{2})|\Big/|(\frac{\pi}{2} - \beta) - \frac{\pi}{2}| \\ &\cong \frac{1}{r}v_\phi(\frac{\pi}{2} - \beta)\Big/\beta \\ &\cong \frac{1}{r}\Omega r\sin(\frac{\pi}{2} - \beta)\Big/\beta \\ &\cong \frac{\Omega}{\beta} \end{aligned} \tag{5.55}$$

Normal Stress

The r-component of the equation of motion:

$$-\rho\frac{v_\phi^2}{r} = \frac{1}{r^2}\frac{\partial}{\partial r}(r^2\tau_{rr}) - \frac{\tau_{\theta\theta} + \tau_{\phi\phi}}{r} \tag{5.56}$$

As before, the $\frac{v_\phi^2}{r}$ is negligible:

$$\frac{1}{r}(2r\tau_{rr} + r^2\frac{\partial \tau_{rr}}{\partial r}) = \tau_{\theta\theta} + \tau_{\phi\phi} \tag{5.57}$$

$$r\frac{\partial \tau_{rr}}{\partial r} = \tau_{\theta\theta} + \tau_{\phi\phi} - 2\tau_{rr} = (\tau_{\phi\phi} - \tau_{\theta\theta}) + 2(\tau_{\theta\theta} - \tau_{rr}) \tag{5.58}$$

$$r\frac{\partial \tau_{rr}}{\partial r} = N_1 + 2N_2 \tag{5.59}$$

Since $N_2 = f_1(\dot\gamma)$, $\dot\gamma \neq f_2(r)$ as $\dot\gamma \cong \frac{\Omega}{\beta}$

$$\frac{\partial N_2}{\partial r} = 0 \implies \frac{\partial \tau_{\theta\theta}}{\partial r} = \frac{\partial \tau_{rr}}{\partial r} \tag{5.60}$$

$$r\frac{\partial \tau_{rr}}{\partial r} = N_1 + 2N_2 = r\frac{\partial \tau_{\theta\theta}}{\partial r} = \frac{\partial \tau_{\theta\theta}}{\partial \ln r} \tag{5.61}$$

$$N_2 = \tau_{22} - \tau_{33} = \tau_{\theta\theta}(R) - \tau_{rr}(R) = \tau_{\theta\theta}(R) - p_0 \tag{5.62}$$

$$\begin{aligned} F_z &= -\int_0^{2\pi}\int_0^R \tau_{\theta\theta}\, r\, \mathrm{d}r\, \mathrm{d}\phi - \pi R^2 p_0 \\ &= -\pi \int_0^R \tau_{\theta\theta}\, \mathrm{d}r^2 - \pi R^2 p_0 \\ &= -\pi \left[\tau_{\theta\theta} r^2 |_0^R - \int_0^R r^2 \frac{\mathrm{d}\tau_{\theta\theta}}{\mathrm{d}r}\, \mathrm{d}r \right] - \pi R^2 p_0 \\ &= -\pi \left[R^2 \tau_{\theta\theta}|_R - \int_0^R r^2 \frac{\mathrm{d}\tau_{\theta\theta}}{\mathrm{d}r}\, \mathrm{d}r \right] - \pi R^2 p_0 \end{aligned} \tag{5.63}$$

$$\because r\frac{\partial \tau_{rr}}{\partial r} = r\frac{\partial \tau_{\theta\theta}}{\partial r} = N_1 + 2N_2 = \tau_{\theta\theta} + \tau_{\phi\phi} - 2\tau_{rr} \tag{5.64}$$

$$\begin{aligned} \therefore F_z &= -\pi R^2 \left[\tau_{\theta\theta}|_R - \frac{\tau_{\theta\theta} + \tau_{\phi\phi} - 2\tau_{rr}}{2}|_R + p_0 \right] \\ &= -\pi R^2 \left[\frac{\tau_{\theta\theta} - \tau_{\phi\phi}}{2}|_R + \tau_{rr}|_R + p_0 \right] \end{aligned} \tag{5.65}$$

Since $\tau_{rr}|_R = -p_0$

$$\therefore F_z = \frac{\pi R^2}{2}(\tau_{\theta\theta} - \tau_{\phi\phi})|_R = \frac{1}{2}\pi R^2 N_1 \tag{5.66}$$

or

$$N_1 = \frac{2F_z}{\pi R^2} \tag{5.67}$$

which is the force exerted on the plate to resist the fluid force.

Problem with Cone and Plate Rheometer

- Edge failure for $\mathrm{De} \gg 1$
- Inertia term $\frac{\rho v_\phi^2}{r}$ at high $\dot{\gamma}$, which needs to be corrected
- Viscous heating at high $\dot{\gamma}$

5.4 Parallel Disk Rheometer

Parallel Disk Rheometry

Assume steady, laminar, isothermal flow, negligible body forces, and cylindrical edge:

$$v_\theta(r,z) = \Omega r \frac{z}{h},\ v_r = v_z = 0 \tag{5.68}$$

The equation of motion in cylindrical coordinates:

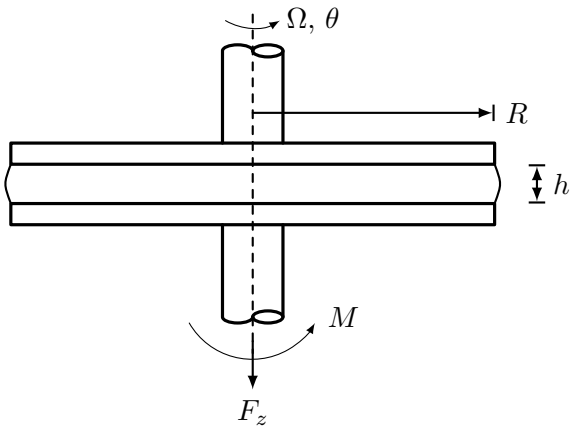


Figure 5.4: Parallel disk rheometry.

$$\frac{\partial \tau_{\theta z}}{\partial z} = 0 \ (\theta\text{-component}) \tag{5.69}$$

$$\frac{\partial \tau_{zz}}{\partial z} = 0 \ (z\text{-component}) \tag{5.70}$$

$$\frac{1}{r}\frac{\partial}{\partial r}(r\tau_{rr}) - \frac{\tau_{\theta\theta}}{r} = -\rho\frac{v_\theta^2}{r} \ (r\text{-component}) \tag{5.71}$$

Shear Rate

$L_{rr} = \frac{\partial v_r}{\partial r} = 0$, $L_{r\theta} = \frac{1}{r}\frac{\partial v_r}{\partial \theta} - \frac{v_\theta}{r} = -\frac{\Omega z}{h}$, $L_{rz} = \frac{\partial v_r}{\partial z} = 0$

$L_{\theta r} = \frac{\partial v_\theta}{\partial r} = \frac{\Omega z}{h}$, $L_{\theta\theta} = \frac{1}{r}\frac{\partial v_\theta}{\partial \theta} + \frac{v_r}{r} = 0$, $L_{\theta z} = \frac{\partial v_\theta}{\partial z} = \frac{\Omega r}{h}$

$L_{zr} = \frac{\partial v_z}{\partial r} = 0$, $L_{z\theta} = \frac{1}{r}\frac{\partial v_z}{\partial \theta} = 0$, $L_{zz} = \frac{\partial v_z}{\partial z} = 0$

$$\therefore \mathbf{L} = \begin{bmatrix} 0 & -\frac{\Omega z}{h} & 0 \\ \frac{\Omega z}{h} & 0 & \frac{\Omega r}{h} \\ 0 & 0 & 0 \end{bmatrix} \tag{5.72}$$

$$\mathbf{L}^T = \begin{bmatrix} 0 & \frac{\Omega z}{h} & 0 \\ -\frac{\Omega z}{h} & 0 & 0 \\ 0 & \frac{\Omega r}{h} & 0 \end{bmatrix}, \ 2\mathbf{D} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & \frac{\Omega r}{h} \\ 0 & \frac{\Omega r}{h} & 0 \end{bmatrix}$$

$$\therefore 2D_{\theta z} = 2D_{z\theta} = \dot{\gamma}_{\theta z} = \dot{\gamma}_{z\theta} = \frac{\Omega r}{h} = \frac{\partial v_\theta}{\partial z} \tag{5.73}$$

Shear Stress

We focus on the shear stress $\tau_{\theta z} = \tau_{12} = \tau_{12}(\dot{\gamma})$. The torque exerted on the disk is:

$$M = 2\pi \int_0^R r\tau_{12}\, r\, \mathrm{d}r \tag{5.74}$$

$\dot{\gamma} = \frac{\Omega r}{h}$, $\dot{\gamma}|_R = \dot{\gamma}_R = \frac{\Omega R}{h} \implies r = \frac{R\dot{\gamma}}{\dot{\gamma}_R}$. In addition, $r = \frac{h}{\Omega}\dot{\gamma} \implies \mathrm{d}r = \frac{h}{\Omega}\mathrm{d}\dot{\gamma}$.

$$\therefore M = 2\pi \int_0^{\dot{\gamma}_R} (\frac{R}{\dot{\gamma}_R})^3 \dot{\gamma}^2 \tau_{12}\, \mathrm{d}\dot{\gamma} \tag{5.75}$$

Apply the Leibniz' rule to differentiate M:

$$\frac{1}{2\pi R^3}\frac{\mathrm{d}M}{\mathrm{d}\dot{\gamma}_R} = \int_0^{\dot{\gamma}_R} [-3\dot{\gamma}_R^{-4}\dot{\gamma}^2\tau_{12}]\, \mathrm{d}\dot{\gamma} + \dot{\gamma}_R^{-1}\tau_{12}|_R \tag{5.76}$$

$$\frac{1}{2\pi R^3}\frac{\mathrm{d}M}{\mathrm{d}\dot{\gamma}_R} + \frac{3\dot{\gamma}_R^{-1}M}{2\pi R^3} = \dot{\gamma}_R^{-1}\tau_{12}|_R \tag{5.77}$$

$$\tau_{12}|_R = \frac{M}{2\pi R^3}\Big[3 + \frac{\mathrm{d}\ln M}{\mathrm{d}\ln\dot{\gamma}_R}\Big] \tag{5.78}$$

- If Newtonian, $\frac{\mathrm{d}\ln M}{\mathrm{d}\ln\dot{\gamma}_R} = 1$
- If non-Newtonian, $\frac{\mathrm{d}\ln M}{\mathrm{d}\ln\dot{\gamma}_R}$ is determined through experiment

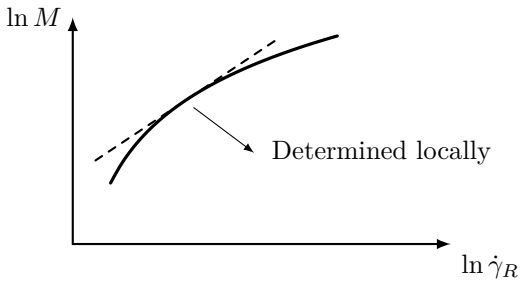


Figure 5.5: Exemplary experimental data of parallel disk rheometry.

Normal Stress

The r-component of the equation of motion:

$$\frac{1}{r}\frac{\partial}{\partial r}(r\tau_{rr}) - \frac{\tau_{\theta\theta}}{r} = -\rho\frac{v_\theta^2}{r} \tag{5.79}$$

Again, we neglect the inertia term:

$$\frac{\partial}{\partial r}(r\tau_{rr}) - \tau_{\theta\theta} = 0 \tag{5.80}$$

Using simpler notations ($1 = \theta$, $2 = z$, $3 = r$):

$$\frac{\mathrm{d}}{\mathrm{d}r}(r\tau_{33}) - \tau_{11} = 0 \tag{5.81}$$

$$\frac{\mathrm{d}\tau_{33}}{\mathrm{d}r} = -\frac{\tau_{33} - \tau_{11}}{r} \tag{5.82}$$

$$\frac{\mathrm{d}\tau_{22}}{\mathrm{d}r} = \frac{\mathrm{d}\tau_{33}}{\mathrm{d}r} + \frac{\mathrm{d}}{\mathrm{d}r}(\tau_{22} - \tau_{33}) \tag{5.83}$$

$$\therefore \frac{\mathrm{d}\tau_{22}}{\mathrm{d}r} = -\frac{\tau_{33} - \tau_{11}}{r} + \frac{\mathrm{d}}{\mathrm{d}r}(\tau_{22} - \tau_{33}) \tag{5.84}$$

$$\int_{\tau_{22}(r)}^{\tau_{22}(R)} \mathrm{d}\tau_{22} = \int_{N_2(r)}^{N_2(R)} \mathrm{d}(\tau_{22} - \tau_{33}) + \int_r^R \frac{(\tau_{11} - \tau_{22}) + (\tau_{22} - \tau_{33})}{\zeta}\,\mathrm{d}\zeta \tag{5.85}$$

$$\tau_{22}(R) - \tau_{22}(r) = N_2(R) - N_2(r) + \int_r^R \frac{N_1 + N_2}{\zeta}\,\mathrm{d}\zeta \tag{5.86}$$

Note that $\tau_{22}(R) = 0$ Pa and $N_2(R) = 0$ (free surface)

$$\therefore \tau_{22}(r) = N_2(r) - \int_r^R \frac{N_1 + N_2}{\zeta}\,\mathrm{d}\zeta \tag{5.87}$$

The total thrust is expressed as $F_z = -2\pi \int_0^R \tau_{22}\, r\,\mathrm{d}r$

$$\begin{aligned} F_z &= -2\pi \int_0^R N_2\, r\,\mathrm{d}r + 2\pi \int_0^R (\int_r^R \frac{N_1 + N_2}{\zeta}\,\mathrm{d}\zeta) r\,\mathrm{d}r \\ &= -2\pi \int_0^R N_2\, r\,\mathrm{d}r + 2\pi \int_0^R \frac{N_1 + N_2}{\zeta} (\int_0^\zeta r\mathrm{d}r)\,\mathrm{d}\zeta \\ &= -2\pi \int_0^R N_2\, r\,\mathrm{d}r + \pi \int_0^R (N_1 + N_2)\zeta\,\mathrm{d}\zeta \\ &= \pi \int_0^R (N_1 - N_2)\, r\,\mathrm{d}r \end{aligned} \tag{5.88}$$

Pay attention to how the order of integration is changed here. We also change the variable: $r = \frac{R\dot{\gamma}}{\dot{\gamma}_R}$, $\mathrm{d}r = \frac{R}{\dot{\gamma}_R}\mathrm{d}\dot{\gamma}$:

$$F_z = \pi \int_0^{\dot{\gamma}_R} (N_1 - N_2) \frac{R^2}{\dot{\gamma}_R^2} \dot{\gamma}\,\mathrm{d}\dot{\gamma} \tag{5.89}$$

Differentiate F_z with $\dot{\gamma}_R$ using the Leibnitz' rule

$$\begin{aligned} \frac{1}{\pi R^2}\frac{\mathrm{d}F_z}{\mathrm{d}\dot{\gamma}_R} &= \int_0^{\dot{\gamma}_R} (N_1 - N_2)(-2\dot{\gamma}_R^{-3})\dot{\gamma}\,\mathrm{d}\dot{\gamma} + \dot{\gamma}_R^{-1}(N_1 - N_2)|_{\dot{\gamma}_R} \\ &= -2\dot{\gamma}_R^{-1} \int_0^{\dot{\gamma}_R} (N_1 - N_2)\dot{\gamma}_R^{-2}\dot{\gamma}\,\mathrm{d}\dot{\gamma} + \dot{\gamma}_R^{-1}(N_1 - N_2)|_{\dot{\gamma}_R} \\ &= \frac{-2\dot{\gamma}_R^{-1}}{\pi R^2} F_z + \dot{\gamma}_R^{-1}(N_1 - N_2)|_{\dot{\gamma}_R} \end{aligned} \tag{5.90}$$

$$\therefore \frac{2F_z}{\pi R^2} + \frac{\dot{\gamma}_R}{\pi R^2}\frac{\mathrm{d}F}{\mathrm{d}\dot{\gamma}_R} = (N_1 - N_2)|_{\dot{\gamma}_R} \tag{5.91}$$

$$(N_1 - N_2)|_{\dot{\gamma}_R} = \frac{F_z}{\pi R^2}[2 + \frac{\mathrm{d}\ln F_z}{\mathrm{d}\ln \dot{\gamma}_R}] \tag{5.92}$$

Since $\dot{\gamma}$ can be adjusted easily by changing Ω and h, we can measure the material functions at a wide range of shear rate, as well as measuring N_1 and N_2.

CHAPTER 6

Shear Rheometry: Pressure Driven Flows

Lecture 6 **Date:** <YYYY-MM-DD>
Topic: Capillary Rheometry; errors in capillary rheometry; slit rheometry **Scribe:** Yang Han

6.1 Capillary Rheometry

There are several advantages of pressure-driven rheometry that allow for the measurement of material functions at high $\dot{\gamma}$:

- Inexpensive and simple
- No free surface (enclosed flow) $\implies$ not limited by high $\dot{\gamma}$
- Online measurement
- Similar to process flows (e.g., pipes, extrusion dies)

Here, we focus on the most widely used pressure-driven apparatus, capillary rheometry.

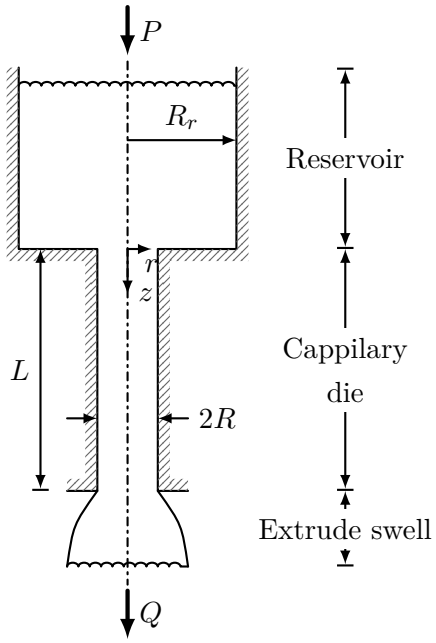


Figure 6.1: Capillary rheometry.

The overarching goal of capillary rheometry is to determine $\eta(\dot{\gamma}_w) = \frac{\tau_w}{\dot{\gamma}_w}$ inside of the capillary region. In order to simplify the momentum equation, we make the following assumptions:

- Fully developed, steady, isothermal, laminar flow
- No slip at capillary wall
- Incompressible ($\eta \neq f(p)$)
- $v_r = v_\theta = 0$, $v_z = v_z(r)$

τ_w in the Capillary

The z-component of the momentum equation (see Table 1.7.1., p.48):

$$0 = -\frac{\partial p}{\partial z} + \frac{1}{r}\frac{\partial (r\tau_{rz})}{\partial r} \tag{6.1}$$

Since $\frac{1}{r}\frac{\partial (r\tau_{rz})}{\partial r} = f(r)$ and $\frac{\partial p}{\partial z} = g(z)$, we know that $\frac{\partial p}{\partial z} = \text{const.} = \frac{\Delta p_c}{L}$.

$$\therefore \frac{\Delta p_c}{L}\int r\,\mathrm{d}r = \int \mathrm{d}(r\tau_{rz}) \tag{6.2}$$

$$\frac{\Delta p_c}{L}\frac{r^2}{2} = r\tau_{rz} + C_1 \tag{6.3}$$

$$\tau_{rz} = \frac{\Delta p_c}{L}\frac{r}{2} - \frac{C_1}{r} \tag{6.4}$$

The boundary condition is $\tau_{rz}|_{r=0} = 0 \implies C_1 = 0$.

$$\therefore \tau_{rz} = \frac{\Delta p_c}{L}\frac{r}{2} \tag{6.5}$$

and

$$\tau_w = \frac{\Delta p_c}{L}\frac{R}{2} \tag{6.6}$$

$\dot{\gamma}_w$ at the Wall

$$\begin{aligned} Q &= \int_0^{2\pi}\int_0^R v_z(r) r \,\mathrm{d}r\mathrm{d}\theta = 2\pi\int_0^R v_z(r) r \,\mathrm{d}r = \pi\int_0^R v_z(r)\,\mathrm{d}r^2 \\ &= \pi v_z(r) r^2|_0^R - \pi\int_0^R r^2\,\mathrm{d}v_z(r) \\ &= -\pi\int_0^R r^2\,\mathrm{d}v_z(r) \\ &= -\pi\int_0^R r^2\frac{\mathrm{d}v_z(r)}{\mathrm{d}r}\,\mathrm{d}r \end{aligned} \tag{6.7}$$

From τ_{rz} and τ_w, we have $r = R\frac{\tau_{rz}(r)}{\tau_w} \implies \mathrm{d}r = \frac{R}{\tau_w}\mathrm{d}\tau_{rz}(r)$.

$$\therefore Q = -\pi\int_0^{\tau_w}\frac{R^2}{\tau_w^2}\tau_{rz}^2\frac{\mathrm{d}v_z(r)}{\mathrm{d}r}\frac{R}{\tau_w}\,\mathrm{d}\tau_{rz} \tag{6.8}$$

$$\therefore \frac{Q\tau_w^3}{\pi R^3} = -\int_0^{\tau_w}\tau_{rz}^2\frac{\mathrm{d}v_z}{\mathrm{d}r}\,\mathrm{d}\tau_{rz} \tag{6.9}$$

Differentiate this equation with respect to τ_w using the Leibniz' rule:

$$\frac{3Q\tau_w^2}{\pi R^3} + \frac{\tau_w^3}{\pi R^3}\frac{\mathrm{d}Q}{\mathrm{d}\tau_w} = \tau_w^2\big(-\frac{\mathrm{d}v_z}{\mathrm{d}r}\Big|_{\tau_w}\big) = \tau_w^2\dot{\gamma}_w \tag{6.10}$$

$$\therefore \dot{\gamma}_w = \frac{Q}{\pi R^3}\big(3 + \frac{\tau_w}{Q}\frac{\mathrm{d}Q}{\mathrm{d}\tau_w}\big) = \frac{Q}{\pi R^3}\big(3 + \frac{\mathrm{d}\ln Q}{\mathrm{d}\ln\tau_w}\big) \tag{6.11}$$

For Newtonian fluid, the shear rate at the wall is $\dot{\gamma}_{aw} = \frac{4Q}{\pi R^3}$. With this, we can rearrange the above equation and obtain the Weissenberg-Rabinowitsch equation:

$$\dot{\gamma}_w = \frac{1}{4}\dot{\gamma}_{aw}\big(3 + \frac{\mathrm{d}\ln Q}{\mathrm{d}\ln\tau_w}\big) \tag{6.12}$$

Clearly, $\frac{\mathrm{d}\ln Q}{\mathrm{d}\ln\tau_w} = 1$ for Newtonian fluid (by letting $\dot{\gamma}_w = \dot{\gamma}_{aw}$). For shear-thinning or shear-thickening fluids, we have

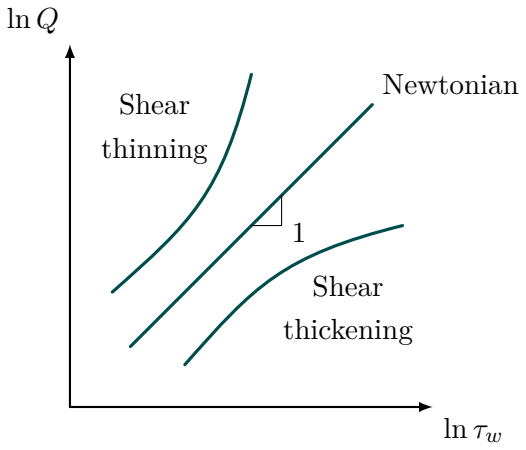


Figure 6.2: Weissenberg-Rabinowitsch plot for capillary rheometry.

Now, we aim to convert the Weissenberg-Rabinowitsch equation to a form with quantities that are directly measurable experimentally.

$$\tau_w = \frac{\Delta p_c}{L}\frac{R}{2} \implies \mathrm{d}\tau_w = \frac{R}{2L}\mathrm{d}\Delta p_c \implies \frac{\mathrm{d}\tau_w}{\tau_w} = \frac{\mathrm{d}\Delta p_c}{\Delta p_c} \implies \mathrm{d}\ln\tau_w = \mathrm{d}\ln\Delta p_c \tag{6.13}$$

$$\therefore \frac{\mathrm{d}\ln Q}{\mathrm{d}\ln\tau_w} = \frac{\mathrm{d}\ln Q}{\mathrm{d}\ln\Delta p_c} = \frac{1}{n'} \tag{6.14}$$

$$\dot{\gamma}_w = \frac{1}{4}\dot{\gamma}_{aw}(3+\frac{1}{n'}) \tag{6.15}$$

By definition

$$\eta = \frac{\tau_w}{\dot{\gamma}_w} = \frac{\frac{\Delta p_c}{L}\frac{R}{2}}{\frac{1}{4}\dot{\gamma}_{aw}(3+\frac{1}{n'})} = \frac{\pi R^4\Delta p_c}{2QL}(\frac{n'}{3n'+1}) \tag{6.16}$$

We can make a few observations:

- For power law fluid, n' is the same as the exponent n
  - From Example 2.4.1, $Q = \frac{\pi R^3}{1/n+3}(\frac{\tau_w}{m})^{1/n} \implies \frac{\mathrm{d}\ln Q}{\mathrm{d}\ln\tau_w} = \frac{1}{n}$
- For Newtonian fluid, $n' = 1$
  - $\eta_a = \frac{\pi R^4\Delta p_c}{8QL}$ (apparent viscosity)

6.2 Errors in Capillary Rheometry

- Wall Slip
  - Wall slip can occur at very high $\dot{\gamma}$ and τ (when $\tau_w > 10^5$ Pa), especially for macromolecules
- Turbulence

  - When Re > 2000 (Re $= \frac{d\rho u}{\eta}$)
  - If capillary rheometry is used for low viscosity fluid, Re can be large, and the analysis might break down
  - In this case, the diameter d needs to be further reduced $\implies$ micro-capillary rheometer, $d \sim 10\ \mu$m

- Shear Heating
  - Capillary is often used to measure η at large $\dot{\gamma}_w$ $\implies$ heating effect can be significant
  - Nahme number Na $= \frac{\beta \tau_w \dot{\gamma}_w R^2}{4k}$
    - β: temperature sensitivity of viscosity $\eta = \eta_0 e^{\beta(T-T_0)}$
    - k: thermal conductivity
    - Viscous heating becomes an issue when Na > 0.1

- Pressure Correction
  - $\Delta p_{\text{total}} = p_{\text{top}} - p_{\text{atm}} = \Delta p_{\text{f}} + \Delta p_{\text{r}} + \Delta p_{\text{c}} + \Delta p_{\text{en}} + \Delta p_{\text{exit}}$
  - Δp_{f}: piston friction, determined with no fluid in the system
  - Δp_{r}: falling pressure from the reservoir, negligible if $\frac{R}{R_r} < 0.2$
  - Δp_{c}: capillary pressure drop
  - Δp_{en}: entrance effect, a function of τ_w and $\frac{R}{R_r}$
  - Δp_{exit}: pressure drop from die swell at exit, caused by normal stress, typically $< 10\%$ of Δp_{en}

Bagley Correction

One method to correct the pressure is the Bagley correction. The pressure drop is measured on a series of dies of the same diameter, but decreasing length (different L/D ratio). A linear fit is carried out on the measured points, enabling an extrapolation to the L/D ratio of 0 length. Note that the flow rate is maintained for the series of capillaries.

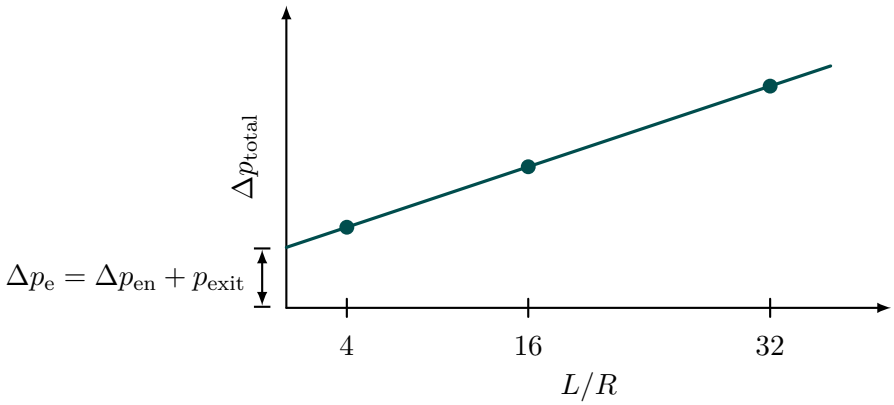


Figure 6.3: Bagley correction.

6.3 Slit Rheometry

Extrude Swell

When an elastic liquid leaves a capillary die, it expands due to tension along streamlines. The extrude swell is often more significant when normal stress is present.

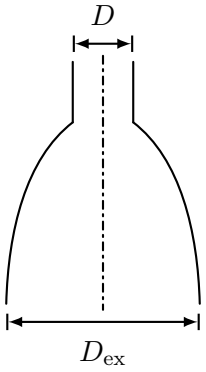


Figure 6.4: Extrude die.

We typically measure extrude swell by

$$B_{\text{extrude}} = \frac{D_{\text{ex}}}{D} \tag{6.17}$$

where D_{ex} is the equilibrium extrude diameter. For Newtonian fluid, $B_{\text{extrude}} = 0.13$ when $\text{Re} \leq 2$. This is often true since elastic liquids are typically extruded in the low Reynolds range. We can further define an elastic swell as:

$$B = B_{\text{extrude}} - 0.13 \tag{6.18}$$

The normal stress can be estimated as:

$$N_1^2 = 8\tau_w^2(B^6 - 1) \tag{6.19}$$

Pressure Hole

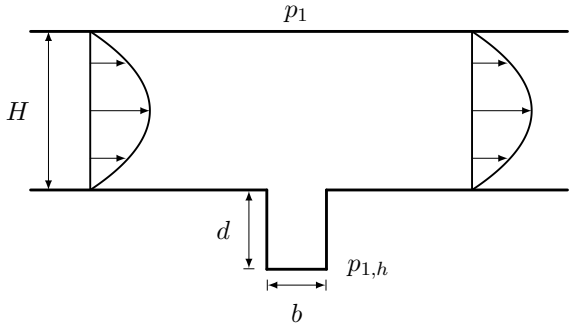


Figure 6.5: Pressure hole.

For a given wall stress, the pressure differential between the bulk and the pressure hole is

$$p_h = p_1 - p_{1,h} \tag{6.20}$$

By changing the flow rate, we can change the wall stress. This leads to a correlation between the pressure differential and wall stress:

$$m = \frac{\mathrm{d} \ln p_h}{\mathrm{d} \ln \tau_w} \tag{6.21}$$

The normal stresses are then:

$$N_1 = 2mp_h \text{ (for slot hole)} \tag{6.22}$$

$$N_1 - N_2 = 3mp_h \text{ (for circular hole)} \tag{6.23}$$

CHAPTER 7

Extensional Rheometry

Lecture 7 **Date:** <YYYY-MM-DD>

Topic: Filament stretching rheometry; lubriated compression; fiber spinning; bubble colllapse; opposed nozzles; entrnace flow **Scribe:** Yang Han

7.1 Filament Stretching Rheometry

Filament stretching is an experiment method that works for fluids $10 - 10000$ times of the viscosity of water.

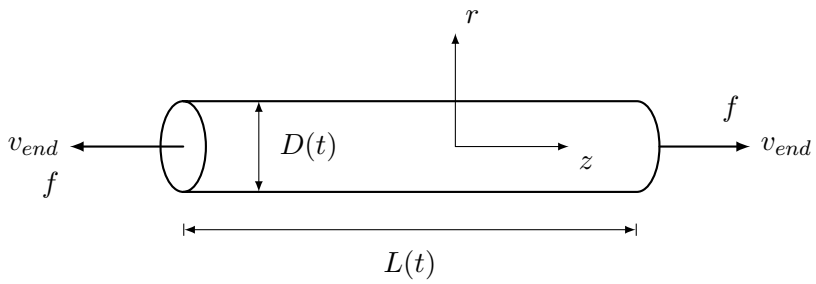


Figure 7.1: Filament stretching.

Experimentally, we employ a filament at rest initially. At $t = 0$, we apply uniaxial extension on the filament with a constant $\dot{\epsilon}$. The measurable quantities are the filament diameter $D(t)$ and the force to maintain the stretching $F_z(t)$.

$$\mathbf{L} = \begin{bmatrix} \frac{\partial v_1}{\partial x_1} & \frac{\partial v_1}{\partial x_2} & \frac{\partial v_1}{\partial x_3} \\ \frac{\partial v_2}{\partial x_1} & \frac{\partial v_2}{\partial x_2} & \frac{\partial v_2}{\partial x_3} \\ \frac{\partial v_3}{\partial x_1} & \frac{\partial v_3}{\partial x_2} & \frac{\partial v_3}{\partial x_3} \end{bmatrix} = \begin{bmatrix} \dot{\epsilon} & 0 & 0 \\ 0 & -\dot{\epsilon}/2 & 0 \\ 0 & 0 & -\dot{\epsilon}/2 \end{bmatrix} \tag{7.1}$$

$$\frac{\partial v_z}{\partial z} = \dot{\epsilon} \tag{7.2}$$

with B.C.: $v_z|_{z=0} = 0$

$$\frac{\partial v_r}{\partial r} = -\frac{\dot{\epsilon}}{2} \tag{7.3}$$

with B.C.: $v_r|_{r=0} = 0$. These lead to

$$v_z = v_z(z) = \dot{\epsilon} z \tag{7.4}$$

$$v_r = v_r(r) = -\frac{\dot{\epsilon}}{2} r \tag{7.5}$$

$$v_{\text{end}} = \frac{\dot{\epsilon} L}{2} = \frac{1}{2}\frac{\mathrm{d}L}{\mathrm{d}t} \tag{7.6}$$

$$\therefore \int_{L_0}^{L} \frac{\mathrm{d}L}{L} = \int_0^t \dot{\epsilon}\, \mathrm{d}t \tag{7.7}$$

$$L = L_0 e^{\dot{\epsilon} t} \tag{7.8}$$

or

$$\epsilon = \dot{\epsilon} t = \ln \frac{L}{L_0} \tag{7.9}$$

The stress causing the filament to elongate is the normal stress difference:

$$\tau_{zz} - \tau_{rr} = \frac{F(t)}{A(t)} \tag{7.10}$$

From continuity, $A(t)L(t) = \text{const.} = \pi R_0^2 L_0$. We know that $L(t) = L_0 e^{\dot{\epsilon} t}$, so

$$A(t) = \frac{\pi R_0^2}{e^{\dot{\epsilon} t}} = \pi R_0^2 e^{-\dot{\epsilon} t} \tag{7.11}$$

$$\tau_{zz} - \tau_{rr} = \frac{F(t)}{A(t)} = \frac{F(t)}{\pi R_0^2} e^{\dot{\epsilon} t} \tag{7.12}$$

$$\eta_e = \frac{\tau_{zz} - \tau_{rr}}{\dot{\epsilon}} = \frac{F(t)}{\pi R_0^2 \dot{\epsilon}} e^{\dot{\epsilon} t} \tag{7.13}$$

What we can extract from extensional rheometry is a transient viscosity (vs. the steady-state viscosity from shear rheometry).

7.2 Lubricated Compression

The viscous behaviors of a fluid under "stretching" and "compression" are usually quite different

- This is polar opposite to shear rheometry; the rheological properties should not depend on which direction the fluid is sheared
- However, many fluids are much more difficult to "compress" than stretch. A good example is a particle suspension, where the repulsion between particles give the suspension extra "resistance to motion" when compressed
- Note that the term "compression" is not used in the context of most fluid dynamics literature. After all, we usually work with incompressible fluids in rheology. Here, it refers to a squeezing flow. "Lubricated compression" is the preferred term in more rigorous literature.

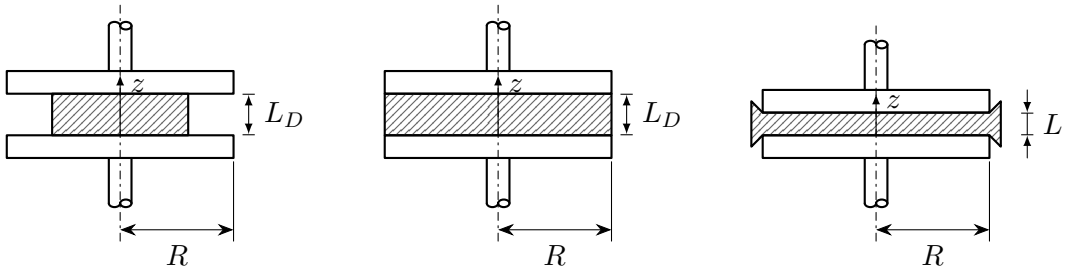


Figure 7.2: Lubricated compression.

We now choose r in the 1 direction with $\epsilon_{11} = \epsilon_{22} = \epsilon_{rr}$.

$$\frac{\partial v_r}{\partial r} = \dot{\epsilon},\ v_r|_{r=0} = 0 \implies v_r(r) = \dot{\epsilon} r \tag{7.14}$$

$$\frac{\partial v_z}{\partial z} = 2\dot{\epsilon},\ v_z|_{z=0} = 0 \implies v_z(z) = 2\dot{\epsilon} z \tag{7.15}$$

$$v_{\text{top}} = 2\dot{\epsilon} L = -\frac{\mathrm{d}L}{\mathrm{d}t} \tag{7.16}$$

$$\dot{\epsilon} = -\frac{1}{2L}\frac{\mathrm{d}L}{\mathrm{d}t} \tag{7.17}$$

$$\therefore -\frac{1}{2}\int_{L_0}^{L} \frac{1}{L}\,\mathrm{d}L = \int_0^t \dot{\epsilon}\,\mathrm{d}t \tag{7.18}$$

$$\epsilon = -\frac{1}{2}\ln\left(\frac{L(t)}{L_0}\right) \tag{7.19}$$

For a gap fully filled by the fluid

$$\tau_{rr} - \tau_{zz} = \frac{F(t)}{\pi R^2} \tag{7.20}$$

For a partially filled gap

$$\tau_{rr} - \tau_{zz} = \frac{F(t)}{\pi r^2(t)} \tag{7.21}$$

The varying radius can be found assuming an incompressible fluid

$$r(t) = r_0 \sqrt{\frac{L_0}{L(t)}} \tag{7.22}$$

Now, we can calculate an "equibiaxial viscosity"

$$\eta_b = \frac{\tau_{rr} - \tau_{zz}}{\dot{\epsilon}} \tag{7.23}$$

7.3 Fiber Spinning

Extensional rheometry for low viscosity fluids ($< 10^3$ Pa $\cdot$ s) is particularly problemtic:

- Nearly impossible to "grab and pull" the fluids like a metallic or polymer melt filament
- However, the extensional effects are also quite strong for polymer solution
- We can use approximate extensional rheometry to assess the extensional effects

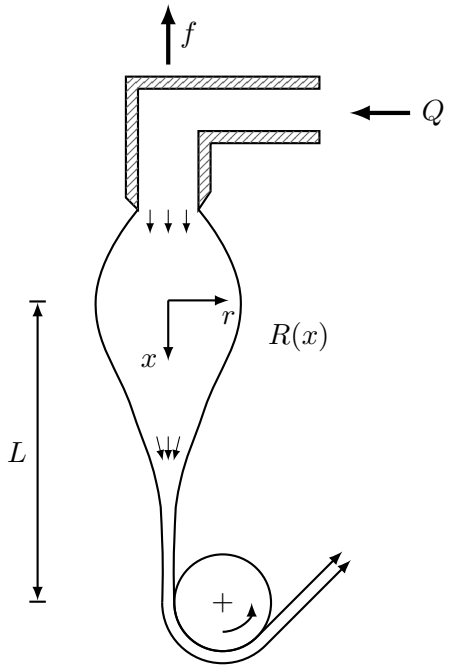


Figure 7.3: Fiber spinning.

$$Q = v_x \pi R^2(x) \tag{7.24}$$

For a constant flow rate, the definition of extension rate gives:

$$\dot{\epsilon} \equiv \frac{\partial v_x}{\partial x} = \frac{\mathrm{d}}{\mathrm{d}x}\left(\frac{Q}{\pi R^2(x)}\right) = -\frac{2Q}{\pi R^3}\frac{\mathrm{d}R}{\mathrm{d}x} \tag{7.25}$$

Differentiating the $R(x)$ profile down the fiber gives the extension rate. However, a simpler analysis can be attained by assuming a constant extension rate everywhere:

$$\dot{\epsilon}_a = \frac{\Delta v_x}{\Delta x} = \frac{v_L - v_0}{L} = \frac{Q}{\pi L}\left(\frac{1}{R_L^2} - \frac{1}{R_0^2}\right) \tag{7.26}$$

Since the final diameter is small, a good approximation is

$$\dot{\epsilon}_a \cong \frac{Q}{\pi R_L^2 L} \tag{7.27}$$

Equating Eq. (7.25) and Eq. (7.26)

$$\frac{\mathrm{d}R}{\mathrm{d}x} = -\frac{R^3}{2L}\left(\frac{1}{R_L^2} - \frac{1}{R_0^2}\right) \tag{7.28}$$

$$\mathrm{d}\left(\frac{1}{R^2}\right) = \frac{\mathrm{d}x}{L}\left(\frac{1}{R_L^2} - \frac{1}{R_0^2}\right) \tag{7.29}$$

$$\int_{R_0}^{R} \mathrm{d}\left(\frac{1}{R^2}\right) = \left(\frac{1}{R_L^2} - \frac{1}{R_0^2}\right)\int_0^x \frac{\mathrm{d}x}{L} \tag{7.30}$$

$$\frac{1}{R^2} - \frac{1}{R_0^2} = \frac{x}{L}\left(\frac{1}{R_L^2} - \frac{1}{R_0^2}\right) \tag{7.31}$$

$$\frac{1}{R^2} \cong \frac{x}{R_L^2 L} \tag{7.32}$$

For the filament stretching experiment, it is apparent to integrate the transient $\dot{\epsilon}$ over time to obtain the total strain ϵ. For steady-state fiber spinning, we typically integrate $\dot{\epsilon}$ spatially

$$\epsilon_a = \int_0^L \dot{\epsilon}\frac{\mathrm{d}t}{\mathrm{d}x}\,\mathrm{d}x = \int_0^L \frac{\dot{\epsilon}}{v_x}\,\mathrm{d}x \tag{7.33}$$

From earlier, we know that

$$\frac{\dot{\epsilon}}{v_x} = \left(-\frac{2Q}{\pi R^3}\frac{\mathrm{d}R}{\mathrm{d}x}\right)\Big/\left(\frac{Q}{\pi R^2}\right) = -\frac{2}{R}\frac{\mathrm{d}R}{\mathrm{d}x} = -2\frac{\mathrm{d}\ln R}{\mathrm{d}x} \tag{7.34}$$

$$\therefore \epsilon_a = \int_0^L -2\frac{\mathrm{d}\ln R}{\mathrm{d}x}\,\mathrm{d}x = -2\int_{R_0}^{R_L} \mathrm{d}\ln R = \ln\frac{R_0^2}{R_L^2} \tag{7.35}$$

Recognizing the constant Q, we can also rewrite the total strain experienced by each material element when it is drawn down the fiber as

$$\epsilon_a = \ln \frac{R_0^2}{R_L^2} = \ln \frac{v_L}{v_0} \tag{7.36}$$

[*Note 1*] You can get the same result by $\epsilon_a = \int_0^L \frac{\partial v_x}{\partial x} \frac{1}{v_x} \, \mathrm{d}x$, which might be more straightforward.

[*Note 2*] Both the filament stretching and fiber spinning have a strain in the form of $\ln \frac{L}{L_0}$ or $\ln(\frac{R_0}{R})^2$. These are called Hencky strain (vs. the engineering strain $\frac{L-L_0}{L_0}$), which is more appropriate when the strain is large.

The force balance (normal stress + body force - inertia + surface tension)

$$\frac{F}{\pi R^2} = (\tau_{xx} - \tau_{rr})_x + \frac{\rho g}{R^2} \int_0^x R^2 \, \mathrm{d}x' - \rho v_x^2 + \frac{\Gamma}{R} \tag{7.37}$$

For highly viscous fluids, the correction terms beyond the normal stress can be neglected, and the data are typically estimated by dividing the force on the nozzle by the area of the die

$$\tau_{xx} - \tau_{rr} = \frac{F}{\pi R_0^2} \tag{7.38}$$

Of course, we can define an apparent viscosity

$$\eta_a = \frac{\tau_{xx} - \tau_{rr}}{\dot{\epsilon}_a} = \frac{\frac{F}{\pi R_0^2}}{\frac{Q}{\pi R_L^2 L}} = \frac{FL}{Q} (\frac{R_L}{R_0})^2 \tag{7.39}$$

7.4 Bubble Collapse

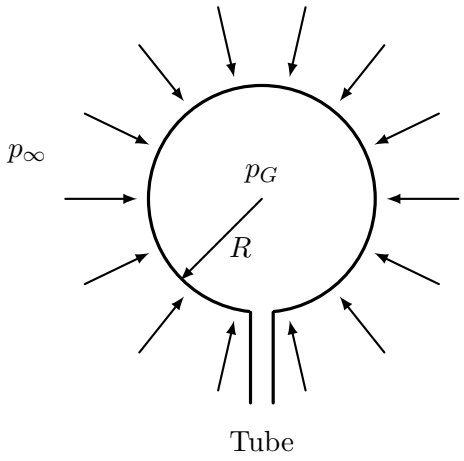


Figure 7.4: Bubble collapse.

Assumptions:

- Negligible diffusion
- Surface tension does not affect bubble collapse
- Symmetrical

We can analyze the mass balance of a layer of the fluid outside of the bubble.

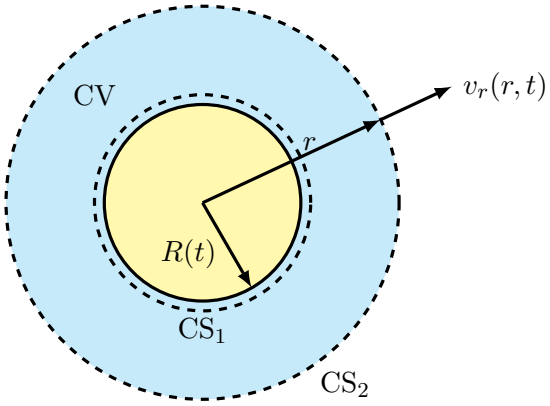


Figure 7.5: Control volume around the bubble.

In the control volume (CV) between the two control surfaces (CS), the integral mass conservation equation is

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathrm{CV}}\rho\,\mathrm{d}V+\int_{\mathrm{CS}}\rho(\mathbf{v}-\mathbf{v_I})\cdot\hat{\mathbf{n}}\,\mathrm{d}A=0 \tag{7.40}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathrm{CV}}\rho\,\mathrm{d}V=\rho\frac{\mathrm{d}V}{\mathrm{d}t}=\frac{4}{3}\pi\rho\frac{\mathrm{d}}{\mathrm{d}t}(r^3-R^3(t))=-4\pi R^2\rho\frac{\mathrm{d}R}{\mathrm{d}t} \tag{7.41}$$

$$\int_{\mathrm{CS_1}}\rho(\mathbf{v}-\mathbf{v_I})\cdot\hat{\mathbf{n}}\,\mathrm{d}A=0 \tag{7.42}$$

since the fluid velocity is the same as the shrinking velocity of the bubble.

$$\int_{\mathrm{CS_2}}\rho(\mathbf{v}-\mathbf{v_I})\cdot\hat{\mathbf{n}}\,\mathrm{d}A=4\pi r^2\rho v_r \tag{7.43}$$

since $\mathbf{v}=v_r\hat{\mathbf{e}}_r$ and $\mathbf{v_I}=\mathbf{0}$.

Together, we have

$$-4\pi R^2\rho\frac{\mathrm{d}R}{\mathrm{d}t}+4\pi r^2\rho v_r=0 \tag{7.44}$$

$$v_r=(\frac{R}{r})^2\frac{\mathrm{d}R}{\mathrm{d}t} \tag{7.45}$$

From the definition of extension rate

$$\dot{\epsilon} = \dot{\epsilon}_{rr} = \frac{\partial v_r}{\partial r} = -\frac{2R^2}{r^3}\frac{\mathrm{d}R}{\mathrm{d}t} \tag{7.46}$$

Clearly, the extension rate is not uniform. The extension rate at the interface is

$$\dot{\epsilon}_R = -\frac{2}{R}\frac{\mathrm{d}R}{\mathrm{d}t} \tag{7.47}$$

Integrating once, we have the strain

$$\epsilon = -2\ln\frac{R}{R_0} \tag{7.48}$$

The force balance at the bubble interface

$$0 = p_G - p_\infty - \frac{2\Gamma}{R} + 2\int_R^\infty \frac{\tau_{rr} - \tau_{\theta\theta}}{r}\,\mathrm{d}r \tag{7.49}$$

We need a constitutive equation to evaluate the integral. This is a serious limitation on using bubble collapse as a rheomter. Assuming Newtonian

$$\tau_{rr} - \tau_{\theta\theta} = -\frac{3}{2}(p_G - p_\infty - \frac{2\Gamma}{R}) \tag{7.50}$$

We can now define an apparent extensional viscosity

$$\eta_a = \frac{3(p_G - p_\infty - 2\Gamma/R)R}{4\,\mathrm{d}R/\mathrm{d}t} \tag{7.51}$$

7.5 Opposed Nozzles

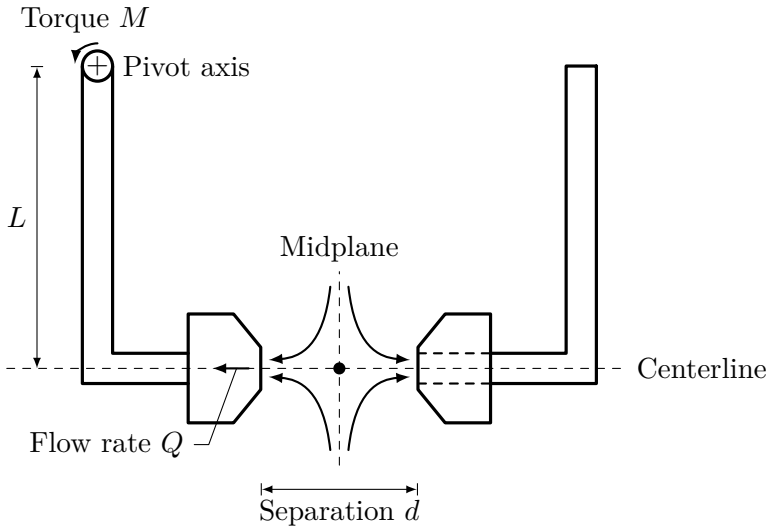


Figure 7.6: Opposed nozzles.

Rheometer setup:

- Opposed nozzles sucking the fluid in
- The flow creates a force that tends to pull the nozzles together, which is measured by the torque on one of the flow tubes

The tensile stress differential is

$$\tau_{11} - \tau_{22} = \tau_{11} - \tau_{33} = \frac{M}{L\pi R^2} \tag{7.52}$$

The apparent extension rate is

$$\dot{\epsilon}_a = \frac{\Delta v_z}{\Delta z} = \frac{Q/\pi R^2 - 0}{d/2 - 0} = \frac{2Q}{\pi R^2 d} \tag{7.53}$$

Adjusting R and Q can generate a wide range of $\dot{\epsilon}_a$. The apparent extensional viscosity is

$$\eta_a = \frac{\tau_{11} - \tau_{22}}{\dot{\epsilon}_a} = \frac{Md}{2QL} \tag{7.54}$$

7.6 Entrance Flow

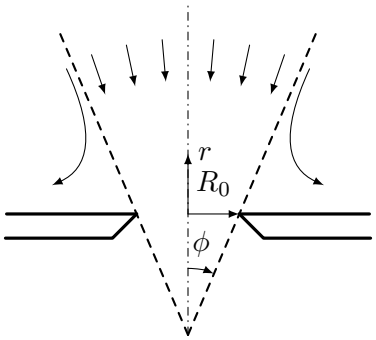


Figure 7.7: Entrance flow.

We choose spherical coordinates

$$v_r = \frac{Q}{A(r)},\ v_\theta = v_\phi = 0 \tag{7.55}$$

where A is the cross-sectional area in the converging region, which is the surface area on a sphere with radius r between two polar angles $-\phi$ and ϕ. The area can then be expressed as

$$A = 2\pi r^2(1 - \cos\phi) \tag{7.56}$$

and thus

$$v_r = \frac{Q}{2\pi r^2(1 - \cos\phi)} \tag{7.57}$$

The extension rate at the orifice is

$$\dot{\epsilon} = \frac{\mathrm{d}v_r}{\mathrm{d}r}|_{r=R_0/\sin\phi} = \frac{Q\sin^3\phi}{\pi R_0^3(1-\cos\phi)} \tag{7.58}$$

The normal stress difference is assumed to be equal to the entrance pressure drop

$$\tau_{11} - \tau_{22} = \Delta p_{\mathrm{en}} \tag{7.59}$$

Therefore, the apparent extensional viscosity is

$$\eta_a = \frac{\Delta p_{\mathrm{en}}}{\dot{\epsilon}} \tag{7.60}$$

The problem with the orifice is that ϕ is typically unknown, which needs to be determined by flow visualization. A common approximation widely is

$$\dot{\epsilon} = \frac{\dot{\gamma}_a}{8} \tag{7.61}$$

where $\phi \cong 15^\circ$, and $\dot{\gamma}_a$ is the apparent Newtonian shear rate assuming Poiseuille flow through a tube of radius R_0:

$$\dot{\gamma}_a = \frac{4Q}{\pi R_0^3} \tag{7.62}$$

[*Note*] $\phi \cong 15^\circ$ was suggested by Cogswell (1972) for analyzing the kinematics of both shear and extensional flow in the contraction region. $\frac{\sin^3\phi}{1-\cos\phi}|_{\phi=15^\circ} \approx 0.5$, which leads to the "1/8" factor in the relation between $\dot{\epsilon}$ and $\dot{\gamma}_a$. There are other flow kinematic theories suggesting different results. For instance, Gibson (1989) assumed a sink flow model and arrived at $\dot{\epsilon} = \frac{\dot{\gamma}_a}{4}$. Cogswell's result was not more or less popular than other theories. However, the situation changed when Macosko published his rheology textbook in 1994, in which he only mentioned the 1/8 ratio. Rheologiests and polymer scientists quickly adapted this recommendation while ignoring the dispute in the literature.

- F.N. Cogswell (1972), Converging flow of polymer melts in extrusion dies, Polym. Eng. Sci. 12, 64–73
- itemize A.G. Gibson (1989), Die entry flows of reinforced polymers. Composites, 20, 57–54

CHAPTER 8

Suspension Rheology

Lecture 10 **Date:** <YYYY-MM-DD>
Topic: Introduction; dilute suspension; non-Newtonian behavior; particle-particle interactions; classic suspension systems **Scribe:** Yang Han

8.1 Introduction to Suspensions

Suspensions are a class of materials with important industrial and biological applications. Some examples of suspensions:

- Milk (fat globules in water, stabilized by proteins like casein)
- Blood (red and white cells and platelets in plasma; plasma itself is also a colloid)
- Paint (solid pigment particles in water or oil; Latex or acrylic paints are more like an emulsion)
- Ink (solid pigment particles in water or alcohol)

Suspensions in modern biomedicine:

- Injectable drug
  - Insulin injections (cloudy suspension, typically combined with protamine for delay absorption; true insulin solutions also exist—no need to mix or shake)
  - Depo-Provera (medroxyprogesterone acetate in water, milky white liquid given as an intramuscular injection)
- Vaccine

  - DTap, Tdap, Hepatitis B, HPV
  - COVID-19 vaccines: Novavax (protein subunit vaccine)
- Cell suspensions in diagnostics and therapy
  - Blood tests
  - cell therapies (for leukemia, lymphoma, inflammatory diseases)
  - T cell therapy (cancer)
- Nanoparticle drug delivery
  - Suspensions of liposomes, polymer nanoparticles, or lipid nanoparticles (mRNA COVID vaccines, where the mRNA is encapsulated in lipid nanoparticles, to get the mRNA through cell membrane)
- Diagnostic agents
  - Barium sulfate suspension (gastrointestinal (GI) imaging)
  - Iron oxide nanoparticles (contrast agents in MRI)

The study of suspension started from Stokes' law (1851) for the settling of particles. The creeping flow around a spherical particle renders a viscous drag on the sphere:

$$F_d = -6\pi\eta R v \tag{8.1}$$

The force balance (drag + buoyancy - gravity = 0):

$$F_d + (\rho_p - \rho_f) g \frac{4}{3}\pi R^3 = 0 \tag{8.2}$$

The terminal velocity of the sphere is

$$v = \frac{2}{9}\frac{\rho_p - \rho_f}{\eta} g R^2 \tag{8.3}$$

The key variables that affect the rheological properties of a suspension:

- Concentration (volume fraction ϕ)
- Particle shape (aspect ratio r_p)
- Interaction forces (hydrodynamic forces, Brownian motion, inter-particle forces)

8.2 Dilute Suspension of Rigid Spheres

8.2.1 Hard Spheres

The purpose of this section is the Einstein equation (not the one about relativity).

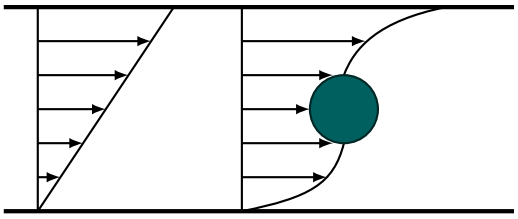


Figure 8.1: Disturbed shear flow by a spherical particle.

Assumptions:

- Solvent is Newtonian
- Creeping flow Re $\ll 1$ (i.e., negligible body forces, torques, and inertia)
- Neutral density, $\rho_s = \rho_p$, no settling
- No slip between particle and fluid
- Rigid, spherical particles
- Dilute (non-interacting) particles
- No influence of walls
- No particle migration
- Average velocity field in surrounding fluid is the same as if no particle presence

The analysis involves 3 length scales:

- Fluid molecules (≤ 1 μm) $\ll$ a, radius of particles
- $a \ll \frac{\mathrm{d}v/\mathrm{d}x}{\mathrm{d}^2v/\mathrm{d}x^2}$, scale of main velocity variation
- $a \ll h$, viscometer gap

For $\phi \ll 0.1$, the Einstein equation for shear viscosity is

$$\eta = \eta_s(1 + \frac{5}{2}\phi) \tag{8.4}$$

To obtain a complete constitutive equation, we can divide the stress tensor into 2 parts

$$\boldsymbol{\tau} = \boldsymbol{\tau}_s + \boldsymbol{\tau}_p \tag{8.5}$$

The stress from the main flow is

$$\boldsymbol{\tau}_s = 2\eta_s\bar{\mathbf{D}} \tag{8.6}$$

where $\bar{\mathbf{D}}$ is averaged over a volume larger than the particle separation, $V \gg a^3/\phi$:

$$\bar{\mathbf{D}} = \frac{1}{V}\int_V \mathbf{D}\,\mathrm{d}V \tag{8.7}$$

The overbar is typically dropped in the literature.

The particle stress is

$$\boldsymbol{\tau}_p = \frac{1}{V}\sum_i \int_{S_i} [\hat{\mathbf{n}}\cdot(\mathbf{T}_\mathbf{r}) - \eta_s(\mathbf{v}\hat{\mathbf{n}} + \hat{\mathbf{n}}\mathbf{v})]\,\mathrm{d}S_i \tag{8.8}$$

where S is the particle surface area, $\hat{\mathbf{n}}$ is the vector normal to the particle surface, and $\mathbf{r}$ is the particle position.

Happel and Brenner shows the stress is

$$\boldsymbol{\tau} = 2\eta_s(1 + \frac{5}{2}\phi)\mathbf{D} \tag{8.9}$$

with $\boldsymbol{\tau}_s = \eta_s 2\mathbf{D}$ and $\boldsymbol{\tau}_p = \frac{5}{2}\phi\eta_s 2\mathbf{D}$. A key observation here is that the particle size does not matter.

8.2.2 Particle Migration

The criterion for neglecting the effect of settling can be obtained from Stokes' law. The time required for a sphere to migrate (settle) 10% of the rheometer gap, h, under the influence of gravity, g, acting perpendicular to the gap is

$$t_{0.1h} = \frac{0.45\eta_s h}{|\rho_p - \rho_s|a^2 g} \tag{8.10}$$

Here are some typical h values:

- Parallel disk: $h \cong 2$ mm
- Cone and plate: $h = r\sin\beta < 3$ mm
- Concentric cylinders: $h \cong 50$ mm (we typically use L for Couette rheometer)

Now consider a suspension in water with $a = 100$ μm, $\rho_s = 1$ g/cm^3, and $\rho_p = 1.02$ g/cm^3

- Parallel disk: $t_{0.1h} = 100$ s (not suitable)
- Cone and plate: $t_{0.1h} = 300$ s (not suitable)
- Concentric cylinders: $t_{0.1h} = 5000$ s

When the particle Reynolds number is large, inertia can alter the velocity field around the sphere

$$\eta = \eta_s(1 + \frac{5}{2}\phi + 1.34\mathrm{Re}_p^{3/2}) \tag{8.11}$$

where $\mathrm{Re}_p = \frac{\rho_p \dot{\gamma} a^2}{\eta_s}$.

Even when the particle Reynolds number is small, the stress field around a sphere can interact with the wall, causing it to migrate inward. Brownian motion can keep the particles uniformly distributed if $K = \frac{\rho_p \bar{v}^2 a^4}{hkT}$ (viscous drag vs. Brownian diffusion) is small enough:

- $K < 0.1$ for Couette
- $K < 0.01$ for plane Poiseuille flow

Here, k is teh Boltzmann constant; $\bar{v} = \frac{1}{2} v_{max}$ in Couette flow and $\bar{v} = \frac{2}{3} v_{max}$ in Poiseuille flow. See Fig. 10.2.1 (p.431) as an example.

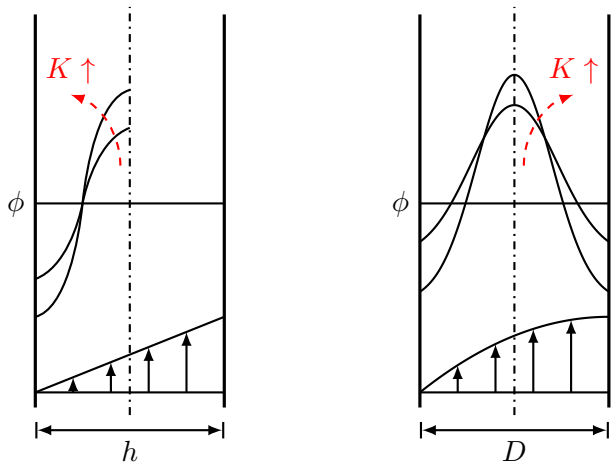


Figure 8.2: Particle migration in a suspension.

Example - Latex Suspension

A polystyrene latex of monodisperse spheres with 1.0 μm diameter is diluted to a volume fraction of 0.05 in water. Specific gravity of the particle is 1.05; $\rho_p = 1.05\rho_s$.

(a) Using the constitutive equation for dilute, non-interacting spheres, estimate its shear and extensional viscosity.

Applying the Einstein equation:

$\eta = \eta_s(1 + \frac{5}{2}\phi) = \eta_s(1 + \frac{5}{2} \times 0.05) = 1.125\eta_s$

Per the assumption for the Einstein equation, this is a Newtonian shear viscosity. Therefore, the extensional viscosity is

$\eta_e = 3\eta = 3.375\eta_s$

(b) Determine whether settling, particle inertia, or migration will present measurement problems in a narrow gap Couette rheometer: $L = 50$ mm, $R_i = 25$ mm, $R_0 = 26$ mm, and $\Omega_i < 100$ rad/s. Assume room temperature at 298 K.

The settling time

$t_{0.1h} = \frac{0.45\eta_s h}{|\rho_p - \rho_s| a^2 g} = \frac{0.45\times10^{-3}\times0.05}{(1.05-1)\times1000\times(0.5\times10^{-6})^2\times9.8} = 1.8\times10^5$ s

The particle Reynolds number $\mathrm{Re}_p = \frac{\rho_p \dot{\gamma} a^2}{\eta_s}$. We need to evaluate the shear rate $\dot{\gamma}$ in the Couette rheometer. From Chapter 5, we know that $\kappa = \frac{R_i}{R_0} = \frac{25}{26} = 0.9615$, $0.5 < \kappa < 0.99$. From Table 5.3.1, we have $\dot{\gamma}(R_i) = \frac{2\Omega_i}{n(1-\kappa^{2/n})}$. Here, $n = \frac{\mathrm{d}\ln M_i}{\mathrm{d}\ln\Omega_i} = 1$ for a Newtonian type suspension.

$\therefore \dot{\gamma}(R_i) = \frac{2\Omega_i}{n(1-\kappa^{2/n})} = \frac{2\Omega_i}{1\times(1-0.9615^{2/1})} = 26.4838\Omega_i$ [s^{-1}]

$\mathrm{Re}_p = \frac{\rho_p \dot{\gamma} a^2}{\eta_s} = \frac{1.05\times10^3\times26.4838\Omega_i\times(0.5\times10^{-6})^2}{10^{-3}} = 6.95\times10^{-6}\Omega_i$

Even with the highest angular velocity $\Omega_i = 100$ rad/s, $\mathrm{Re}_p = 6.95\times10^{-4} \ll 1$. Therefore, the inertia effects are negligible.

For the migration criterion $K = \frac{\rho_p \bar{v}^2 a^4}{hkT}$

$\bar{v} = \frac{1}{2}v_{max} = \frac{1}{2}R_i\Omega_i$, $h = R_0 - R_i$

$\therefore K = \frac{\rho_p \bar{v}^2 a^4}{hkT} = \frac{\rho_p(\frac{1}{2}R_i\Omega_i)^2 a^4}{(R_0-R_i)kT} = \frac{1.05\times10^3\times1/4\times(0.025\Omega_i)^2\times(0.5\times10^{-6})^4}{(0.026-0.025)\times1.38\times10^{-23}\times298} = 0.0025\Omega_i^2$

To ignore particle migration effect, $\Omega_i < 6.32$ rad/s.

8.2.3 Beyond the Dilute Limit

When $\phi > 0.1$, the Einstein equation is usually expanded as a power series:

$$\eta = \eta_s(1 + \frac{5}{2}\phi + k\phi^2 + \cdots) \tag{8.12}$$

See Fig. 10.2.2, p.432. The higher order terms are due to hydrodynamic interactions between spheres and other interparticle forces. This equation can be rearranged to:

$$\frac{\eta - \eta_s}{\eta_s\phi} = \frac{5}{2} + k\phi + \cdots \tag{8.13}$$

A few useful definitions:

$$\eta_{sp} = \frac{\eta - \eta_s}{\eta_s} = \frac{5}{2}\phi + k\phi^2 + \cdots \text{ (specific viscosity)} \tag{8.14}$$

$$\eta_r = \frac{\eta}{\eta_s} = 1 + \frac{5}{2}\phi + k\phi^2 + \cdots \text{ (relative or reduced viscosity)} \tag{8.15}$$

$$[\eta] = \lim_{\phi \to 0} \frac{\eta_{sp}}{\phi} = \frac{5}{2} \text{ (intrinsic viscosity)} \tag{8.16}$$

$$\eta_{inh} = \frac{\eta_{sp}}{\phi} = \frac{5}{2} + k\phi + \cdots \text{ (inherent viscosity)} \tag{8.17}$$

8.3 Non-Newtonian Behaviors in Emulsions

Emulsions

Compared to rigid spheres, emulsions are unique in the following ways:

- The liquid inside the droplets also flows (in a tank-tread like motion)
- This circulation causes extra viscous dissipation
- A useful measure is the relative/reduced viscosity $\eta_{dr} = \frac{\eta_d}{\eta_s}$, where η_d is the droplet viscosity

Hydrodynamic forces can overcome interfacial tension and cause the droplet to deform and even to break up. For small deformation, an elliptical form is also assumed for the deformed droplet.

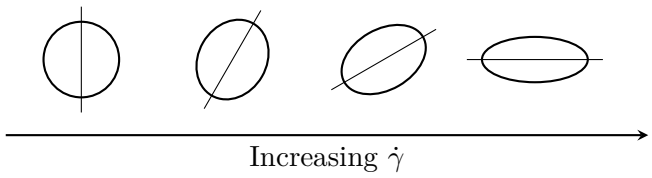


Figure 8.3: Droplet deformation.

The difference between major axes of the ellipse is

$$D = \frac{a-b}{a+b} = 2\lambda_d I I_{2D}^{1/2} \Big(\frac{1 + 19\eta_{dr}/16}{1 + \eta_{dr}} \Big) \tag{8.18}$$

The droplet relaxation time is $\lambda_d = \frac{a\eta_s}{\Gamma}$, where Γ is the interfacial tension:

- For typical oil-in-water emulsion, $\eta_s = 1$ Pa $\cdot$ s, $\eta_{dr} \cong 3$, $\Gamma = 0.02$ N/m, and $a \cong 1$ μm
- $\lambda_d \cong 5 \times 10^{-8}$ s, very small deformation

If $\eta_{dr} \gg 1$, effect of interfacial tension can be neglected. At high deformation rates, the droplet will align with the flow

$$\lim_{\dot{\gamma}\to\infty} D = \frac{5}{2(2\eta_{dr}+3)} \tag{8.19}$$

The droplet breaks when the hydrodynamic force exceeds the interfacial tension, or $D_{burst} > 1/2$.

Deformable Spheres

For small deformations, the constitutive equation of the emulsion is

$$\boldsymbol{\tau} = 2\eta_s \mathbf{D}\Big[1 + \Big(\frac{1+\frac{5}{2}\eta_{dr}}{1+\eta_{dr}}\Big)\phi + F\Big] \tag{8.20}$$

where $F = F(\eta_{dr}, \lambda_d, \overset{\triangledown}{\mathbf{D}})$. Here, $\overset{\triangledown}{\mathbf{D}}$ represents the history of deformation (the origin of non-Newtonian behaviors).

For steady-state simple shear, a viscosity independent with shear rate can be derived:

$$\eta = \eta_s\Big[1 + \Big(\frac{1+\frac{5}{2}\eta_{dr}}{1+\eta_{dr}}\Big)\phi\Big] \tag{8.21}$$

It is easy to spot two limiting cases. $\eta_{dr} \to \infty, \eta = \eta_s(1+\frac{5}{2}\phi)$, which is equivalent to the Einstein equation for rigid sphere. $\eta_{dr} \to 0,\ \eta = \eta_s(1+\phi)$, which is for gas bubble or foam.

Under steady shear, the constitutive equation also gives a positive first normal stress coefficient and a negative normal stress coefficient:

$$\Psi_1 = \frac{\tau_{11}-\tau_{22}}{\dot{\gamma}^2} = 2f(\eta_{dr})\eta_s\lambda_d\phi \tag{8.22}$$

$$\Psi_2 = \frac{\tau_{22}-\tau_{33}}{\dot{\gamma}^2} = [\frac{g}{2}(\eta_{dr}) - f(\eta_{dr})]\eta_s\lambda_d\phi \tag{8.23}$$

where $f(\eta_{dr}) = \frac{1}{80}\Big(\frac{19\eta_{dr}+16}{\eta_{dr}+1}\Big)^2$ and $g(\eta_{dr}) = \frac{3(19\eta_{dr}+16)(25\eta_{dr}^2+=41\eta_{dr}+4)}{560(\eta_{dr}+1)^3}$.

For steady uniaxial extension

$$\eta_u = 3\eta_s\Big[1 + \Big(\frac{1+\frac{5}{2}\eta_{dr}}{1+\eta_{dr}}\Big)\phi + g(\eta_{dr})\lambda_d\dot{\epsilon}\Big] \tag{8.24}$$

The deformable spheres result in non-Newtonian physical effects: (1) time-dependent shear stress (via F), (2) normal stresses, and (3) extension thickening

- Largely caused by the interfacial tension
- Interfacial tension tends to restore the spherical shape that is distorted by the viscous forces
- The former shape serves as a "memory" of the equilibrium condition $\implies$ viscoelastic effects

8.4 Particle-Particle Interactions

For non-dilute suspensions, interparticle forces make the rheological behaviors deviate from Newtonian. These forces typically depend on the interparticle distance, thereby potential forces.

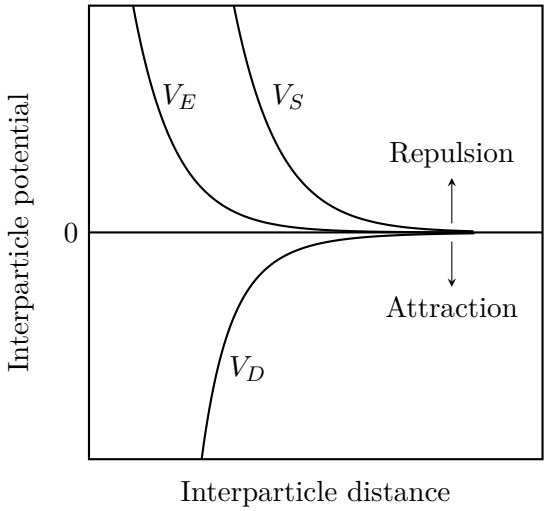


Figure 8.4: Interaction potentials.

Dispersion Forces

Dispersion forces are a type of van der Waals force. The potential is

$$V_D = -(A_p^2 - A_i^2)^{1/2} H_g \tag{8.25}$$

where A_p and A are the Hamaker constant (a measure of strength of the vdW force) of the particle and medium, respectively. Here, H_g is a function of particle geometry and interparticle distance H. $V_D \propto H^{-6}$ for spheres at large distances, and $V_D \propto H^{-1}$ for spheres at close distances.

Electrostatic Forces

$$V_E = 4\pi\epsilon \frac{a}{2 + H/a} \Psi_0^2 \exp(-\kappa H) \tag{8.26}$$

where Ψ_0 is the surface potential, κ is the Debye-Huckel constant, andϵ is the dielectric constant of the medium.

Polymeric (Steric) Forces

This is a steric force originated from the Flory-Huggins theory. Two polymer chains would rather become more compact than mix and occupy the same "lattice space". [Note: Paul Flory, Nobel laureate, PhD at Ohio State]

$$V_S = \frac{akT(1/2 - \chi)\delta^2}{H_s v_s} \tag{8.27}$$

where χ is the interaction parameter in Flory-Huggins theory, H_s is a function of interparticle distance, δ is the thickness of stabilized polymer layer (~ 10 nm), and v_s is the volume of solvent molecule.

Here, χ needs to be smaller than 1/2 to provide a repulsion (i.e., positive potential). A solvent as such is called a good solvent.

Dimensionless Group Numbers

The extent of Brownian motion vs. hydrodynamic forces is described by the Peclet number:

$$\mathrm{Pe} = \frac{\eta_s \dot{\gamma} a^3}{kT} \tag{8.28}$$

Dispersion forces vs. Brownian motion:

$$\frac{(A_p^2 - A_i^2)^{1/2}}{kT} \tag{8.29}$$

Electrostatic repulsion vs. Brownian motion:

$$\frac{\epsilon \Psi_0^2 a}{kT} \tag{8.30}$$

Polymeric repulsion vs. Brownian motion:

$$\frac{(1/2 - \chi) a \delta^2}{v_s} \tag{8.31}$$

8.5 Classic Suspension Systems

8.5.1 Brownian Hard Particles

For monodisperse hard spheres, the potential forces between particles are zero whenever the particles are not touching. Once contact, an infinite repulsion occurs. This is a classic Newtonian suspension.

A semi-empirical Krieger-Dougherty relation is commonly used

$$\eta_{rx} = (1 - \frac{\phi}{\phi_m})^{-[\eta]\phi_m} = (1 - \frac{\phi}{\phi_m})^{-2.5\phi_m} \tag{8.32}$$

For the law shear plateau, $x = 0,\ \phi_{m0} = 0.63$; for the high shear plateau, $x = \infty,\ \phi_{m\infty} = 0.71$.

This equation reduces to the Einstein equation when ϕ is small. To show this, we employ the Taylor expansion series:

$$(1-x)^{-a} = 1 + ax + \frac{a(a+1)}{2}x^2 + \cdots \tag{8.33}$$

Let $x = \frac{\phi}{\phi_m}$ and $a = [\eta]\phi_m$, we have

$$\eta_{rx} = 1 + [\eta]\phi + \frac{[\eta]([\eta]\phi_m + 1)}{2\phi_m^2}\phi^2 + O(\phi^3) \tag{8.34}$$

A more specific case is the Batchelor equation

$$\eta_r = 1 + 2.5\phi + 6.2\phi^2 + O(\phi^3) \tag{8.35}$$

The ϕ^2 term represents the particle-particle interactions from hydrodynamic interaction theory. From the Krieger-Dougherty relation, $\frac{[\eta]([\eta]\phi_m+1)}{2\phi_m^2} = 6.8 - 8.1$.

8.5.2 Stable Colloidal Suspensions

Electrostatic Stabilization

When electrostatically stabilized particles approach each other, the repulsion forces increase gradually (contrary to Brownian hard spheres). During flow, the repulsion forces keep particles further apart than in the neutrally stable systems. Therefore, the energy dissipation (i.e., the viscosity) becomes larger.

To account for this, the "6.2" coefficient in the Batchelor equation should be modified to account for the electrostatic repulsion:

$$H_0 = (\frac{1}{\kappa}) \ln \Big[\frac{\alpha}{\ln(\alpha/\ln\alpha)}\Big] \tag{8.36}$$

where $\alpha = 4\pi\Psi_0 a^2 \kappa \exp(2a\kappa)/kT$.

The repulsion tends to cause viscoelastic behaviors. If the repulsion is strong enough, colloidal crystals might form, leading to a lattice structure and a frequency-independent storage modulus (as in sinusoidal oscillation).

Polymeric Stabilization

A short-range force that increase rapidly with decreasing interparticle distance and drops to zero when the polymer layers do not overlap anymore. If teh polymer layers do not deform much, the

Brownian hard sphere model can be applied by replace ϕ with an effective volume fraction:

$$\phi_{eff} = \phi\Big(1 + \frac{\delta}{a}\Big)^3 \tag{8.37}$$

The polymeric forces also translate to the storage modulus (i.e., elasticity) in Maxwell-type linear viscoelasticity models.

8.5.3 Flocculated Systems

Structure in flocculated dispersions:

- Attraction forces $\gg$ repulsion forces $\gg$ Brownian motion
- Particles can remain together when they collide
- Many flocculated systems shows Bingham-type behaviors

Thixotropy is a time-dependent shear thinning property, which is commonly observed in flocculated systems. This irreversible flow behavior is demonstrated in Figure 8.5.

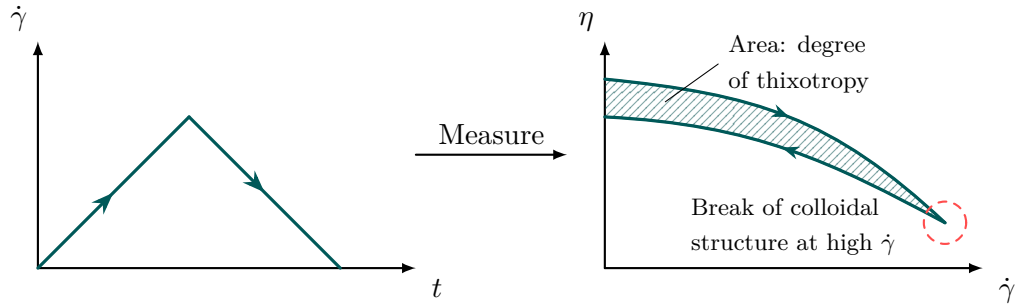


Figure 8.5: Thixotropy in flocculated system.

As shown, the shear breaks down the flocculated structure to smaller flocs, leading to shear thinning. When shear is reduced, the flocs will grow again by "sticking" together rather than a reversible process. Hence, the breakdown and recovery of the system depends on the shear history.

CHAPTER 9

Rheology of Polymeric Fluids

Lecture 11 **Date:** <YYYY-MM-DD>
Topic: Dilute polymer solutions; Concentrated polymer solutions **Scribe:** Yang Han

9.1 Dilute Polymer Solutions

9.1.1 Polymer Chain Conformation

Random coil in a solvent can be modeled as a random free walk.

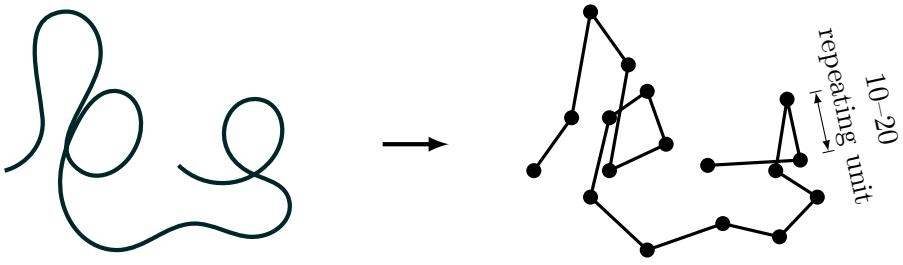


Figure 9.1: Representation of a random coil by random free walk.

The mean square end-to-end vector is

$$\bar{\mathbf{r}^2} = 2nl^2 \tag{9.1}$$

where n is the number of segments and l is the length of segment. Assume the whole coil is a sphere with radius of $\sqrt{\bar{\mathbf{r}^2}}$. Apply the Einstein equation

$$\eta = \eta_s(1 + 2.5\phi) \tag{9.2}$$

$$\eta_{sp} = \frac{\eta - \eta_s}{\eta_s} = 2.5\phi = 2.5 \underbrace{(\frac{n_2}{V})V_{sphere}}_{\text{polymer vol. frac.}} \tag{9.3}$$

$$\frac{n_2}{V} = \frac{\#\text{ of polymer molecules}}{\text{volume of solution}} = \frac{cN_{Av}}{M} \tag{9.4}$$

Here, c is the polymer mass concentration, N_{Av} is the Avogadro constant, M is the polymer molecular weight.

Combining with $V_{sphere} = k_1(\bar{\mathbf{r}^2})^{3/2}$, we have

$$\frac{\eta - \eta_s}{\eta_s c} = [\eta] = \frac{2.5k_1N_{Av}(\bar{\mathbf{r}^2})^{3/2}}{M} \tag{9.5}$$

The Flory-Fox equation gives

$$\Phi = 2.5k_1N_{Av} \tag{9.6}$$

Here, Φ is experimentally determined to be constant for all synthetic polymers. Therefore

$$[\eta] = \Phi\frac{(\bar{\mathbf{r}^2})^{3/2}}{M} \tag{9.7}$$

We further "know" that $\bar{\mathbf{r}^2} \propto M$, and thus

$$[\eta] \propto M^{1/2} \tag{9.8}$$

This leads to the famous Mark-Houwink equation

$$[\eta] = KM^a \tag{9.9}$$

Here, K and a are functions of polymer and solvent types. a is typically between 0.5 and 0.8.

This gives a way to measure polymer molecular weight by its intrinsic viscosity. Note here that no hydrodynamic forces have been considered so far. Therefore, $[\eta]$ here refers to the zero-shear viscosity. Realistically, it may be necessary to obtain values of $[\eta]$ at several shear rates and extrapolate to zero shear rate.

Generally speaking, we should write $(\bar{\mathbf{r}^2})^{1/2} \propto M^\nu$, where ν is related to the polymer–solvent interaction. In a good solvent, polymer coils swell due to repulsive excluded volume interactions, thereby occupying a larger hydrodynamic volume. This leads to a larger ν. For theta-solvent, $\nu = 0.5$; for a good solvent, $\nu > 0.5$. With this, the Mark Houwink equation becomes

$$[\eta] = KM^{3\nu-1} \tag{9.10}$$

9.1.2 Constitutive Equations

In order to model a polymer, we need something which can in some way remember the flow it has been through. We do this by creating something which can change its physical configuration as it responds to the flow. Then when the flow stops, its configuration is the way it carries the information about the flow history. This is exactly what real polymer chains do.

A polymeric kinetic theory typically starts from single-elastic dumbbell model:

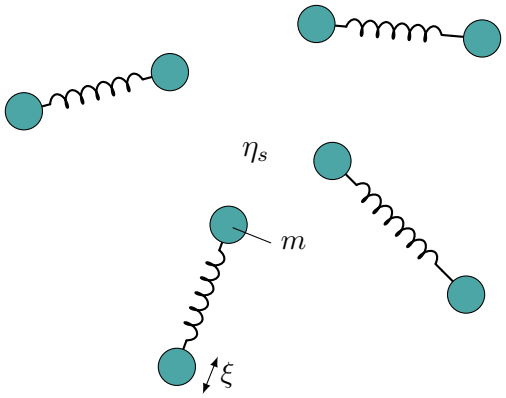


Figure 9.2: Single elastic dumbbell model.

- η_s - viscosity of Newtonian solvent, in which the dumbbells are suspended
- n_0 - number of dumbbells per unit volume
- m - mass of one bead of dumbbell
- ξ - friction coefficient of a bead as if moves through the solvent
  - $\xi = \frac{F_d}{v} = 6\pi\eta_s R$ if Stokes' law applies
- H - spring constant of the Hookean spring
  - $H = \frac{3kT}{R^2}$ since the energy stored in the spring is balanced by the thermal energy kT

The equation of motion for the beads leads to a constitutive equation for the polymer contribution:

$$\boldsymbol{\tau}^p + \frac{\xi}{4H}\overset{\triangledown}{\boldsymbol{\tau}}^p = \frac{n_0 kT\xi}{4H} 2\mathbf{D} \tag{9.11}$$

$\frac{\xi}{4H}$ has a unit of time and is referred to as the relaxation time for the dumbbell, λ. The above equation becomes:

$$\boldsymbol{\tau}^p + \lambda\overset{\triangledown}{\boldsymbol{\tau}}^p = n_0 kT\lambda 2\mathbf{D} \tag{9.12}$$

This is identical to the upper-convected Maxwell (UCM) model.

Recall the derivation of the Oldroyd-B model, we can write the total stress as $\boldsymbol{\tau} = \boldsymbol{\tau}^p + \boldsymbol{\tau}^s = \boldsymbol{\tau}^p + \eta_s 2\mathbf{D}$. The Oldroyd-B model leads to

$$\eta_p = n_0 kT\lambda \tag{9.13}$$

$$\eta_0 = \eta_p + \eta_s = n_0 kT\lambda + \eta_s \tag{9.14}$$

$$\lambda_1 = \lambda \tag{9.15}$$

$$\lambda_2 = \frac{\eta_s}{\eta_0}\lambda \tag{9.16}$$

[*Note*] $\eta_p = n_0 kT\lambda$ comes from the kinetic theory of the Hookean dumbbell model. Here, kT represents the polymer's entropic elasticity (an entropic force to resist deformation). λ represents hwo fast the polymer (or the spring) returns to equilibrium. Higher kT and λ make the polymer resist the flow more or longer, thereby contributing more to the viscoelastic stress.

Recall the example for the Oldroyd-B model, we have shown that for steady-state shear, the model leads to

$$\eta_{s.s.} = \frac{\tau_{12}}{\dot{\gamma}} = \eta_0 = n_0 kT\lambda + \eta_s \tag{9.17}$$

$$\Psi_{1,s.s.} = \frac{\tau_{11} - \tau_{22}}{\dot{\gamma}^2} = 2(\lambda_1 - \lambda_2)\eta_0 = 2\lambda\eta_p = 2n_0 kT\lambda^2 \tag{9.18}$$

$$\Psi_{2,s.s.} = \frac{\tau_{22} - \tau_{33}}{\dot{\gamma}^2} = 0 \tag{9.19}$$

Clearly, this model predicts η independent of shear rate. This serious deficiency results from the oversimplified molecular model. Inclusion of intra-molecular effects (hydrodynamic interaction, reduced excluded volume effects, nonlinear spring force law, and internal viscosity) will fix this issue.

The same example of the Oldroyd-B model shows that the steady-state uniaxial extensional viscosity is

$$\begin{aligned}\eta_u &= 3\eta_0\frac{1-\lambda_2\dot{\epsilon}-2\lambda_1\lambda_2\dot{\epsilon}^2}{(1-2\lambda_1\dot{\epsilon})(1+\lambda_1\dot{\epsilon})} = 3\eta_0\frac{1-(\eta_s/\eta_0)\lambda\dot{\epsilon}-2\lambda^2(\eta_s/\eta_0)\dot{\epsilon}^2}{(1-2\lambda\dot{\epsilon})(1+\lambda\dot{\epsilon})} \\ &= 3\frac{(\eta_p+\eta_s)-\eta_s\lambda\dot{\epsilon}-2\lambda^2\eta_s\dot{\epsilon}^2}{(1-2\lambda\dot{\epsilon})(1+\lambda\dot{\epsilon})} = 3\frac{\eta_s(1-2\lambda\dot{\epsilon})(1+\lambda\dot{\epsilon})+\eta_p}{(1-2\lambda\dot{\epsilon})(1+\lambda\dot{\epsilon})} = 3\eta_s + \frac{3n_0kT\lambda}{(1-2\lambda\dot{\epsilon})(1+\lambda\dot{\epsilon})}\end{aligned} \tag{9.20}$$

9.1.3 Small-Amplitude Oscillatory Shear of Dilute Polymer Solution

For the small-amplitude oscillatory shear experiment as described in Chapter 3, we impose a sinusoidal shear $\gamma = \gamma_0 \sin \omega t$ on the top plate. The rheometer is initially stationary with a dilute polymer solution sandwiched in between. Our goal is to apply the single-elastic dumbbell model and derive expressions for G', G'', η', and η'' in terms of η_s and $\eta_p = n_0 kT\lambda$.

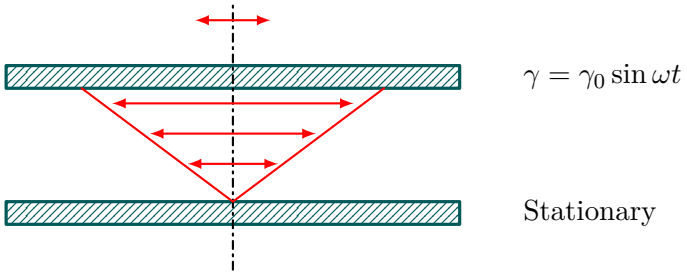


Figure 9.3: Small-amplitude oscillatory shear.

We define the shear rate as $\dot{\gamma} = \gamma_0 \omega \cos \omega t$. Here, $\gamma_0 \omega$ is the same as $\dot{\gamma}_0$ in Chapter 3. Similar to the simple shear, the velocity vector is

$$\mathbf{v} = \begin{bmatrix} \dot{\gamma} y & 0 & 0 \end{bmatrix} \tag{9.21}$$

The $x - y - z$ coordinates seat on the center of the bottom plate. The kinematics gives

$$\mathbf{L} = (\boldsymbol{\nabla}\mathbf{v})^T = \begin{bmatrix} \frac{\partial v_x}{\partial x} & \frac{\partial v_x}{\partial y} & \frac{\partial v_x}{\partial z} \\ \frac{\partial v_y}{\partial x} & \frac{\partial v_y}{\partial y} & \frac{\partial v_y}{\partial z} \\ \frac{\partial v_z}{\partial x} & \frac{\partial v_z}{\partial y} & \frac{\partial v_z}{\partial z} \end{bmatrix} = \begin{bmatrix} 0 & \gamma_0 \omega \cos \omega t & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{9.22}$$

$$\mathbf{L}^T = \boldsymbol{\nabla}\mathbf{v} = \begin{bmatrix} 0 & 0 & 0 \\ \gamma_0 \omega \cos \omega t & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{9.23}$$

$$\mathbf{D} = \frac{1}{2}(\mathbf{L} + \mathbf{L}^T) = \begin{bmatrix} 0 & \frac{1}{2}\gamma_0 \omega \cos \omega t & 0 \\ \frac{1}{2}\gamma_0 \omega \cos \omega t & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{9.24}$$

$\overset{\triangledown}{\mathbf{D}} = \frac{\partial \mathbf{D}}{\partial t} + \mathbf{v} \cdot \boldsymbol{\nabla}\mathbf{D} - (\boldsymbol{\nabla}\mathbf{v})^T \cdot \mathbf{D} - \mathbf{D} \cdot \boldsymbol{\nabla}\mathbf{v}$

- $\frac{\partial \mathbf{D}}{\partial t} = \begin{bmatrix} 0 & -\frac{1}{2}\gamma_0 \omega^2 \sin \omega t & 0 \\ -\frac{1}{2}\gamma_0 \omega^2 \sin \omega t & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$
- $\mathbf{v} \cdot \boldsymbol{\nabla}\mathbf{D} = \mathbf{0}$ (uniform flow, shear rate not a function of space)

- $(\boldsymbol{\nabla}\mathbf{v})^T \cdot \mathbf{D} = \begin{bmatrix} 0 & \gamma_0\omega\cos\omega t & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \cdot \begin{bmatrix} 0 & \frac{1}{2}\gamma_0\omega\cos\omega t & 0 \\ \frac{1}{2}\gamma_0\omega\cos\omega t & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} = \begin{bmatrix} \frac{1}{2}\gamma_0^2\omega^2\cos^2\omega t & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$
- $\mathbf{D} \cdot \boldsymbol{\nabla}\mathbf{v} = \begin{bmatrix} 0 & \frac{1}{2}\gamma_0\omega\cos\omega t & 0 \\ \frac{1}{2}\gamma_0\omega\cos\omega t & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \cdot \begin{bmatrix} 0 & 0 & 0 \\ \gamma_0\omega\cos\omega t & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} = \begin{bmatrix} \frac{1}{2}\gamma_0^2\omega^2\cos^2\omega t & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$

$$\therefore \overset{\triangledown}{\mathbf{D}} = \begin{bmatrix} 0 & -\frac{1}{2}\gamma_0\omega^2\sin\omega t & 0 \\ -\frac{1}{2}\gamma_0\omega^2\sin\omega t & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} - \begin{bmatrix} \gamma_0^2\omega^2\cos^2\omega t & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{9.25}$$

$\overset{\triangledown}{\boldsymbol{\tau}} = \frac{\partial \boldsymbol{\tau}}{\partial t} + \mathbf{v} \cdot \boldsymbol{\nabla}\boldsymbol{\tau} - (\boldsymbol{\nabla}\mathbf{v})^T \cdot \boldsymbol{\tau} - \boldsymbol{\tau} \cdot \boldsymbol{\nabla}\mathbf{v}$

Like before, we assume a stress tensor in the form of $\boldsymbol{\tau} = \begin{bmatrix} \tau_{11} & \tau_{12} & 0 \\ \tau_{21} & \tau_{22} & 0 \\ 0 & 0 & \tau_{33} \end{bmatrix}$. Note that none of our nonlinear viscoelastic models (NLVE) so far can yield non-zero τ_{23}. This out-of-plane stress is extremely rare. Th only NLVE model mentioned in this course that can render a non-zero τ_{23} is the Giesekus model.

- $\frac{\partial \boldsymbol{\tau}}{\partial t} = \frac{\partial}{\partial t} \begin{bmatrix} \tau_{11} & \tau_{12} & 0 \\ \tau_{21} & \tau_{22} & 0 \\ 0 & 0 & \tau_{33} \end{bmatrix}$
- $\mathbf{v} \cdot \boldsymbol{\nabla}\boldsymbol{\tau} = \mathbf{0}$
- $(\boldsymbol{\nabla}\mathbf{v})^T \cdot \boldsymbol{\tau} = \begin{bmatrix} 0 & \gamma_0\omega\cos\omega t & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \cdot \begin{bmatrix} \tau_{11} & \tau_{12} & 0 \\ \tau_{21} & \tau_{22} & 0 \\ 0 & 0 & \tau_{33} \end{bmatrix} = \begin{bmatrix} \tau_{21}\gamma_0\omega\cos\omega t & \tau_{22}\gamma_0\omega\cos\omega t & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$
- $\boldsymbol{\tau} \cdot \boldsymbol{\nabla}\mathbf{v} = \begin{bmatrix} \tau_{11} & \tau_{12} & 0 \\ \tau_{21} & \tau_{22} & 0 \\ 0 & 0 & \tau_{33} \end{bmatrix} \cdot \begin{bmatrix} 0 & 0 & 0 \\ \gamma_0\omega\cos\omega t & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} = \begin{bmatrix} \tau_{12}\gamma_0\omega\cos\omega t & 0 & 0 \\ \tau_{22}\gamma_0\omega\cos\omega t & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$

$$\therefore \overset{\triangledown}{\boldsymbol{\tau}} = \frac{\partial}{\partial t} \begin{bmatrix} \tau_{11} & \tau_{12} & 0 \\ \tau_{21} & \tau_{22} & 0 \\ 0 & 0 & \tau_{33} \end{bmatrix} - \begin{bmatrix} 2\tau_{12}\gamma_0\omega\cos\omega t & \tau_{22}\gamma_0\omega\cos\omega t & 0 \\ \tau_{22}\gamma_0\omega\cos\omega t & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{9.26}$$

We use the Oldroyd-B model here as a surrogate

$$\boldsymbol{\tau} + \lambda_1 \overset{\triangledown}{\boldsymbol{\tau}} = 2\eta(\mathbf{D} + \lambda_2 \overset{\triangledown}{\mathbf{D}}) = \eta 2\mathbf{D} + 2\lambda_2\eta \overset{\triangledown}{\mathbf{D}} = \eta 2\mathbf{D} + 2\lambda_1\eta_s \overset{\triangledown}{\mathbf{D}} \tag{9.27}$$

Here, we replace λ_1 with λ to be consistent with the single dumbbell model

$$\boldsymbol{\tau} + \lambda \overset{\triangledown}{\boldsymbol{\tau}} = \eta 2\mathbf{D} + 2\lambda\eta_s \overset{\triangledown}{\mathbf{D}} \tag{9.28}$$

Expanding this equation gives

$$\begin{bmatrix} \tau_{11} & \tau_{12} & 0 \\ \tau_{21} & \tau_{22} & 0 \\ 0 & 0 & \tau_{33} \end{bmatrix} + \lambda \frac{\partial}{\partial t} \begin{bmatrix} \tau_{11} & \tau_{12} & 0 \\ \tau_{21} & \tau_{22} & 0 \\ 0 & 0 & \tau_{33} \end{bmatrix} - \lambda \begin{bmatrix} 2\tau_{12}\gamma_0\omega\cos\omega t & \tau_{22}\gamma_0\omega\cos\omega t & 0 \\ \tau_{22}\gamma_0\omega\cos\omega t & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$
$$= \eta \begin{bmatrix} 0 & \gamma_0\omega\cos\omega t & 0 \\ \gamma_0\omega\cos\omega t & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} + 2\lambda\eta_s \begin{bmatrix} 0 & -\frac{1}{2}\gamma_0\omega^2\sin\omega t & 0 \\ -\frac{1}{2}\gamma_0\omega^2\sin\omega t & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} - 2\lambda\eta_s \begin{bmatrix} \gamma_0^2\omega^2\cos^2\omega t & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{9.29}$$

Obviously, $\tau_{22} = \tau_{33} = 0$.

The "12" component gives

$$\frac{\mathrm{d}\tau_{12}}{\mathrm{d}t} + \frac{1}{\lambda}\tau_{12} = \frac{\eta}{\lambda}\gamma_0\omega\cos\omega t - \eta_s\gamma_0\omega^2\sin\omega t \tag{9.30}$$

with I.C.: $\tau_{12}(0) = 0$. This ODE can be solved with the integrating factor method ($e^{t/\lambda}$). The full solution is

$$\tau_{12}(t) = \tau_{12}(t) = \gamma_0 \frac{\lambda^2}{1+\lambda^2\omega^2}\Big[(\frac{\eta\omega}{\lambda^2} + \eta_s\omega^3)\cos\omega t + \frac{\omega^2}{\lambda}(\eta - \eta_s)\sin\omega t\Big] - \frac{\gamma_0\lambda^2}{1+\lambda^2\omega^2}(\frac{\eta\omega}{\lambda^2} + \eta_s\omega^3)e^{-t/\lambda} \tag{9.31}$$

Note that the exponential term vanishes when $t \to \infty$. The long-time solution only contains the oscillatory terms

$$\tau_{12}(t) = \gamma_0 \frac{\lambda^2}{1+\lambda^2\omega^2}\Big[(\frac{\eta\omega}{\lambda^2} + \eta_s\omega^3)\cos\omega t + \frac{\omega^2}{\lambda}(\eta - \eta_s)\sin\omega t\Big] \tag{9.32}$$

It is clear that we cannot ignore the $\frac{\partial\boldsymbol{\tau}}{\partial t}$ term even if we only need the long-time solution. This is quite different from the steady-state simple shear or uniaxial extensional flows that we have worked on in Chapter 4.

By definition, we should rewrite the long-time solution in the form of

$$\tau_{12}(t) = G'\gamma_0\sin\omega t + G''\gamma_0\cos\omega t \tag{9.33}$$

By comparison, we have

$$G' = (\frac{\lambda^2}{1+\lambda^2\omega^2})\frac{\omega^2}{\lambda}(\eta - \eta_s) = \frac{\lambda\omega^2\eta_p}{1+\lambda^2\omega^2} = \frac{n_0kT\lambda^2\omega^2}{1+\lambda^2\omega^2} \tag{9.34}$$

$$\begin{aligned} G'' &= \frac{\lambda^2}{1+\lambda^2\omega^2}\left(\frac{\eta\omega}{\lambda^2}+\eta_s\omega^3\right) = \frac{\lambda^2\omega}{1+\lambda^2\omega^2}\left(\frac{\eta_p+\eta_s}{\lambda^2}+\eta_s\omega^2\right) \\ &= \frac{\lambda^2\omega}{1+\lambda^2\omega^2}\left(\frac{\eta_p}{\lambda^2}+\frac{1+\lambda^2\omega^2}{\lambda^2}\eta_s\right) = \omega\eta_s + \frac{n_0kT\lambda\omega}{1+\lambda^2\omega^2} \end{aligned} \tag{9.35}$$

$$\eta' = \frac{G''}{\omega} = \eta_s + \frac{n_0kT\lambda}{1+\lambda^2\omega^2} \tag{9.36}$$

$$\eta'' = \frac{G'}{\omega} = \frac{n_0kT\lambda^2\omega}{1+\lambda^2\omega} \tag{9.37}$$

Now, we compare the G' and G'' with those we derived in Chapter 3 using the single-mode Maxwell model: $G' = G_0\frac{\omega^2\lambda^2}{1+\omega^2\lambda^2}$ and $G'' = G_0\frac{\omega\lambda}{1+\omega^2\lambda^2}$. Clearly, the storage moduli take the same form, with $G_0 = \frac{\eta_p}{\lambda} = n_0kT$. This is not surprising, as the elastic characteristics can only stem from the polymer contribution. For the loss moduli, the Oldroyd-B model contains an extra term of $\omega\eta_s$. This represents the additional viscous dissipation caused by the non-negligible solvent viscosity.

Interpretation of the Results

We know that the Oldroyd-B is equivalent to a combination of UCM model for the polymer and a Newtonian model for the solvent. Let's now solve for the Newtonian contribution for the same flow: $2\mathbf{D} = \begin{bmatrix} 0 & \gamma_0\omega\cos\omega t & 0 \\ \gamma_0\omega\cos\omega t & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$.

$$\boldsymbol{\tau}^s = \eta_s 2\mathbf{D} = \begin{bmatrix} 0 & \gamma_0\omega\eta_s\cos\omega t & 0 \\ \gamma_0\omega\eta_s\cos\omega t & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{9.38}$$

or simply

$$\tau_{12}^s = \gamma_0\omega\eta_s\cos\omega t \tag{9.39}$$

Let's take a look at the long-time solution for τ_{12} from above. We only focus on the $\cos\omega t$ term

$$\begin{aligned} \gamma_0\frac{\lambda^2}{1+\lambda^2\omega^2}\left(\frac{\eta\omega}{\lambda^2}+\eta_s\omega^3\right)\cos\omega t &= \gamma_0\frac{\omega\lambda^2}{1+\lambda^2\omega^2}\left(\frac{\eta_p}{\lambda^2}+\frac{\eta_s}{\lambda^2}+\eta_s\omega^2\right)\cos\omega t \\ &= \gamma_0\frac{\omega}{1+\lambda^2\omega^2}\eta_p\cos\omega t + \gamma_0\frac{\omega\lambda^2}{1+\lambda^2\omega^2}\left(\frac{1+\lambda^2\omega^2}{\lambda^2}\right)\eta_s\cos\omega t \\ &= \gamma_0\frac{\omega}{1+\lambda^2\omega^2}\eta_p\cos\omega t + \gamma_0\omega\eta_s\cos\omega t \\ &= \gamma_0\frac{\omega}{1+\lambda^2\omega^2}\eta_p\cos\omega t + \tau_{12}^s \end{aligned} \tag{9.40}$$

It is not difficult to speculate that the remainder of the $\tau_{12}(t)$ is the polymer contribution

$$\tau_{12}^p = \gamma_0 \frac{\omega}{1+\lambda^2\omega^2}\eta_p(\cos\omega t + \lambda\omega\sin\omega t) \tag{9.41}$$

This solution can also be obtained from solving the UCM directly for $\boldsymbol{\tau}^p$ (and only retain the long-time part of the solution).

Let's now take a look at the exponential decay term in the full solution of $\tau_{12}(t)$:

$$-\frac{\gamma_0\lambda^2}{1+\lambda^2\omega^2}(\frac{\eta\omega}{\lambda^2}+\eta_s\omega^3)e^{-t/\lambda} = -\gamma_0\frac{\omega}{1+\lambda^2\omega^2}\eta_p e^{-t/\lambda} - \gamma_0\omega\eta_s e^{-t/\lambda} \tag{9.42}$$

The full solution for τ_{12}^p from the UCM is

$$\tau_{12}^p(t) = \gamma_0\frac{\omega}{1+\lambda^2\omega^2}\eta_p(\cos\omega t + \lambda\omega\sin\omega t - e^{-t/\lambda}) \tag{9.43}$$

The $-\gamma_0\omega\eta_s e^{-t/\lambda}$ term is an artifact for enforcing $\tau_{12}(0)=0$, as $\tau_{12}^s(0)=\gamma_0\omega\eta_s$. This can be fixed by recognizing that the Newtonian behavior of the solvent leads to a non-zero shear stress at $t=0$. Accordingly, we can change the I.C. to $\tau_{12}(0)=\gamma_0\omega\eta_s$.

Alternatively, we can also change the oscillation to $\gamma(t)=\gamma_0(1-\cos\omega t)$. In this case, $\dot\gamma(t)=\gamma_0\omega\sin\omega t$, and we can ensure that $\gamma(0)=\dot\gamma(0)=0$ and $\tau_{12}(0)=0$.

9.1.4 Rouse Model

N beads and $N-1$ springs to introduce multiple relaxation times

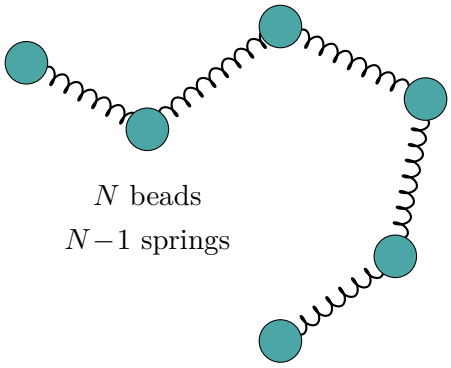


Figure 9.4: Multi-spring model.

The relaxation time distribution:

$$\lambda_i = \frac{\lambda}{2\sin^2(i\pi/2N)} \approx \lambda\Big(\frac{2N^2}{i^2\pi^2}\Big) \tag{9.44}$$

for large N ($\lim_{x\to 0}\sin x = x$).

The constitutive equation and conclusions above would be exactly the same if λ is replaced by $\sum_{i=1}^{N} \lambda_i$:

$$\boldsymbol{\tau}_i^p + \lambda_i \overset{\triangledown}{\boldsymbol{\tau}}_i^p = \eta_{pi} 2\mathbf{D} \tag{9.45}$$

$$\boldsymbol{\tau}^p = \sum_{i=1}^{N} \boldsymbol{\tau}_i^p \tag{9.46}$$

9.2 Concentrated Polymer Solutions

Appendix

A.1 Component Form of Certain Tensor Equations

The table below gives the components of $\mathbf{F}$ in several coordinate systems.

Table A.1: Components of $\mathbf{F}$.

Rectangular coordinates (x, y, z)		
$F_{xx} = \partial x/\partial x'$	$F_{xy} = \partial x/\partial y'$	$F_{xz} = \partial x/\partial z'$
$F_{yx} = \partial y/\partial x'$	$F_{yy} = \partial y/\partial y'$	$F_{yz} = \partial y/\partial z'$
$F_{zx} = \partial z/\partial x'$	$F_{zy} = \partial z/\partial y'$	$F_{zz} = \partial z/\partial z'$
Cylindrical coordinates (r, θ, z)		
$F_{rr} = \partial r/\partial r'$	$F_{r\theta} = (1/r')(\partial r/\partial \theta')$	$F_{rz} = \partial r/\partial z'$
$F_{\theta r} = r\partial\theta/\partial r'$	$F_{\theta\theta} = (r/r')(\partial\theta/\partial\theta')$	$F_{\theta z} = r\partial\theta/\partial z'$
$F_{zr} = \partial z/\partial r'$	$F_{z\theta} = (1/r')(\partial z/\partial\theta')$	$F_{zz} = \partial z/\partial z'$
Spherical coordinates (r, θ, ϕ)		
$F_{rr} = \partial r/\partial r'$	$F_{r\theta} = (1/r')(\partial r/\partial\theta')$	$F_{r\phi} = (1/r'\sin\theta')(\partial r/\partial\phi')$
$F_{\theta r} = r\partial\theta/\partial r'$	$F_{\theta\theta} = (r/r')(\partial\theta/\partial\theta')$	$F_{\theta\phi} = (r/r'\sin\theta')(\partial\theta/\partial\phi')$
$F_{\phi r} = r\sin\theta\partial\phi/\partial r'$	$F_{\phi\theta} = (r\sin\theta/r')\partial\phi/\partial\theta'$	$F_{\phi\phi} = (r\sin\theta/r'\sin\theta')(\partial\phi/\partial\phi')$

The table below gives the components of $\mathbf{L}$ in several coordinate systems.

Table A.2: Components of $\mathbf{L}$.

Rectangular coordinates (x, y, z)		
$L_{xx} = \partial v_x/\partial x$	$L_{xy} = \partial v_x/\partial y$	$L_{xz} = \partial v_x/\partial z$
$L_{yx} = \partial v_y/\partial x$	$L_{yy} = \partial v_y/\partial y$	$L_{yz} = \partial v_y/\partial z$
$L_{zx} = \partial v_z/\partial x$	$L_{zy} = \partial v_z/\partial y$	$L_{zz} = \partial v_z/\partial z$
Cylindrical coordinates (r, θ, z)		
$L_{rr} = \partial v_r x/\partial r$	$L_{r\theta} = (1/r)(\partial v_r/\partial\theta) - v_\theta/r$	$L_{rz} = \partial v_r/\partial z$
$L_{\theta r} = \partial v_\theta/\partial r$	$L_{\theta\theta} = (1/r)(\partial v_\theta/\partial\theta) + v_r/r$	$L_{\theta z} = \partial v_\theta/\partial z$
$L_{zr} = \partial v_z/\partial r$	$L_{r\theta}(1/r)(\partial v_z/\partial\theta)$	$L_{zz} = \partial v_z/\partial z$
Spherical coordinates (r, θ, ϕ)		
$L_{rr} = \partial v_r x/\partial r$	$L_{r\theta} = (1/r)(\partial v_r/\partial\theta) - v_\theta/r$	$L_{r\phi} = (1/r\sin\theta)(\partial v_r/\partial\phi) - v_\phi/r$
$L_{\theta r} = \partial v_\theta/\partial r$	$L_{\theta\theta} = (1/r)(\partial v_\theta/\partial\theta) + v_r/r$	$L_{\theta\phi} = (1/r\sin\theta)(\partial v_\theta/\partial\phi) - (v_\phi/r)\cot\theta$
$L_{\phi r} = \partial v_\phi/\partial r$	$L_{\phi\theta} = (1/r)(\partial v_\phi/\partial\theta)$	$L_{\phi\phi} = (1/r\sin\theta)(\partial v_\phi/\partial\phi) + v_r/r + (v_\theta/r)\cot\theta$

The momentum balance equation in different coordinate systems are given in the table below.

Table A.3: Components of equation of motion.

Rectangular coordinates (x, y, z)

x-Component

$$\rho\Big(\frac{\partial v_x}{\partial t}+v_x\frac{\partial v_x}{\partial x}+v_y\frac{\partial v_x}{\partial y}+v_z\frac{\partial v_x}{\partial z}\Big)=-\frac{\partial p}{\partial x}+\Big(\frac{\partial \tau_{xx}}{\partial x}+\frac{\partial \tau_{yx}}{\partial y}+\frac{\partial \tau_{zx}}{\partial z}\Big)+\rho g_x$$

y-Component

$$\rho\Big(\frac{\partial v_y}{\partial t}+v_x\frac{\partial v_y}{\partial x}+v_y\frac{\partial v_y}{\partial y}+v_z\frac{\partial v_y}{\partial z}\Big)=-\frac{\partial p}{\partial y}+\Big(\frac{\partial \tau_{xy}}{\partial x}+\frac{\partial \tau_{yy}}{\partial y}+\frac{\partial \tau_{zy}}{\partial z}\Big)+\rho g_y$$

z-Component

$$\rho\Big(\frac{\partial v_z}{\partial t}+v_x\frac{\partial v_z}{\partial x}+v_y\frac{\partial v_z}{\partial y}+v_z\frac{\partial v_z}{\partial z}\Big)=-\frac{\partial p}{\partial z}+\Big(\frac{\partial \tau_{xz}}{\partial x}+\frac{\partial \tau_{yz}}{\partial y}+\frac{\partial \tau_{zz}}{\partial z}\Big)+\rho g_z$$

The continuity equation:

$$\boldsymbol{\nabla}\cdot\mathbf{v}=\frac{\partial v_x}{\partial x}+\frac{\partial v_y}{\partial y}+\frac{\partial v_z}{\partial z}=0$$

Cylindrical coordinates (r, θ, z)

r-Component

$$\rho\Big(\frac{\partial v_r}{\partial t}+v_r\frac{\partial v_r}{\partial r}+\frac{v_\theta}{r}\frac{\partial v_r}{\partial \theta}-\frac{v_\theta^2}{r}+v_z\frac{\partial v_r}{\partial z}\Big)=-\frac{\partial p}{\partial r}+\Big(\frac{1}{r}\frac{\partial}{\partial r}(r\tau_{rr})+\frac{1}{r}\frac{\partial \tau_{\theta r}}{\partial \theta}-\frac{\tau_{\theta\theta}}{r}+\frac{\partial \tau_{zr}}{\partial z}\Big)+\rho g_r$$

θ-Component

$$\rho\Big(\frac{\partial v_\theta}{\partial t}+v_r\frac{\partial v_\theta}{\partial r}+\frac{v_\theta}{r}\frac{\partial v_\theta}{\partial \theta}+\frac{v_r v_\theta}{r}+v_z\frac{\partial v_\theta}{\partial z}\Big)=-\frac{1}{r}\frac{\partial p}{\partial \theta}+\Big(\frac{1}{r^2}\frac{\partial}{\partial r}(r^2\tau_{r\theta})+\frac{1}{r}\frac{\partial \tau_{\theta\theta}}{\partial \theta}+\frac{\partial \tau_{\theta z}}{\partial z}+\frac{\tau_{\theta r}-\tau_{r\theta}}{r}\Big)+\rho g_\theta$$

z-Component

$$\rho\Big(\frac{\partial v_z}{\partial t}+v_r\frac{\partial v_z}{\partial r}+\frac{v_\theta}{r}\frac{\partial v_z}{\partial \theta}+v_z\frac{\partial v_z}{\partial z}\Big)=-\frac{\partial p}{\partial z}+\Big(\frac{1}{r}\frac{\partial}{\partial r}(r\tau_{rz})+\frac{1}{r}\frac{\partial \tau_{\theta z}}{\partial \theta}+\frac{\partial \tau_{zz}}{\partial z}\Big)+\rho g_z$$

The continuity equation:

$$\boldsymbol{\nabla}\cdot\mathbf{v}=\frac{1}{r}\frac{\partial}{\partial r}(rv_r)+\frac{1}{r}\frac{\partial v_\theta}{\partial \theta}+\frac{\partial v_z}{\partial z}=0$$

Spherical coordinates (r, θ, ϕ)

r-Component

$$\rho\Big(\frac{\partial v_r}{\partial t}+v_r\frac{\partial v_r}{\partial r}+\frac{v_\theta}{r}\frac{\partial v_r}{\partial \theta}+\frac{v_\phi}{r\sin\theta}\frac{\partial v_r}{\partial \phi}-\frac{v_\theta^2+v_\phi^2}{r}\Big)$$

$$=-\frac{\partial p}{\partial r}+\Big(\frac{1}{r^2}\frac{\partial}{\partial r}(r^2\tau_{rr})+\frac{1}{r\sin\theta}\frac{\partial}{\partial \theta}(\tau_{\theta r}\sin\theta)+\frac{1}{r\sin\theta}\frac{\partial \tau_{r\phi}}{\partial \phi}-\frac{\tau_{\theta\theta}+\tau_{\phi\phi}}{r}\Big)+\rho g_r$$

θ-Component

$$\rho\Big(\frac{\partial v_\theta}{\partial t}+v_r\frac{\partial v_\theta}{\partial r}+\frac{v_\theta}{r}\frac{\partial v_\theta}{\partial \theta}+\frac{v_\theta}{r\sin\theta}\frac{\partial v_\theta}{\partial \phi}+\frac{v_r v_\theta}{r}-\frac{v_\phi^2\cot\theta}{r}\Big)$$

$$=-\frac{1}{r}\frac{\partial p}{\partial \theta}+\Big(\frac{1}{r^3}\frac{\partial}{\partial r}(r^3\tau_{r\theta})+\frac{1}{r\sin\theta}\frac{\partial}{\partial \theta}(\tau_{\theta\theta}\sin\theta)+\frac{1}{r\sin\theta}\frac{\partial \tau_{\theta\phi}}{\partial \phi}+\frac{(\tau_{\theta r}-\tau_{r\theta})-\cot\theta\tau_{\phi\phi}}{r}\Big)+\rho g_\theta$$

ϕ-Component

$$\rho\Big(\frac{\partial v_\phi}{\partial t}+v_r\frac{\partial v_\phi}{\partial r}+\frac{v_\theta}{r}\frac{\partial v_\phi}{\partial \theta}+\frac{v_\phi}{r\sin\theta}\frac{\partial v_\phi}{\partial \phi}+\frac{v_r v_\phi}{r}+\frac{v_\theta v_\phi\cot\theta}{r}\Big)$$

$$=-\frac{1}{r\sin\theta}\frac{\partial p}{\partial \phi}+\Big(\frac{1}{r^3}\frac{\partial}{\partial r}(r^3\tau_{r\phi})+\frac{1}{r\sin\theta}\frac{\partial}{\partial \theta}(\tau_{\theta\phi}\sin\theta)+\frac{1}{r\sin\theta}\frac{\partial \tau_{\phi\phi}}{\partial \phi}+\frac{(\tau_{\phi r}-\tau_{r\phi})+2\cot\theta\tau_{\theta\phi}}{r}\Big)+\rho g_\phi$$

The continuity equation:

$$\boldsymbol{\nabla}\cdot\mathbf{v}=\frac{1}{r^2}\frac{\partial}{\partial r}(r^2v_r)+\frac{1}{r\sin\theta}\frac{\partial}{\partial \theta}(v_\theta\sin\theta)+\frac{1}{r\sin\theta}\frac{\partial v_\phi}{\partial \phi}=0$$

A.2 Calculus Tools

Integration by Parts

The integration by parts formula states:

$$\int_a^b u(x)v'(x)\,\mathrm{d}x = \Big[u(x)v(x)\Big]_a^b - \int_a^b u'(x)v(x)\,\mathrm{d}x = u(b)v(b) - u(a)v(a) - \int_a^b u'(x)v(x)\,\mathrm{d}x \quad \text{(A.1)}$$

The indefinite integral form is:

$$\int u\,\mathrm{d}v = uv - \int v\,\mathrm{d}u \quad \text{(A.2)}$$

Leibniz Integral Rule

The Leibniz' rule is to perform differentiation under the integral sign:

$$\frac{\mathrm{d}}{\mathrm{d}x}\int_{u(x)}^{v(x)} f(x,t)\,\mathrm{d}t = f(x,v(x))\frac{\mathrm{d}v}{\mathrm{d}x} - f(x,u(x))\frac{\mathrm{d}u}{\mathrm{d}x} + \int_{u(x)}^{v(x)} \frac{\partial f(x,t)}{\partial x}\,\mathrm{d}t \quad \text{(A.3)}$$

Ordinary Differential Equations

Separation of variables should be firstly attempted for most ordinary differential equations (ODEs) encountered in this course. Generally, the ODE take a form as:

$$\frac{1}{P(y)}\frac{\mathrm{d}y}{\mathrm{d}x} = Q(x) \quad \text{(A.4)}$$

Separation of variables recasts the ODE to two integrals:

$$\int \frac{1}{P(y)}\,\mathrm{d}y = \int Q(x)\,\mathrm{d}x \quad \text{(A.5)}$$

For ODEs taking the form

$$\frac{\mathrm{d}y}{\mathrm{d}x} + P(x)y = Q(x) \quad \text{(A.6)}$$

we can apply an integrating factor, $e^{\int P(x)\,\mathrm{d}x}$, on both sides of the equation:

$$e^{\int P(x)\,\mathrm{d}x}\frac{\mathrm{d}y}{\mathrm{d}x} + e^{\int P(x)\,\mathrm{d}x}P(x)y = Q(x)e^{\int P(x)\,\mathrm{d}x} \quad \text{(A.7)}$$

By applying the product rule in reverse, we can see that the left-hand side can be expressed as a single derivative

$$\frac{\mathrm{d}}{\mathrm{d}x}\Big(e^{\int P(x)\,\mathrm{d}x}y\Big) = Q(x)e^{\int P(x)\,\mathrm{d}x} \quad \text{(A.8)}$$

This equation can be solved by the separation of variables method:

$$e^{\int P(x)\,\mathrm{d}x} y = \int Q(x) e^{\int P(x)\,\mathrm{d}x}\,\mathrm{d}x + C \tag{A.9}$$

or

$$y = e^{-\int P(x)\,\mathrm{d}x} \int Q(x) e^{\int P(x)\,\mathrm{d}x}\,\mathrm{d}x + C e^{-\int P(x)\,\mathrm{d}x} \tag{A.10}$$

If the ODE is homogeneous, i.e., $Q(x) = 0$, no integrating factor is needed and the ODE can be solved directly by separation of variables.

A.3 Curve Fitting

In rheology, we often have a dataset (e.g., stress-shear rate data) and need to fit them using a specific constitutive equation. There are many curve fitting tools. Here, we use python as an example.

Scipy is the scientific computing module of Python providing in-built functions on a lot of well-known Mathematical functions. The *scipy.optimize* package equips us with multiple optimization procedures. Among the most used are Least-Square minimization, curve-fitting, minimization of multivariate scalar functions, etc. Here is a curve fitting example.

```
import numpy as np
from scipy.optimize import curve_fit
import matplotlib.pyplot as plt

# --------------------------------
# 1. Define the model function
# --------------------------------
def model(x, a, b, c):
return a * np.exp(-b * x) + c

# --------------------------------
# 2. Generate synthetic data
# --------------------------------
np.random.seed(0)
x = np.linspace(0, 5, 50)
y_true = model(x, a=2.5, b=1.3, c=0.5)
y_noisy = y_true + 0.2 * np.random.normal(size=len(x))

# --------------------------------
# 3. Fit with constraints (bounds)
# --------------------------------
# a > 0, b between 0 and 5, c between -1 and 1
bounds_lower = [0.0, 0.0, -1.0]
bounds_upper = [np.inf, 5.0, 1.0]
```

```
25
26          popt, pcov = curve_fit(
27          model, x, y_noisy,
28          p0=[1.0, 1.0, 0.0],   # initial guess
29          bounds=(bounds_lower, bounds_upper)
30          )
31
32          a_fit, b_fit, c_fit = popt
33
34          print("Fitted parameters:")
35          print(f"a = {a_fit:.4f}")
36          print(f"b = {b_fit:.4f}")
37          print(f"c = {c_fit:.4f}")
38
39          # --------------------------------
40          # 4. Plot
41          # --------------------------------
42          plt.scatter(x, y_noisy, label="data")
43          plt.plot(x, model(x, *popt), label="fit", linewidth=2)
44          plt.legend()
45          plt.show()
```