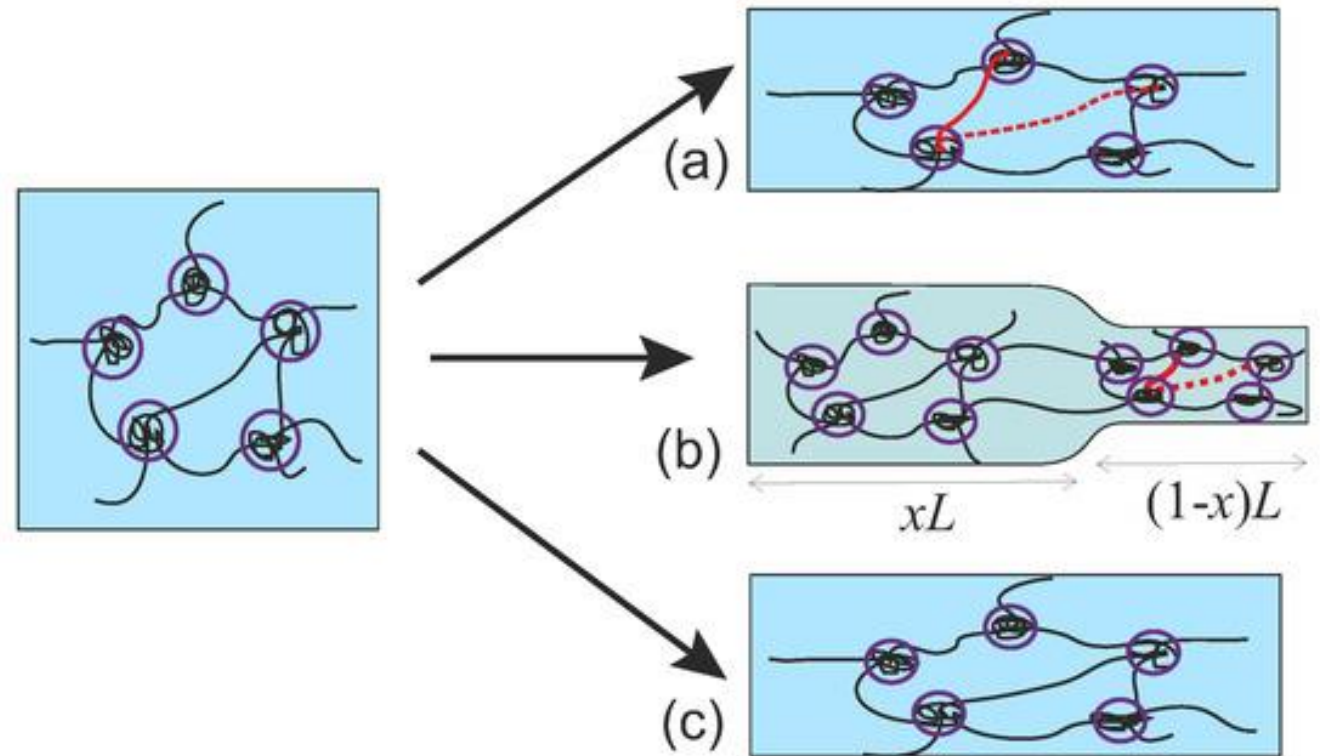


Finite Linear Viscoelasticity

The Rubberlike liquid

or

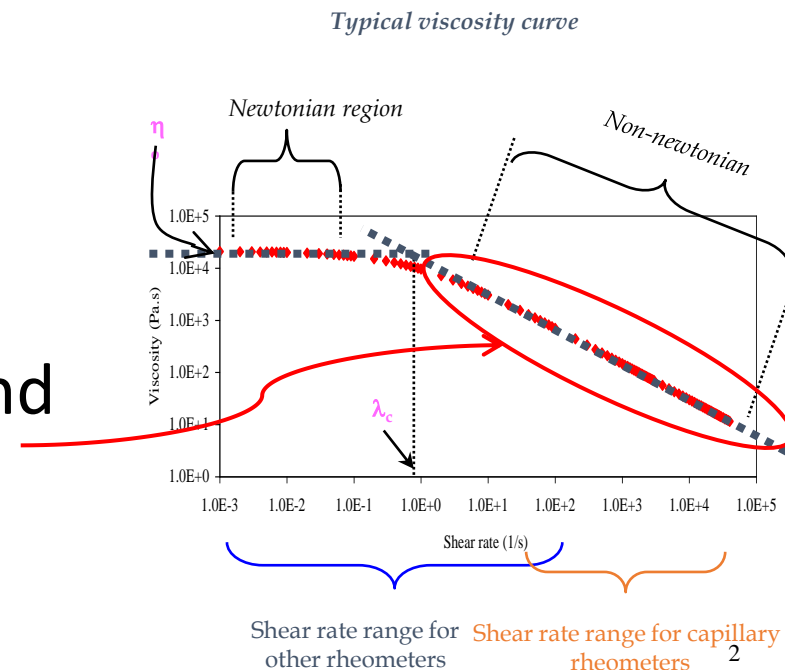
The Lodge's Network Theory



But...

It is well known that:

- there is a dependence of the viscosity on the shear rate and that



- there is a non-zero normal stress difference as the shear rate increases (Weissenberg effect)

$$\dot{\gamma}_{ij}(t \geq 0) = \begin{bmatrix} 0 & \dot{\gamma} & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

Then...

a different theory or a
modification of the
infinitesimal theory is
required:

*The Finite Linear Viscoelasticity or
The Rubberlike liquid or
Lodge Network Theory*

The Rubberlike liquid or the Finite Linear Viscoelasticity Model

- Experimental observation shows that the Finger tensor gives the best description for the deformation just beyond the region of linear infinitesimal viscoelasticity.
- The rubberlike liquid model:
 - uses the Finger strain tensor,
 - assumes that the Boltzman Superposition Principle is valid
 - and formulates a theory which results in the following equation:

$$\tau_{ij}(t) = \int_{-\infty}^t m(t - t') B_{ij}(t, t') dt'$$

Finite Measures of Strain

- Principle of Material Indifference:

The material's rheological behavior reflects a basic physical property and therefore cannot depend on the frame of reference used to describe the behavior as long as the material is isotropic in its rest state.

- Two measures of strain that satisfy this criterion in Rheology are:

- the Cauchy-Green tensor, $C_{ij}(t_1, t_2)$ and
- the Finger tensor $B_{ij}(t_1, t_2)$

The Cauchy and Finger Strain Tensors for simple shear

The diagonal is non-zero

$$C_{ij}(t_1, t_2) = \begin{bmatrix} 1 & [\gamma(t_2) - \gamma(t_1)] & 0 \\ [\gamma(t_2) - \gamma(t_1)] & \{1 + [\gamma(t_2) - \gamma(t_1)]^2\} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Compare to simple shear in the
LIVE range

$$\gamma_{ij}(t \geq 0) = \begin{bmatrix} 0 & \gamma & 0 \\ \gamma & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

The diagonal is non-zero

$$B_{ij}(t_1, t_2) = \begin{bmatrix} \{1 + [\gamma(t_1) - \gamma(t_2)]^2\} & [\gamma(t_1) - \gamma(t_2)] & 0 \\ [\gamma(t_1) - \gamma(t_2)] & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

The Cauchy and Finger Strain Tensors for simple extension

$$C_{ij}(t_1, t_2) = \begin{bmatrix} e^{2[\varepsilon(t_2) - \varepsilon(t_1)]} & 0 & 0 \\ 0 & e^{-[\varepsilon(t_2) - \varepsilon(t_1)]} & 0 \\ 0 & 0 & e^{-[\varepsilon(t_2) - \varepsilon(t_1)]} \end{bmatrix}$$

Compare to simple extension in the
LIVE range

$$\gamma_{ij}(t \geq 0) = \begin{bmatrix} 2\varepsilon_0 & 0 & 0 \\ 0 & -\varepsilon_0 & 0 \\ 0 & 0 & -\varepsilon_0 \end{bmatrix}$$

$$B_{ij}(t_1, t_2) = \begin{bmatrix} e^{2[\varepsilon(t_1) - \varepsilon(t_2)]} & 0 & 0 \\ 0 & e^{-[\varepsilon(t_1) - \varepsilon(t_2)]} & 0 \\ 0 & 0 & e^{-[\varepsilon(t_1) - \varepsilon(t_2)]} \end{bmatrix}$$

Remember the scalar invariants?

A vector has one “scalar invariant”:
its magnitude.

A second order Cartesian tensor has three scalar invariants
(I_1 , I_2 and I_3)

Which are the invariants of the Finger Tensor ?

The Finger tensor invariants are:

$$I_1(\mathbf{B}_{ij}) = B_{11} + B_{22} + B_{33}$$

$$I_2(\mathbf{B}_{ij}) = C_{11} + C_{22} + C_{33}$$

$$I_3(\mathbf{B}_{ij}) = 1$$

Note: since B_{ij} depends on t_2 and t_1 , then their scalar invariants depend also on t_2 and t_1 ,
...therefore

Scalar invariants of the Finger Tensor for simple shear and simple extension

- For simple shear:

$$I_1(\mathbf{B}_{ij}) = I_2(\mathbf{B}_{ij}) = [\gamma(t_2) - \gamma(t_1)]^2 + 3$$

- For simple extension:

$$I_1(\mathbf{B}_{ij}) = e^{-2[\varepsilon(t_2) - \varepsilon(t_1)]} + 2e^{[\varepsilon(t_2) - \varepsilon(t_1)]}$$

$$I_2(\mathbf{B}_{ij}) = e^{2[\varepsilon(t_2) - \varepsilon(t_1)]} + 2e^{-[\varepsilon(t_2) - \varepsilon(t_1)]}$$

Remember that

- Experimental observation shows that the Finger tensor gives the best description for the deformation just beyond the region of linear infinitesimal viscoelasticity.
- The rubberlike liquid model:
 - uses the Finger strain tensor,
 - assumes that the Boltzman Superposition Principle is valid
 - and formulates a theory which results in the following equation:

$$\tau_{ij}(t) = \int_{-\infty}^t m(t - t') B_{ij}(t, t') dt'$$

The Rubberlike liquid or the Finite LVE,

$$\tau_{ij}(t) = \int_{-\infty}^t m(t - t') B_{ij}(t, t') dt'$$

- For simple shear deformation

- the strain is:

$$B_{21}(t, t') = [\gamma(t) - \gamma(t')]$$

- the stress is:

$$\tau_{21}(t) = \sigma(t)$$

- then

$$\sigma(t) = \int_{-\infty}^t m(t - t') [\gamma(t) - \gamma(t')] dt'$$

- if the deformation at $t=0$, $[\gamma(t) - \gamma(t')] = \gamma$

- then:

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

- or

$$\frac{\sigma(t)}{\gamma} = \int_{-\infty}^t m(t - t') dt' = G(t)$$

Therefore...

The memory function can be obtained by taking the derivative...

$$m(t - t') = \frac{dG(t - t')}{dt'}$$

$$\tau_{ij}(t) = \int_{-\infty}^t m(t - t') B_{ij}(t, t') dt'$$

- Then,
 - the relaxation modulus of the rubberlike liquid is independent of strain
 - it means that the memory function is a linear viscoelastic property and
 - it can be written in terms of the relaxation spectrum

$$m(s) = \int_{-\infty}^{\infty} \frac{H(\lambda)}{\lambda} e\left(\frac{-s}{\lambda}\right) d\ln(\lambda)$$

where

$$s = t - t'$$

Lodge's Network Theory (LNT)

- Stress calculation for simple shear strain:

$$\tau_{ij}(t) = \int_{-\infty}^t m(t - t') B_{ij}(t, t') dt'$$

$$\sigma(t) = \tau_{21}(t) = \int_{-\infty}^t m(t - t') [\gamma(t) - \gamma(t')] dt'$$

- Upon integration by parts

$$\sigma(t) = \tau_{21}(t) = \int_{-\infty}^t G(t - t') d\gamma(t')$$

- This is similar to the LiVE

Lodge's Network Theory (LNT)

$$\tau_{ij}(t) = \int_{-\infty}^t m(t-t') B_{ij}(t, t') dt'$$

- First normal stress difference ($\tau_{11}-\tau_{22}$) calculation for simple shear strain:

$$\tau_{11}(t) = \int_{-\infty}^t m(t-t') \left\{ 1 + [\gamma(t) - \gamma(t')]^2 \right\} dt'$$

$$\tau_{22}(t) = \int_{-\infty}^t m(t-t') \{1\} dt'$$

$$\tau_{11}(t) - \tau_{22}(t) = \int_{-\infty}^t m(t-t') \left\{ [\gamma(t) - \gamma(t')]^2 \right\} dt' = N_1(t)$$

Better than predicted by LIVE BSP

$$\tau_{33}(t) = \int_{-\infty}^t m(t-t') \{1\} dt'$$

Similarly for ($\tau_{22}-\tau_{33}$):

$$\tau_{22}(t) - \tau_{33}(t) = \int_{-\infty}^t m(t-t') \{0\} dt' = 0 = N_2(t)$$

Not good

Lodge's Network Theory (LNT)

Solving the previous equations for step strain for $t > 0$:

$$\tau_{ij}(t) = \int_{-\infty}^t m(t - t') B_{ij}(t, t') dt'$$

$$[\gamma(t) - \gamma(t')] = \gamma \quad \text{for } t' < 0$$

$$[\gamma(t) - \gamma(t')] = \gamma \quad \text{for } t' > 0$$

Stress $\sigma(t) = G(t) \gamma$

N1
$$\tau_{11}(t) - \tau_{22}(t) = \int_{-\infty}^t m(t - t') \{[\gamma]^2\} dt'$$

$$N_1(t) = \gamma^2 \int_{-\infty}^t m(t - t') dt'$$

$$N_1(t) = \gamma^2 G(t)$$

N2

$$N_2(t) = 0$$

Finger strain tensor for uniaxial elongation

$$C_{ij}^{-1}(t') = \begin{vmatrix} \exp[2\dot{\epsilon} s] & 0 & 0 \\ 0 & \exp[-\dot{\epsilon} s] & 0 \\ 0 & 0 & \exp[-\dot{\epsilon} s] \end{vmatrix}$$

where $s = (t - t')$

and $C_{ij}^{-1}(t') = B_{ij}(t')$

Finger strain tensor for uniaxial elongation

Stress calculation for constant strain rate
in simple extension for $t > 0$:

$$\sigma_E(t) = \sigma_{11}(t) - \sigma_{22}(t)$$

$$\tau_{ij}(t) = \int_{-\infty}^t m(t-t') B_{ij}(t, t') dt'$$

$$\tau_{11}(t) = \int_{-\infty}^t m(s) \left\{ 2e^{2[\dot{\varepsilon}s]} \right\} d\varepsilon(s)$$

$$\tau_{22}(t) = \int_{-\infty}^t m(s) \left\{ -1e^{[-\dot{\varepsilon}(s)]} \right\} d\varepsilon(s)$$

$$\tau_{11}(t) - \tau_{22}(t) = \int_{-\infty}^t m(s) \left\{ 2e^{[2\dot{\varepsilon}(s)]} + 1e^{[-\dot{\varepsilon}(s)]} \right\} \dot{\varepsilon} ds = \sigma_E(t, \dot{\varepsilon})$$

$$\frac{\sigma_E(t, \dot{\varepsilon})}{\dot{\varepsilon}} = \int_{-\infty}^t m(s) \left\{ 2e^{[2\dot{\varepsilon}(s)]} + 1e^{[-\dot{\varepsilon}(s)]} \right\} ds = \eta_E(t, \dot{\varepsilon})$$

The rubber-like liquid model (RLM)

- The RLM does not provide a quantitative description of the behavior of molten polymers experiencing large and/or rapid deformations
- Disadvantages:
 - The viscosity is shear rate independent
 - The first normal stress coefficient is shear rate independent
 - The second Normal Stress is zero at all shear rates
 - The tensile stress growth function increases without limit when the strain exceeds the reciprocal of twice the relaxation time
 - The tensile stress growth function always lies above the linear viscoelastic curve at non-zero values of strain rate.

The rubber-like liquid model (RLM)

- Advantages:
 - It is a simple equation
 - It gives the correct low shear rate limiting dependence of N_1 on shear rate and provides relationships between $\Psi_{1,0}$ and the material functions of LVE
 - It provides a basis of comparison for describing the non-LVE behavior of real materials
 - Any observed deviation can be later used as a non-linear characterizing function.
 - It is the simplest theory of non-LVE able to predict most of the features first observed, when both the size and the rate of the deformation exceed the ranges in which LVE is observed.

The BKZ equation

- Bernstein, Kearsley and Zapas, based on concepts used in the development of the theory of rubber viscoelasticity, they proposed the following form of the constitutive equation for a viscoelastic material.

$$\tau_{ij}(t) = \int \left[2 \frac{\partial u}{\partial I_1} C_{ij}(t, t') - 2 \frac{\partial u}{\partial I_2} B_{ij}(t, t') \right] dt'$$

where $u = u(I_1, I_2, t - t')$

is a time-dependent elastic energy potential function
which has to be determined experimentally

The BKZ equation

- The energy potential function can be factored by introducing a time independent potential function:

$$u = u(I_1, I_2, t - t') = m(t - t')U(I_1, I_2)$$

Giving a “factorable BKZ model”

$$\tau_{ij}(t) = \int_{-\infty}^t m(t - t') \left[2 \frac{\partial U}{\partial I_1} C_{ij}(t, t') - 2 \frac{\partial U}{\partial I_2} B_{ij}(t, t') \right] dt'$$

To get the function, it requires to measure shear stress and N1 in simple shear.

The Wagner's equation

- The memory function is allowed to depend on variables affecting the deformation process:
 - The history of the strain rate in the interval t' to t .
 - The history of the strain in the interval from t' to t
 - The history of the stress in the interval from t' to t
 - The history of the elastic energy in the interval from t' to t
- The most favorable approach is to allow the memory function to depend on the strain as well as on time.
- Since, the memory function is a scalar quantity, while the strain is a tensor valued quantity then:
 - This can only be accomplished by letting the memory function to depend on the scalar invariants of the Finger tensor; and the memory function becomes:

$$M = M[(t - t'), I_1(B_{ij}), I_2(B_{ij})]$$

The Wagner's equation

$$\tau_{ij}(t) = \int_{-\infty}^t M[(t - t'), I_1(B_{ij}), I_2(B_{ij})] [B_{ij}(t, t')] dt'$$

- As you may have noticed, this model drops the Cauchy's tensor.
- White and Tokita suggested (based on experimental observations on crosslinked rubbers) that the memory function might be expressed as the product of the strain independent function of time and a function of strain
- Then Wagner proposed:

$$M[(t - t'), I_1(B_{ij}), I_2(B_{ij})] = m(t - t') h(I_1, I_2)$$