

# Constitutive Models for viscoelasticity

Presented by:

Ayush Tripathi

Under the guidance of

Dr Syed Nizamudddin Khaderi

Department of Mechanical & Aerospace Engineering



భారతీయ సాంకేతిక విజ్ఞాన సంస్థ హైదరాబాద్  
भारतीय प्रौद्योगिकी संस्थान हैदराबाद  
Indian Institute of Technology Hyderabad



- Framework
- Internal variable model
- Continuum mechanics model
- Rheological model
- Strain energy density functions
- Micro macro model
- Statistical mechanics framework
- Honeywell project
- Roadblocks
- course of action



- Development of constitutive models based on two approaches
  - Continuum Mechanics framework
    - Internal variable
    - Thermodynamic variable
  - Statistical Mechanics framework
    - Micro-mechanism



- Also referred as phenomenological models.
- Such models assume that the hyperelastic properties can be described by means of a strain energy density function that involves either strain invariants or principal stretches.
- All hyperelastic material models are based on a strain energy function that determines how much energy is stored in the material as a function of the applied deformation
- Since the energy must be independent of rigid body rotations, the strain energy function is often written in terms of its invariants
- Lack microstructural justification



- Directly link the macroscopic behavior of the materials to their microstructure.
- The parameters of polymer physics and chemistry, such as the cross-linking density, the molecular weight of the monomers, the chain extensibility, the polymerisation degree and the amount of entanglements of polymer chains, reflect the microstructure of the material
- Micro-mechanical based hyperelastic models
- Preserve the affinity of network deformation induced by the macroscopic deformation
- Affine network models fail to fully capture the entanglement effect of polymer chains, hence cannot represent the real molecular structure of the elastomers.



- Current state of thermoelastic material
  - $F$  and  $\theta$
  - Measurable and controllable (External variable)
- Material involving dissipation
  - Internal variable
    - Describes aspects of the internal structure of a material
    - History variable for dissipative materials
  - Thermodynamic state variable  $\zeta$
- Current state of dissipative material :  $F, \theta, \zeta$



- Current thermodynamic state: fictitious state of thermodynamic equilibrium described by their current value and not by their past history
- phenomenological variable constructed mathematically (Thermal, chemical, mechanical)
- Describe structural property within a macroscopic framework
  - Dashpot displacement in viscoelastic models
  - Damage, inelastic strains, dislocation densities
- The existence of non-equilibrium states that evolve with time is an essential feature of inelastic materials
- A viscoelastic behaviour of a material is characterised by hysteresis



- Helmholtz free energy function defines the thermodynamic state by
  - Deformation Gradient (F)
  - Internal history variable specified for a particular problem

$$\psi = \psi(F, \zeta_1, \zeta_2, \dots, \zeta_m)$$

- Number of variables depend on theory and boundary condition





it is essential to make sure that the stress-strain law satisfies two conditions:

- (i) It must obey the laws of thermodynamics.
- (ii) It must satisfy the condition of objectivity, or material frame indifference.

- **Thermodynamic restrictions:** The laws of thermodynamics impose two restrictions on stress-strain laws:

- The first law requires that the work done by stresses must either be stored as recoverable internal energy in the solid, or be dissipated as heat (or a combination of both).
- The second law requires that if a sample of the material is subjected to a cycle of deformation that starts and ends with an identical strain and internal energy (at constant temperature, or without heat exchange with the surroundings) the total work done must be positive or zero.

$$\mathcal{D}_{\text{int}} = \mathbf{P} : \dot{\mathbf{F}} - \dot{e} + \Theta \dot{\eta} \geq 0$$



For purely mechanical theory  $\mathcal{D}_{int} = w_{int} - \dot{\Psi} \geq 0$

- Local entropy production must always be greater than zero
- Work conjugate pair; rate of internal mechanical work per unit volume (stress power)
- Rate of change of internal energy

$$W_{int} = P : \dot{F}$$

$$\frac{d\varphi}{dt}(F, \zeta_1, \zeta_2 \dots \zeta_m) = \frac{\partial \psi}{\partial F} : \dot{F} + \sum_{\alpha=1}^m \frac{\partial \psi}{\partial \zeta_{\alpha}} : \dot{\zeta}_{\alpha}$$



$$\mathcal{D}_{int} = \left( P - \frac{\partial \psi(F, \zeta_1, \zeta_2 \dots \zeta_m)}{\partial F} \right) : \dot{F} - \sum_{\alpha=1}^m \frac{\partial \psi(F, \zeta_1, \zeta_2 \dots \zeta_m)}{\partial \zeta_\alpha} : \dot{\zeta}_\alpha \geq 0$$

Splitting the terms

$$P = \frac{\partial \psi(F, \zeta_1, \zeta_2 \dots \zeta_m)}{\partial F}$$

$$\mathcal{D}_{int} = \sum_{\alpha=1}^m \Xi_\alpha : \dot{\zeta}_\alpha \geq 0$$

$$\Xi_\alpha = - \frac{\partial \psi(F, \zeta_1, \zeta_2 \dots \zeta_m)}{\partial \zeta_\alpha} \quad \alpha = 1, 2, \dots, m$$

Gradient of free energy wrt to internal variable

- Must hold for all times at every point of the continuum body
- $\Xi_\alpha$  Conjugate to  $\zeta_\alpha$
- Tensor variables  $F$  and  $\zeta_\alpha$  are associated with thermodynamics forces  $P$  and  $\Xi_\alpha$
- If  $\zeta_\alpha$  is not needed to characterize thermodynamic state of the system, then the material is perfectly elastic



- Describes the evolution of the internal variable and associated dissipation mechanism
- Required to describe how an irreversible process evolves
- Thermodynamic admissibility is the only restriction

$$\dot{\zeta}_{\alpha}(t) = \mathcal{A}_{\alpha}\left(F, \zeta_1, \zeta_2 \cdots \zeta_m\right)$$

- Rate at which the internal variables tend towards equilibrium
- Tensor valued function with 1+m variables
- Every system tends to thermodynamic equilibrium
  - Observable and internal variable reach equilibrium under prescribed stress and strain
  - Remain constant at all points if the system with time
- For an elastic continuum, every state is in equilibrium



- Process involving relaxation and creep
  - Non equilibrium thermodynamics
  - Thermoplastic elastomers
- Thermodynamic state is characterized by internal variables
- External variables not suitable for finite element realization
- 3D viscoelastic model for finite strains and small perturbations away from equilibrium
- Not restricted to isotropy



- Decoupled representation of Helmholtz free energy function
  - Dilational
  - Isochoric
- Change of free energy within an isothermal framework given by

$$\psi\left(C, I_1, I_2 \dots I_m\right) = \underbrace{\psi^{\infty}_{vol}(J)}_{\text{Equilibrium state}} + \underbrace{\psi^{\infty}_{iso}(C)}_{\text{Configurational}} + \sum_{\alpha=1}^m \gamma_{\alpha}(C, I_{\alpha})$$

- Normalization condition

$$\psi^{\infty}_{vol}(1) = 0 \qquad \psi^{\infty}_{iso}(I) = 0 \qquad \sum_{\alpha=1}^m \gamma_{\alpha}(I, I) = 0$$



- Third term  $\sum_{\alpha=1}^m \gamma_{\alpha}(C, \Gamma_{\alpha})$ 
  - Represents configurational free energy
  - Characterizes non equilibrium state (behaviour of relaxation and creep)

$\gamma_{\alpha}(C, \Gamma_{\alpha}) \rightarrow$  function of strain like internal variables (inelastic,  $r$ ) akin to  $C$

# Decoupled volumetric-isochoric State



- Second Piola-Kirchoff

$$S = 2 \frac{\partial \psi(C, \Gamma_1, \Gamma_2 \dots \Gamma_m)}{\partial C}$$

- Additive decomposition

$$S = 2 \frac{\partial \psi(C, \Gamma_1, \Gamma_2 \dots \Gamma_m)}{\partial C} = S_{vol}^{\infty} + S_{iso}$$

- Where,

$$S_{vol}^{\infty} = J \frac{\partial \psi_{iso}^{\infty}(C)}{\partial J} C^{-1} \quad S_{iso} = S_{iso}^{\infty} + \sum_{\alpha=1}^m Q_{\alpha} \quad S_{iso}^{\infty} = J^{-2/3} \mathbb{P} : 2 \frac{\partial \psi_{iso}^{\infty}(C)}{\partial C}$$

- Q represents non-equilibrium stresses in the sense of non-equilibrium thermodynamics
- P is the projection tensor



# Viscoelastic material at large strains



$$S_{iso} = \underbrace{S^{\infty}_{iso}}_{\text{Equilibrium}} + \sum_{\alpha=1}^m \underbrace{Q_{\alpha}}_{\text{Non-Equilibrium}}$$

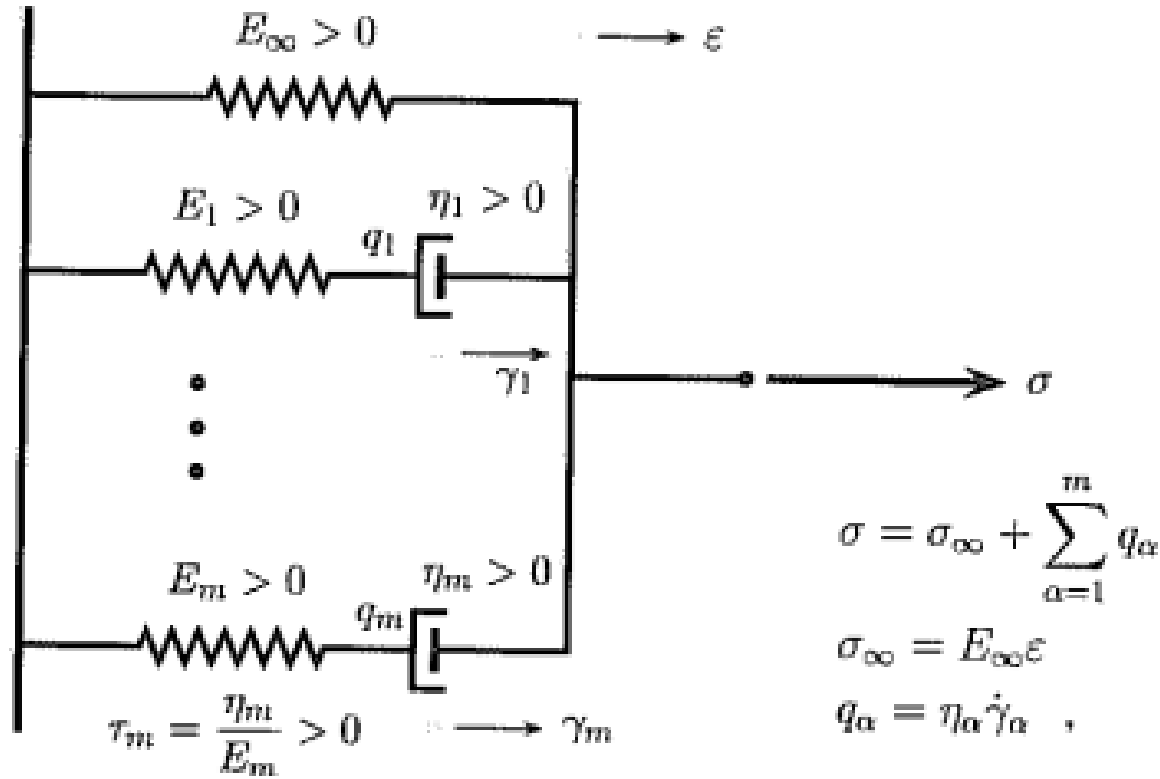
- $Q$  are the conjugate to  $\Gamma_{\alpha}$
- The conditions restrict configurational free energy
- As  $t \rightarrow \infty$  the isochoric stress reaches equilibrium
- $Q$  represents distance from equilibrium
- Dissipation at equilibrium is zero
- At thermodynamic equilibrium the material responds perfectly elastic

$$Q_{\alpha} = -2 \frac{\partial \Upsilon_{\alpha}(C, \Gamma_{\alpha})}{\partial \Gamma}$$

Fictitious Non Equilibrium Stress

$$\mathcal{D}_{int} = \sum_{\alpha=1}^m Q_{\alpha} : \frac{\dot{\Gamma}_{\alpha}}{2} \geq 0$$

# Rheological models



$$\sigma = \sigma_{\infty} + \sum_{\alpha=1}^m q_{\alpha}$$

$$\sigma_{\infty} = E_{\infty} \epsilon$$

$$q_{\alpha} = \eta_{\alpha} \dot{\gamma}_{\alpha} \quad , \quad \alpha = 1, \dots, m$$

$\sigma$  → Total Stress applied  
 $\epsilon$  → Total linear strain due to strain  
 $\gamma_{\alpha}$  → inelastic strain(internal variable)  
 $\dot{\gamma}_{\alpha}$  → Strain rate  
 $\eta_{\alpha}$  → Viscosity  
 $q_{\alpha}$  → Non equilibrium stress(internal variable) at each dashpot

- $\tau_m$  = Relaxation Time of the subnetwork
- Solid behaviour is modelled by set of springs responding linearly according to hooke's law
- The stiffness of the free spring and springs of  $\alpha$ -maxwell element are determined by young's moduli  $E_{\infty} > 0$   $E_{\alpha} > 0$
- Flow behaviour is modelled by viscous fluid like dashpot



- The Mechanical device is assumed to have unit area and unit length
  - Stress and strain interpreted as force and extension

- Total stress applied

$$\sigma = \sigma_{\infty} + \sum_{\alpha=1}^m q_{\alpha}$$

- @ equilibrium

$$\sigma_{\infty} = E_{\alpha} \mathcal{E}$$

- Stress in the spring of  $\alpha$ -maxwell element

$$q_{\alpha} = E_{\alpha}(\mathcal{E} - \gamma_{\alpha})$$

- Stress acting on each dashpot

$$q_{\alpha} = \eta_{\alpha} \dot{\gamma}_{\alpha} = E_{\alpha}(\mathcal{E} - \gamma_{\alpha})$$

- Differentiating, we get

$$\dot{q}_{\alpha} + \frac{q_{\alpha}}{\tau_{\alpha}} = E_{\alpha} \dot{\mathcal{E}}$$



- $q_\alpha \rightarrow$  stress on each dashpot
- $\dot{\gamma}_\alpha \rightarrow$  strain rate on each dashpot

$$\mathcal{D}_{int} = \sum_{\alpha=1}^m q_\alpha \dot{\gamma}_\alpha \geq 0$$

Always non-negative

$$= \sum_{\alpha=1}^m \eta_\alpha (\dot{\gamma}_\alpha)^2 \geq 0$$

Condition for Thermodynamic admissibility of non-equilibrium stress



- Defining Strain energies

$$\psi(\mathcal{E}, \gamma_1, \dots, \gamma_m) = \psi_\infty(\mathcal{E}) + \sum_{\alpha=1}^m \vartheta_\alpha(\mathcal{E}, \gamma_\alpha)$$

- Where, the quadratic forms

$$\psi_\infty(\mathcal{E}) = \frac{1}{2} E_\alpha \mathcal{E}^2 \qquad \vartheta_\alpha(\mathcal{E}, \gamma_\alpha) = \frac{1}{2} E_\alpha (\mathcal{E} - \gamma_\alpha)^2$$

- Normalization condition

$$\psi_\infty(0) = 0 \qquad \vartheta_\alpha(0, 0) = 0$$



$\psi_{\infty}(\mathcal{E}) \rightarrow$  Energy stored elastically in springs

$\vartheta_{\alpha}(\mathcal{E}, \gamma_{\alpha}) \rightarrow$  Viscoelastic contribution to strain energy and is related to relaxation (retardation) process with relaxation time ( $\tau_{\alpha}$ )

- Differentiating ( $\psi$ ) wrt total strain ( $\mathcal{E}$ ) gives the total stress ( $\sigma$ ) applied

$$\frac{\partial \psi(\mathcal{E}, \gamma_1, \dots, \gamma_m)}{\partial \mathcal{E}} = \sigma_{\alpha}(\mathcal{E}) + \sum_{\alpha=1}^m q_{\alpha}(\mathcal{E}, \gamma_{\alpha}) = \sigma$$

$$\sigma_{\alpha} = \frac{\partial \psi_{\infty}(\mathcal{E})}{\partial \mathcal{E}} = E_{\alpha} \mathcal{E}$$

Linear Stress

$$q_{\alpha} = - \frac{\partial \vartheta_{\alpha}(\mathcal{E}, \gamma_{\alpha})}{\partial \gamma_{\alpha}} = E_{\alpha} (\mathcal{E} - \gamma_{\alpha})$$

Non-Linear Stress

The internal dissipation becomes

$$\mathcal{D}_{int} = - \sum_{\alpha=1}^m \frac{\partial \vartheta_{\alpha}(\mathcal{E}, \gamma_{\alpha})}{\partial \gamma_{\alpha}} \dot{\gamma}_{\alpha} \geq 0$$



- Necessary to specify complementary equations of evolution
  - Describes evolution of a viscoelastic process
  - Local entropy production inequality is satisfied
- Law needs to govern internal variable  $Q_\alpha$ 
  - $Q_\alpha$  -- Isochoric non-equilibrium stress
- Evolution equation needs to have physical basis
- Should be suitable for time integration algorithm
- Good approximation to the observed physical behaviour for large strain

$$\dot{Q}_\alpha + \frac{Q_\alpha}{\tau_\alpha} = \dot{S}_{iso\alpha} \quad t \in (0, T]$$



- we start from stress free configuration @  $t=0$   $Q_\alpha = 0$
- $S_{iso\ \alpha} \rightarrow$  Isochoric second PK corresponding to strain energy  $\psi_{iso}(C)$ 
  - Depends only on external variable  $C$
  - Responsible for relaxation(retardation) process with relaxation(retardation) time( $\tau_\alpha$ )
  - constitutive equation for fictitious second PK
  - Both  $Q$  and  $S$  contribute to the isochoric response

$$S_{iso\ \alpha} = J^{-2/3} \mathbb{P} : S_\alpha$$

$$S_\alpha = 2 \frac{\partial \psi(C)}{\partial C}$$



# Solution to linear evolution equation



- Solution to the evolution equation valid for semi-open interval  $t \in (0, T]$

$$Q_{\alpha} = \exp\left(-\frac{T}{\tau}\right)Q_{\alpha 0} + \int_{0^+}^T \exp\left[-\frac{(t-t)}{\tau_{\alpha}}\right]\dot{S}_{\text{iso } \alpha} dt \quad \alpha = 1, 2, \dots, m$$

- Instantaneous response  $Q_{\alpha 0^+}$  is given by

$$Q_{\alpha 0^+} = J_{\alpha 0^+}^{-2/3} \mathbb{P}:2 \frac{\partial \Upsilon_{\alpha}\left(C_{0^+}, \Gamma_{\alpha 0^+}\right)}{\partial C_{0^+}}$$

- Evolution of internal variable is governed by strain energy density function  $\psi_{\text{iso } \alpha}$

# Solution to linear evolution equation



- If the viscoelastic medium such as thermoplastic elastomer is composed of identical polymer chains, we replace  $\psi_{\text{iso}} \rightarrow \psi_{\text{iso}}^{\infty}$
- The expression becomes  $\Psi_{\text{iso } \alpha}(\bar{\mathbf{C}}) = \beta_{\alpha}^{\infty} \Psi_{\text{iso}}^{\infty}(\bar{\mathbf{C}}) \quad \alpha = 1, 2, \dots, m$
- $\beta_{\alpha}^{\infty} \in [0, \infty)$  Are given non-dimensional strain energy factors associated with  $(\tau_{\alpha}) \in [0, \infty)$  (Simo and Govindjee)



- Cauchy's equation of motion  $\operatorname{div} \sigma + b = \rho \dot{v}$
- We need an update algorithm to obtain total stress
- Update procedure recognized in reference configuration
  - Numerical integration of convolution integral
- Algorithmic update of the second Piola Kirchhoff stress  $S$
- Time discretization of the closed time interval  $t \in [0^+, T]$

$$\bigcup_{n=0}^m [t_n, t_{n+1}]$$

# Time integration algorithm



- For a time sub interval  $[t_n, t_{n+1}]$   $\Delta t = t_{n+1} - t_n$
- Assuming that upto a certain time  $t_n$  the stress  $S_n$ , satisfies the equilibrium equation and displacement field  $U_n$ 
  - $F_n = I + \text{Grad } U_n$
  - $C_n = F_n^T F_n$
  - $S_n \rightarrow$  Determined previously
- $J_n = \det F_n$
- $\bar{C}_n = J_n^{-2/3} C_n$
- Are specified uniquely by a given motion  $X_n$  at time  $t_n$
- Strain driven type of numerical procedure



- We advance the procedure to time  $t_{n+1} = \Delta t + t_n$ 
  - Update all relevant quantities
  - Make an initial guess  $X_{n+1} \rightarrow$  trial solution
  - Update all prescribed loads
- The new motion  $X_{n+1}$  at time  $t_{n+1}$  is corrected iteratively until all balance principles are satisfied
- To check equilibrium at  $t_{n+1}$  all the tensor variables are updated

$$\mathbf{F}_{n+1} = \mathbf{I} + \mathbf{Grad} \mathbf{U}_{n+1}$$
$$\mathbf{C}_{n+1} = \mathbf{F}_{n+1}^T \mathbf{F}_{n+1}$$

$$\mathbf{J}_{n+1} = \det \mathbf{F}_{n+1}$$
$$\mathbf{C}_{n+1} = \mathbf{J}_{n+1}^{-2/3} \mathbf{C}_{n+1}$$



- $S_{n+1}$  at  $t_{n+1}$  is determined uniquely via associated constitutive relation

$$S_{n+1} = [S_{\text{iso}}^{\infty} + S_{\text{vol}}^{\infty} + \sum_{\alpha=1}^m Q_{\alpha}]_{n+1}$$

$$S_{\text{vol } n+1}^{\infty} = 2 \frac{\partial \Psi_{\text{vol}}^{\infty}(J_{n+1})}{\partial \mathbf{C}_{n+1}}, \quad S_{\text{iso } n+1}^{\infty} = 2 \frac{\partial \Psi_{\text{iso}}^{\infty}(\bar{\mathbf{C}}_{n+1})}{\partial \mathbf{C}_{n+1}}$$

- All strain measures are known at  $t_{n+1}$



- For  $Q_\alpha$  using the approach followed by (Simo 1987), which bypasses the need for incremental objectivity (frame indifference) during superimposed rigid body motion

- Splitting the convolution integral

$$\int_{t_n}^{t_{n+1}} (\bullet) dt = \int_{0^+}^{t_n} (\bullet) dt + \int_{t_n}^{t_{n+1}} (\bullet) dt$$

$$\begin{aligned} \mathbf{Q}_{\alpha n+1} = & \exp(-t_{n+1}/\tau_\alpha) \mathbf{Q}_{\alpha 0^+} + \int_{t=0^+}^{t=t_n} \exp[-(t_{n+1} - t)/\tau_\alpha] \dot{\mathbf{S}}_{\text{iso } \alpha}(t) dt \\ & + \int_{t=t_n}^{t=t_{n+1}} \exp[-(t_{n+1} - t)/\tau_\alpha] \dot{\mathbf{S}}_{\text{iso } \alpha}(t) dt, \quad \alpha = 1, \dots, m. \end{aligned}$$

# Time integration algorithm



- To simplify we substitute  $\Delta t = t_{n+1} - t_n$

$$\exp[-(\Delta t + \beta)/\tau_\alpha] = \exp(-\Delta t/\tau_\alpha)\exp(-\beta/\tau_\alpha)$$

- $\beta$  takes values  $t_n$  and  $t_n - t$
- Using second order accurate mid point rule on the third term  $t = \frac{t_{n+1} + t_n}{2}$

$$\begin{aligned} \mathbf{Q}_{\alpha n+1} = & \exp(-\Delta t/\tau_\alpha) \left[ \exp(-t_n/\tau_\alpha) \mathbf{Q}_{\alpha 0+} + \int_{t=0+}^{t=t_n} \exp[-(t_n - t)/\tau_\alpha] \dot{\mathbf{S}}_{\text{iso } \alpha}(t) dt \right] \\ & + \exp(-\Delta t/2\tau_\alpha) \int_{t=t_n}^{t=t_{n+1}} \dot{\mathbf{S}}_{\text{iso } \alpha}(t) dt, \quad \alpha = 1, \dots, m. \end{aligned}$$





$$\mathbf{Q}_{\alpha n+1} = \exp(2\xi_{\alpha})\mathbf{Q}_{\alpha n} \\ + \exp(\xi_{\alpha})\beta_{\alpha}^{\infty}(\mathbf{S}_{iso n+1}^{\infty} - \mathbf{S}_{iso n}^{\infty}) \quad , \quad \xi_{\alpha} = -\frac{\Delta t}{2\tau_{\alpha}} \quad ;$$

Dimensionless parameter

- Rearranging and substituting we get,

$$\mathbf{Q}_{\alpha n+1} = \beta_{\alpha}^{\infty}\exp(\xi_{\alpha})\mathbf{S}_{iso n+1}^{\infty} + \mathcal{H}_{\alpha n} \quad , \quad \alpha = 1, \dots, m \quad ,$$

- where

$$\mathcal{H}_{\alpha n} = \exp(\xi_{\alpha})[\exp(\xi_{\alpha})\mathbf{Q}_{\alpha n} - \beta_{\alpha}^{\infty}\mathbf{S}_{iso n}^{\infty}] \quad ,$$

History term determined by Q and S from previous iteration.



- Elastomers consist of polymer networks formed by the cross-linking of highly mobile and flexible polymer chains
- typically characterized by their high compliance and capability of sustaining large deformation
- Non linear stress behaviour
  - Sustain strain upto few hundred percent (Hyperelasticity)
  - Rate dependent behaviour(viscoelasticity)
- Decompose stress
  - Elastic + Inelastic



- Phenomenological model
  - Properties of material defined using strain energy density function
  - Strain invariants and principal stretches
- Models sufficient to describe empirical relationship between stress and strain
  - Lack microstructural justification



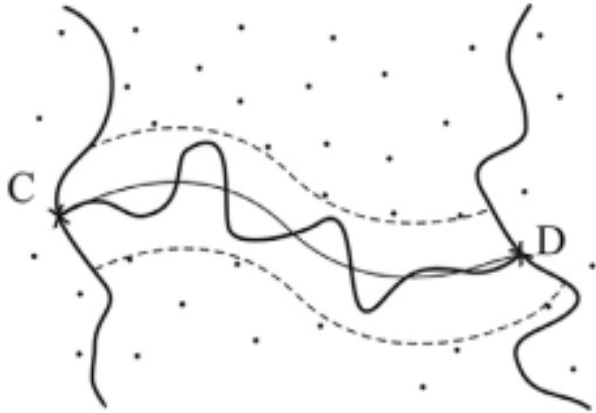
- Directly link macroscopic behaviour to their microstructure
- Considering parameters of polymer physics and chemistry
  - Cross-linking density
  - Molecular weight of monomers
  - Chain extensibility
  - Polymerization degree
  - Amount of entanglement of polymer chains
- Gaussian: chain length  $\ll$  extension limit
- Non-gaussian: chain length approaches maximum extension
- Fail to capture entanglement effects of chain

# Multiplicative decomposition of deformation gradient

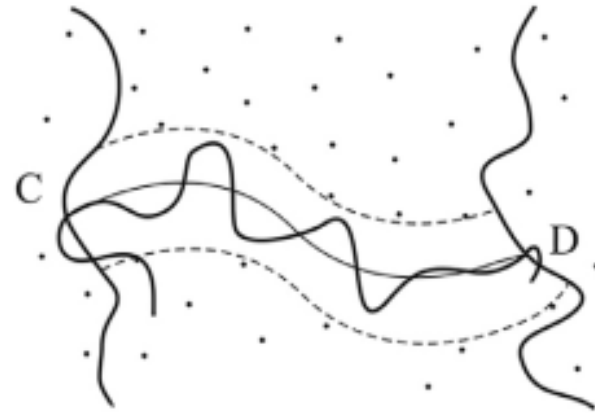


- Stress or strain like internal variable
- Similar to finite deformation plasticity
- Multiplicative decomposition of deformation gradient
- Microstructure details are not reflected by the material parameter
- Capable of qualitatively predicting
  - Time dependent inelastic deformation
  - Stress response of elastomers
- Distinguish between them by
  - Numerical modelling on macroscopic viscoelastic behaviour
  - Fitting to experimental behaviour
- Lack underlying physical mechanism of viscoelasticity

# Polymer Dynamics: Tube model



Cross Linked with chains at C and D



Entanglement with chains at C and D

- Topological constraint: Polymer chain is confined in a tube like region
- Primitive chain: Axis of tube confining chain C-D



- For short time scales
  - motion of polymer chain can be considered as wriggling around its primitive chain
- Wriggling represented by
  - Dia of tube
  - Contour length of primitive chain
  - Motion forgotten once parameters are defined
- For long time scales
  - Polymer chain reptates along the tube
  - Destroying and creating ends of the tube



- Under deformation
  - Ground network sustains elastic stress
  - Inelastic stress is generated by reptation
  - Dia of tube changes significantly
  - Affects the reptation ability and hence relaxation process
- Needs to be developed statistically
  - All parameters have microscopic foundation
  - Obtained by fitting experimental data/ simulation
- cannot be used to capture the energy dissipation during finite deformation





- Micro macro constitutive model
  - Combines continuum mechanics and statistical mechanics
  - Incorporates non-linear viscosity into state of art continuum mechanics
  - Adopts thermodynamic evolution model
  - adopts most of the hyperelastic constitutive equations
  - Captures the relaxation and non-linear viscosity of polymer chains under large deformations
  - Insights into tailoring the microstructure to application



- Elastic ground network
- Subnetwork of different types of polymer chains
- Each subnetwork represents a type of polymer chains with similar diffusion behaviour
- Subnetworks  $B_1 - B_m$  relax with time and dissipate energy
- Deformation gradient is  $\mathbf{F} = \frac{\partial \mathbf{x}}{\partial \mathbf{X}}$
- Since deformation acts on all the polymer network

$$\mathbf{F} = \mathbf{F}_A = \mathbf{F}_{B_n} \quad (n = 1, 2, \dots, M).$$



- For each subnetwork,  $F$  can be decomposed into
  - Elastic Component
  - Inelastic component

$$\mathbf{F}_{B_n} = \mathbf{F}_{B_n}^e \mathbf{F}_{B_n}^i$$

$\mathbf{F}_{B_n}^e \rightarrow$  Deformation gradient of the spring

$\mathbf{F}_{B_n}^i \rightarrow$  Deformation gradient of the damper in the subnetwork



$W_A(F_A)$  &  $W_{B_n}(F_{B_n}^e)$  Helmholtz free energy densities of the spring in ground and sub network respectively

- Total free energy density of the elastomer

$$W(\mathbf{F}_A, \mathbf{F}_{B_1}^e, \mathbf{F}_{B_2}^e, \dots, \mathbf{F}_{B_n}^e) = W_A(\mathbf{F}_A) + \sum_{n=1}^M W_{B_n}(\mathbf{F}_{B_n}^e).$$

- Cauchy stress tensor is given by

$$\mathbf{T} = J^{-1} \frac{\partial W}{\partial \mathbf{F}} \mathbf{F}^T = \mathbf{T}_A + \sum_{n=1}^M \mathbf{T}_{B_n},$$



- Where,

$$J = \det \mathbf{F} \quad \mathbf{T}_A = J^{-1} \frac{\partial W_A(\mathbf{F}_A)}{\partial \mathbf{F}} \mathbf{F}^T \quad \mathbf{T}_{B_n} = J^{-1} \frac{\partial W_{B_n}(\mathbf{F}_{B_n}^e)}{\partial \mathbf{F}} \mathbf{F}^T.$$

- First piola Kirchhoff stress tensor is given by

$$\mathbf{P} = J \mathbf{T} \mathbf{F}^{-T}$$

# Thermodynamic requirement



- free energy of a material system must never increase under isothermal conditions.
  - internal variables of the time-dependent polymer networks must fulfil the entropy inequality

$$\delta G = \int [\delta W(\mathbf{F}_A, \mathbf{F}_{B_1} \mathbf{H}_{B_1}^i, \mathbf{F}_{B_2} \mathbf{H}_{B_2}^i, \dots, \mathbf{F}_{B_n} \mathbf{H}_{B_n}^i) - \mathbf{P} : \delta \mathbf{F}] dV \leq 0,$$

where  $\mathbf{F}_{B_n}^e = \mathbf{F}_{B_n} \mathbf{H}_{B_n}^i$ ,  $\mathbf{H}_{B_n}^i$  is the inverse of  $\mathbf{F}_{B_n}^e$ ,  $\delta G$  is the change of the total free energy, and  $dV$  is the volume of a material particle.

$$\left( \mathbf{P} - \frac{\partial W}{\partial \mathbf{F}} \right) : \delta \mathbf{F} - \sum_{n=1}^M \frac{\partial W}{\partial (\mathbf{F}_{B_n} \mathbf{H}_{B_n}^i)} : \frac{\partial (\mathbf{F}_{B_n} \mathbf{H}_{B_n}^i)}{\partial \mathbf{F}_{B_n}^i} : \delta \mathbf{F}_{B_n}^i \geq 0.$$

$$P = \frac{\partial W}{\partial F} \quad \text{Even when the system is in a non-equilibrium state}$$

$$\sum_{n=1}^M \frac{\partial W}{\partial \mathbf{F}_{B_n}^e} : (\mathbf{F}_{B_n}^e \delta \mathbf{F}_{B_n}^i \mathbf{H}_{B_n}^i) \geq 0$$

# Internal variable evolution equation



- We know that  $P = \frac{\partial W}{\partial F^e_{B_n}} = 2 \frac{\partial W}{\partial C^e_{B_n}} (F^e_{B_n})$   $C^e_{B_n} = (F^e_{B_n})^T F^e_{B_n}$

Material time derivative of internal variable,

$$-\tau_{B_n} : \frac{1}{2} \mathbf{F}_{B_n} \frac{d[(\mathbf{C}^i_{B_n})^{-1}]}{dt} (\mathbf{F}_{B_n})^T (\mathbf{b}^e_{B_n})^{-1} \geq 0$$

Where,

$$\tau_{B_n} = 2 \mathbf{F}^e_{B_n} \frac{\partial W}{\partial \mathbf{C}^e_{B_n}} (\mathbf{F}^e_{B_n})^T, \mathbf{b}^e_{B_n} = \mathbf{F}^e_{B_n} (\mathbf{F}^e_{B_n})^T \text{ and } \mathbf{C}^i_{B_n} = (\mathbf{F}^i_{B_n})^T \mathbf{F}^i_{B_n}$$

- Load is applied simultaneously to all networks simultaneously
- Relaxation of different subnetwork is independent of each other



- A sufficient condition for fulfilling the inequality is that the internal variable satisfy the thermodynamic evolution equation

$$-\frac{1}{2}\mathbf{F}_{B_n}\frac{d\left[(\mathbf{C}_{B_n}^i)^{-1}\right]}{dt}(\mathbf{F}_{B_n})^T(\mathbf{b}_{B_n}^e)^{-1} = \gamma^{-1} : \tau_{B_n},$$

*where  $\gamma^{-1}$  takes the form*

$$\gamma^{-1} = \frac{1}{2\eta_{B_n}}\left(\mathbf{I}^4 - \frac{1}{3}\mathbf{I} \otimes \mathbf{I}\right).$$

$\eta_{B_n}$  is the viscosity of the individual polymer subnetwork





$$\Psi = C_{10}(I_1^* - 3) + C_{01}(I_2^* - 3) + \frac{\kappa}{2}(J - 1)^2.$$

- Linear dependence on first and second invariance
- applicable for small strains only
- Cannot capture strain hardening or softening
- Lack of frequency dependence
- Parameters lack physical basis



$$U = \frac{\mu_1}{2}(I_1 - 3) + \frac{K_1}{2}(J - 1)^2$$

- $\mu$  and  $k$  are material parameters
- For small strain, they are shear and bulk modulus respectively
- $\mu = NkT$ ; where  $N$  is the number of polymer chains per unit volume,  $k$  is the Boltzmann constant, and  $T$  is temperature.
- Limited compressibility
- Does not account for variation in Material parameters with strain rate
- Not suitable for finite deformation



$$\bar{U} = \sum_{i=1}^N \frac{2\mu_i}{\alpha_i^2} (\lambda_1^{\alpha_i} + \lambda_2^{\alpha_i} + \lambda_3^{\alpha_i} - 3) + \frac{K_1}{2} (J - 1)^2$$

where  $\bar{\lambda}_i = \lambda_i / J^{1/3}$  and  $\mu_i, \alpha_i, K$  are material properties.

- Stretch based
- Modified principle stretches associated with volume changing deformations
- Choices of independent variable complicate the mathematical analysis associated with it
- Versatile (compressible and incompressible material)
- Highly parameterisable
- Suitable for finite deformation; high strain range
- Limited capture of nonlinearities
- Parameters does not have physical basis
- Can be reduced to Rivlin-Mooney



- Singularity when the first invariant of the left Cauchy-Green deformation tensor reaches a limiting value
- Finite stretchability
- Accounts for chain extensibility

$$\bar{U} = -\frac{GJ_{lim}}{2} \ln\left(1 - \frac{\bar{I}_1 - 3}{J_{lim}}\right) + \frac{1}{D_1} (J - 1)^2$$

Shear modulus (input)

Extensibility (input)

Equal to  $\frac{2}{K}$  (input)



$$\sigma_{ij} = \frac{1}{J} F_{ik} \frac{\partial W}{\partial F_{kj}}$$



- The viscosity  $\eta_{B_n}$  of subnetwork  $B_n$  must be constitutively prescribed to obtain inelastic deformation
- viscosity of a polymer network can be expressed in terms of the shear relaxation modulus  $G_n$

$$\eta_{B_n} = \int_0^{\infty} G_n dt.$$

- Relaxation of elastomers originate from the polymer chains  $B_1 \dots B_n$

# Non-linear viscosity of free chains



- For short time scale ( $t < t_e$ )
  - Diffusion of the polymer chain can be represented as Brownian motion
- For ( $t = t_e$ )
  - Brownian motion restricted by topological constraint (tube region)
- For ( $t > t_e$ )
  - Due to restriction on the tube, the polymer chain starts to reptate and disengages from the original tube
- Assuming smooth transition from rouse behaviour to reptation behaviour,  $G$  in terms of polymer structure parameter

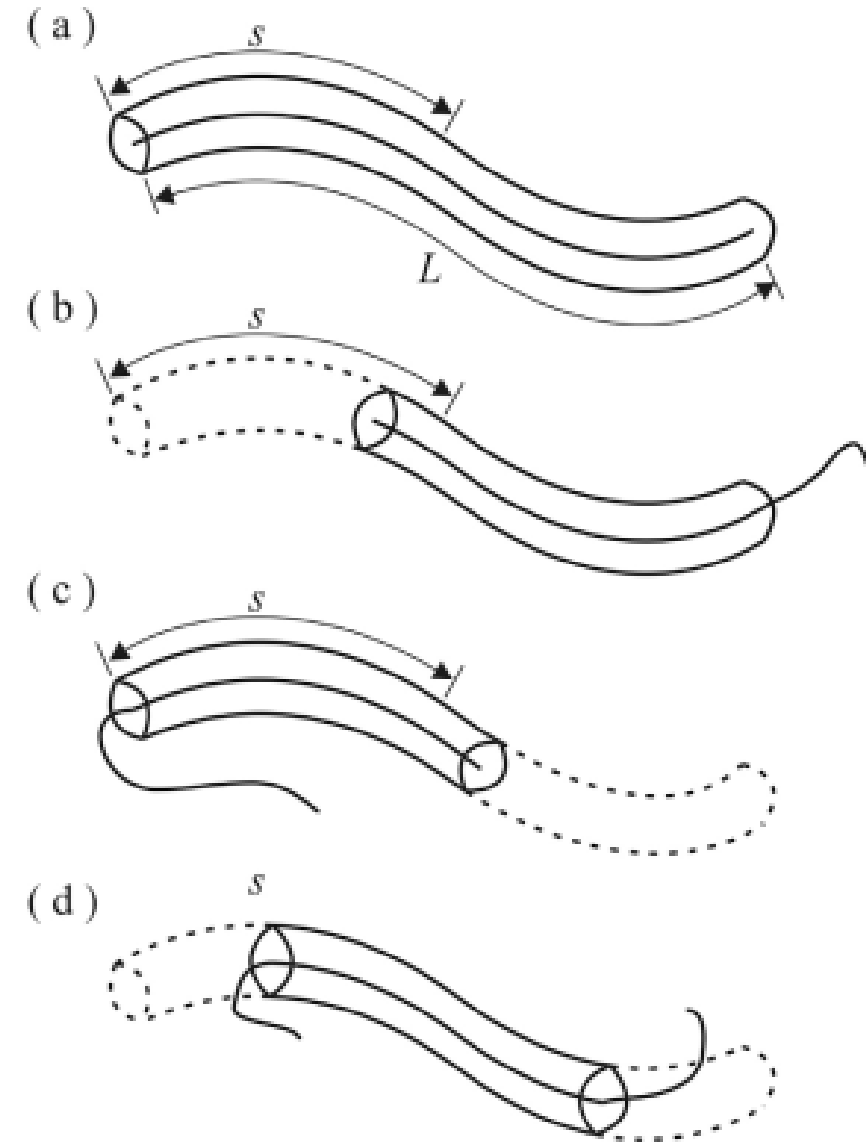
$$G_n^0 \cong G_n(\tau_n^e) \cong n_{B_n} k_B T \left( \frac{\tau_n^e}{\tau_n^R} \right)^{1/2},$$

where  $n_{B_n}$  is the number of chains per unit volume in subnetwork  $B_n$ ,  $k_B$  is the Boltzmann constant,  $T$  is the temperature,  $\tau_n^R$  is the relaxation time of the contour length of the primitive chain

# Non-linear viscosity of free chains



- During reptation
  - Parts of chain disengage from tube
  - Only the parts still confined in the tube contribute to the stress
  - The relaxation modulus  $G_n$  is proportional to the fraction  $\varphi(t)$  of the chain still confined in the tube at time  $t$  (i.e.  $G_n(t) = G_n^0(t)$ )
- We define  $(s)$  as the contour position of the segment on the primitive chain and  $\psi(\xi, t; s)$  as the probability that the primitive chain moves  $\xi$  while its ends have not reached the segment  $(s)$  of the original tube







- $\psi(\xi, t; s)$  must satisfy the one dimensional diffusion equation

$$\frac{\partial \Psi}{\partial t} = D_c \frac{\partial^2 \Psi}{\partial \xi^2},$$

- $D_c$  is the diffusion coefficient of the polymer chain
- When  $\xi = s$ , segment  $s$  disengages from the original tube and  $\psi(\xi, t; s) = 0$
- Similarly  $\psi(\xi, t; s) = 0$  when  $\xi = s - L$ , where  $L$  is contour length of the primitive chain at time  $t$
- The solution using the boundary conditions

$$\Psi(\xi, t; s) = \sum_{p=1}^{\infty} \frac{2}{L} \sin\left(\frac{p\pi s}{L}\right) \sin\left[\frac{p\pi(s - \xi)}{L}\right] \exp\left(\frac{-p^2 t}{\tau_n^d}\right)$$

# Non-linear viscosity of free chains



- Where  $\tau_n^d$  is the disengagement time of the free chain
  - Time needed for complete disengagement of the polymer chain from the tube it is confined or finish the relaxation process
- Fraction of chain confined in the tube at time (t)

$$\varphi(t) = \frac{1}{L} \int_0^L \int_{s-L}^s \Psi(\xi, t; s) d\xi ds.$$

- Combining, we get

$$\eta_{B_n} = \int_0^\infty G_n^0 \varphi(t) dt = \frac{\pi^2}{12} G_n^0 \tau_n^d.$$

- where

$$\tau_n^d = \frac{\zeta N_{B_n}^3 b_0^4}{\pi^2 k_B T \langle a_n \rangle^2}$$

$a_n \rightarrow$  Tube diameter

$\zeta \rightarrow$  monomer friction coefficient

$N_{B_n} \rightarrow$  Polymerisation degree of network  $B_n$

$b_0 \rightarrow$  effective bond length between monomers

# Non-linear viscosity of free chains



- $a_n$  of the tube and primitive chain length are assumed to be unchanged under deformation (Doi and Edwards 1986)
  - Which yields a constant  $\tau_n^d$
  - Works well for small deformations

- To capture the nonlinear viscosity under finite deformation
  - The primitive chain length  $L$  must change with macroscopic deformation
  - Average over all possible initial tangent vectors  $\mathbf{u}_0$  is formulated as

$$\langle L \rangle = \int \frac{|\mathbf{F} \cdot \mathbf{u}_0|}{4\pi} L_0 d^2 \mathbf{u}_0,$$

- The mean diameter ( $a_n$ ) also changes with deformation
  - Linked to mean square end-to-end distance of the primitive chain
- Assumptions have been verified using molecular dynamics simulation

$$(a_n) = \frac{(R_{ee}^2)}{(L)}$$



- In this model, the disengagement time  $\tau_n^d$  in the equation of viscosity varies with macroscopic deformation
- Leading to non-linearity of viscosity
- Here, the mean square end-to-end distance of the primitive chain is calculated as

$$\langle \mathbf{R}_{ee}^2 \rangle = \int |\mathbf{F} \cdot \mathbf{R}|^2 f_0(\mathbf{R}) d^3 R,$$

- $f_0(\mathbf{R})$  is the statistical distribution function on end-to-end vector  $\mathbf{R}$  of the primitive chain in reference state

# Non-linear viscosity of free chains



- Assumed that the primitive chain in the current state is deformed in the same way as the microscopic deformation therefore,

$$\frac{\langle a_n \rangle}{a_0} = \frac{\int |\mathbf{F} \cdot \mathbf{R}|^2 f_0(\mathbf{R}) d^3 R}{\langle \mathbf{R}_{ee}^2 \rangle_0 \int \frac{|\mathbf{F} \cdot \mathbf{u}_0|}{4\pi} d^2 \mathbf{u}_0}, \quad (\mathbf{R}_{ee}^2)_0 = \int |\mathbf{R}|^2 f_0(\mathbf{R}) d^3 R$$

- $a_n$  = diameter in the primitive chain
- $(\mathbf{R}_{ee}^2)_0$  = mean square end-to-end vector of the primitive chain in the reference state
- Substituting in the equation for non-linear viscosity

$$\eta_{B_n} = \frac{\eta_n}{\alpha(\mathbf{F})^2}, \quad \eta_n = \frac{\zeta n_{B_n}^4 b_0^4}{12 a_0^2} \left( \frac{\tau_{R_n}}{\tau_{en}} \right)^{1/2}, \quad \alpha(\mathbf{F}) = \frac{\int |\mathbf{F} \cdot \mathbf{R}|^2 f_0(\mathbf{R}) d^3 R}{\langle \mathbf{R}_{ee}^2 \rangle_0 \int \frac{|\mathbf{F} \cdot \mathbf{u}_0|}{4\pi} d^2 \mathbf{u}_0}$$

Viscosity in reference state

Dimensionless parameter



- Helmholtz free energy density functions must be specified first
- $W_A(F_A)$  Governed by elastic ground network of the polymer
  - Should be able to capture elastic response of the elastomer
  - Material parameters can be obtained by fitting them to quasi-static experiments
- The material parameters of  $W_A(F_{B_n}^e)$  can be determined by fitting them to loading-unloading experiments conducted at different strain rates
- Considering homogenous isochoric deformation  $\det \mathbf{F}_A = \det \mathbf{F}_{B_n} = \det \mathbf{F}_{B_n}^e = \det \mathbf{F}_{B_n}^i = 1$ .

$$\mathbf{F}_A = \mathbf{F}_{B_n} = \mathbf{F}_{B_n}^e \mathbf{F}_{B_n}^i = \begin{bmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{bmatrix}, \mathbf{F}_{B_n}^e = \begin{bmatrix} \lambda_{1_n}^e & 0 & 0 \\ 0 & \lambda_{2_n}^e & 0 \\ 0 & 0 & \lambda_{3_n}^e \end{bmatrix}, \mathbf{F}_{B_n}^i = \begin{bmatrix} \lambda_{1_n}^i & 0 & 0 \\ 0 & \lambda_{2_n}^i & 0 \\ 0 & 0 & \lambda_{3_n}^i \end{bmatrix},$$

# Honeywell project: Gel preparation



- Prepared 36 Gel samples replicating bird material
- Cut 75 mm dia plastic tubes with 180 mm length
  - To be used as a mould
  - Prepare wheat dough with a dry consistency for sealing
  - Spread the dough 10mm thick on a rigid tray
  - Stick the pipes in dough to obtain a proper seal
  - Spray silicon nitride to prevent gel from sticking to the pipe
- Prepared gel with  $1000 \text{ kg/m}^3$  density
  - 10 % Gelatine (w/w)% in water
  - Mix thoroughly and let it sit for 1-2 hours
  - Heat the beaker in water bath maintaining  $55 \pm 5 \text{ }^\circ\text{C}$  until homogenous solution is obtained
  - Pour the solution in the pipes till 155mm height from dough surface
  - Refrigerate at  $5\text{-}15 \text{ }^\circ\text{C}$  for 18 to 36 hours



- Mould removal
  - Dip the cast in warm water briefly
  - Use a long thin metal wire to slowly debond the curved surface of the pipe
  - Gently apply pressure from free end to obtain the required gel cylinder
- Helped in the initial setup of the
  - Strain gauge
  - Gas gun
  - Barrel
  - Momentum trap