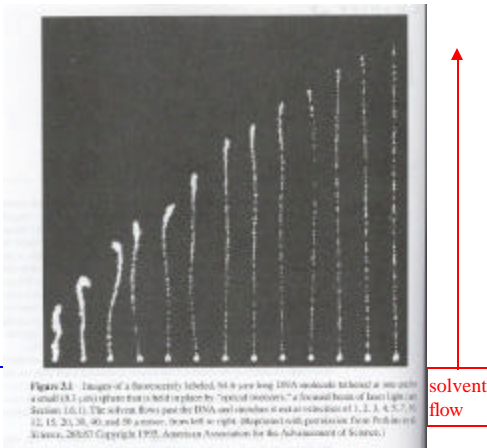


Molecular Origins of Viscoelasticity

Polymer molecules are stretchable even in slow flows.

One end of a DNA molecule held stationary



solvent flow

Effect of stretchable molecules on bulk properties

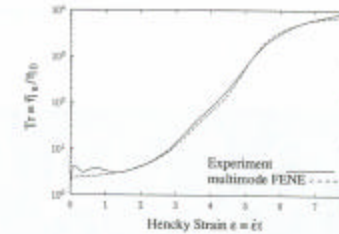


Figure 3.2 Trouton ratio, Tr , of uniaxial extensional viscosity η_u , to zero-shear viscosity η_0 after start-up of steady uniaxial extension at a rate of $\dot{\epsilon} \approx 1 \text{ sec}^{-1}$ for a "Boger fluid" consisting of a 0.185 wt% solution of flexible polyisobutylene ($M_w = 2.11 \times 10^6$) in a solvent composed mostly of viscous polybutene with some added ketone (solid line). The dashed line is a fit of a "multimode" FENE dumbbell model, where each mode is represented by a FENE dumbbell model, with a spring law given by Eq. (3-56), without preaveraging, as described in Section 3.6.2.2.1. The relaxation times were obtained by fitting the linear viscoelastic data, $G'(\omega)$ and $G''(\omega)$. The slowest mode, with $\tau_1 = 5 \text{ sec}$, dominates the behavior at large strains; the best fit is obtained by choosing for it an extensibility parameter of $B = 40,000$. The value of $B = 3L^2/(R^2)$, $= 3(0.82)^2\eta/C_{\infty}$, predicted from the molecular characteristics, is around 20,000. This value is obtained using $n = M_w/28 = 75,000$ backbone bonds and $C_{\infty} = 6.8$ (see Table 3-3). (From Verhoef et al. (1997), with kind permission from Elsevier Science - NL, Sara Burgerhartstraat 25, 1055 KV Amsterdam, The Netherlands.)

Molecular origins of viscoelasticity

Entanglements:
Topological interactions that prevent polymer chains from moving very far perpendicular to their contours.

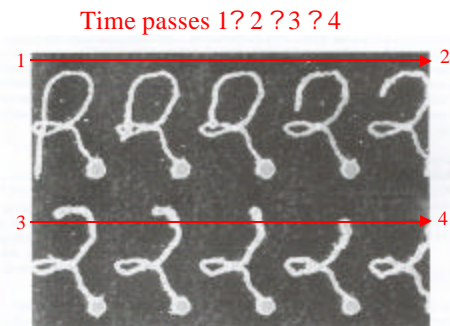


Figure 3.3 Time sequence of images showing retraction of one end of a fluorescent 90-pair-long DNA molecule entangled in a solution of other, non-fluorescing DNA molecules. The fluorescent molecule was attached at one end to a small sphere that was pulled through the solution using a laser-optical trap, to form the letter R. The free end then retracts through a "tube-like" region formed by the surrounding mesh of other, invisible DNA chains. (Reprinted with permission from the cover of Science, May 6, 1994. Copyright 1994, American Association for the Advancement of Science.)

Effect of entanglements on viscoelasticity

Entanglements prevent significant lateral movements of an entangled polymer chain. Therefore in order to relax stress the only motion that is available to a polymer molecule is along its own contour. This reptation along its contour is very slow and the bulk viscosity is very high.

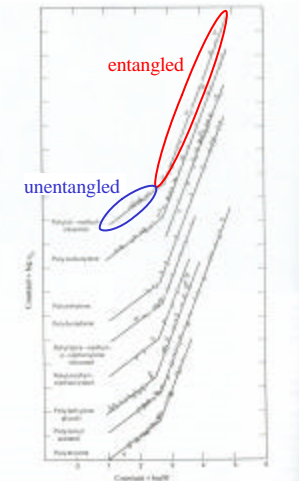


Figure 3.4 Relationship between compliance viscosity and molecular weight for several entangled polymer marks. The curves are shifted along the x-axis after dividing both the abscissa and ordinate. (From Berry and Fox, 1968, reprinted with permission from Springer, Berlin.)

Mechanical stress and molecular orientations

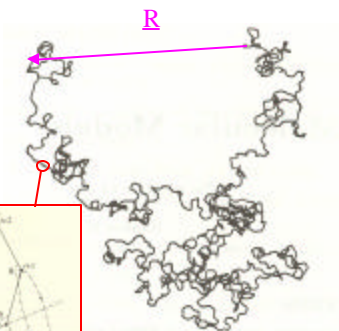
Mechanical stress is the bulk manifestation of anisotropies in molecular orientations. The contribution of a molecule to the total stress increases as the degree of orientation and stretch increases. Therefore in order to calculate the stress from molecular information we must know the conformations of all of the molecules.

The bulk mechanical stress is the sum of all of the contributions of all of the molecules in the system. Closed-form molecular models always result from considering an approximate average behavior or finding an average of all the possible behaviors.

Equilibrium Conformation

At equilibrium (i.e. in the absence of flow) polymer molecules prefer to adopt a random coil configuration.

$\underline{\mathbf{R}}$ is the end to end vector. The molecule is continually moving and $\underline{\mathbf{R}}$ is continually changing. We can define a time-averaged-mean-square-end-to-end distance: $\langle R^2 \rangle_0 = \langle \underline{\mathbf{R}} \cdot \underline{\mathbf{R}} \rangle_0$



Adjacent bonds are restricted to a particular angle. The angle between two nonadjacent bonds can take on any value as long as there are ~10 or more adjacent bonds in between them.



Freely Jointed Chain

We can model a polymer chain as a freely jointed chain as long as sufficient backbone bonds are included in each link for the angle between two adjacent links to be unrestricted.

Khun Length, b_K : common choice for the link length

$b_K = \frac{C_\infty}{0.82} \ell$ where C_∞ is a monomer chemistry dependant parameter (ranges between 5-10) and ℓ is the length of one bond ($\sim 1.54 \text{ \AA}$).

Mean-square-end-to-end-distance:

$\langle \underline{\mathbf{R}}^2 \rangle_0 = N_K b_K^2$ where N_K is the number of links in the chain and is related to the molecular weight of the chain.

$N_K = \frac{(0.82)^2}{C_\infty} n = \frac{(0.82)^2}{C_\infty} j \frac{M}{M_0}$ where n is the number of backbone bonds in the molecule, j is the number of backbone bonds per monomer, M is the molecular weight of the molecule, and M_0 is the molecular weight of the monomer.

Freely Jointed Chain Continued

Root-mean-square-radius of gyration: Root-mean-square average distance separating a monomer from the center of mass of the molecule.

$$R_g = \frac{\langle \underline{\mathbf{R}}^2 \rangle_0^{1/2}}{\sqrt{6}}$$

Equilibrium configuration distribution function for a Gaussian chain:

$$\psi_0(\underline{\mathbf{R}}) \equiv \left(\frac{\beta}{\sqrt{\pi}} \right)^3 \exp(-\beta^2 \underline{\mathbf{R}} \cdot \underline{\mathbf{R}})$$

$$\beta^2 \equiv \frac{3}{2N_K b_K^2}$$

The probability that if one end of the chain is at the origin the other end is at a position between $\underline{\mathbf{R}}$ and $\underline{\mathbf{R}} + d\underline{\mathbf{R}}$ is: $\psi_0(\underline{\mathbf{R}}) dR_1 dR_2 dR_3$

The number of configurations that can have end-to-end vector $\underline{\mathbf{R}}$ at equilibrium is Ω :

$$\Omega = c \psi_0(\underline{\mathbf{R}}) \quad \text{where } c \text{ is a constant.}$$

Relation between stress and molecular configuration

Look back at extra stress tensor: The molecular tension force, $\tilde{\underline{f}}$, acting on an arbitrary surface dA with unit normal, $\hat{\underline{n}}$, is:

$\tilde{\underline{f}} = -dA \hat{\underline{n}} \cdot \underline{\tau}$ This tension force results from the deformation of the polymer chains away from the random coil shape. The tension force due to one chain is:

$$\underline{F} = 2k_B T \beta^2 \underline{R}$$

Therefore a Gaussian chain acts like a Hookean spring with the force proportional to the displacement.

Relation between stress and configuration

Consider a cube of unit volume containing v chains. One of the surfaces is dA with a unit normal, $\hat{\underline{n}}$.

$$\tilde{\underline{f}} = \iiint (\hat{\underline{n}} \cdot \underline{R}) (v \psi(\underline{R}) dR_1 dR_2 dR_3) \underline{F}$$

tension force on unit surface dA due to all polymer chains

probability that a chain with end-to-end vector \underline{R} intersects surface dA .

number of chains in cube with end-to-end vectors between \underline{R} and $\underline{R}+d\underline{R}$.

tension force due to one chain of end-to-end vector \underline{R}

Where $\psi(\underline{R})$ is a non-equilibrium configuration distribution function.

$$\underline{\tau} = -2k_B T \beta^2 v \langle \underline{R} \underline{R} \rangle$$

Rubber Elasticity Theory

Consider an ideal crosslinked network in which, between each 2 crosslinks there is a polymer strand that can be represented by a freely jointed chain of N_K steps of length b_K . At equilibrium (i.e. at time t' before deformation) each strand is characterized by the same configuration distribution.

Realistic rubber network structure:



Figure 5.8 Schematic of a cross-linked polymer network. (Reprinted from Flory-Ciffo di Gennaro, *Scaling Concepts in Polymer Physics*, Copyright © 1979, by Cornell University. Used by permission of the publisher, Cornell University Press.)

Elongational deformation of an ideal polymer network

Inverse deformation gradient tensor:

$$\underline{\underline{F}}^{-1} = \begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{pmatrix}$$

where λ_i are the elongation ratios in the three coordinated directions

Assume that the deformation is affine: This means that the crosslinks all follow the macroscopic deformation and therefore the macroscopic deformation can be applied to the microscopic motion. Then the elongation ratios relate the end-to-end vectors before (\underline{R}_i') and after (\underline{R}_i) deformation:

$$\lambda_i = \frac{R_i}{R_i'} \quad \text{and} \quad \underline{R}(t) = \begin{pmatrix} \lambda_1 R_1' \\ \lambda_2 R_2' \\ \lambda_3 R_3' \end{pmatrix} = \text{end-to-end vector after deformation}$$

Non-equilibrium configuration distribution function for affine deformation of an ideal polymer network

Every strand with initial end-to-end vector \underline{R}' will map to a deformed state with end-to-end vector \underline{R} . (This is a consequence of affine deformation) Therefore the probability that the end-to-end vector of a strand in the deformed state is between \underline{R} and $\underline{R} + d\underline{R}$ is given by the equilibrium distribution function:

$$\left(\begin{array}{l} \text{probability of end to} \\ \text{end vector between } \underline{R} \\ \text{and } \underline{R} + d\underline{R} \end{array} \right) = \psi(\underline{R}) dR_1 dR_2 dR_3 = \psi_0(\underline{R}') dR'_1 dR'_2 dR'_3$$

$$\psi(\underline{R}) = \left(\frac{\beta}{\sqrt{\pi}} \right)^3 \exp \left[-\beta^2 \sum_{i=1}^3 \left(\frac{R_i}{\lambda_i} \right)^2 \right]$$

Stress tensor for affine deformation of an ideal polymer network

$$\begin{aligned} \underline{\tau} &= -\frac{3kTv}{Na^2} (\underline{R} \underline{R}) \\ &= -\frac{3kTv}{Na^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \underline{R} \underline{R} \psi(\underline{R}) dR_1 dR_2 dR_3 \\ &= -vkT \lambda_i^2 \hat{e}_i \hat{e}_i \end{aligned}$$

Finger tensor for elongation: $\begin{pmatrix} \lambda_1^2 & 0 & 0 \\ 0 & \lambda_2^2 & 0 \\ 0 & 0 & \lambda_3^2 \end{pmatrix} = \underline{C}^{-1}$

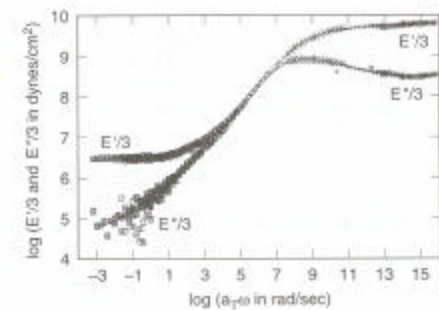
General constitutive equation for affine deformation of an ideal polymer network:

$$\underline{\tau} = -vk_B T \underline{C}^{-1}$$

This is the same as the finite strain version of Hooke's law with the modulus $G = vk_B T$.

Comments on the Ideal Rubber Elasticity Theory

- Describes a purely elastic material, i.e. $G'(\omega) = G = \text{constant}$ and $G''/G' = 0$
- We only see this behavior with cross linked rubbers at low frequencies.
- At higher frequencies G' is frequency dependant and $G''/G' \sim 1$. This behavior occurs because the strands between cross-links are not able to relax their conformations fast enough to keep up with the imposed deformation.



Storage and loss moduli for a cross-linked polyurethane rubber. Small amplitude oscillatory elongation was performed and results were converted to shear moduli, $G' = E'/3$ and $G'' = E''/3$.

Temporary Network Model

Green and Tobolsky

Intended for polymer melts but can be used for elastic rubbers at high rates or frequencies. Polymer chains are restrained by temporary junctions that spontaneously break and reform allowing relaxation of non-equilibrium conformations. The average concentration of junctions, ν , is constant. (In a polymer melt the junction points are physical entanglements)

Assumptions:

- during deformation each strand is stretched affinely until it breaks free from a junction point
- when it breaks free it relaxes to an equilibrium conformation
- as often as one strand breaks free and relaxes another strand becomes rejoined to the network

Green-Tobolsky Model

$$\underline{\underline{\tau}} = \int_{-\infty}^t m(t-t') \underline{\underline{C}}^{-1}(t', t) dt'$$

where

$$m(t-t') = \frac{G}{\lambda} \exp[-(t-t')/\lambda]$$

where

$$G = \nu k_B T$$

and $1/\lambda$ = rate at which junctions break apart

Polymer Solutions

If a high molecular weight polymer is dissolved in a solution the viscosity of the solution increases approximately linearly with concentration at low concentrations. At higher concentrations it increases much more quickly. The critical concentration is called the **overlap concentration** and it is the minimum concentration for entanglements to exist.

$$1 = \nu R_g^3 = \frac{c^* N_A}{M} \left(\sqrt{\frac{N_K}{6}} b_K \right)^3$$

coils per unit volume

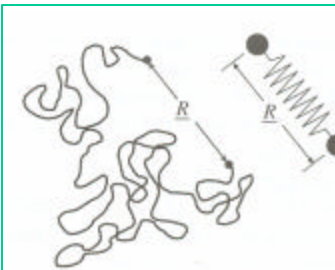
volume of one coil

Applies only at theta conditions where the solvent does not swell the polymer coil.

$$c^* = \left(\frac{6M_0}{jC_\infty} \right)^{3/2} \frac{1}{N_A M^{1/2} \ell^3}$$

Elastic Dumbbell Model

Applies for dilute solutions (i.e. $c \ll c^*$)



The polymer coil is modeled as two beads connected by a spring. The beads account for the viscous forces and the spring accounts for the elastic forces. The forces that cause the spring to stretch are the solvent drag force on the bead and the Brownian motion force caused by collisions between solvent molecules and the chain. These forces are resisted by the restoring force of the spring.

This model gives the upper-convected Maxwell model if the solvent effects on stress are neglected and the Oldroyd-B model if solvent effects on stress are included.

Elastic Dumbbell Model

With solvent contribution:

$$\underline{\underline{\tau}} + \lambda \underline{\underline{\dot{\tau}}} = -[G\lambda + \eta_s] \underline{\underline{\dot{\gamma}}} - \lambda \eta_s \underline{\underline{\dot{\gamma}}}$$

Without solvent contribution:

$$\underline{\underline{\tau}} + \lambda \underline{\underline{\dot{\tau}}} = -G\lambda \underline{\underline{\dot{\gamma}}}$$

Where:

$$\lambda = \frac{\zeta}{8k_B T \beta^2} \quad \zeta = \text{bead friction coefficient}$$

$$G = \nu k_B T \quad \nu = \text{number of dumbbells per unit volume}$$

$$\eta_s = \text{solvent viscosity} \quad \beta = \text{randomwalk parameter}$$

Rouse Model

Extension of the Dumbbell model where each molecule is represented by several springs and beads.



Assumptions:

- does not include effects of entanglements or any other physical restrictions between chains (ie. applies to dilute solutions of low molecular weight melts, also to high molecular weight melts at time scales faster than reptation dynamics)
- coil has a Gaussian equilibrium distribution of conformations
- deformations are not so severe that they distort the chain beyond the limit of Gaussian behavior
- frictional drag of a bead is proportional to the difference between the velocity of the bead and the ambient velocity of the solvent
- hydrodynamic interactions are neglected
- Brownian forces keep each bead in thermal equilibrium with the solvent

Rouse Constitutive Equation

$$\underline{\underline{\tau}}_i + \lambda \underline{\underline{\dot{\tau}}}_i = -G_i \lambda_i \underline{\underline{\dot{\gamma}}}$$

where

$$\underline{\underline{\tau}} = \sum_{i=1}^N \underline{\underline{\tau}}_i \quad G_i = G = \nu k_B T \quad \lambda_i \equiv \frac{\zeta_0 N^2 b^2}{6\pi^2 i^2 k_B T}$$

ζ_0 = drag coefficient per monomer

N = number of monomers per chain

b = statistical segment length

ν = number of chains per unit volume

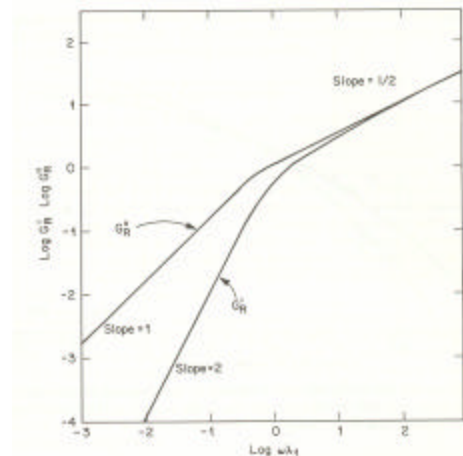
This theory applies to a monodisperse polymer.

Rouse Model Predictions

$$G'_R = \frac{G'}{\nu k_B T}$$

$$G''_R = \frac{G''}{\nu k_B T}$$

$$\lambda_1 = \frac{\zeta_0 N^2 b^2}{6\pi^2 k_B T}$$



Entangled Polymers: melts and concentrated solutions

Complication: entanglements are very important

Simplification: chain configuration distribution really is Gaussian, hydrodynamic interactions are not important

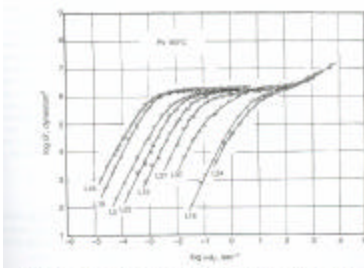


Figure 3.22 Storage modulus, G' , as a function of frequency obtained on 1.00°C for nearly monodisperse polyisobutylene of molecular weight ranging from 560,000 to 47,000, from left to right. (Reprinted with permission from Chang et al., *Macromolecules* 1:181, Copyright 1978, American Chemical Society.)

- plateau in G' that broadens as molecular weight increases
- entanglement plateau modulus: G_N
- Over the frequency range of the plateau, the melt behaves as a cross-linked rubber with a constant modulus
- molecular weight where plateau in G' begins to occur is $\sim M_c$ which is the critical molecular weight for η_0 – M_w relationship

Tube Theory



Real situation: each polymer molecule is entangled with many other molecules

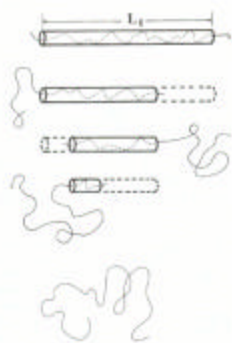


Simplification: represent the system by a single test chain surrounded by a tube that represents all of the other chains

Reptation

For linear, entangled chains the primary mechanism for relaxation within the tube is reptation. Reptation is a diffusive movement of the chain through its tube.

time passes



Initially the chain is constrained within its tube.

The chain slides along its contour in one direction, the portion of the tube that is vacated is forgotten and the stress maintained by this portion of the chain is relaxed. The chain then moves in the opposite direction and forgets about more of its tube.

This continues until the entire original tube has been forgotten about and the chain has obtained an equilibrium configuration.

Doi-Edwards LVE constitutive equation

Linear relaxation modulus: Equations on this slide are from Likhtman and McLeish, *Macromolecules*, 2002, 35, 6332-6343

$$G(t) = G_e \sum_{p, \text{ odd}} \frac{8}{\pi^2 p^2} \exp\left(-\frac{p^2 t}{\tau_{d0}}\right)$$

where

$$\tau_{d0} = \text{reptation time} = \frac{(M/M_e)^3 (M_e/M_0)^2 \zeta b_K^2}{\pi^2 k_B T}$$

$$G_e \equiv \frac{5}{4} G_N^0$$

$$M_e = \frac{\rho R T}{G_e} \equiv \frac{4}{5} \frac{\rho R T}{G_N^0}$$

Zero shear viscosity:

$$\eta_0 = \int_0^{\infty} G(t) dt = \frac{8 G_e \tau_{d0}}{\pi^2} \sum_{p, \text{ odd}} \frac{1}{p^4}$$

Limit on sum, p^* :

$$p^* \equiv \sqrt{\frac{M}{10 M_e}}$$

Doi-Edwards NLVE constitutive eqn

K-BKZ type constitutive eqn

Factorized
K-BKZ
equation

$$\underline{\underline{\tau}} = \int_{-\infty}^t M(t-t') \left[2 \frac{\partial U}{\partial I_2} \underline{\underline{C}}(t, t') - 2 \frac{\partial U}{\partial I_1} \underline{\underline{C}}^{-1}(t', t) \right] dt'$$

where

$$M(t-t') \equiv \frac{dG(t-t')}{dt'}$$

$$U(I_1, I_2) \equiv \frac{5}{2} \ln \left(\frac{J-1}{7} \right)$$

$$J \equiv I_1 + 2(I_2 + 13/4)^{1/2}$$

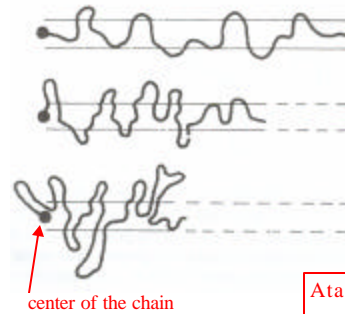
$$I_1 = \text{tr}(\underline{\underline{C}}^{-1})$$

$$I_2 = \text{tr}(\underline{\underline{C}})$$

Nonreptative relaxation mechanisms

Primitive path fluctuations (aka contour length fluctuations):

Consider one half of a chain in its tube at times shorter than the reptation time. At these time scales the chain cannot release stress by reptating.



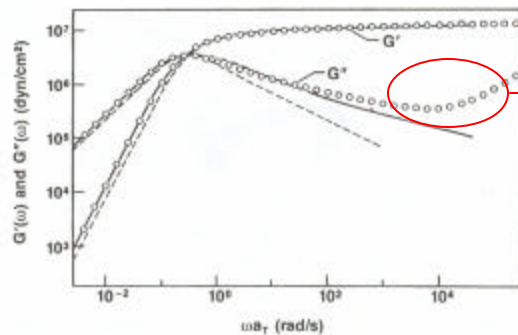
A primitive path fluctuation occurs when the end of the chain is randomly pulled towards the center of the chain. The portion of the tube that is vacated is forgotten about and when re-extended the end of the chain can take on its equilibrium configuration.

Initial time scale for CLF:

$$\tau(s) = \frac{22\pi}{256} s^4 \left(\frac{M}{M_e} \right)^4 \left(\frac{M_e}{M_0} \right)^2 \frac{\zeta b_K^2}{3k_B T}$$

At a certain time, τ_{df} , reptation will takeover the relaxation process and CLF will no longer occur.

Effect of CLF on Predictions



Upturn in G' is related to Rouse relaxation of entanglement sections within the tube and to reorganization of monomers within the tube.

Points are experimental data for a monodisperse polybutadiene ($M=360,000$ g/mol). Dashed line represents Doi-Edwards prediction (reptation only) and solid line represents reptation + CLF.

Likhtman and McLeish LVE constitutive eqn

Includes reptation and CLF: Equations in this section are from Likhtman and McLeish, *Macromolecules*, 2002, 35, 6332-6343

$$\underline{\underline{G}}(t) = G_e \mu(t)$$

where

$$\mu(t) = \sum_{p=1, \text{ odd}}^{p^*} \frac{8\tilde{G}_f}{\pi^2 p^2} \exp\left(-\frac{p^2 t}{\tau_{df}}\right) + \int_{\tilde{e}^*}^{\infty} \frac{0.306}{Z v_e^4 \epsilon^{3/4}} \exp(-\epsilon t) d\epsilon$$

where

$$Z = \frac{M}{M_e}$$

$$\tau_e = \left(\frac{M_e}{M_0} \right)^2 \frac{\zeta b_K^2}{3\pi^2 k_B T}$$

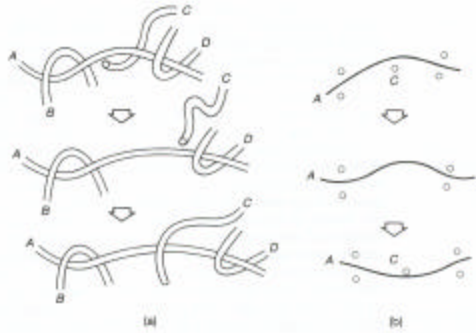
$$\tau_{df} = \text{renormalized reptation time} = \tau_{d0} \left(1 - \frac{2C_1}{\sqrt{Z}} + \frac{C_2}{Z} + \frac{C_3}{Z^{3/2}} \right)$$

$$\tilde{G}_f = \text{renormalized dimensionless plateau modulus} = 1 - \frac{C_1}{\sqrt{Z}} + \frac{C_4}{Z} + \frac{C_5}{Z^{3/2}}$$

$$C_1 = 1.69, C_2 = 4.17, C_3 = -1.55, C_4 = 2.0, C_5 = -1.24$$

Nonreptative relaxation mechanisms

Constraint Release: when the end of one of the surrounding chains (making up the tube) moves past the test chain a constraint on the test chain is released. A portion of the test chain is then free to reorient.



Likhtman and McLeish LVE constitutive eqn

Includes reptation, CLF, constraint release, redistribution of monomers within the tube (aka longitudinal modes relaxation) and Rouse relaxation of the entanglement lengths within the tube: Equations in this section are from Likhtman and McLeish, *Macromolecules*, 2002, 35, 6332-6343

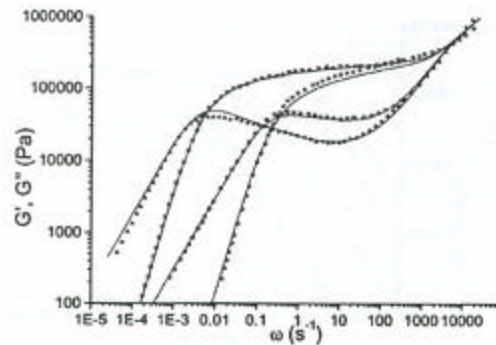
$$G(t) = G_e \left(\frac{4}{5} \mu(t) R(t) + \frac{1}{5Z} \sum_{p=1}^{Z-1} \exp\left(-\frac{p^2 t}{\tau_R}\right) + \frac{1}{Z} \sum_{p=Z}^N \exp\left(-\frac{2p^2 t}{\tau_R}\right) \right)$$

where

$$\tau_R = Z^2 \tau_e$$

$R(t)$ = term representing constraint release. It is similar in shape to $\mu(t)$. To neglect constraint release set $R(t) = 1$.

Performance of the Likhtman-McLeish Constitutive Eqn



Points are for 2 monodisperse polystyrenes of different molecular weights. Curves represent the full L-M constitutive eqn.