Physical Picture for Diffusion of Polymers

- *Low Molecular Weight ($M < M_e$)* chains shown moving past one another.
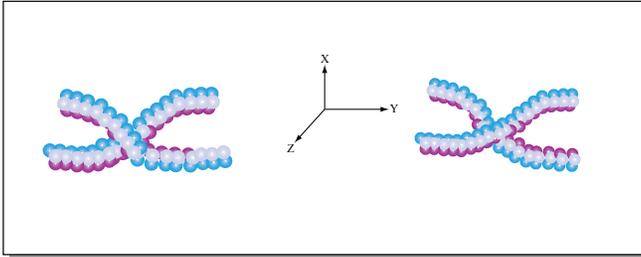
Rouse chains, unentangled

Figure by MIT OCW.

- *High Molecular weight ($M > M_e$)*
- Entanglements in a polymer melt (a short portion of one chain is outlined in bold).
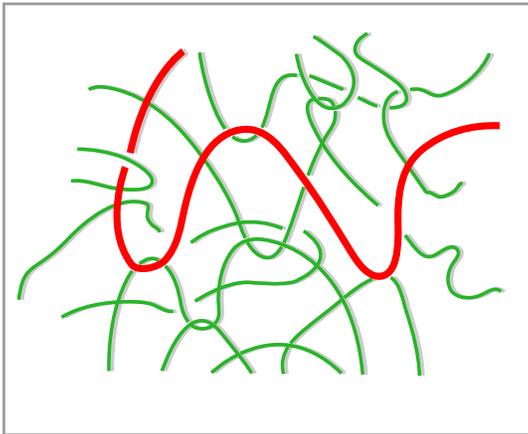- Lateral chain motion is severely restricted by the presence of neighboring chains.

Reptating chains, entangled

- Portion of an effective constraining tube defined by entanglements $\otimes$ about a given chain
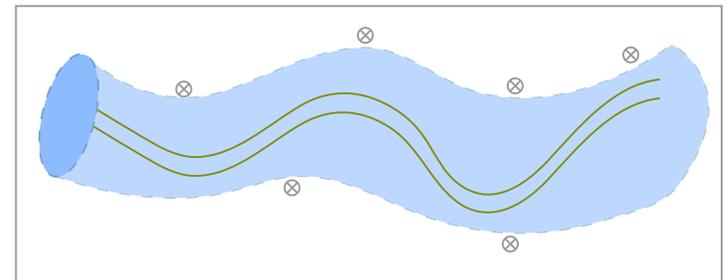
Figure by MIT OCW.

Figure by MIT OCW.

Rouse Chain

- A flexible string comprised of connected Brownian particles that interact with a featureless viscous medium.

- Number of repeat units is less than the entanglement limit, small N, where $N < N_e$

- Viscosity depends on monomeric friction factor ξ_M and x_2

$$\eta \sim \xi \sim \xi_M x_2 \sim M$$

- Diffusivity depends on friction factor via Einstein equation: $D = kT/\xi \sim kT/M$

(Self) Diffusivity Regimes
(Two more scaling laws !)

- Small N or M – Rouse Regime
  - (follows directly from Einstein definition of D)

$$D \sim N^{-1}$$

- Large N or M – Reptation Regime
  - (see derivation in next section)

$$D \sim N^{-2}$$

Reptating Chains

- Key idea: Consider a Rouse chain moving inside a tube defined by the surrounding topological constraints.

- The number of repeat units in the chain is much larger than the entanglement limit, i.e. large N, where $N > N_e$

  In this regime,
  zero shear rate viscosity

  $$\eta_0 \sim M^{3.4}$$

- Basics

  $\langle x^2 \rangle = D\,t$ Fundamental equation of Brownian notion

  $$D = \frac{kT}{\xi}$$ Einstein relation for diffusion of Brownian particle with a friction factor ξ in host medium

  $F = \xi\,v$ Frictional force for particle moving with velocity v in host medium

Reptation (P. de Gennes, S. Edwards, 1971)

1)   Identify set of topological constraints to chain motion.

2)   Construct a "tube" of diameter a_{tube} about the contour of the "test chain" which meanders through these constraints. (Edwards, 1967).

   N_e is the average number of segments between entanglements. There are Z pieces of the tube such that the tube contour length L is the same as that of the diffusing chain Nb = L

$$Za^2 = Nb^2 \quad \text{(tube itself is a random walk; treat entangled chain as physicist's universal chain)}$$

3)   Test chain moves by continuous creation/destruction of its tube. As the chain moves, one end comes out of the tube and a new part of the tube is created. The end of the tube from which the chain has withdrawn is considered destroyed since it no longer has any influence on the mobility of the test chain.
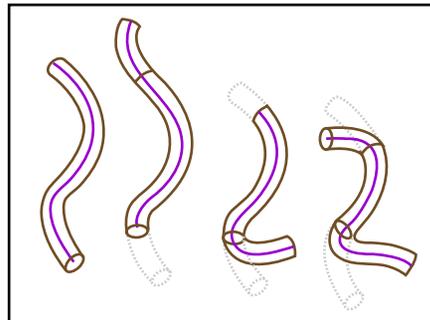
reptating string
inside tube

Figure by MIT OCW.

4) The diffusion coefficient of the Rouse-like chain within the tube (not entangled) is given by:

$$D_{tube} = \frac{kT}{N\xi_M}$$

where N is the number of statistical segments of the chain and ξ_M is the friction factor per statistical segment.

5) As a result of the local wiggling of the chain, the tube migrates. The time τ for the chain to completely escape its "old" tube of total length L is approximately:

$$\tau = \frac{L^2}{D_{tube}}$$

where L is the length of the tube which is also the contour length of the chain, L = N b. **_τ is called the "longest relaxation time",_** since it characterizes the motion of the entire chain. The relaxation time for the chain to exit its old tube thus scales with N^3 since Nb = L.

$$\tau \sim N^3$$

Recall viscosity scales with flow time, so we predict that for an entangled melt

$$\eta \sim M^3$$

Reptation cont'd

6) *Diffusion coefficient for entangled chains*: Center of mass motion of the chain defines a reptation diffusion coefficient, D_{rept}. The distance diffused for a time t is given by

$$<x^2> = D_{rept}\ t$$

For $t = \tau$, the chain center of mass can be estimated to have moved a distance of approximately the radius of gyration.

$$R_g{}^2 = D_{rept}\ \tau$$

Therefore D_{rept} scales with chain length as

$$D_{rept} \approx \frac{N}{\tau} \approx \frac{1}{N^2}$$

Note $D_{rept} = D_{self}$

Experimentally, for well entangled polymer melts, the self-diffusion coefficient is found to scale as 1/(molecular weight)^2 in accord with the reptation model.

Polymer-Polymer Diffusion

Entropic Effects - consider diffusion of chains with *different molecular weights: 2 scenarios:*

1. "Fixed obstacles":   diffusion of short chain in matrix of large, entangled chains

2. "Constraint release":   diffusion of long chain in matrix of short chains

Enthalpic Effects

Self diffusion (same species)	
$\chi = 0$	No effect
Mutual diffusion (different species)	
$\chi > 0$	Slows or stops inter-diffusion
$\chi < 0$	Thermodynamic *acceleration* of inter-diffusion of species in addition to Brownian motion

Ass't Prof ELT DeGennes' Prediction: PVC/PCL

Enthalpic Influence on Diffusion cont'd (Mutual Diffusion)

- Recall F-H free energy of mixing per lattice site:

$$\frac{\Delta G_M}{N_o kT} = \frac{\phi_1}{x_1} \ln \phi_1 + \frac{\phi_2}{x_2} \ln \phi_2 + \phi_1 \phi_2 \chi_{12}$$

- In the case of the mutual interdiffusion of two (miscible) high MW polymers with $x_1 = x_2 \gg 1$, the free energy of mixing for a negative χ is dominated by the enthalpic term. For chains comprised of N monomers,

$$\Delta G_M \sim N\chi_{12} \, \phi_1 \phi_2$$

- This enthalpic effect influences the scaling dependence of the diffusion coefficients by increasing the diffusion scaling law by a factor of N for compatible, negative chi blends.

(self) Diffusion and Viscosity Scaling Laws

Property	$N < N_e$	$N > N_e$
η	N	N^3
D	N^{-1}	N^{-2}

Where N_e is the number of statistical segments between entanglements. Note $M_e = N_e M_o$, where M_o is the molecular weight per monomer.

Rubber Elasticity

Assumptions:
1. Gaussian subchains between permanent crosslinks
2. Temperature is above T_g
3. Flexible chains with relatively low backbone bond rotation potentials
4. Deformation occurs by conformational changes only
5. No relaxation (permanent network is fixed on time scale of experiment)
6. Affine deformation (microscopic deformation : macroscopic deformation)
7. No crystallization at large strains
8. No change in volume (density) with deformation
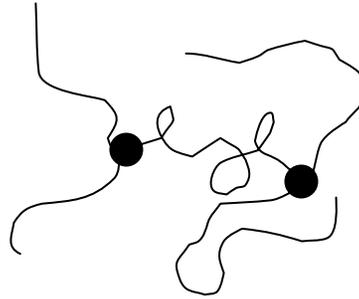
Ideal Rubber Elasticity cont'd

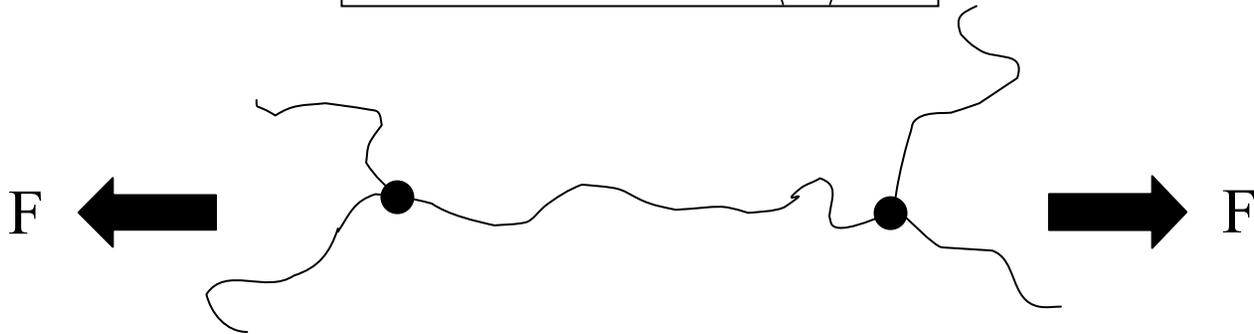## 3D Gaussian Subchain Network

Relaxed subchains

M_x = Average Molecular weight between Xlinks

crosslink

Gaussian subchain
(n segments, segment step size l)
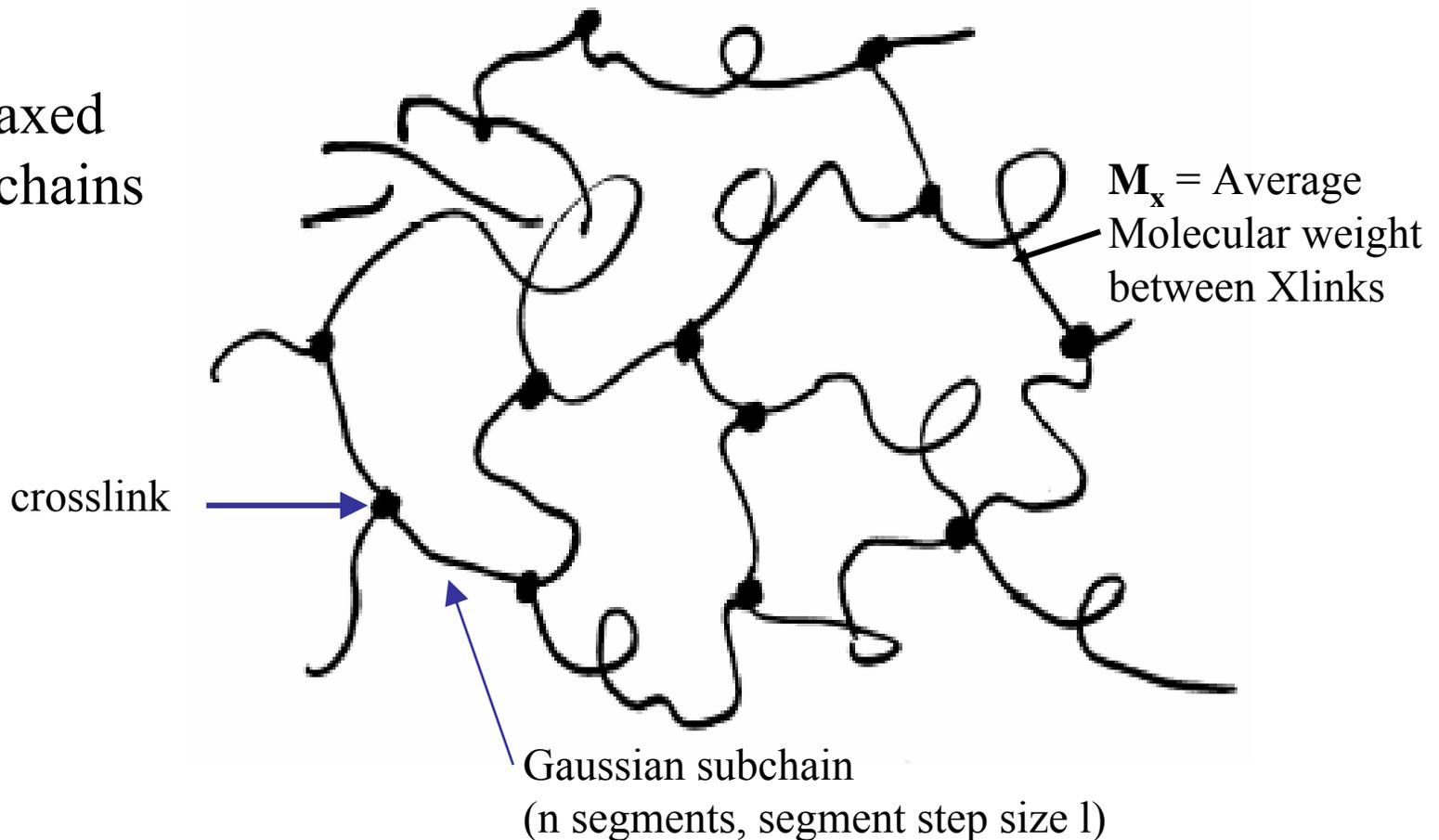
Relaxed vs Extended Subchain Conformations

Relaxed $\qquad \langle r_0{}^2 \rangle^{1/2}$

Extended $\qquad \langle r^2 \rangle^{1/2}$

F $\longleftarrow$ $\qquad\qquad\qquad\qquad$ $\longrightarrow$ F

Entropic Elastic Force

$$F = -T \left(\frac{\partial S}{\partial \ell} \right)_{T,P}$$
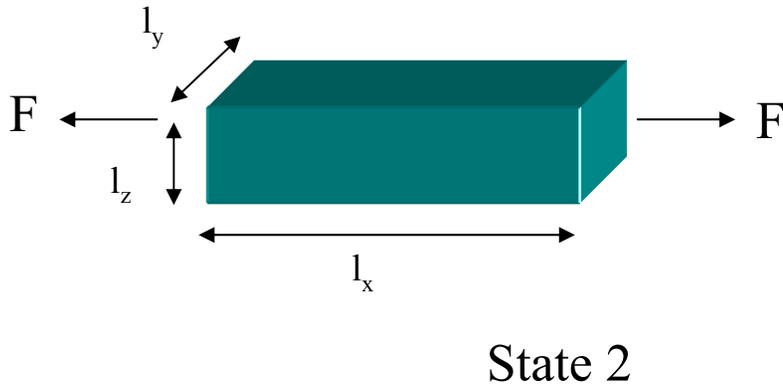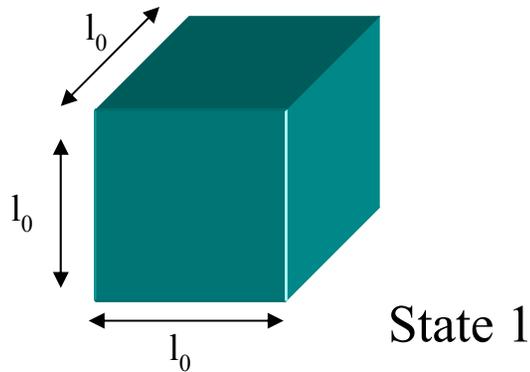
State 1

State 2

State 1:	Relaxed
	$F = 0$
	Ω_1
	$\langle r_0^2 \rangle^{1/2}$
	x, y, z

State 2:	Extended
	$F > 0$
	Ω_2
	$\langle r^2 \rangle^{1/2}$
	x', y', z'

Extension Ratio, α_i

$\alpha_x, \alpha_y, \alpha_z$ are the 3 orthogonal extension ratios which depend on the type of loading geometry.

Local coordinates

$$x' = \alpha_x x \qquad y' = \alpha_y y \qquad z' = \alpha_z z$$

Assumption #6:   *Affine Deformation*

Macro coordinates

$$\alpha_x = \frac{l_x}{l_0} \qquad \alpha_y = \frac{l_y}{l_0} \qquad \alpha_z = \frac{l_z}{l_0}$$

Assumption #8:   *the rubber is incompressible*

$$\Delta V = 0 \qquad\qquad \textit{during deformation}$$
$$\Rightarrow$$
$$\alpha_x \alpha_y \alpha_z = 1$$

Entropic Elastic Force cont'd

The entropic elastic force is derived by considering the change in the conformational entropy of the extended vs. the relaxed state

$$S_2 - S_1 = \Delta S = k \ln \frac{\Omega_2}{\Omega_1}$$

$$x^2 + y^2 + z^2 = r_0^2$$

$$\Omega_1 = const \cdot \exp\left(\frac{-3r_0^2}{2nl^2}\right) \qquad \Omega_2 = const \cdot \exp\left(\frac{-3(\alpha_x^2 x^2 + \alpha_y^2 y^2 + \alpha_z^2 z^2)}{2nl^2}\right)$$

$$\overbrace{\qquad\qquad}^{r^2}$$

$$\Delta S = k \ln \frac{\Omega_2}{\Omega_1} = k \ln \exp\left(\frac{-3[x^2(\alpha_x^2 - 1) + y^2(\alpha_y^2 - 1) + z^2(\alpha_z^2 - 1)]}{2nl^2}\right)$$

It's all about entropy…again

Entropic Elastic Force cont'd

$$x^2 + y^2 + z^2 = r_0^2 \text{ and } \langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle = \frac{\langle r_0^2 \rangle}{3} \quad \text{(for the relaxed subchain)}$$

n steps of size l in subchain $\quad nl^2 = r_0^2$

$$\therefore \quad \Delta S(\alpha_i) = -\frac{k}{2}\left(\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3\right)$$

per sub-chain
(***general relationship***)

$$\Delta F_i = -T\left(\frac{\partial \Delta S(\alpha_i)}{\partial l_i}\right)_{T,P}$$

$\Delta S(\alpha_i)$ depends on details of initial
sample shape and applied loads and this in turn controls ΔF_i

Example: Uniaxial Deformation

With Axi-symmetric sample cross-section

Deform along $\vec{x}$ $\quad l_0 \to l_x$, $\quad \alpha_x = \dfrac{l_x}{l_0}, \quad d\alpha_x = \dfrac{dl_x}{l_0}$

$\alpha_x = \alpha_x, \quad \alpha_y = \alpha_z = \dfrac{1}{\sqrt{\alpha_x}}$ Poisson contraction in lateral directions

since $\alpha_x \alpha_y \alpha_z = 1$

Rewriting $\Delta S(\alpha_i)$ explicitly in terms of α_x

$$\Delta S(\alpha_i) = -\frac{k}{2}\left(\alpha_x^2 + \frac{1}{\alpha_x} + \frac{1}{\alpha_x} - 3 \right)$$

$$F_x = -T \frac{\partial}{\partial l_x}\left(\Delta S(\alpha_x) \right)\Big|_{T,P} = \frac{kT}{2}\frac{\partial}{\partial l_x}\left(\alpha_x^2 + \frac{2}{\alpha_x} - 3 \right)$$

Uniaxial Deformation cont'd

$$F_x = \frac{kT}{2l_0}\left(2\alpha_x - \frac{2}{\alpha_x{}^2}\right) = \frac{kT}{l_0}\left(\alpha_x - \frac{1}{\alpha_x{}^2}\right)$$

At small extensions, the stress behavior is Hookean ($F_x \sim$ const α_x)

Stress-Extension Relationship

$$\sigma_{xx} = \text{total } \frac{F_x(\alpha_x)}{A_0} = \frac{zkT}{A_0 l_0}\left(\alpha_x - \frac{1}{\alpha_x{}^2}\right) \quad \text{for z subchains in volume V}$$

$$A_0 l_0 = V \qquad \frac{z}{V} = \# \text{ of subchains per unit volume } = N_{xlinks}$$

Usually the entropic stress of an elastomeric network is written in terms of M_x where M_x = avg. molecular weight of subchain between x-links

$$\frac{mass/vol}{moles of crosslinks/volume} = M_x = \frac{\rho}{N_x/N_A}$$

$$\boxed{\sigma_{xx}(\alpha_x) = \frac{\rho N_A kT}{M_x}\left(\alpha_x - \frac{1}{\alpha_x{}^2}\right) \quad \text{uniaxial}}$$

Young's Modulus of a Rubber

$$E \equiv \lim_{\alpha_x \to 1} \frac{d\sigma_{xx}}{d\alpha_x} = \frac{\rho R T}{M_x}\left(1 + \frac{2}{\alpha_x^3}\right)$$

$$\boxed{E = 3\rho RT/M_x}$$

Notice that Young's Modulus of a rubber is :
1. Directly *proportional* to temperature
2. Indirectly proportional to M_x

• Can measure modulus of crosslinked rubber to derive $\underline{\underline{M_x}}$

• In an analogous fashion, the entanglement network of a melt, gives rise to entropic restoring elastic force provided the time scale of the measurement is sufficiently short so the chains do not slip out of their entanglements. In this case, we can measure modulus of non-crosslinked rubber melt to derive M_e !

Stress-Uniaxial Extension Ratio Behavior of Elastomers
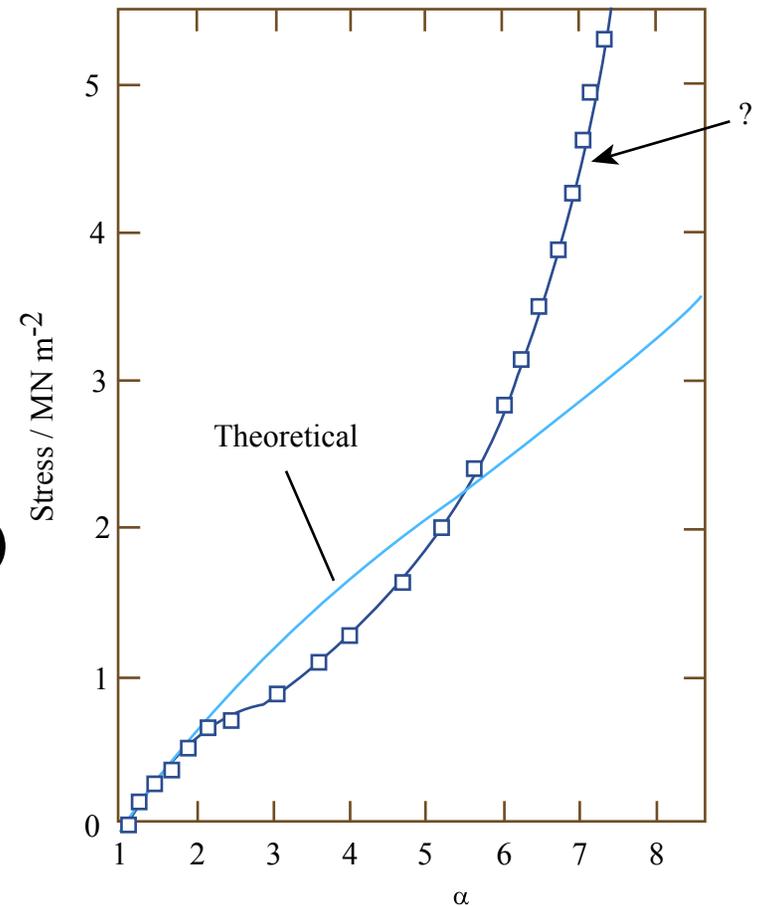
Uniaxial

tensile

$\sigma(\alpha)$

Image removed due to copyright restrictions.

Please see Fig. 5 in Treloar, L. R. G. "Stress-Strain Data for Vulcanised Rubber Under Various Types of Deformation." *Transactions of the Faraday Society* 40 (1944): 59-70

$\sigma(\alpha)$

compressive

Small deformations

High tensile elongations

Theoretical

?

Stress / MN m^{-2}

α