

# Elasticity of Polymer Networks

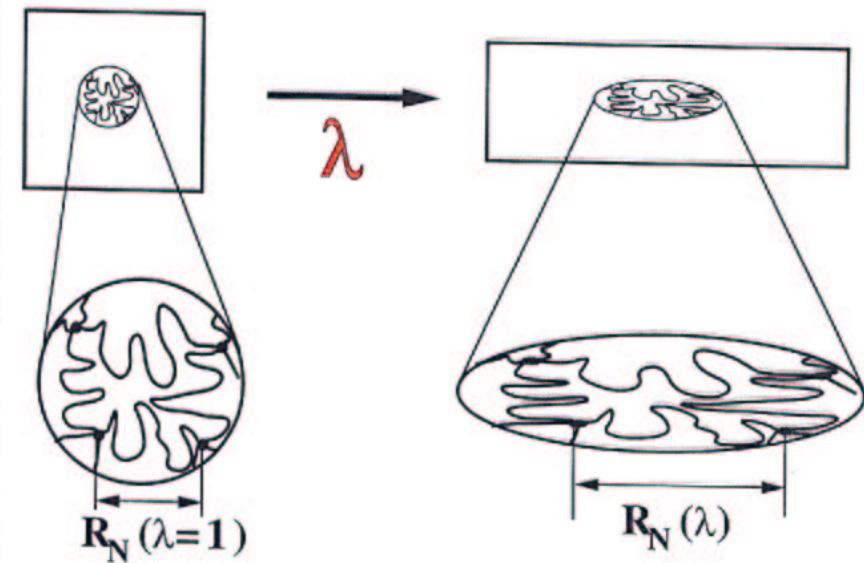
M. Rubinstein and S. Panyukov

## Outline

1. Classical Models of Rubber Elasticity
2. Slip-Tube Model
3. Comparison with experiments

## Elasticity of Networks

Origin - entropic elasticity  
of network strands.



How is the macroscopic deformation of the network transmitted down to individual strands?

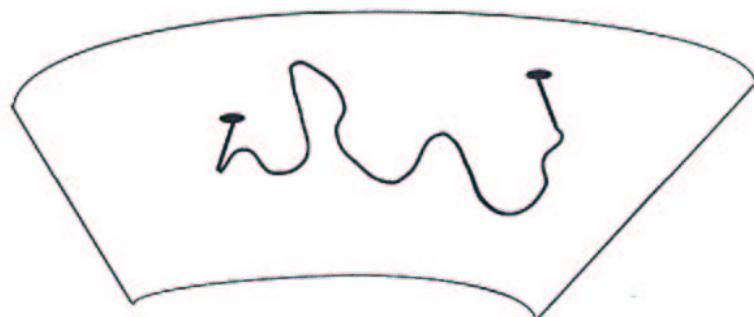
N - degree of polymerization between cross-links

## Affine Strand

Deformation of an affine strand is proportional to the macroscopic deformation of the network

$$\mathbf{R}_N(\lambda) = \lambda \mathbf{R}_N(\lambda=1)$$

as if the ends of the strand are nailed to the elastic non-fluctuating solid.



## Affine Networks



Wall '42  
Flory &  
Rehner '43

Cross-links are displaced affinely as if they are nailed to the elastic non-fluctuating solid.

Network strand is the affine stand

Free energy  $F_{af} = \frac{kT}{2} \frac{c}{N} (\lambda_x^2 + \lambda_y^2 + \lambda_z^2)$

Incompressible network  $\lambda_x \lambda_y \lambda_z = 1$

Uniaxial deformation  $\lambda_x = \lambda, \lambda_y = \lambda_z = \bar{\lambda}^{1/2}$

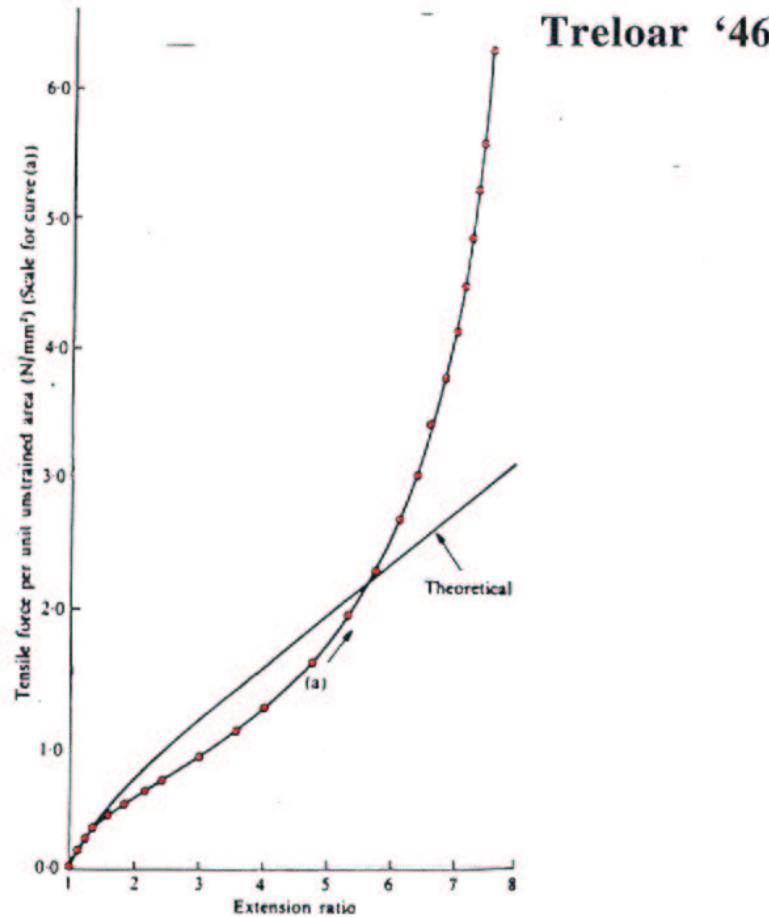
$$F_{af} = \frac{kT}{2} \frac{c}{N} (\lambda^2 + 2/\lambda)$$

Stress  $\sigma$  - force per unit unstrained area

$$\sigma_{af} = G_{af}(\lambda - 1/\lambda^2)$$

Modulus of affine networks  $G_{af} = kT \frac{c}{N}$

## Elasticity of Rubber

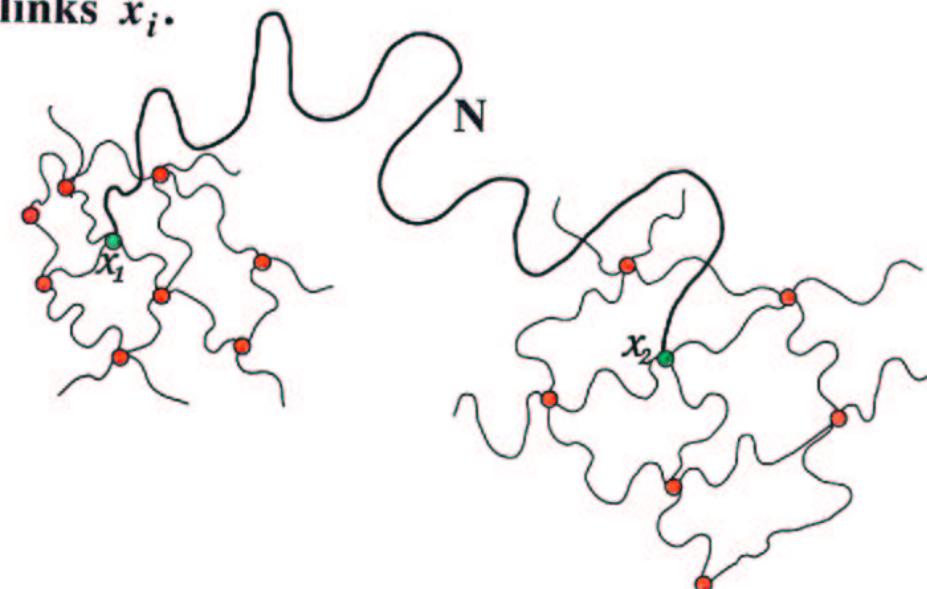


Molecular origin of anomalous stress-strain behavior of polymer networks?

## Phantom Networks

James & Guth '43

Strand is “aware” that it is a part of a network only through its ends - cross-links  $x_i$ .



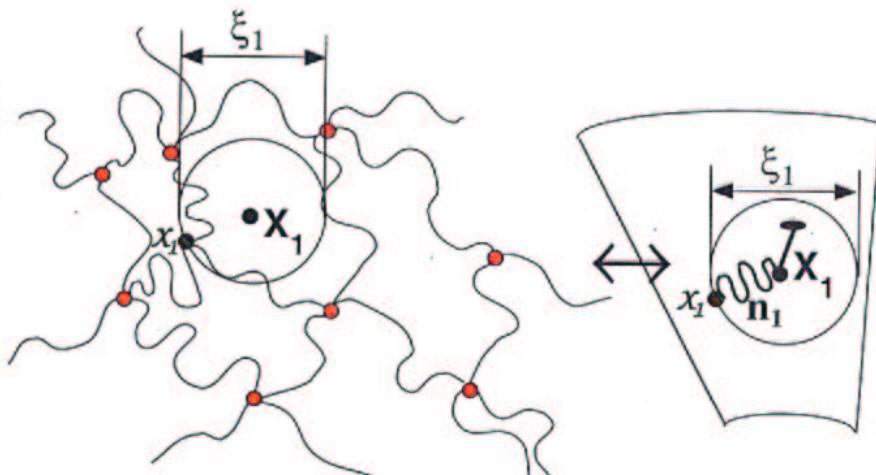
The ends are not “nailed” but can fluctuate around their average positions.

The amplitudes of fluctuations depend on:

- (i) the elasticity of N-mer;
- (ii) the local stiffness of the network.

## Local Stiffness of the Network

- can be characterized by mean square fluctuations  $\xi_i$  of potential cross-links  $x_i$  around their average positions  $X_i$  in the absence of the test chain.

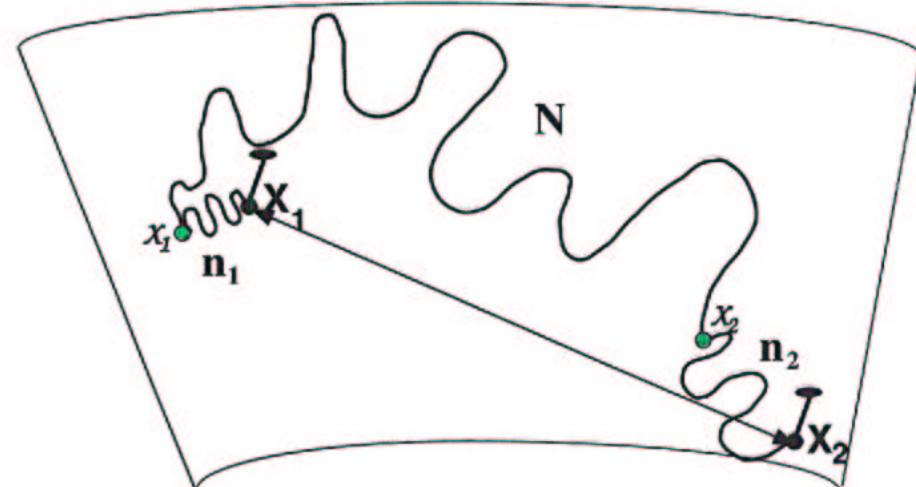


Represent local stiffness by virtual Gaussian chains of  $n_i$  monomers attached to non-fluctuating solid at  $X_i$

$$\xi_i^2 = b^2 n_i$$

$b$  - monomer size

## Combined Chain



Affine strand is the combined chain consisting of  $N$  monomers of network strand and  $n_1 + n_2$  monomers of two virtual chains.

Simple estimates  $n_1 = n_2 = N/(f-2)$

$f$  - functionality of cross-links

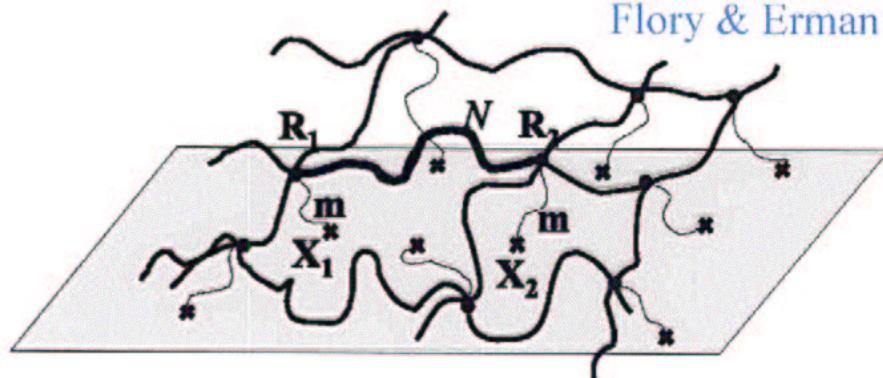
Stress  $\sigma_{ph} = G_{ph}(\lambda - 1/\lambda^2)$

Modulus of phantom networks

$$G_{ph} = kT \frac{f-2}{f} \frac{c}{N}$$

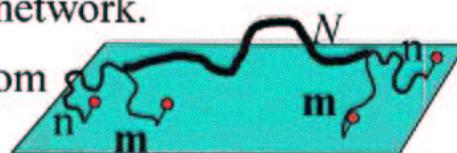
## Constrained-Junction Model

Ronca & Allegra '75  
Flory & Erman '78

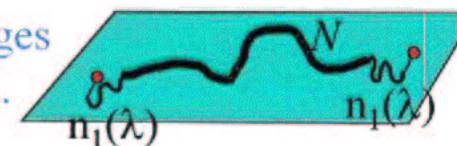


Constraining effect of surrounding chains is modeled by an additional harmonic potential acting on the cross-links of the phantom network.

Two virtual chains of phantom network with  $n=N/(f-2)$



Additional virtual chains with  $m$  monomers represent additional constraining potential.



Constraining potential changes with network deformation  $\lambda$ .

$$m = m_0 \lambda^2$$

Fluctuations of virtual  $m$ -mers deform affinely with network.

## Stress – Strain Relations

### Affine and Phantom Models

Stress  $\sigma \sim (\lambda - 1/\lambda^2)$

Flory & Rehner '43  
James & Guth '43

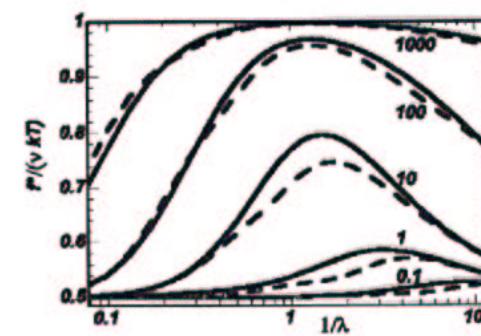
Mooney stress  $f^* = \frac{\sigma}{\lambda - 1/\lambda^2}$

Affine model  $f^* = v k T$

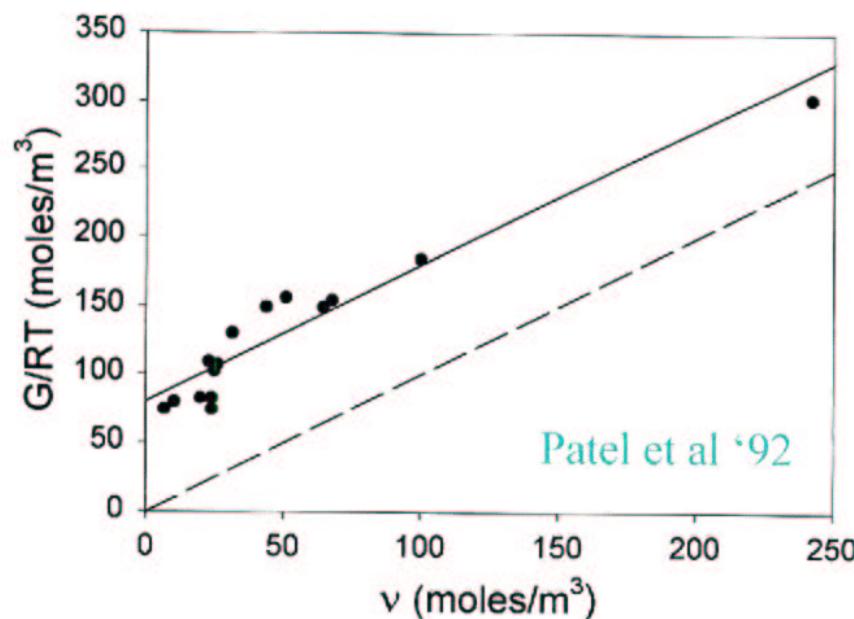
Phantom model  $f^* = v k T (1-2/f) = v k T / 2$  for  $f=4$

### Constrained-Junction Model

Strength of constraining potential  $N/m_0$

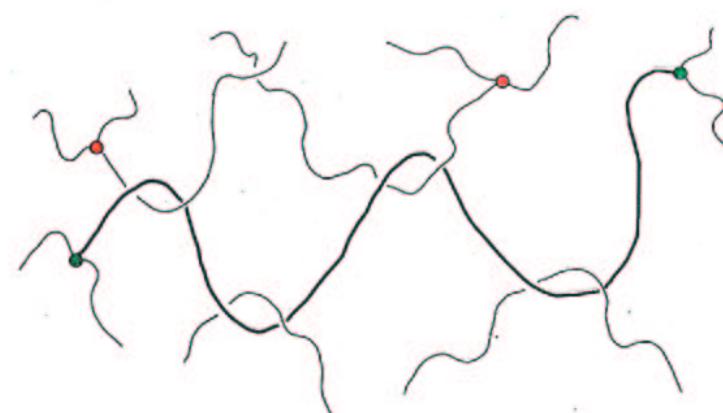


# Entanglements



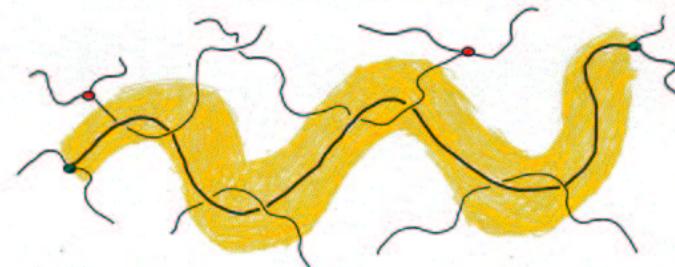
# Entangled Networks

Stress is transmitted to the chain not only through its ends (cross-links), but also through the topological constraints along the whole chain.



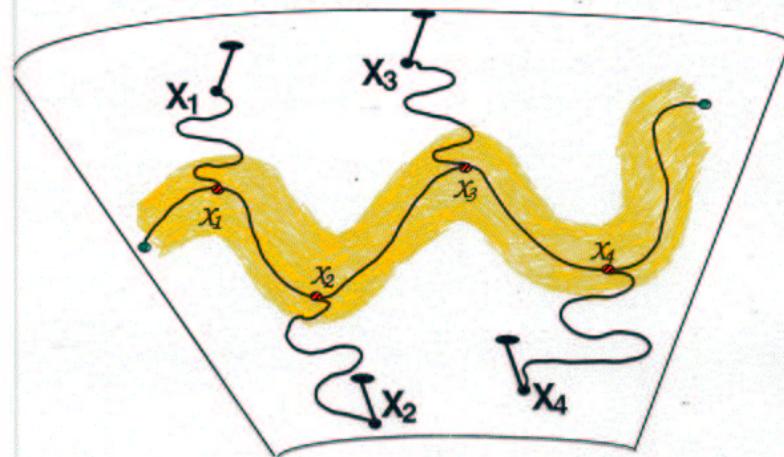
Topological constraints of the neighboring chains confine the test one to the tube-like region.

## Confining Tube



Confining tube can be represented by an effective topological potential (virtual chains) acting on the monomers of the test one.

Edwards '67

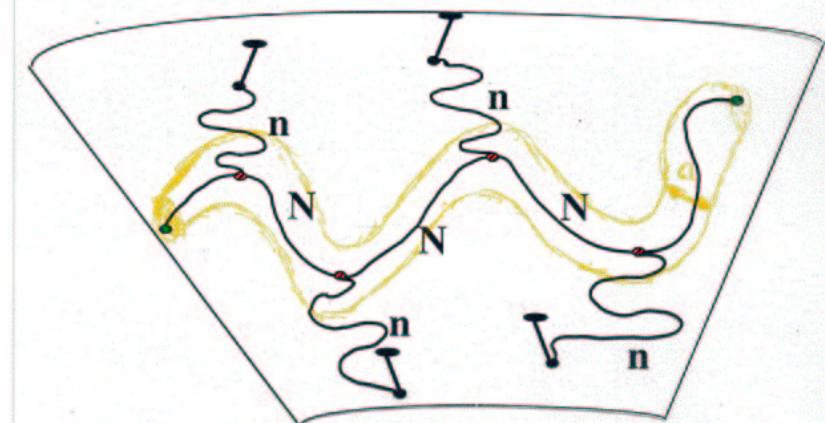


## Tube Diameter

Topological potential restricts fluctuations of monomers of the test chain to confining tube of diameter  $a$ .

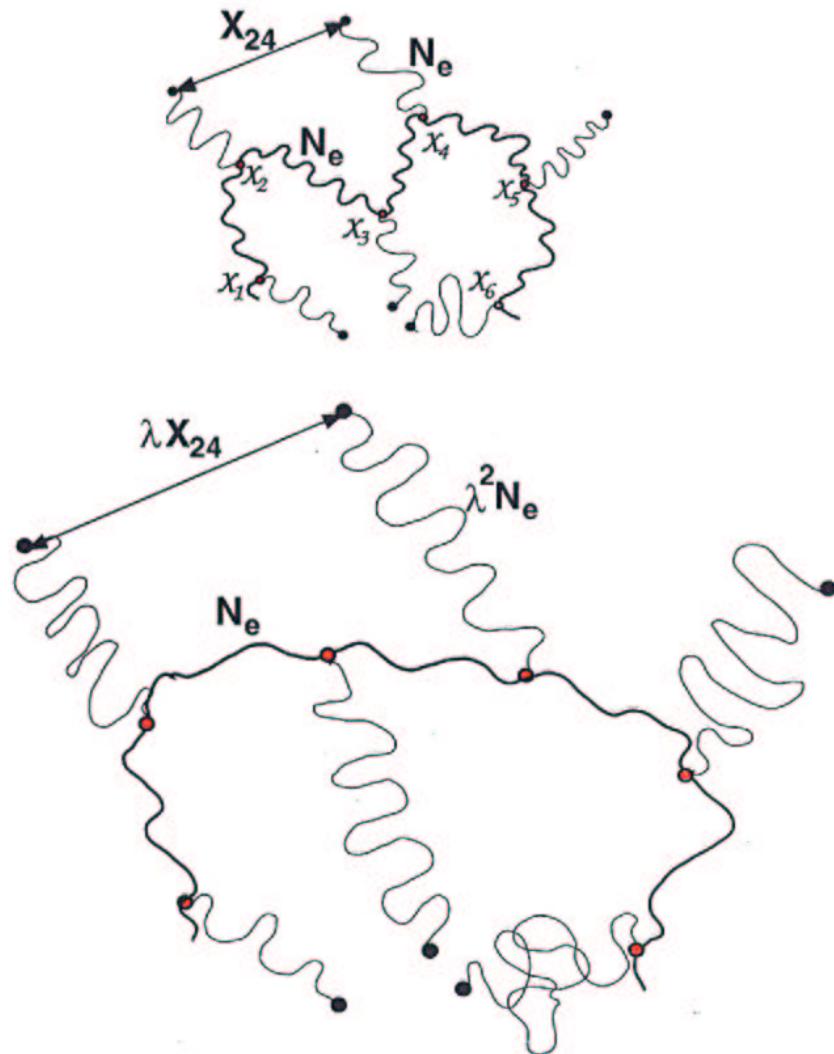
If virtual  $n$ -mers are attached to the test chain  $N$  monomers apart, the mean square fluctuations of test chain monomers are

$$a^2 \approx b^2 (Nn)^{1/2} \quad \text{for } n \geq N$$



Any pair of parameters  $N$  and  $n$ , such that  $Nn = N_e^2$  and  $n \geq N$  will represent similar confinement.

## Deformation of a Strand



## Deformed Confining Tube

Confining tube deforms non-affinely.

$$\mathbf{n}|_{\lambda} = \lambda^2 \mathbf{N}_e$$

$$\mathbf{N}|_{\lambda} = \mathbf{N}_e$$

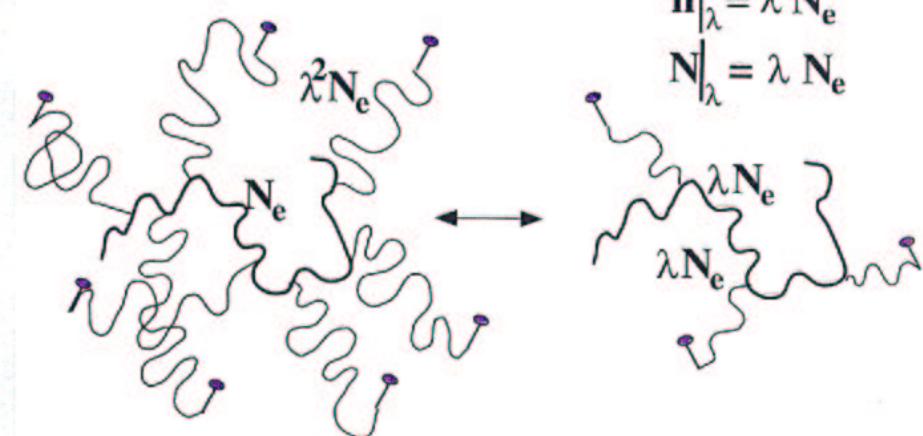
$$\mathbf{N}|_{\lambda} \mathbf{n}|_{\lambda} = \lambda^2 \mathbf{N}_e^2$$

$$\mathbf{a}^2 \approx \mathbf{b}^2 (\mathbf{N}_e)^{1/2}$$

$$\mathbf{a}|_{\lambda} = \lambda^{1/2} \mathbf{a}|_{\lambda=1}$$

$$\mathbf{n}|_{\lambda} = \lambda \mathbf{N}_e$$

$$\mathbf{N}|_{\lambda} = \lambda \mathbf{N}_e$$



Affine strand contains  $\lambda N_e$  monomers.

Fluctuations of the affine strand  
are of the order of the deformed  
tube diameter  $a(\lambda)$ .

$$a(\lambda) = b(\lambda N_e)^{1/2}$$

## Non-Affine Deformation

Affine strand contains  $\lambda N_e$  monomers.

Affine length - size of the affine strand

$$\lambda b(\lambda N_e)^{1/2} = bN_e^{1/2} \lambda^{3/2}$$

On larger length scales chain deforms affinely.

On shorter length scales chain is stretched by the virtual chains.

Entanglement strand is stretched to the size of the deformed tube diameter

$$bN_e^{1/2} \lambda^{3/2} \frac{N_e}{\lambda N_e} = a(\lambda) = b(\lambda N_e)^{1/2}$$

Fluctuations of the monomers of the test chain are limited by the distance between entanglements.

## Free Energy Density

Phantom Gaussian network

$$F_{ph} \approx kT \frac{c}{N_x} (\lambda_x^2 + \lambda_y^2 + \lambda_z^2)$$

$c$  - monomer concentration

$N_x$  - strand between cross-links

Entangled network

(i) stretched -  $kT\lambda^2$  per affine strand  $\lambda N_e$

$$kT \lambda^2 \frac{c}{\lambda N_e} = kT \frac{c}{N_e} \lambda$$

(ii) compressed -  $kT$  per strand  $\lambda N_e$

$$kT \frac{c}{\lambda N_e} = kT \frac{c}{N_e} \frac{1}{\lambda}$$

Cross-over expression for each direction

$$kT \frac{c}{N_e} \left( \lambda + \frac{1}{\lambda} \right)$$

$$F_{ent} \approx kT \frac{c}{N_e} \sum_i \left( \lambda_i + \frac{1}{\lambda_i} \right)$$

Total free energy density

$$F_{tot}(\lambda) = F_{ph}(\lambda) + F_{ent}(\lambda)$$

# Tube Models

## Edwards Tube Model

Confining potential and tube diameter  
do not change upon network deformation.

$$\text{Mooney stress } f^* = \frac{\sigma}{\lambda - 1/\lambda^2} = G_c + G_e$$

$G_c$  – modulus due to cross-links

$G_e$  – modulus due to entanglements

## Non-affine Tube Model

Confining potential and tube diameter  
change upon network deformation.

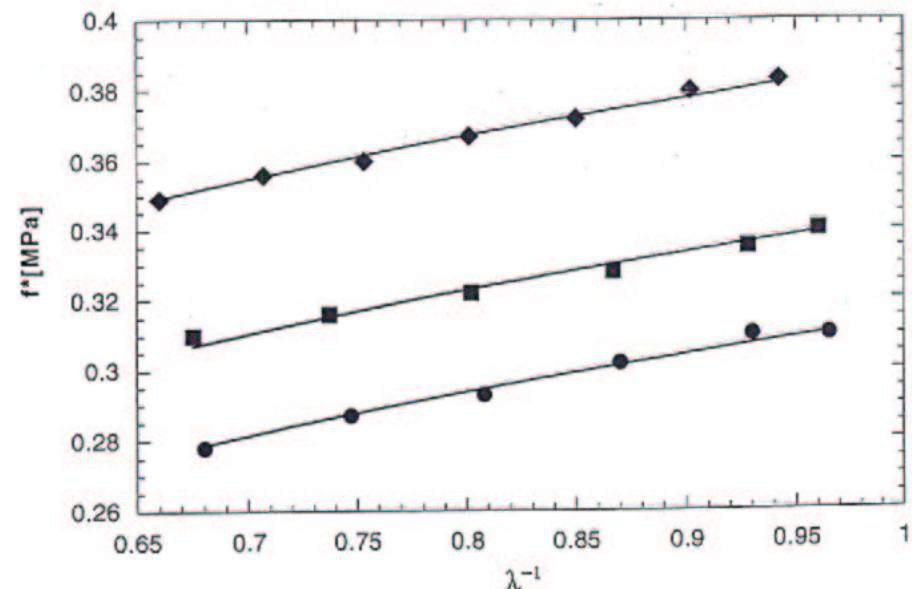
$$\text{Number of monomers in virtual chains } n = n_0 \lambda^2$$

$$\text{Tube diameter } a = b(Nn)^{1/4} = a_0 \lambda^{3/2}$$

$$\text{Mooney stress } f^* = \frac{\sigma}{\lambda - 1/\lambda^2} = G_c + G_e \frac{1}{\lambda - \lambda^{1/2} + 1}$$

# Mooney-Rivlin Plot

Dossin & Graessley '79



Polybutadiene networks cured in  
50% tetradecane solutions  
 $M_w = 168,000$  g/mol

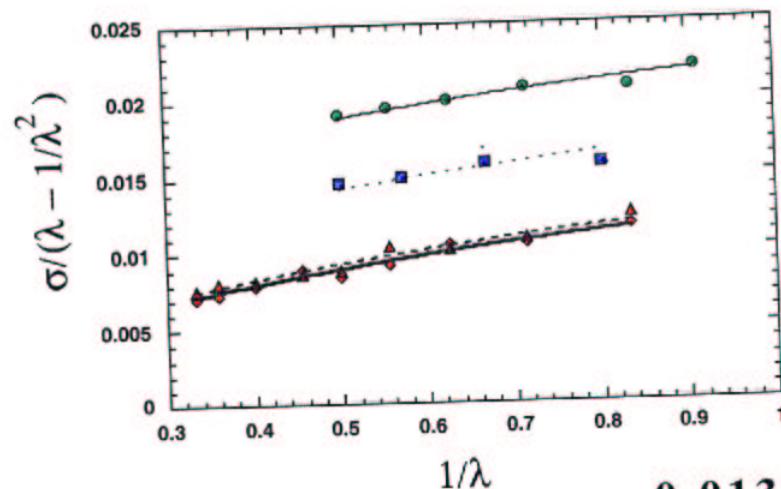
$$\text{Fit: } G_e \approx 0.17 \text{ MPa} \quad G_c \approx \begin{array}{l} 0.22 \text{ MPa} \\ 0.17 \text{ MPa} \\ 0.14 \text{ MPa} \end{array}$$

## Computer Simulations

G. Grest

- 1000 chains of 35 beads each
- 500 chains of 100 beads each
- 120 chains of 350 beads each

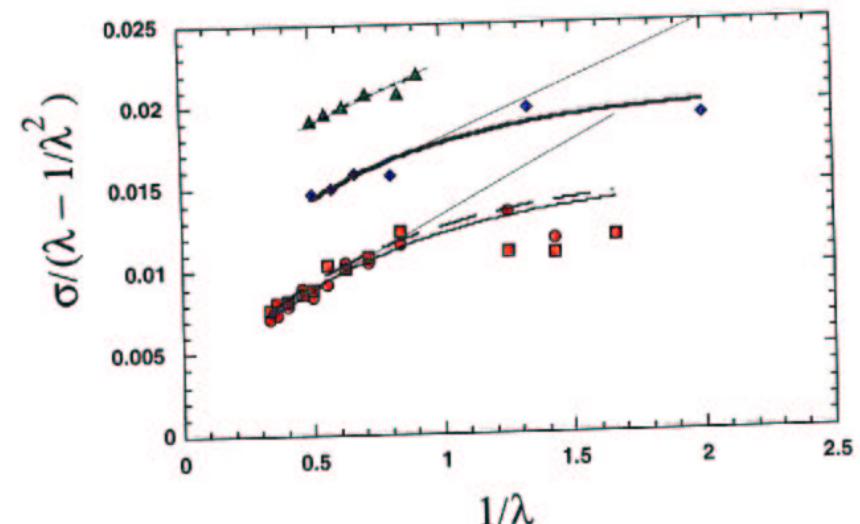
### Mooney-Rivlin Plot



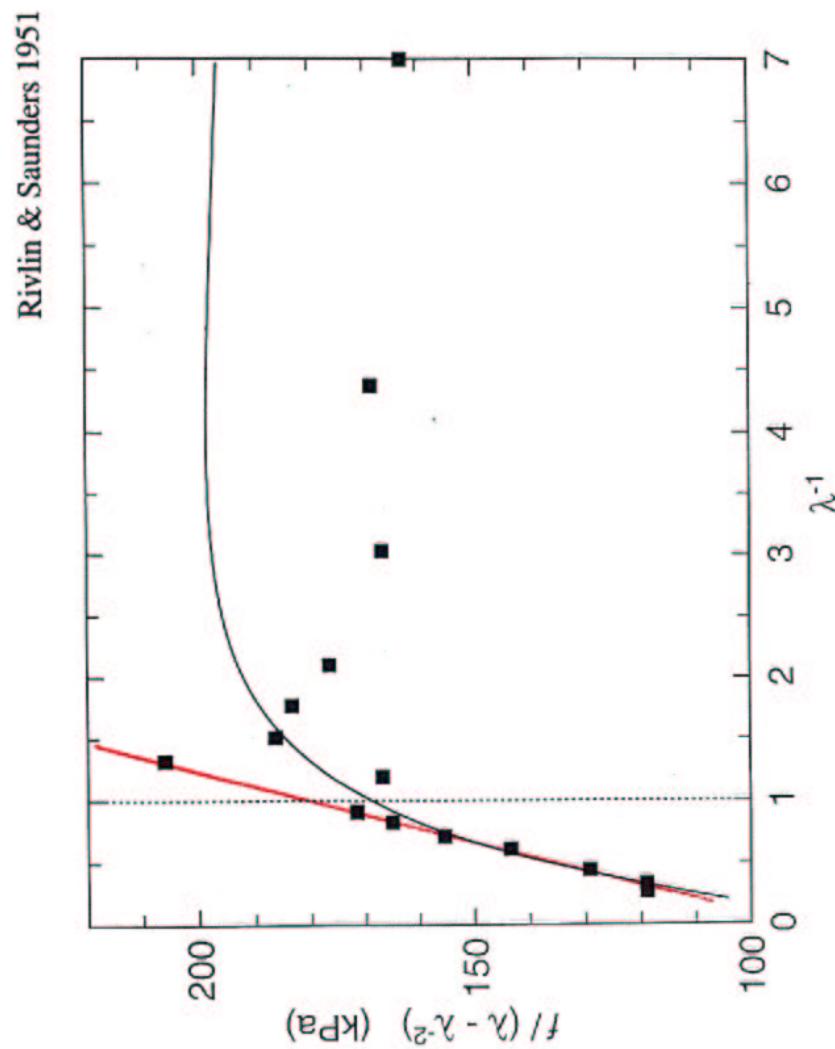
Fit:  $G_e \approx 0.009$        $G_c \approx 0.013$   
                                  $G_e \approx 0.009$   
                                  $G_c \approx 0.0035$

## Simulations of Compression

G. Grest



No additional adjustable parameters



## Summary of Ideas

Edwards Tube model – virtual chains connect many monomers of the network strand to the non-fluctuating elastic background.

Constrained-Junction Model – fluctuations of virtual chains change affinely with network deformation.

New Slip-Tube model accounts for redistribution of stored length along the confining tube.

The predictions of the slip-tube model are in a very good agreement with the experimental data on uniaxial deformation of polybutadiene, PDMS and natural rubber networks.

# Non-Affine Tube Model



## Phantom Network Model      Non-Affine Network Model

### Free Energy

$$F_{ph}^{el}(\lambda) = \frac{kT}{2} \frac{c}{N} \left(1 - \frac{2}{f}\right) \sum_{\alpha} \lambda_{\alpha}^2 \quad F_{naf}^{el}(\lambda) = F_{ph}^{el}(\lambda) + \frac{kT}{2} \frac{c}{N_e} \sum_{\alpha} \left( \lambda_{\alpha} + \frac{1}{\lambda_{\alpha}} \right)$$

### Stress

$$\sigma_{\alpha\beta}^{el} = kT \frac{c}{N} \left(1 - \frac{2}{f}\right) \delta_{\alpha\beta} \lambda_{\alpha}^2 \quad \sigma_{\alpha\beta}^{el} = \left(\sigma_{\alpha\beta}^{el}\right)_{ph} + \frac{kT}{2} \frac{c}{N_e} \delta_{\alpha\beta} \left( \lambda_{\alpha} - \frac{1}{\lambda_{\alpha}} \right)$$

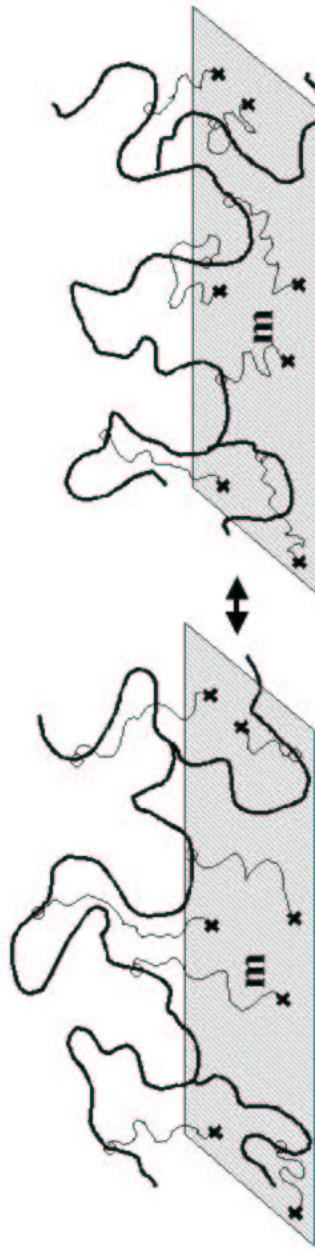
### Mooney Stress

$$f^*(\lambda_z^{-1}) = \frac{\sigma_{zz}^{el} - \sigma_{xx}^{el}}{\lambda^2 - \lambda_z^{-1}}$$

$$f_{ph}^* = G_c = kT \frac{c}{N} \left(1 - \frac{2}{f}\right)$$

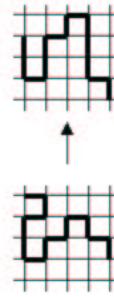
$$f_{naf}^* = G_c + \frac{G_e}{\lambda + \lambda^{-1/2} + 1}$$

# Slip-Tube Model



## Slip-Tube Model

Number of monomers in  $\alpha$ -direction along the tube  $N_\alpha = g_\alpha N_\alpha^0$



Re-assemble monomers in groups of  $g_\alpha$

Same number of renormalized monomers in each direction

$$s_\alpha \rightarrow s'_\alpha = \frac{s_\alpha}{g_\alpha} \quad b \rightarrow b'_\alpha = b g_\alpha^{1/2} \quad \lambda_\alpha \rightarrow \lambda'_\alpha = \frac{b}{b'_\alpha} \lambda_\alpha = \frac{\lambda_\alpha}{g_\alpha^{1/2}}$$

$$F_{st}^{el}(\lambda) = F_{ph}^{el}(\lambda) + \frac{kT}{2} \frac{c}{N_e} \sum_\alpha \left( \frac{\lambda_\alpha}{g_\alpha^{1/2}} + \frac{g_\alpha^{1/2}}{\lambda_\alpha} \right) - \frac{c}{N_e} TS\{g_\alpha\}$$

$$S\{g_\alpha\} = \frac{k}{3} \sum_\alpha \ln(N_{e,\alpha}) = \frac{k}{3} \sum_\alpha \ln\left(N_e^3 \prod_\alpha g_\alpha\right)$$

$N_e$  – average number of monomers between slip-links

# Slip-Tube Model

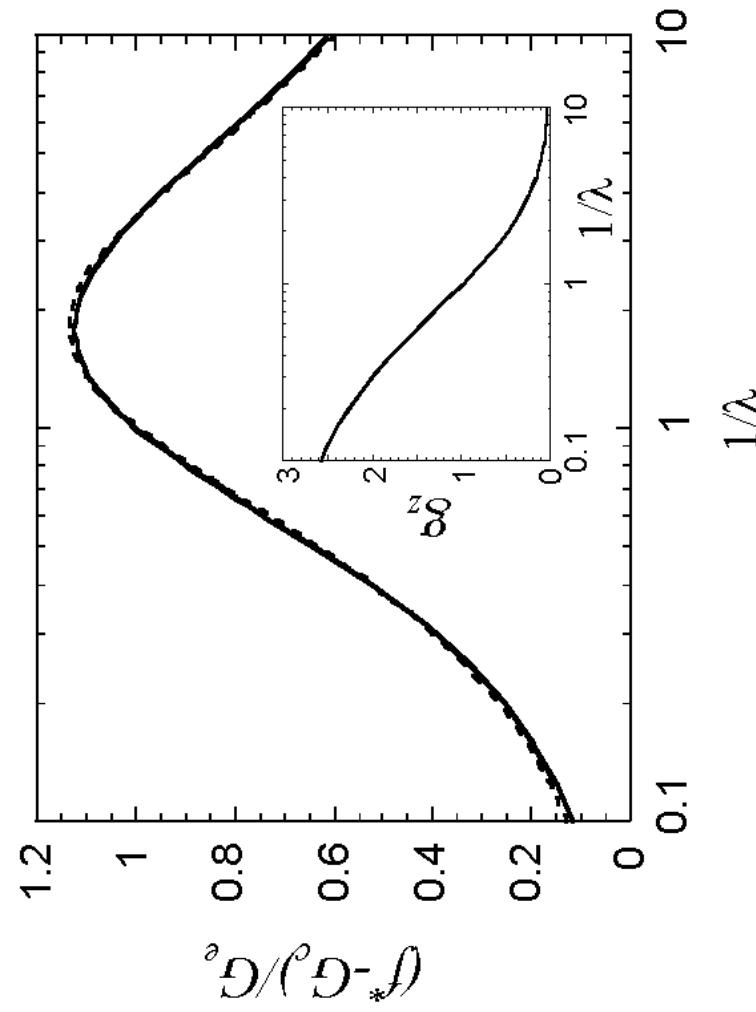
Slippage of monomers along the tube

$$g_\alpha = 1 + \frac{6}{7} \left( \lambda_\alpha - \frac{1}{3} \sum_\beta \lambda_\beta \right) \quad \text{for} \quad |\lambda_\alpha - 1| << 1$$

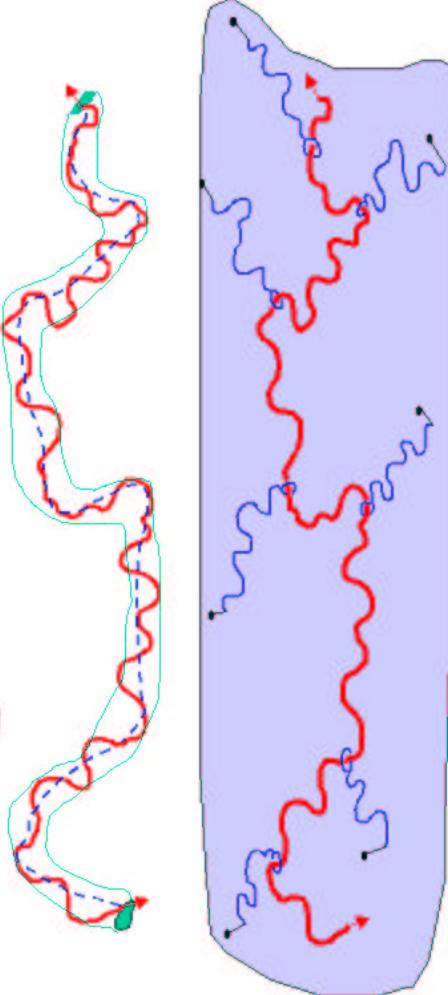
$$f^*(1) = G_c + G_e \quad G_c = kT \frac{c}{N} \left( 1 - \frac{2}{f} \right) \quad G_e = \frac{4}{7} kT \frac{c}{N_e}$$

$$f^*(\lambda^{-1}) = \begin{cases} \lambda^{-1} & \text{for } \lambda \gg 1 \\ \lambda^{1/2} & \text{for } \lambda \ll 1 \end{cases}$$

$$\text{Mooney stress} \quad f^* = \frac{\sigma}{\lambda - 1/\lambda^2} = G_c + \frac{G_e}{0.74\lambda + 0.61\lambda^{-1/2} - 0.35}$$



## Slip-Tube Model

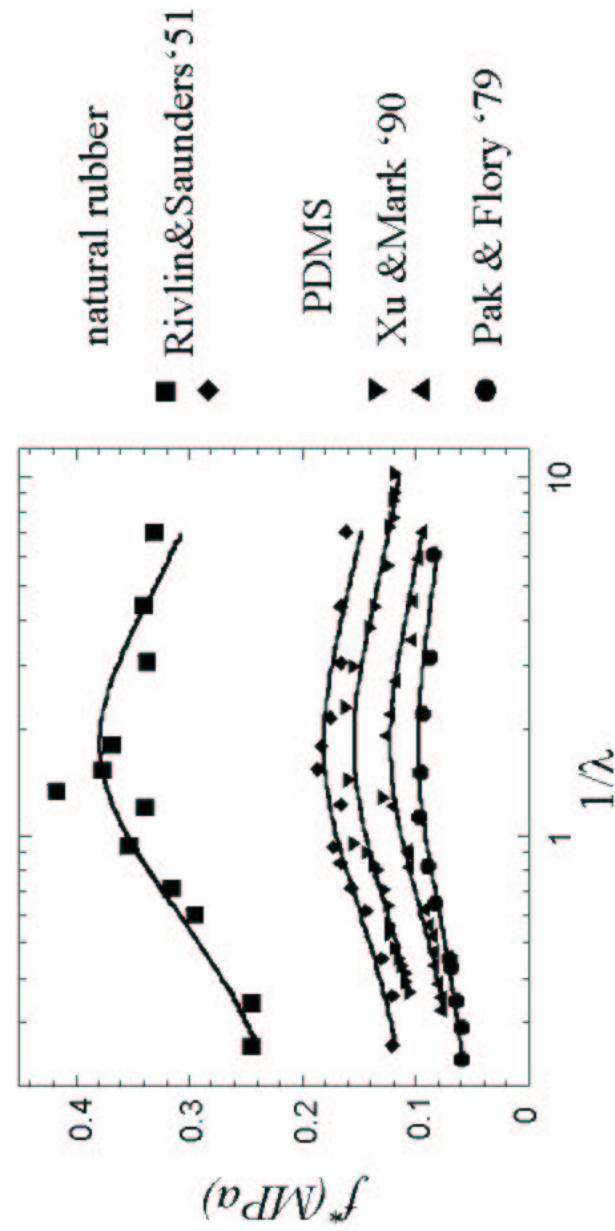


Junction points between network chains and virtual chains are replaced by slip-links attached to fluctuating ends of virtual chains.

These slip-links are allowed to slide along the contour of network chains, but not allowed to pass through each other.

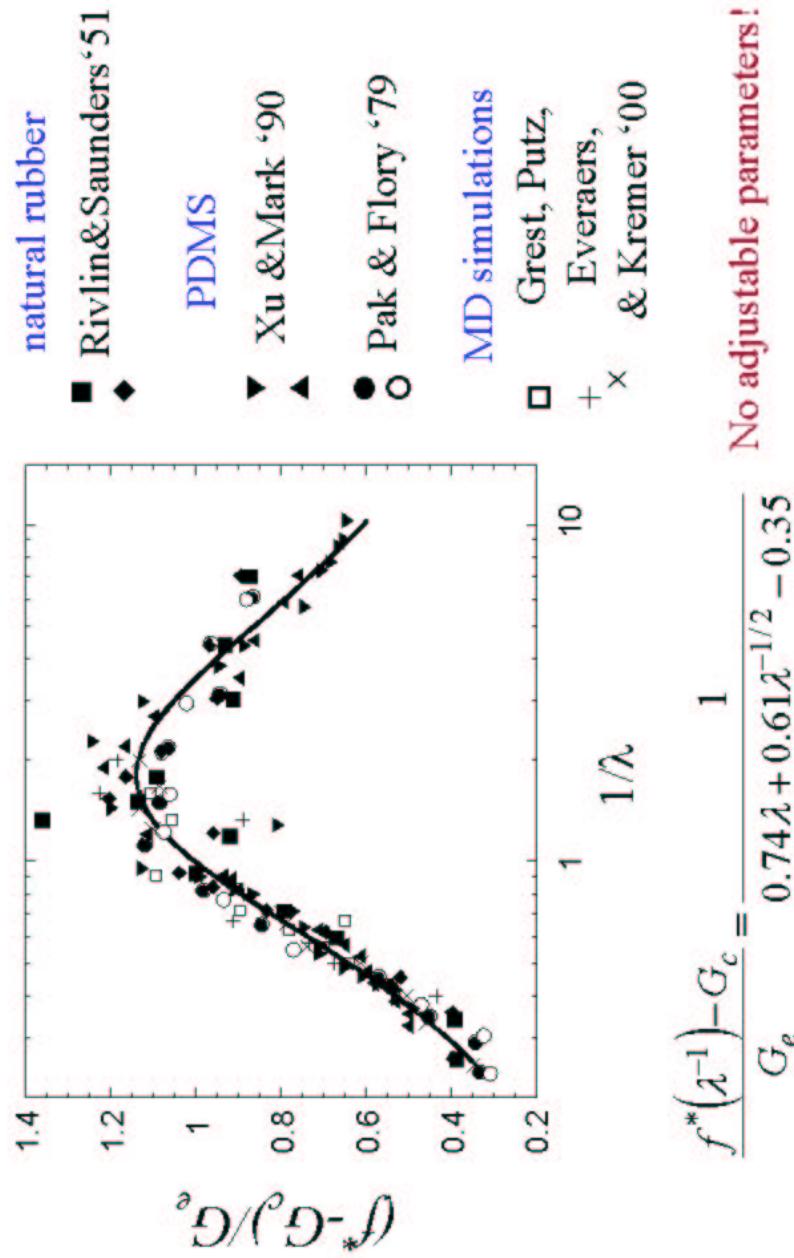
$$\text{Mooney stress} \quad f^* = \frac{\sigma}{\lambda - 1/\lambda^2} = G_c + \frac{G_e}{0.74\lambda + 0.61\lambda^{-1/2} - 0.35}$$

## Slip-Tube Model



2 parameter fits ( $G_c$  &  $G_e$ )

# Universal Plot



## Summary of Ideas

**Edwards Tube model** – virtual chains connect many monomers of the network strand to the non-fluctuating elastic background.

**Constrained-Junction Model** – fluctuations of virtual chains change affinely with network deformation.

**New Slip-Tube model** accounts for redistribution of stored length along the confining tube.

The predictions of the slip-tube model are in a very good agreement with the experimental data on uniaxial deformation of polybutadiene, PDMS and natural rubber networks as well as with computer simulations.

## Acknowledgements

Collaboration

Sergei Panyukov

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