SAND2006-5468P

Chemical Aging of Rubber: Constitutive Modeling Using Molecular Dynamics

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1814, Computational Materials Science and Engineering
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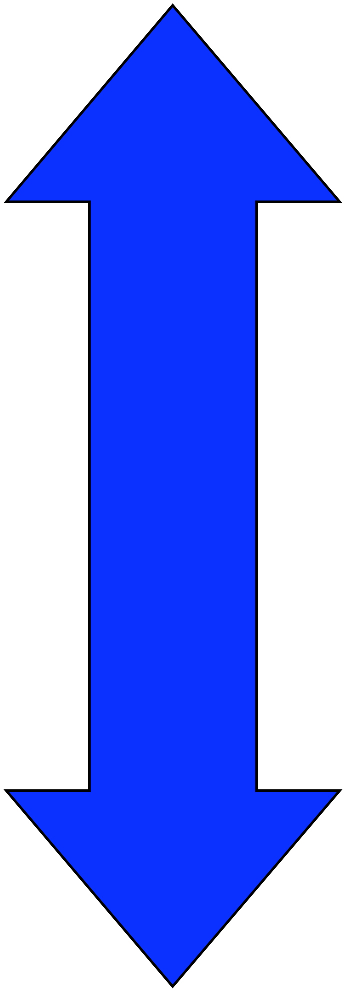
under contract DE-AC04-94AL85000.

Collaborators

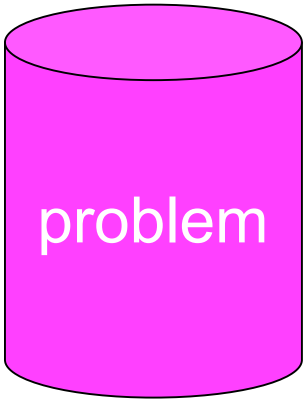
FE calculations



MD simulations

- David Lo
  (1523, Materials Mechanics)
- Joanne Budzien
  (1814, Computational Materials Science and Engineering)
- John Curro
  (1815, Ceramic Processing and Inorganic Materials)
- Dana Rottach
  (UNM, Department of Chemical and Nuclear Engineering)
- Gary Grest
  (1114, Surface and Interface Sciences)
- Aidan Thompson
  (1435, Multiscale Computational Materials Methods)

Map



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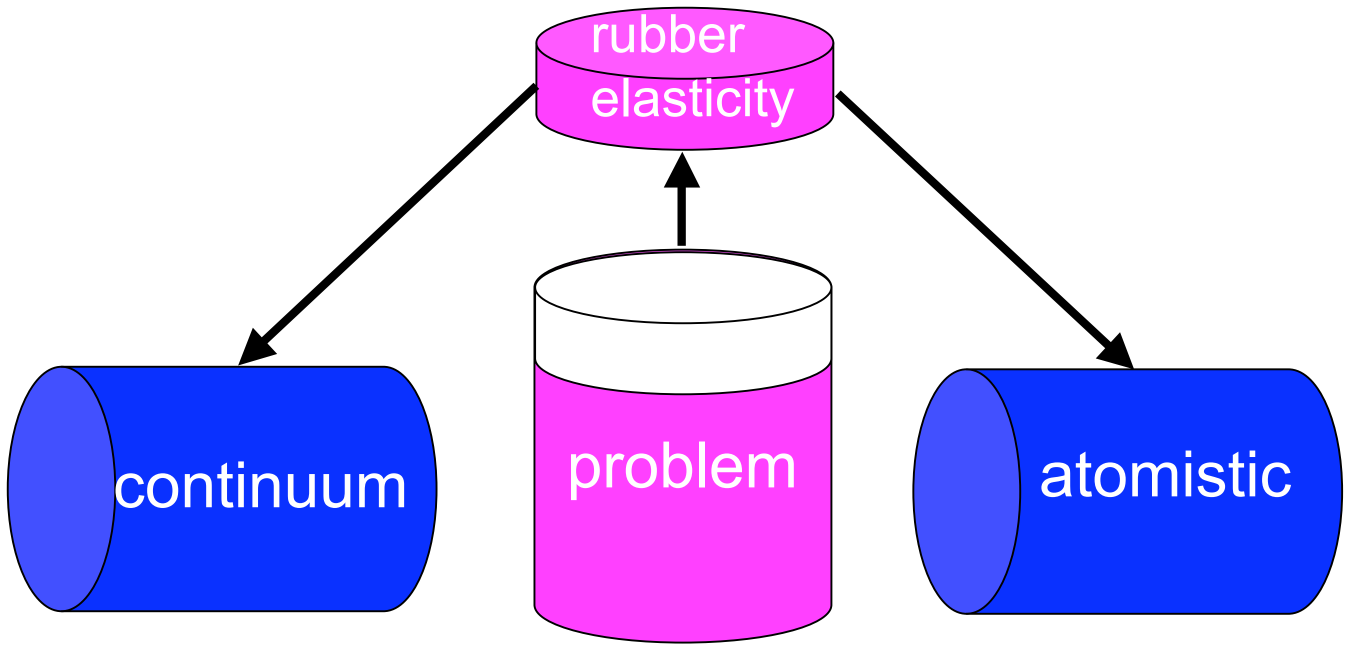

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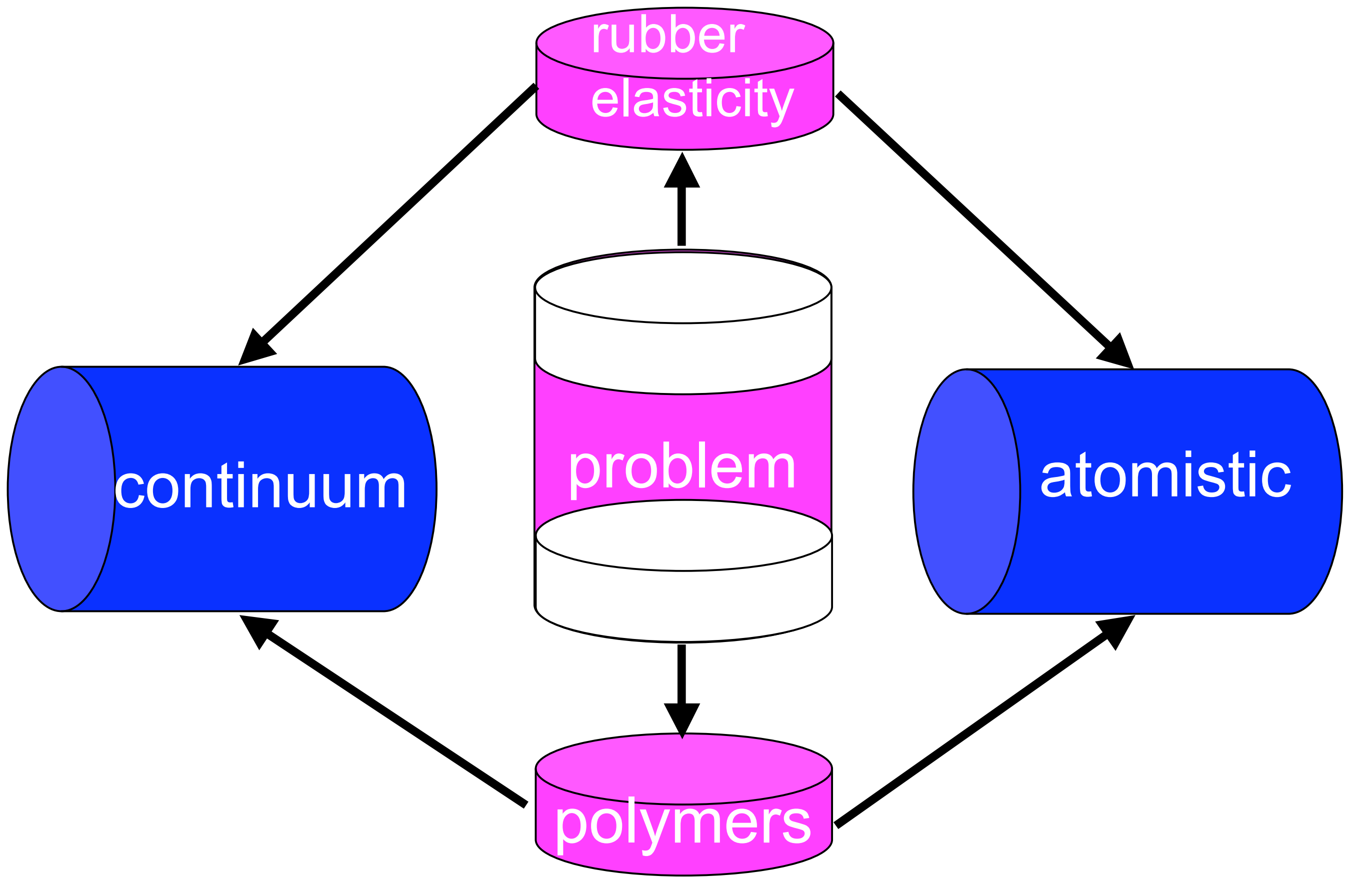

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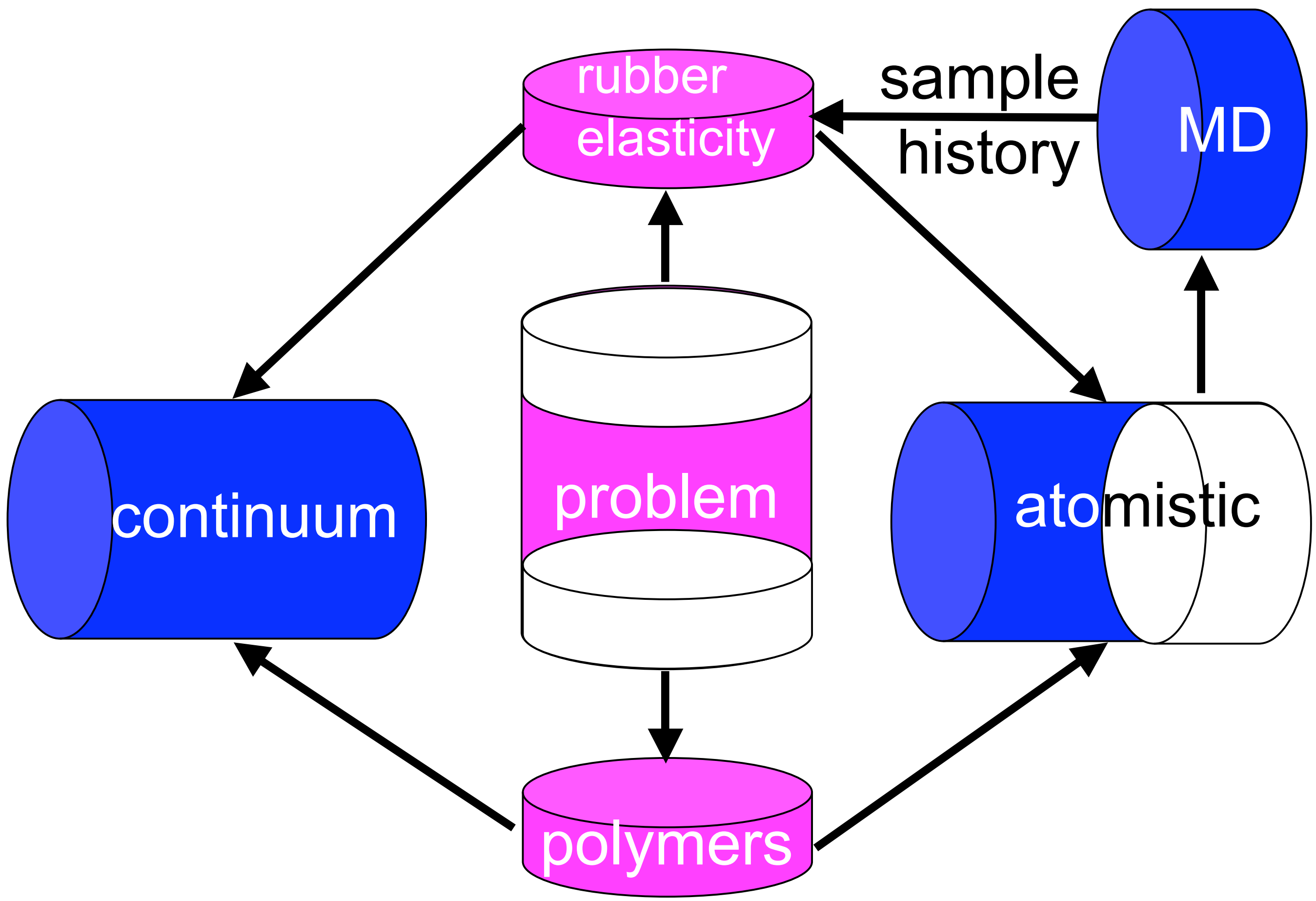
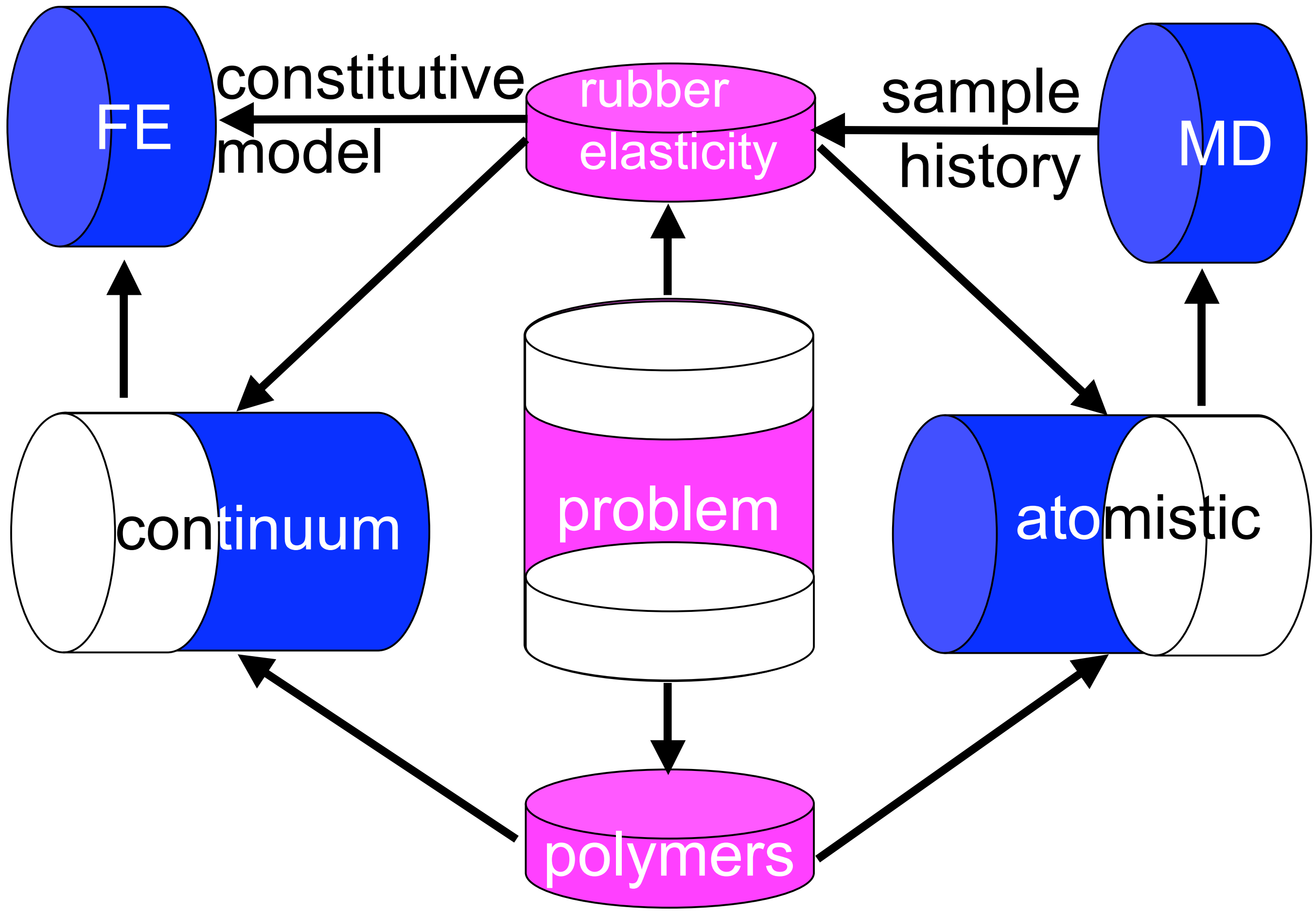

rubber
elasticity
sample
history
MD
continuum
problem
atomistic
polymers

Map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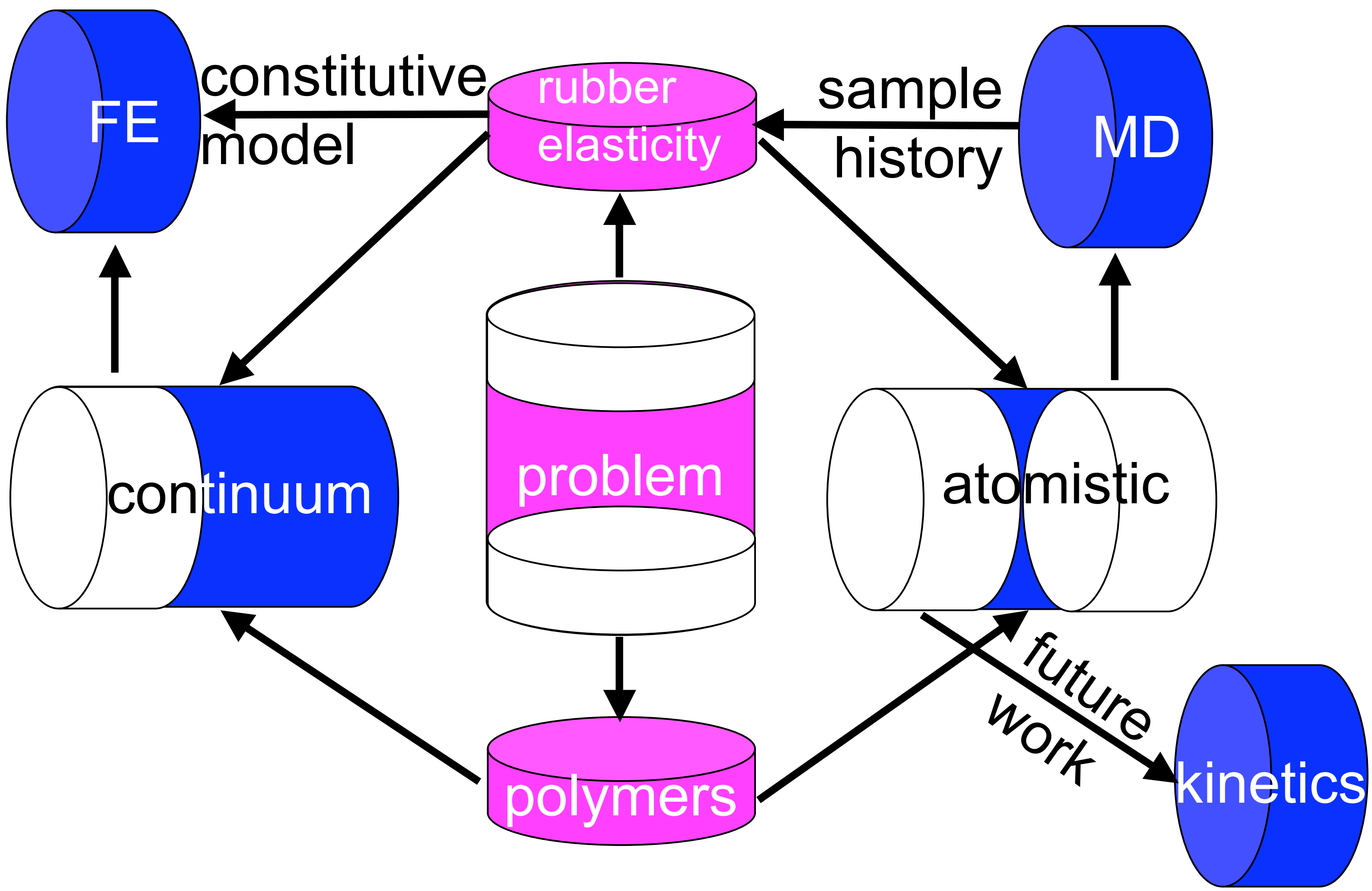
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history
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continuum
problem
atomistic
future
work
kinetics
polymers

Motivation

rubber + compression

time

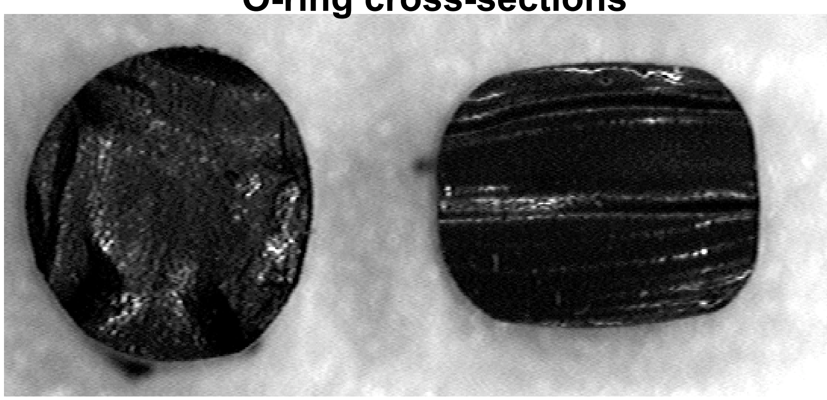
permanent set ⟷ loss of sealing force

o-ring fails

best case:
damaged electronics

worst case:
Challenger blows up

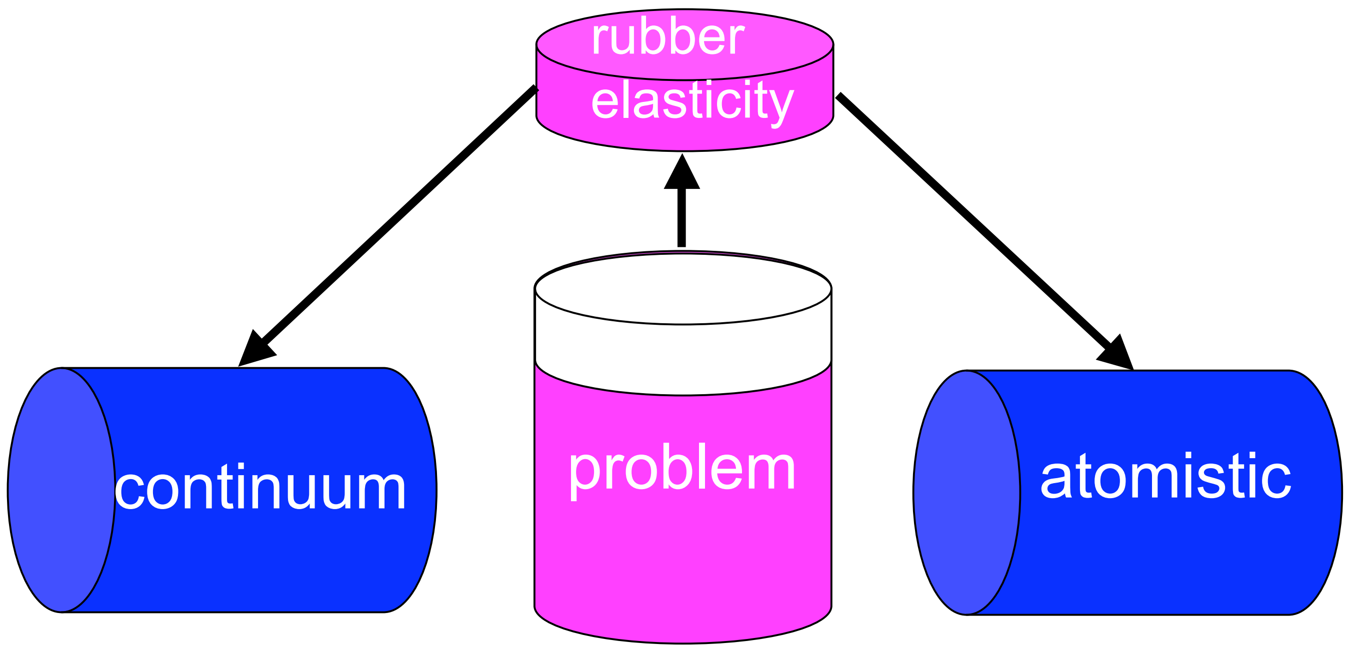
O-ring cross-sections



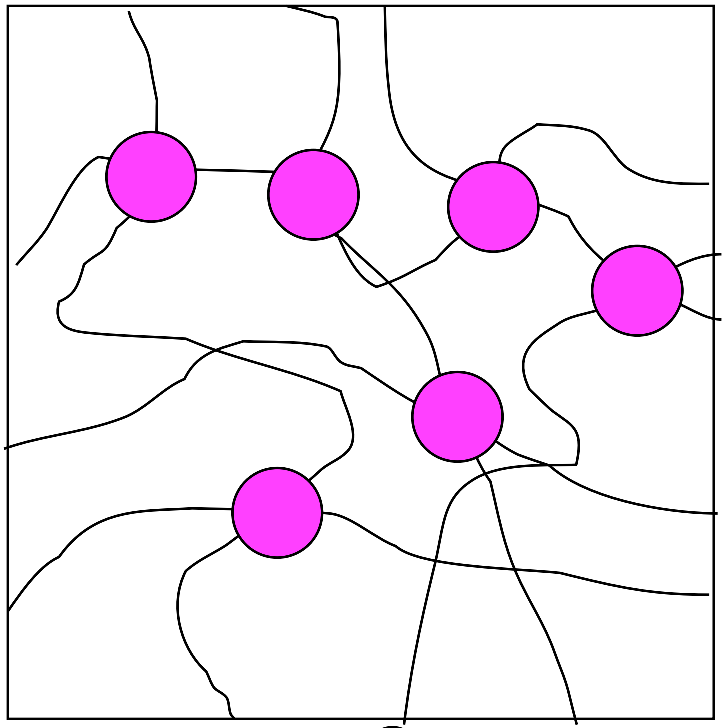
unaged **aged 15 years**

KT Gillen

Map

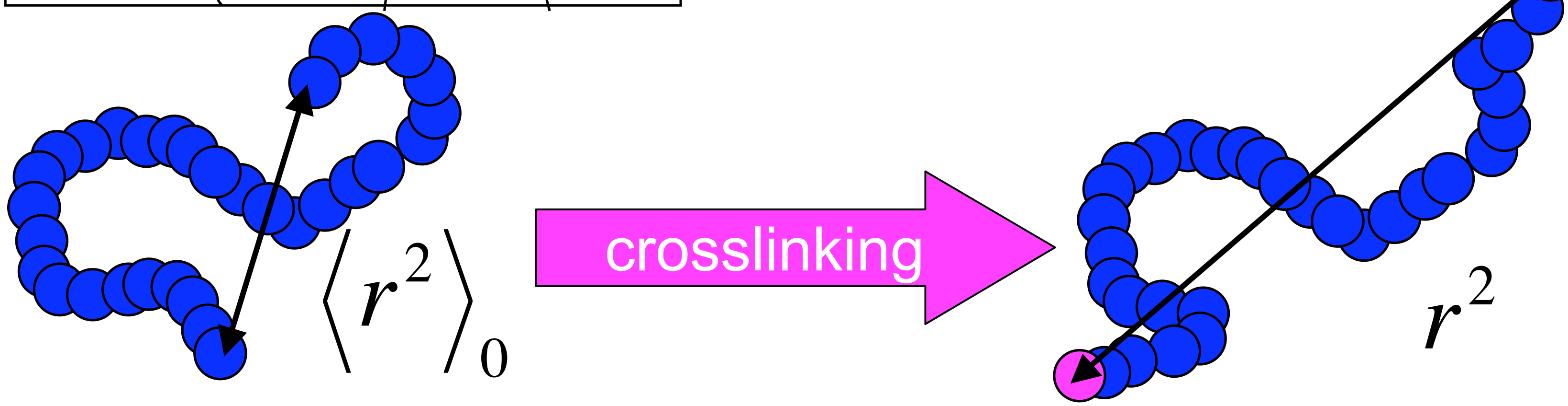


Rubber Elasticity (Atomistic)



Networks carry stress

$$\frac{F^{el}}{k_B T} = \frac{3}{2} \sum_{chains} \left[\frac{r_t^2}{\langle r_t^2 \rangle_0} - 1 \right]$$



Changes in the average chain dimensions affect the stress

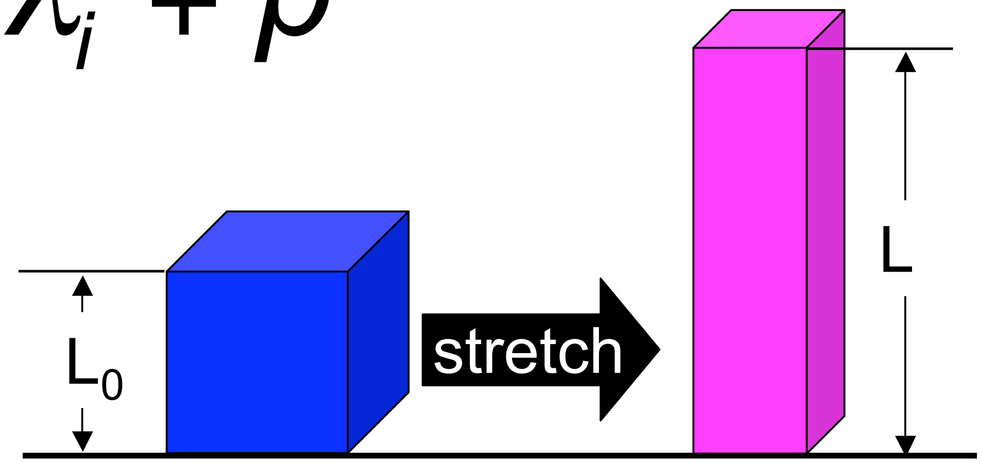
Rubber Elasticity (Continuum)

G= material-specific modulus

p~hydrostatic pressure

$$\sigma_i = G\lambda_i^2 + p$$

$$\lambda_i = \frac{L_i}{L_{0i}}$$

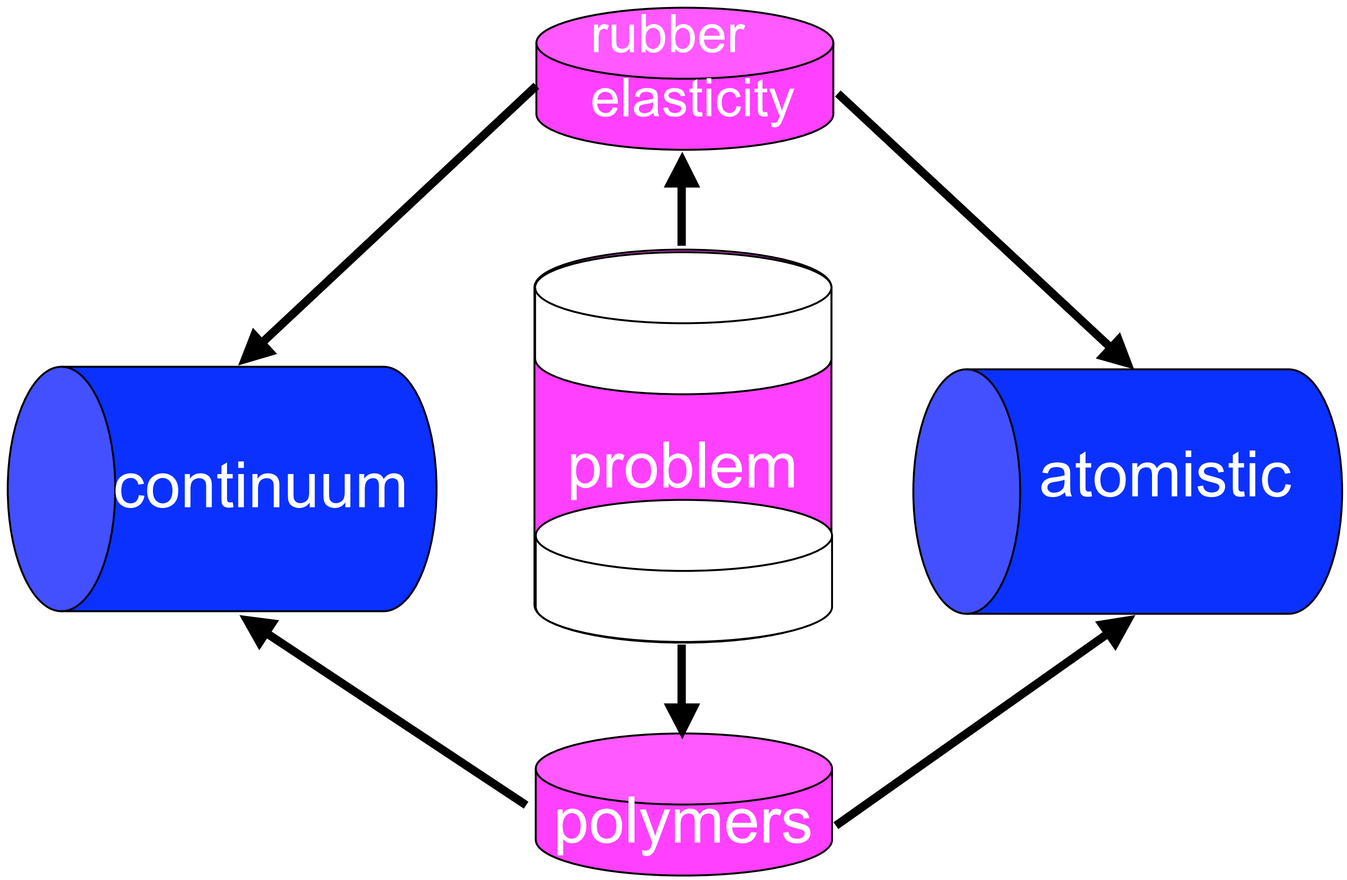


Changes in sample dimensions affect the stress

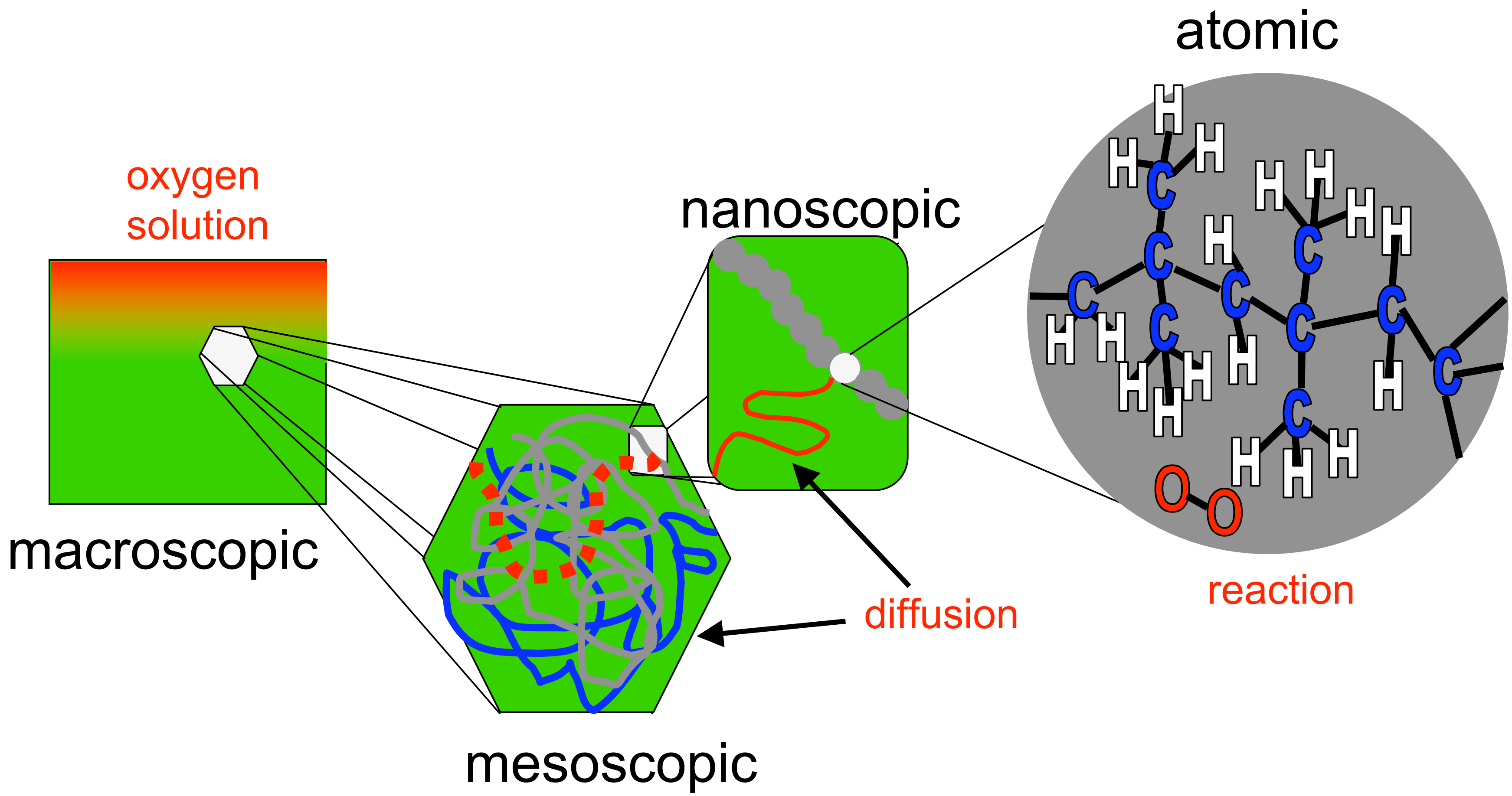
stretched sample → heat → contraction

polymer nature → entropic effect

Map



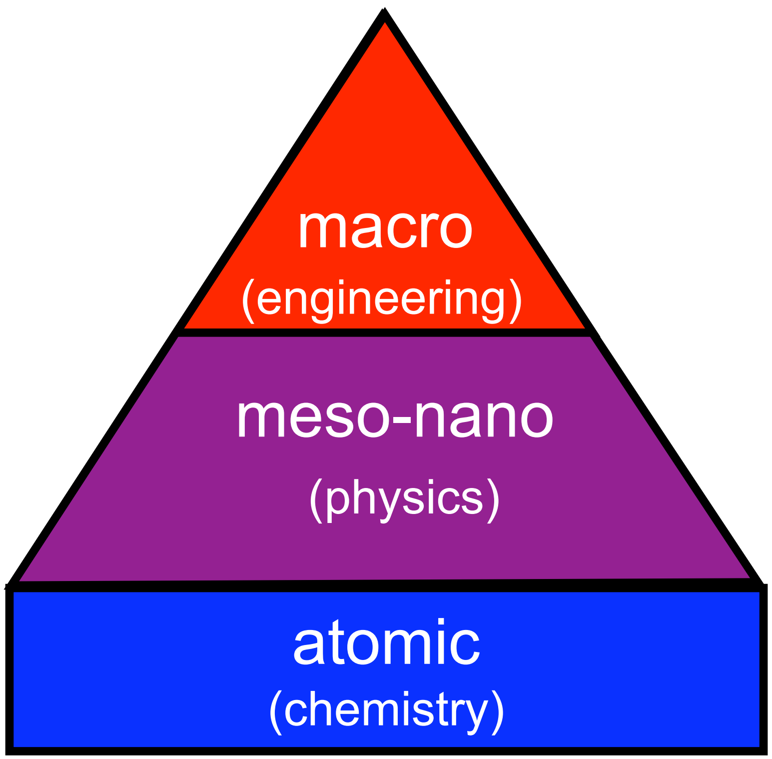
Goal: Predict Material Properties for Engineering Applications

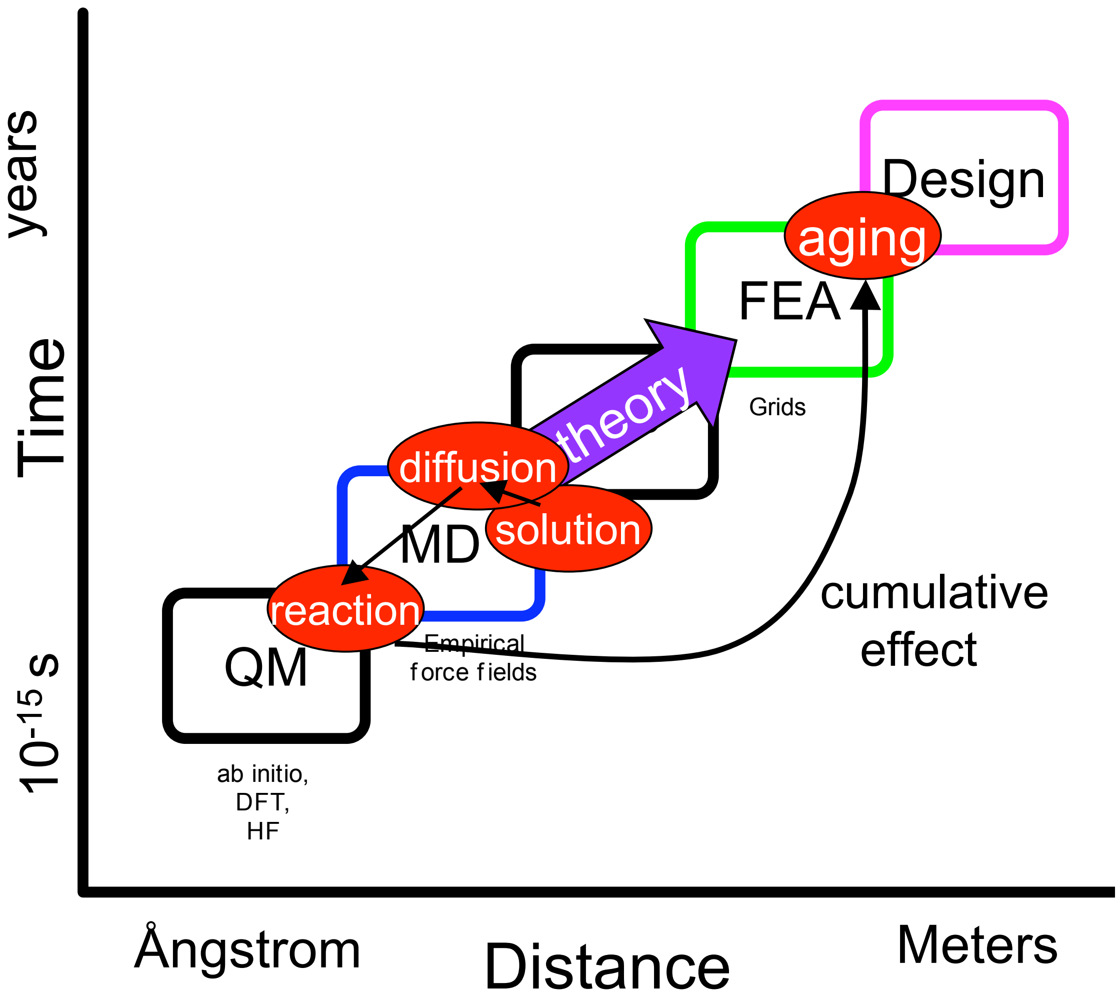


Good predictions at the macroscopic level require knowledge of chemistry and physics at smaller levels!

Problem: Processes of Interest Span Multiple Scales

Hierarchical Approach





Strategy

MD Simulations
Coarse-Grained Model
Controlled Reactions

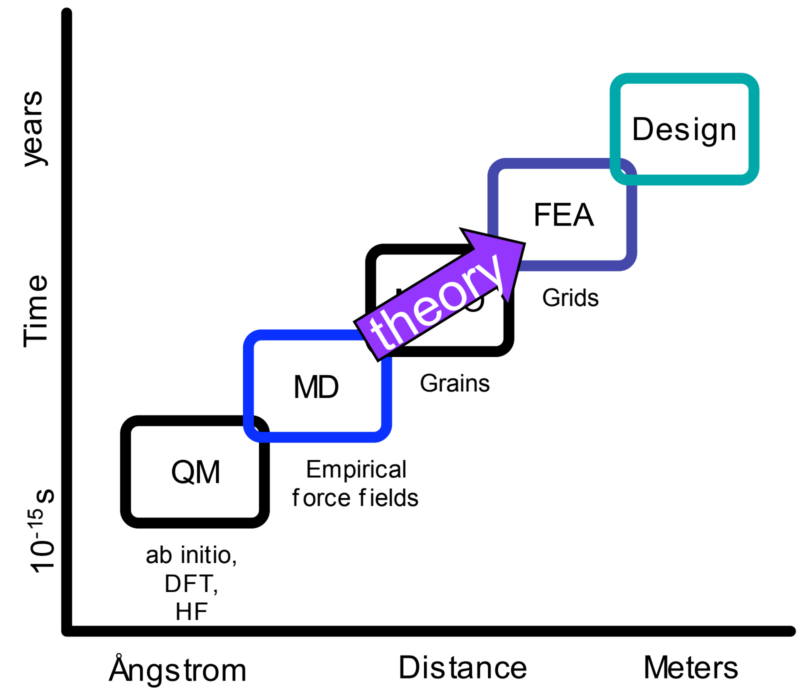
Controlled
Deformation History

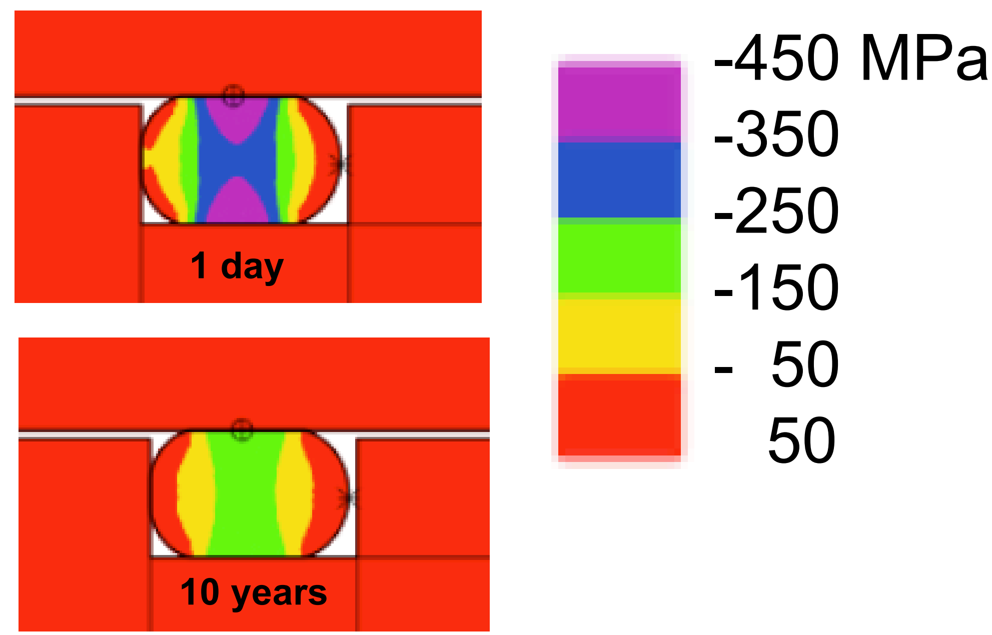
Stress Contributions
Crosslinks
Entanglements
Stress Transfer

Constitutive
Model

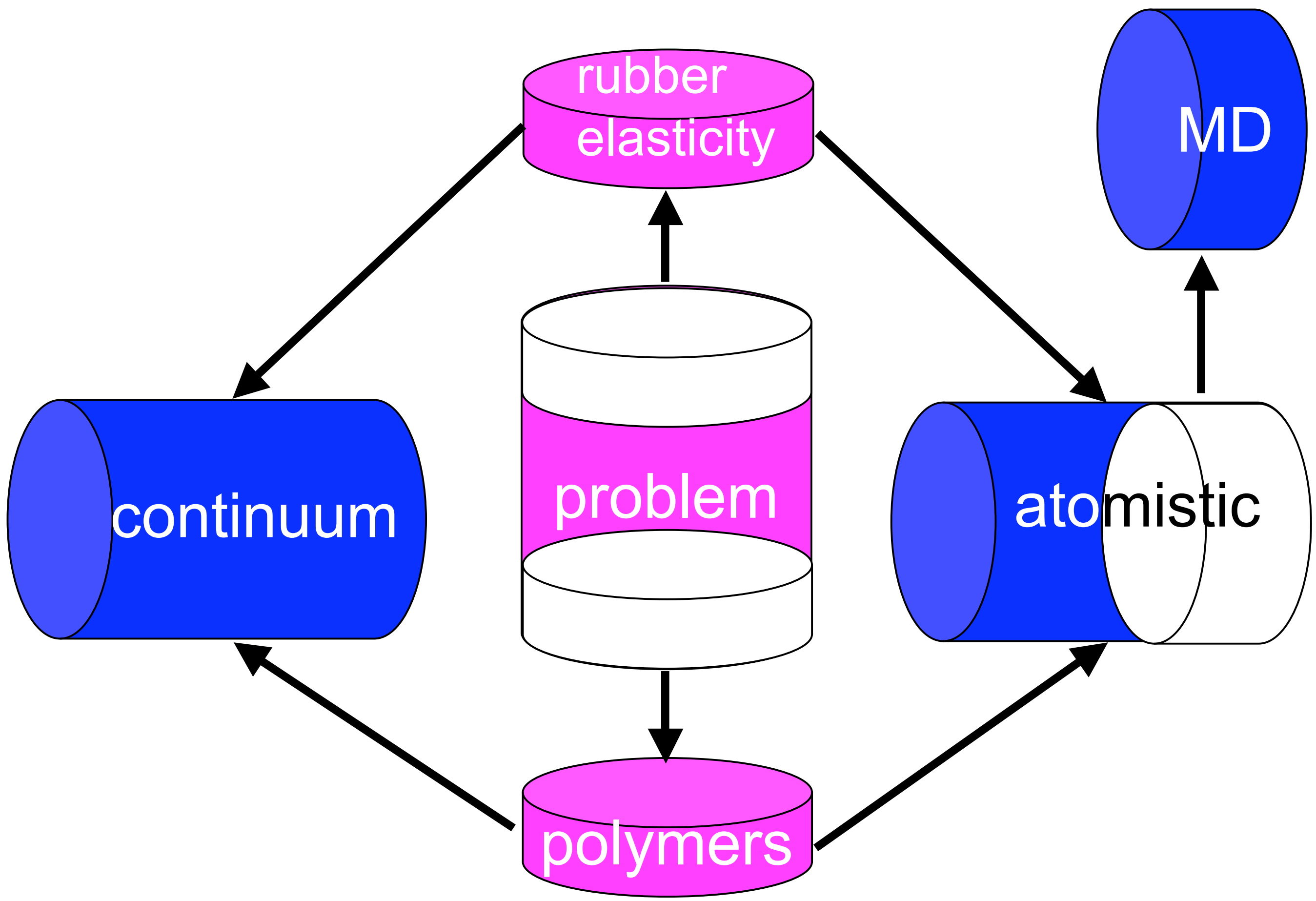
Finite Element
Calculations

O-ring
Aging





Map


rubber
elasticity
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Coarse-grained polymers

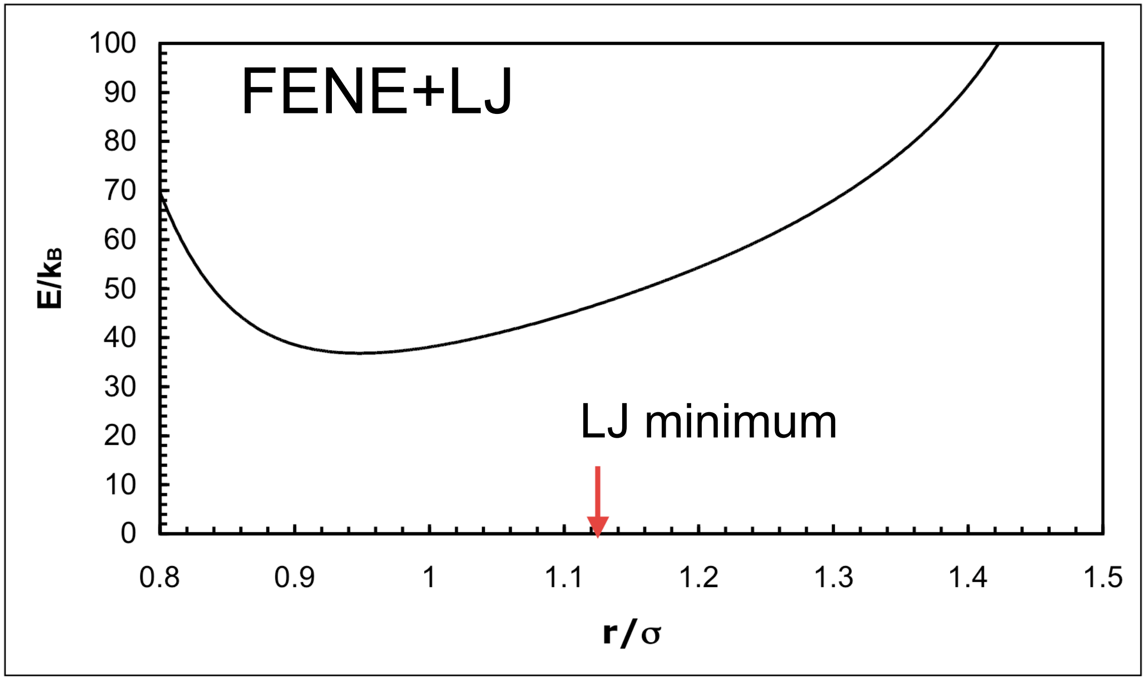
Essential Physics
- bonded
- excluded volume

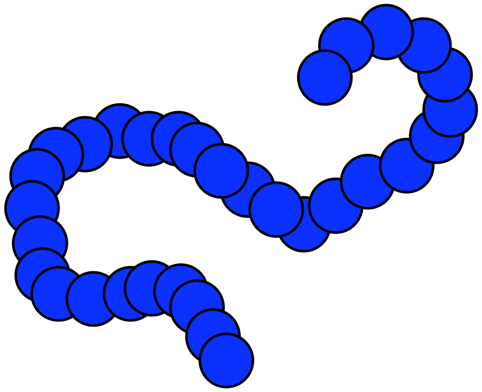
$$U_{LJ} = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] + \varepsilon \qquad r \le 2^{1/6}\sigma$$

$$U_{LJ} = 0 \qquad r > 2^{1/6}\sigma$$

$$U_{FENE} = -\frac{HR_0^2}{2}\ln\left[1 - \frac{r}{R_0}\right] \qquad r < R_0$$

$$U_{FENE} = \infty \qquad r \ge R_0$$





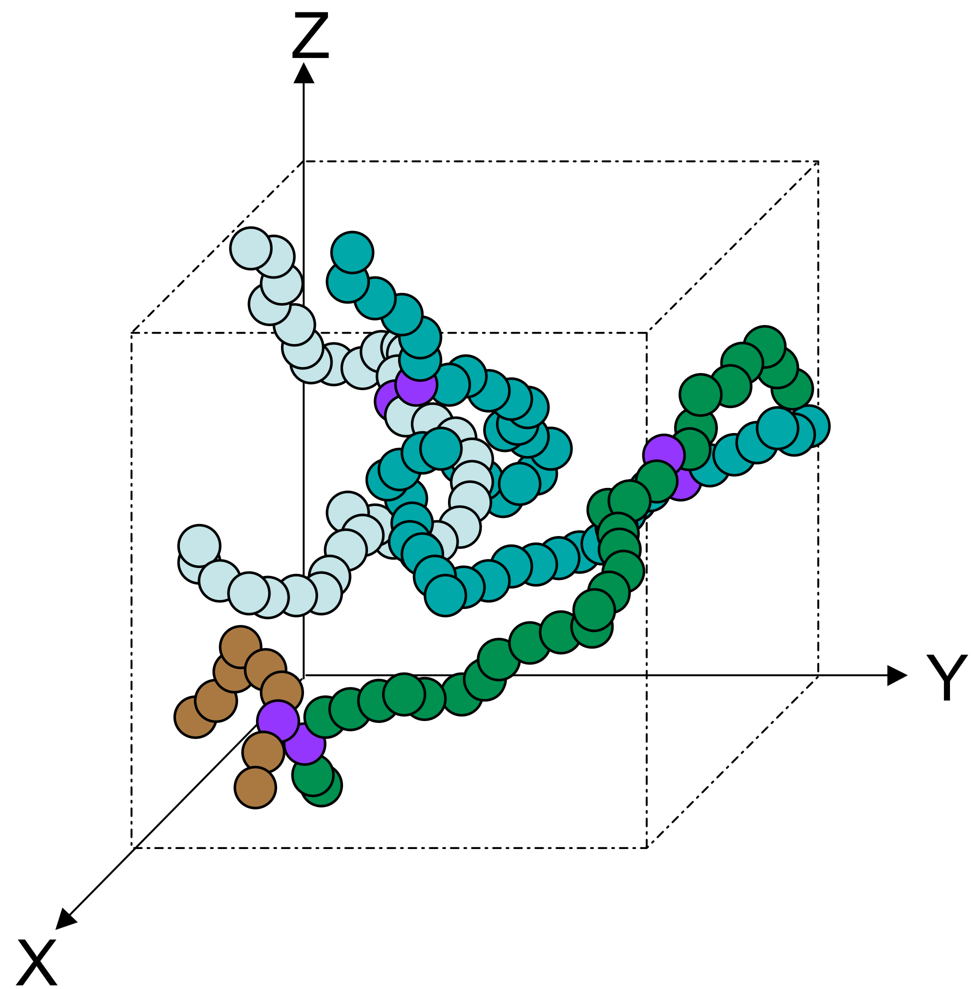
MD System Specifics

500 chains, 500 sites each, 20 reactive sites/chain

ρ=0.85 sites/volume
T*=1.0

1. Equilibrate
2. React
3. Equilibrate
4. Deform
5. Equilibrate
6. React
7. Equilibrate

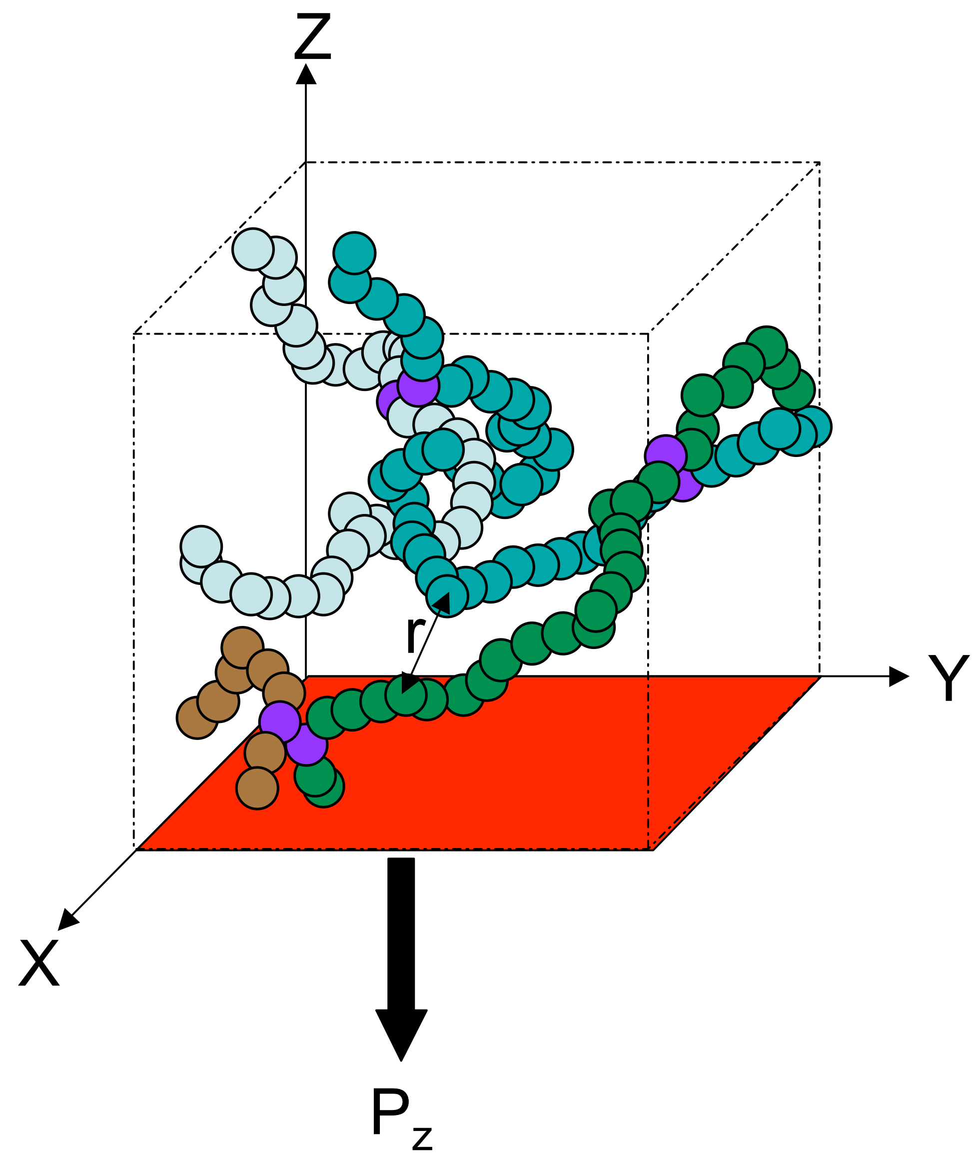
LAMMPS



Stress from MD

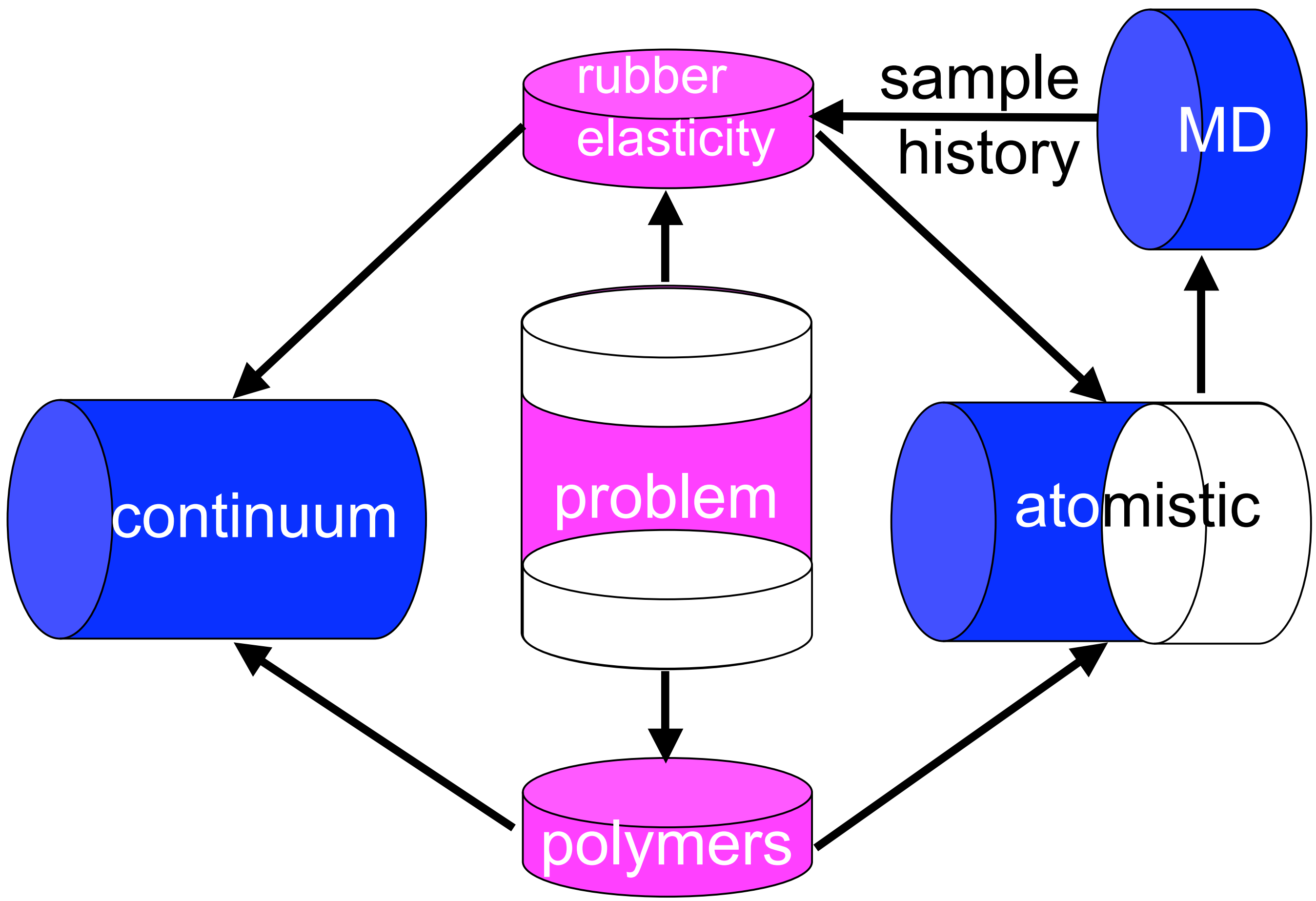
$$P = \left\langle \rho k_B T + \frac{1}{3V} \sum_i \sum_{j>i} r_{ij} \bullet f_{ij} \right\rangle$$

$$\sigma_{zz}^{dev} = P_z - \frac{1}{3} Tr \underline{\underline{P}}$$



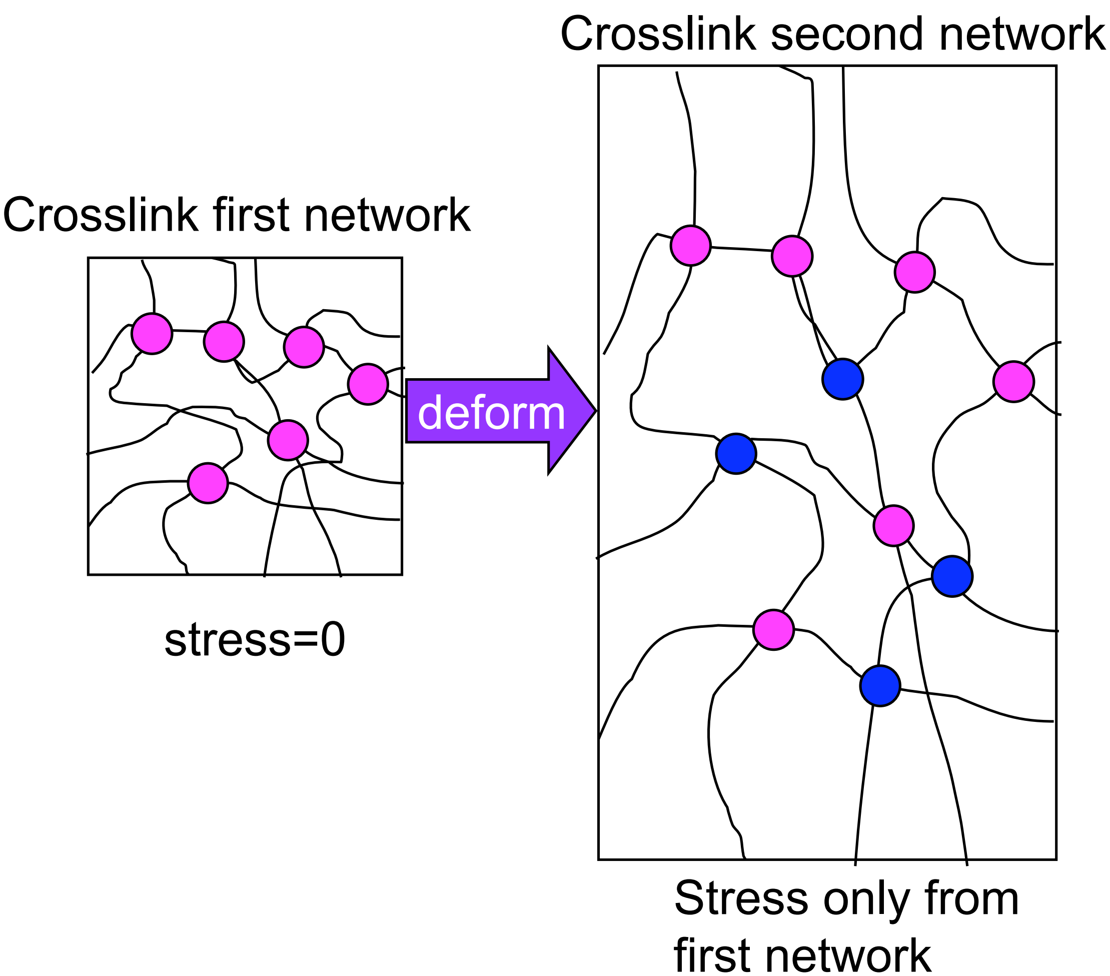
Calculate stress components from pressure components

Map



rubber elasticity
sample history
MD
continuum
problem
atomistic
polymers

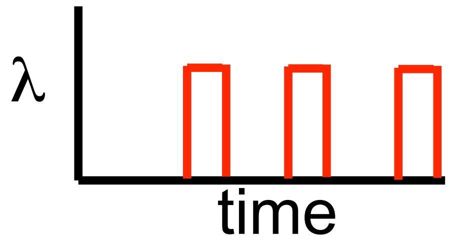
Independent Network Hypothesis

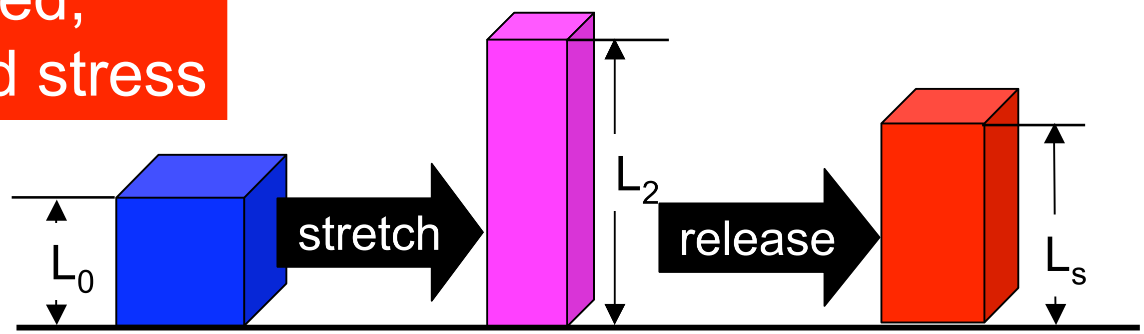


Reaction and strain histories are coupled

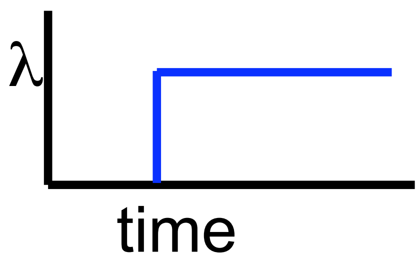
Experimental Data for INH

Intermittent: hold unstrained, periodic check of strained stress



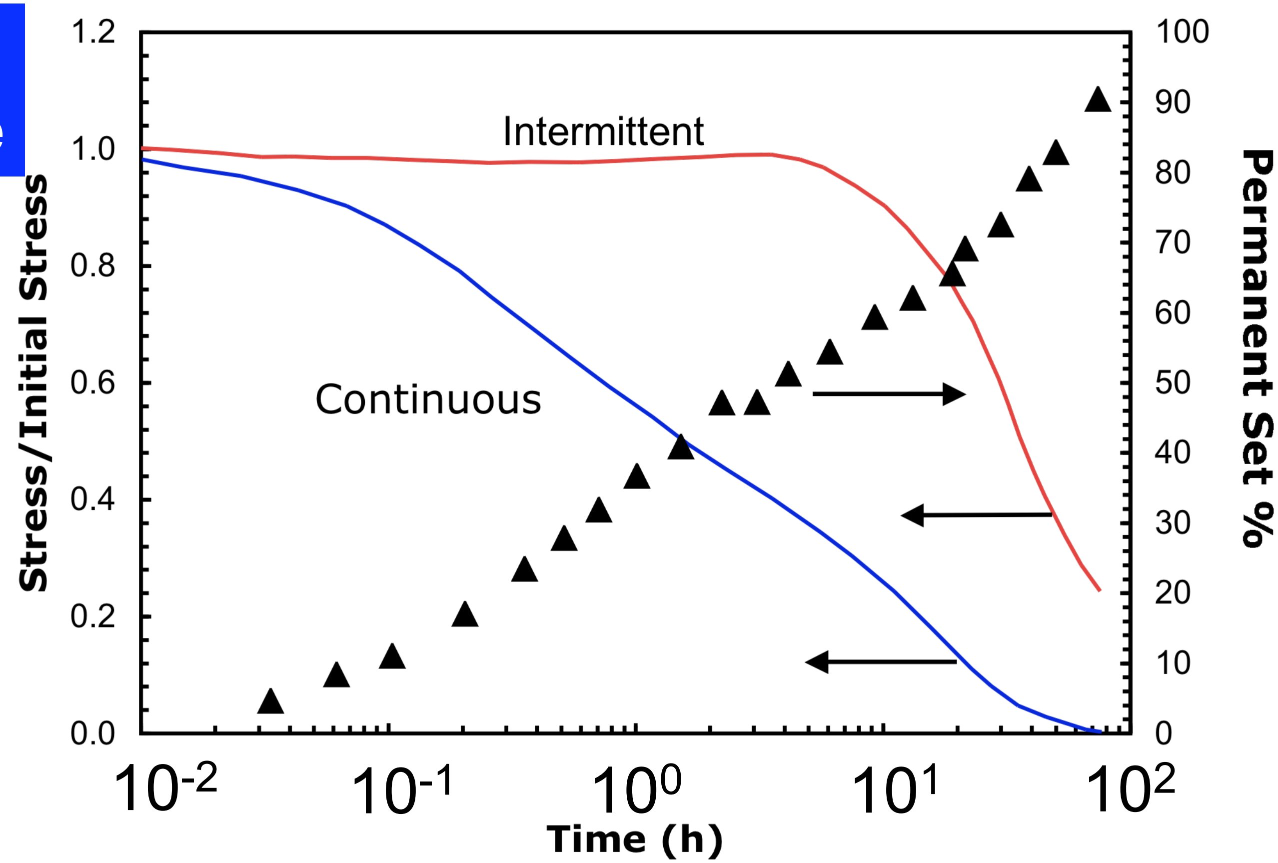


Continuous: hold in strained state



Butyl Rubber
130^0C, λ=1.5

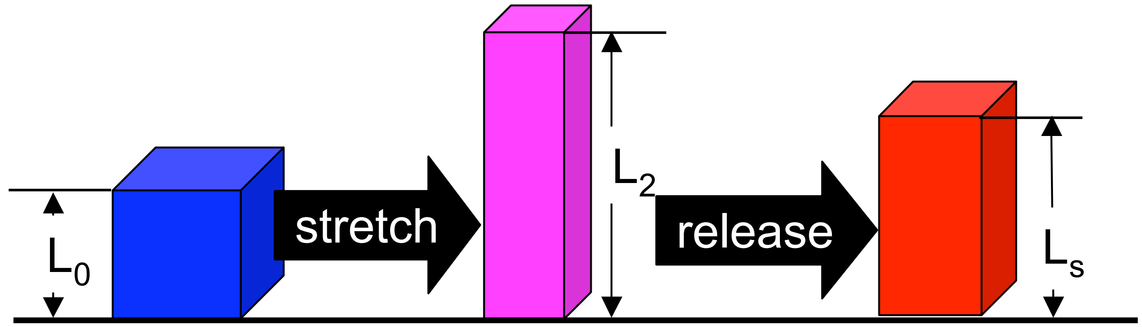
Andrews, Tobolsky, Hanson
J. Appl. Phys. 17, 352 (1946)



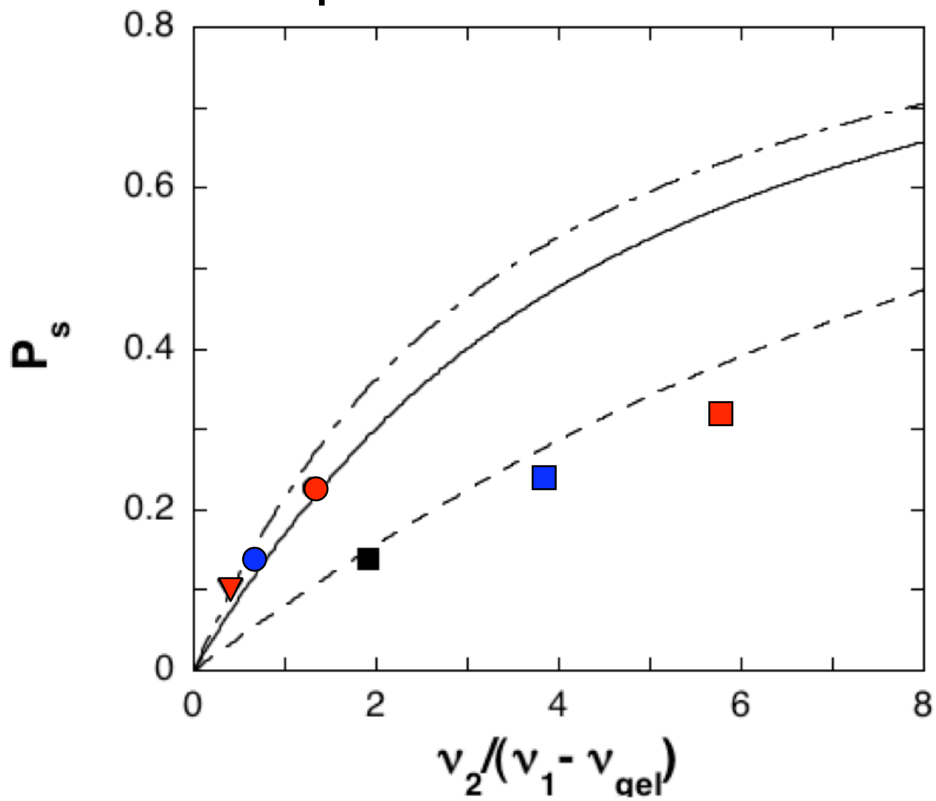
Permanent Set from MD

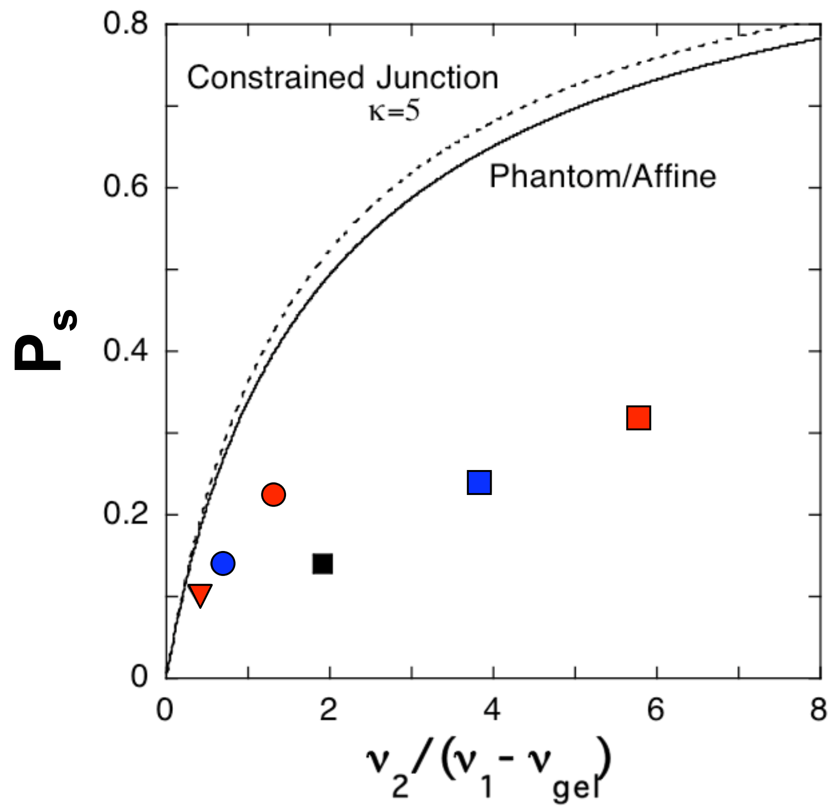
Uniaxial extension

$$P_s = \frac{\lambda_s - \lambda_0}{\lambda_2 - \lambda_0}$$



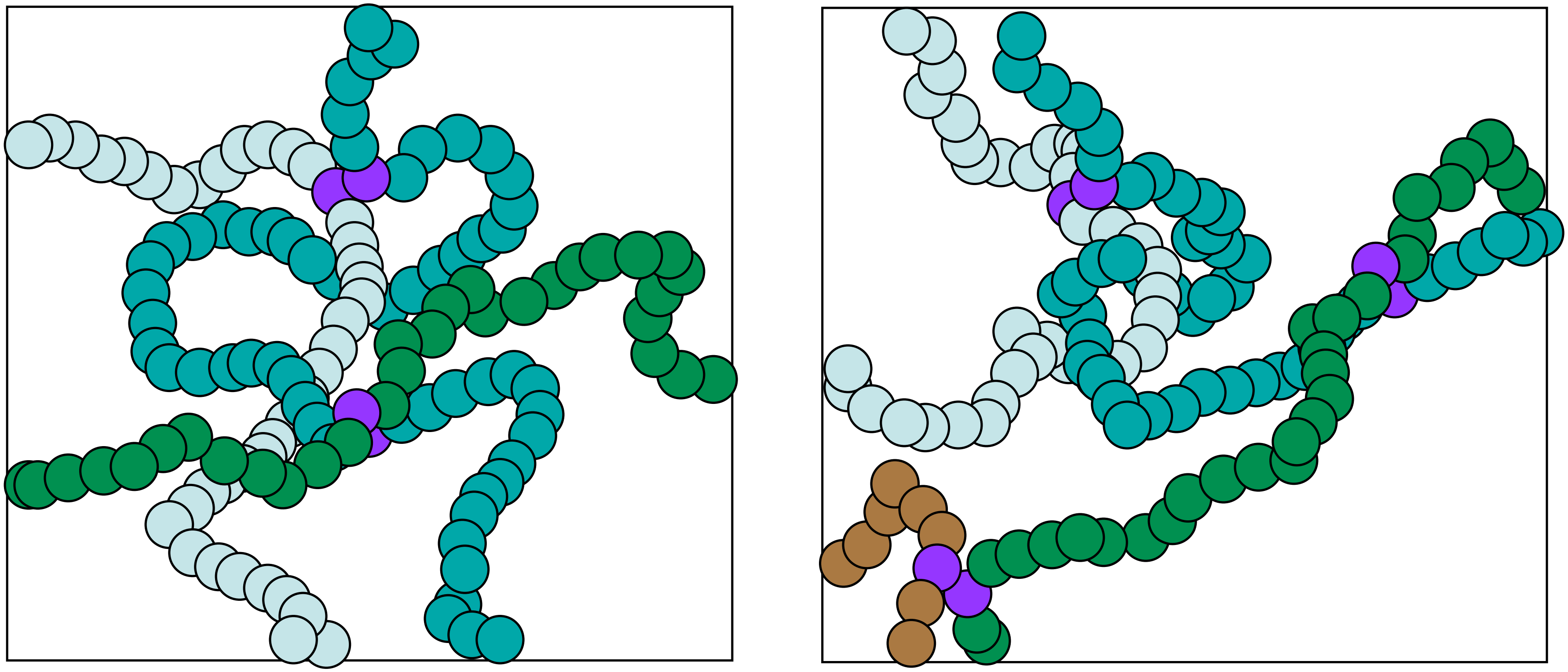
Slip-tube model





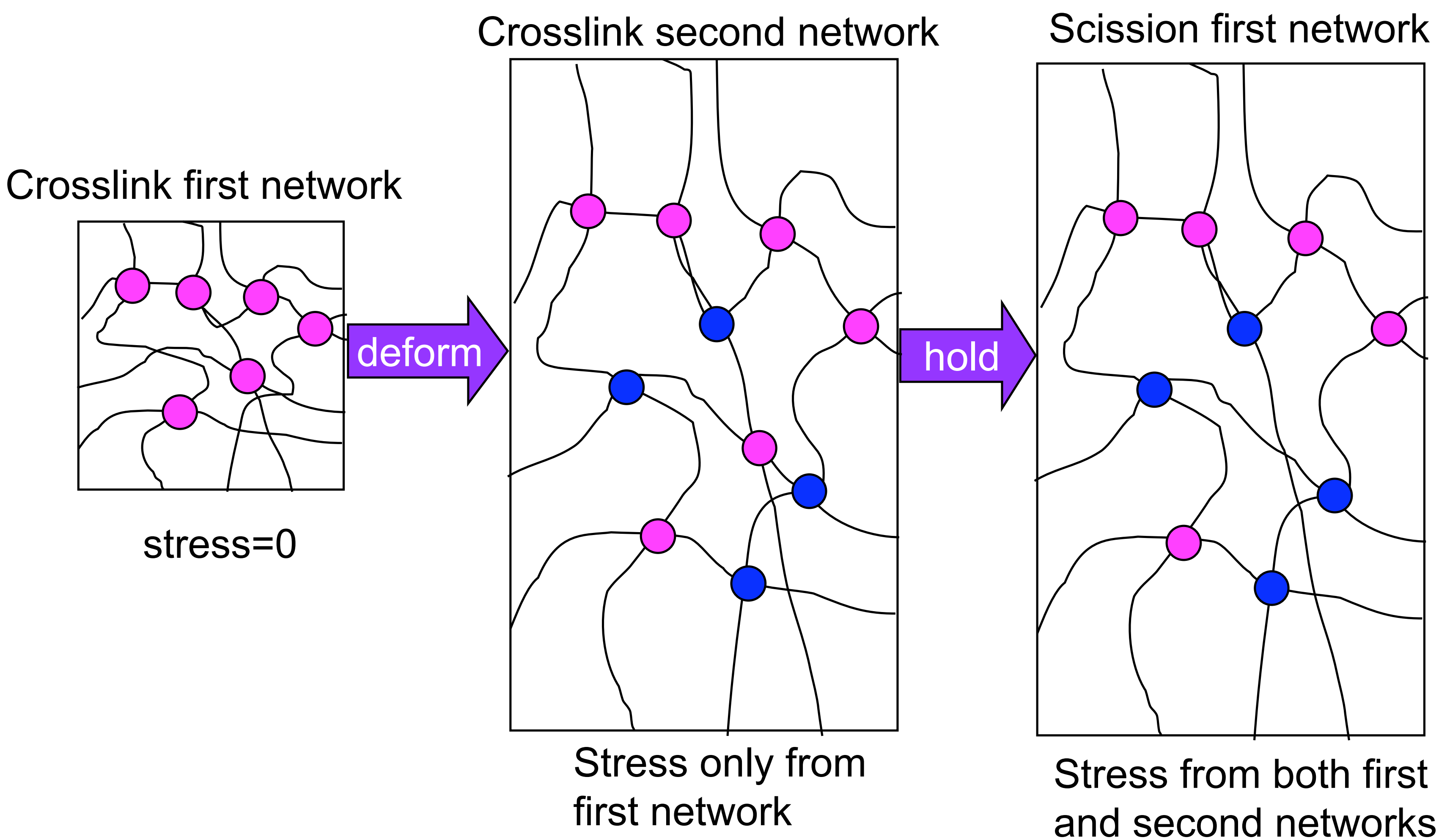
Rottach et al. Submitted to Macromolecules Spring 2006

Entanglements



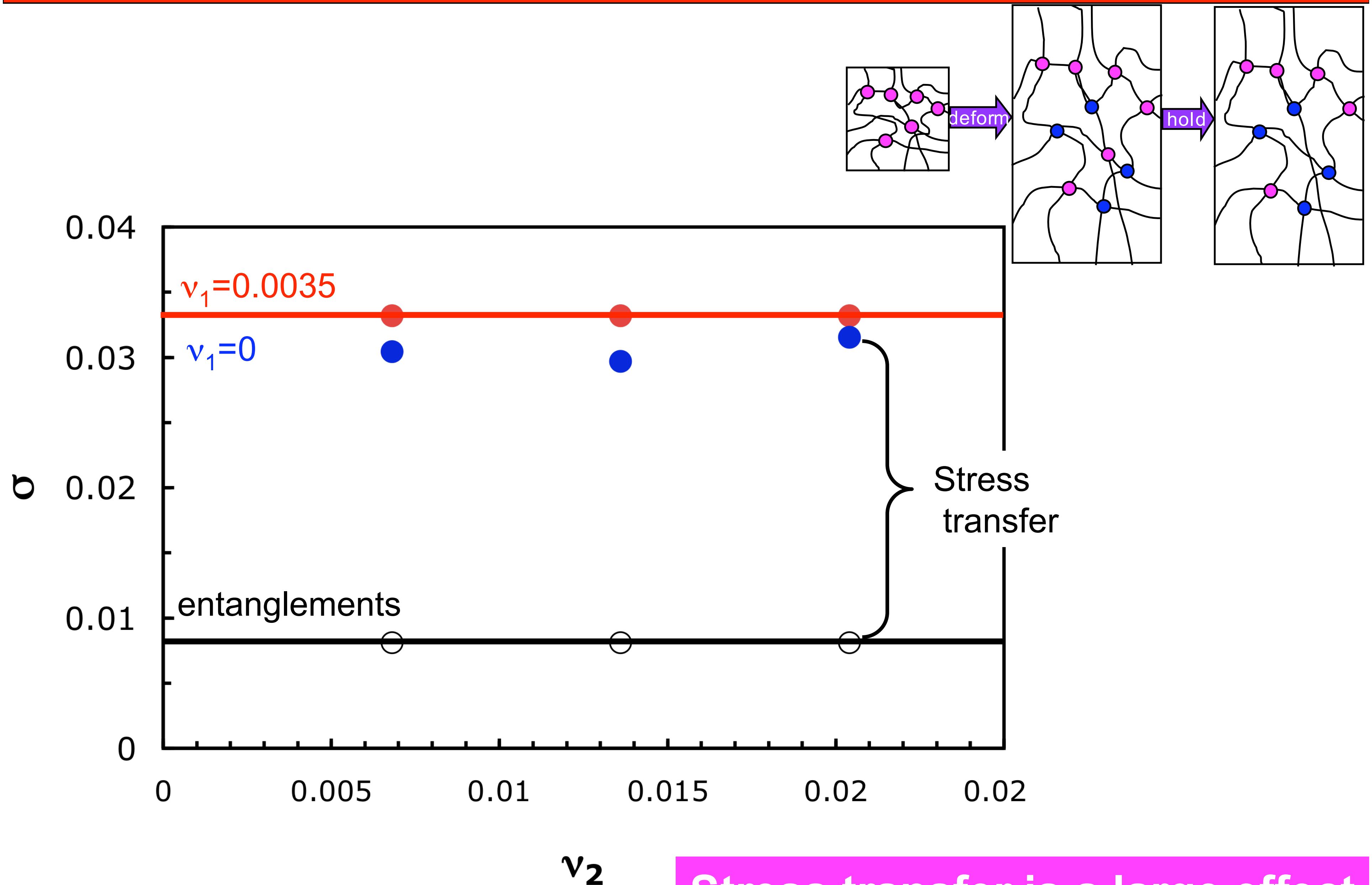
Trapped entanglements also contribute to stress

Independent Network Hypothesis (Revisited)



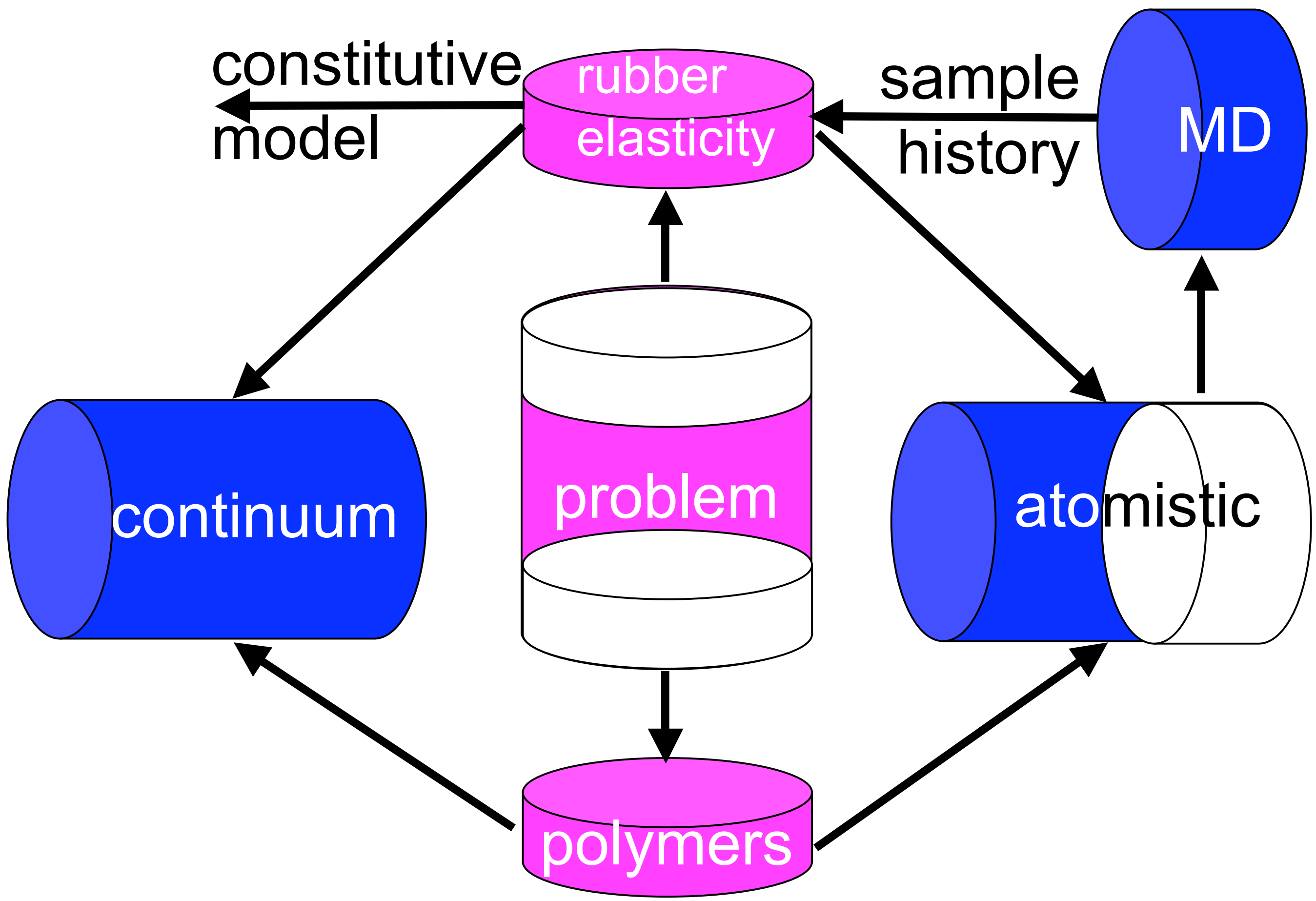
Sample retains memory of crosslinking and strain history

MD Simulation with Scission



Stress transfer is a large effect

Map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elasticity
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General Constitutive Model

crosslinks   entanglements

$$W\left(\lambda_x,\lambda_y,\lambda_z\right)=\sum_{k=1}^{n}W_c\left(\nu_k^{eff},\lambda_x/\lambda_{xk},\lambda_y/\lambda_{yk},\lambda_z/\lambda_{zk}\right)+W_e\left(\nu_e,\lambda_x,\lambda_y,\lambda_z\right)$$

standard phantom model
with effective crosslink density

slip-tube model

$$\nu_k^{eff}=\nu_k\left(1-\sum_{i=1}^{k-1}\sum_{p=k}^{n}\Phi_i^p\right)+\sum_{i=k+1}^{n}\nu_i\sum_{p=i}^{n}\Phi_k^p$$

Rubinstein,Panyukov
Macromolecules 35, 6670 (2002)

stress transfer functions

Flory Trans. Faraday Soc. **56**, 722 (1960)
Fricker Proc. R. Soc. Lond. A. **335**, 267 (1973)

$$\Phi_i^j\approx\frac{\text{stage i crosslinks removed in stage j}}{\text{total number of crosslinks added up through stage j}}$$

Use independent network hypothesis to formulate strain energy.
Use common form of principal stretches.

Entanglement Network

Sample most likely between 30% and 300% of original dimensions

Slip-tube model computationally demanding for arbitrary strain

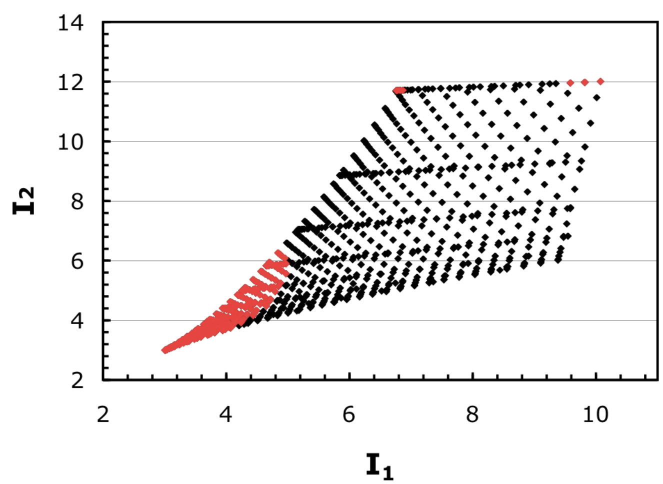
fit strain energy for expected deformations

Use invariant fit in FE to calculate stress

$$W = \frac{A}{2}\sum_{\alpha}\left(\frac{\lambda_\alpha}{\sqrt{g_\alpha}} + \frac{\sqrt{g_\alpha}}{\lambda_\alpha}\right) - \frac{A}{3}\sum_{\alpha}\ln\left(\frac{Ng_\alpha}{L}\right)$$

Rubinstein,Panyukov
Macromolecules 35, 6670 (2002)

$$0.3 \le \{\lambda_1, \lambda_2, \lambda_3\} \le 3$$



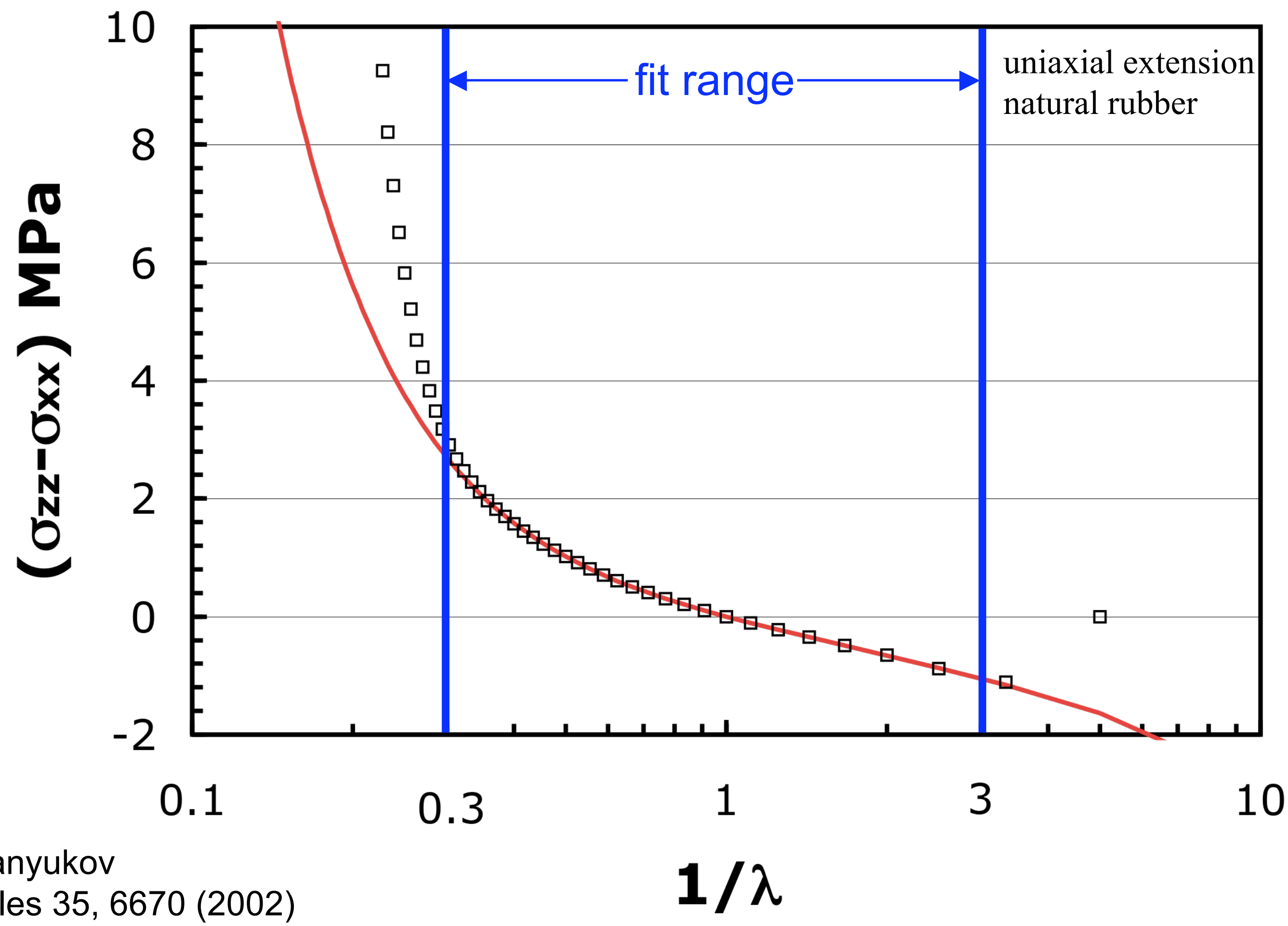
$$W = \sum_{i=1}^{3}\sum_{k=1}^{3} c_{ik}(I_1 - 3)^i (I_2 - 3)^k$$

$$I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2$$

$$I_2 = \lambda_1^2\lambda_2^2 + \lambda_2^2\lambda_3^2 + \lambda_3^2\lambda_1^2$$

MD shows that only first stage networks trap entanglements

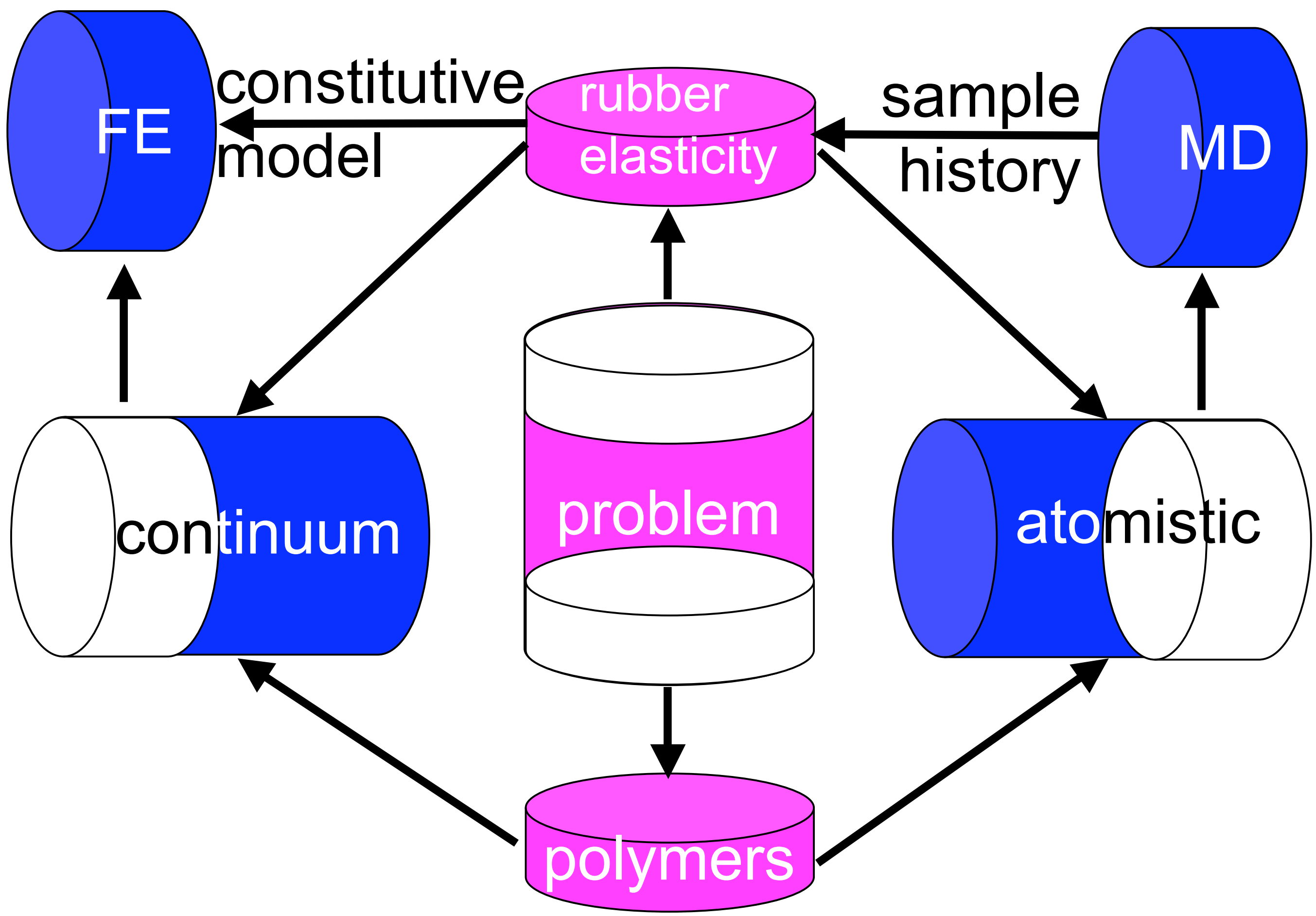
Comparing W to Experiment



Rubinstein,Panyukov
Macromolecules 35, 6670 (2002)

Strain energies were fit to $0.3 \le \{\lambda_1, \lambda_2, \lambda_3\} \le 3$ (arbitrary deformation)
Good agreement found between prediction and experiment

Map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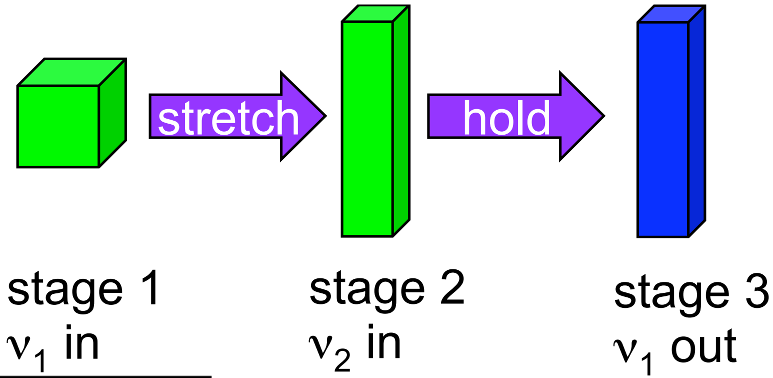
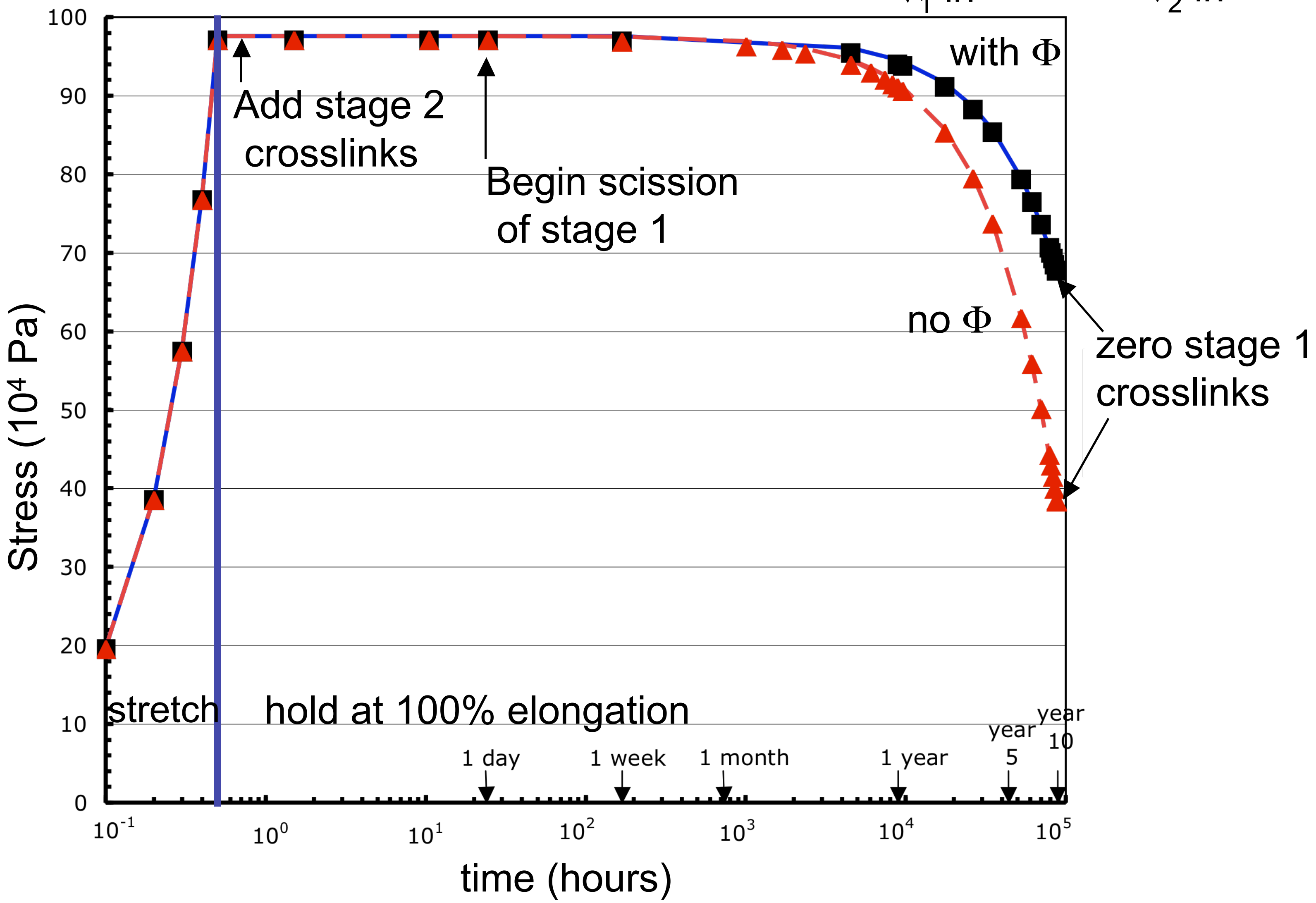
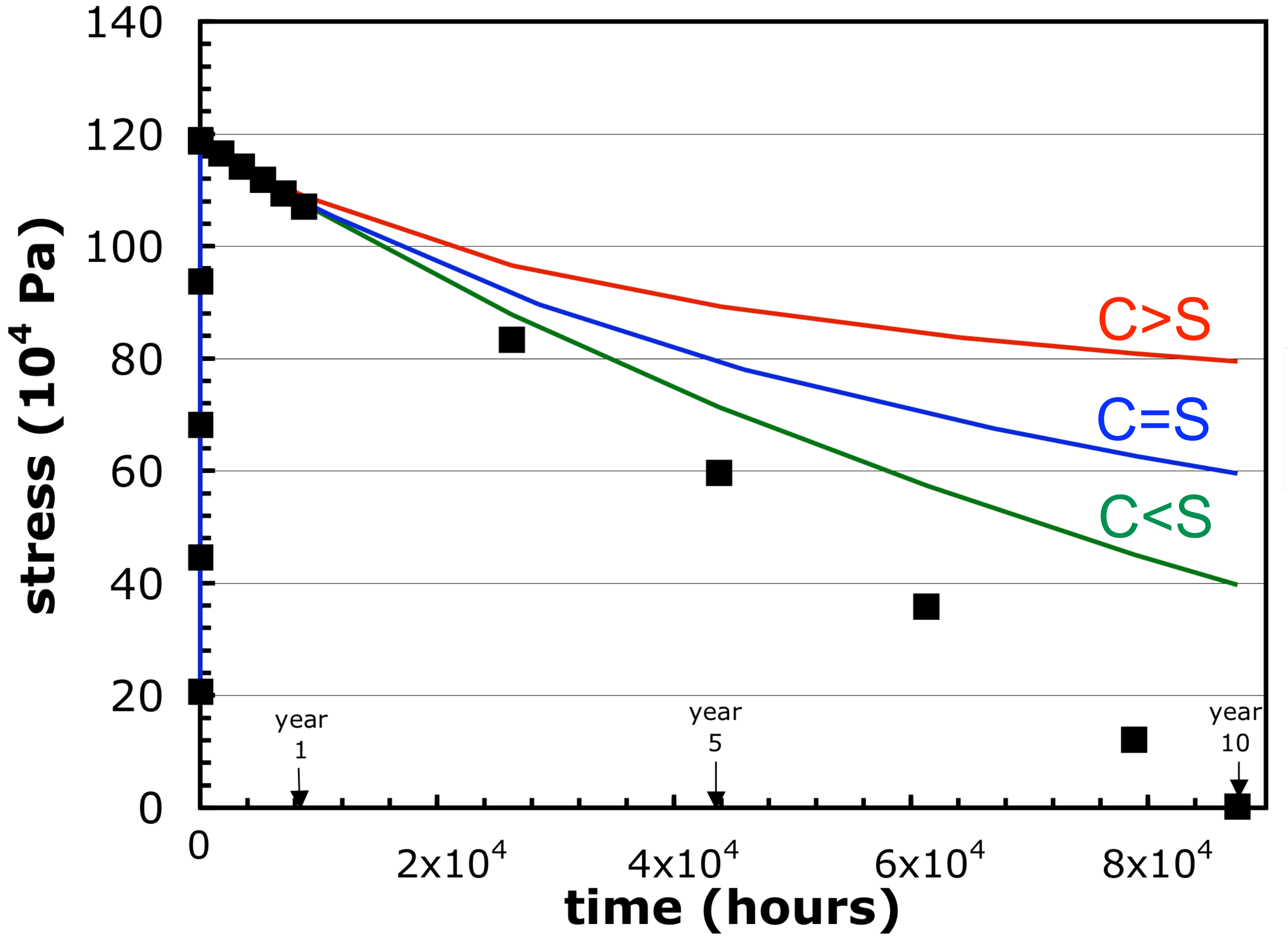
Finite Element



Final stress 80% higher using Φ

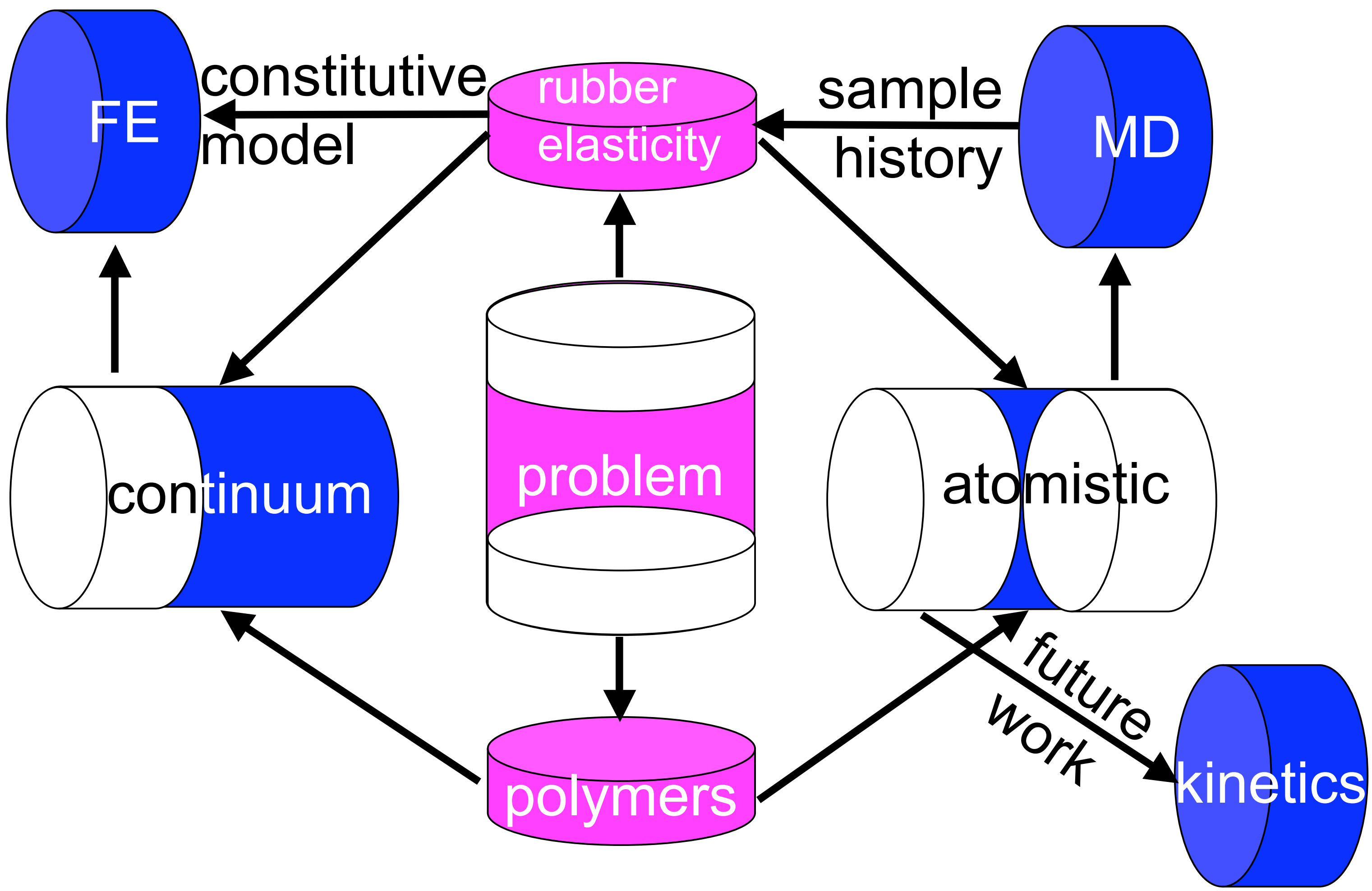


Simultaneous Crosslinking and Scission



Relative rates of scission and crosslinking make a large difference in the resulting stress

Map



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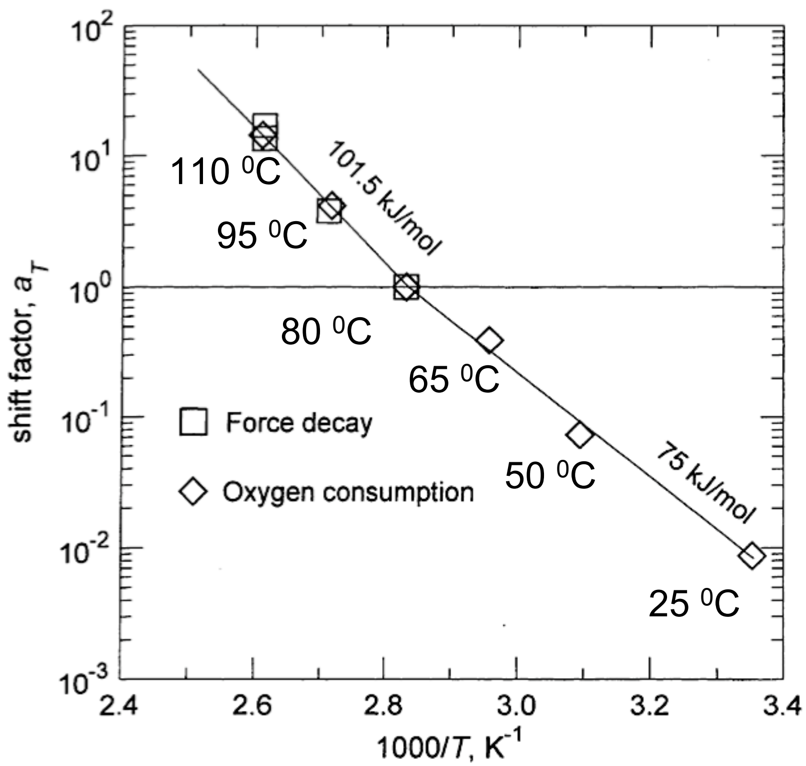
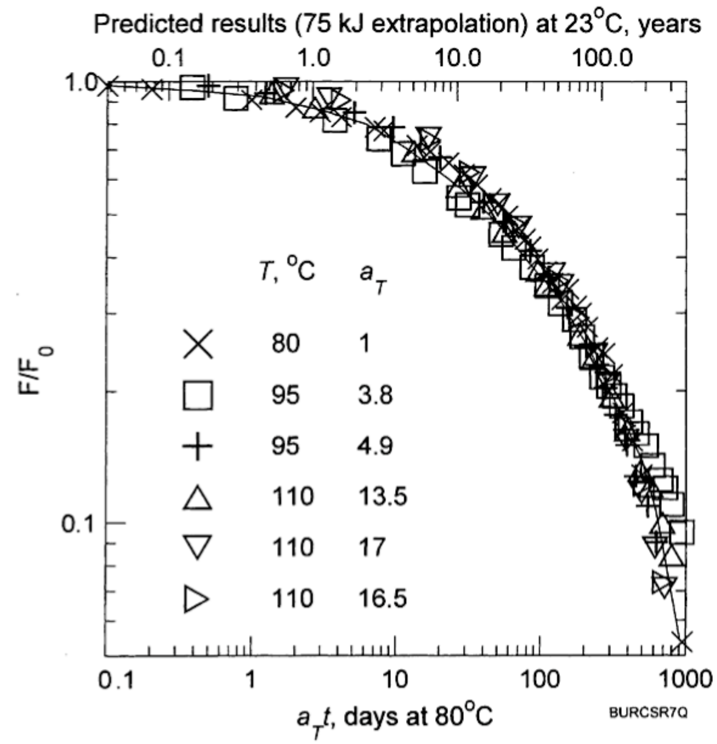
Experimental Kinetics

Butyl o-rings with accelerated aging

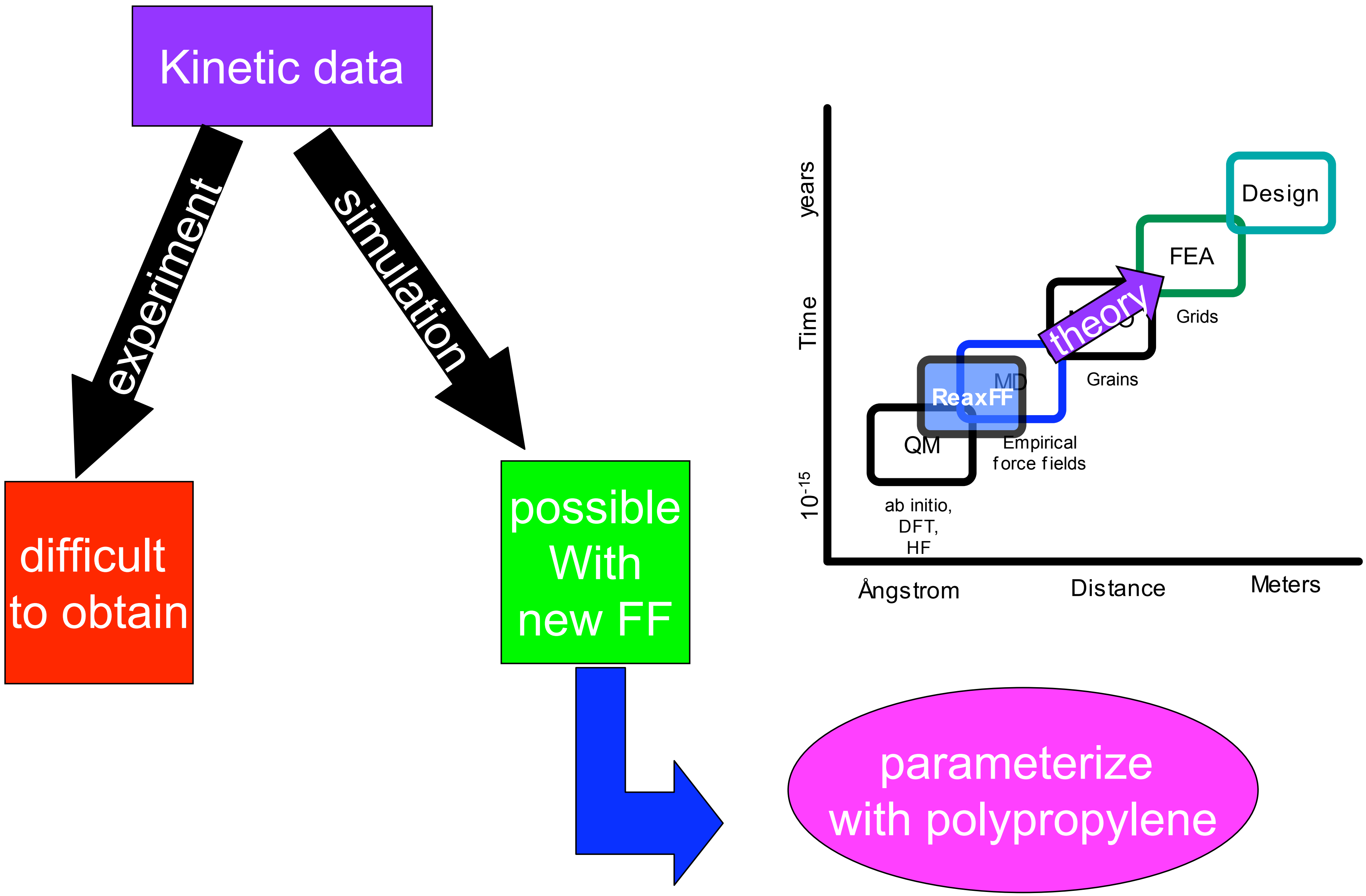




Gillen et al. Polym. Degrad. Stab. 82, 25 (2003)

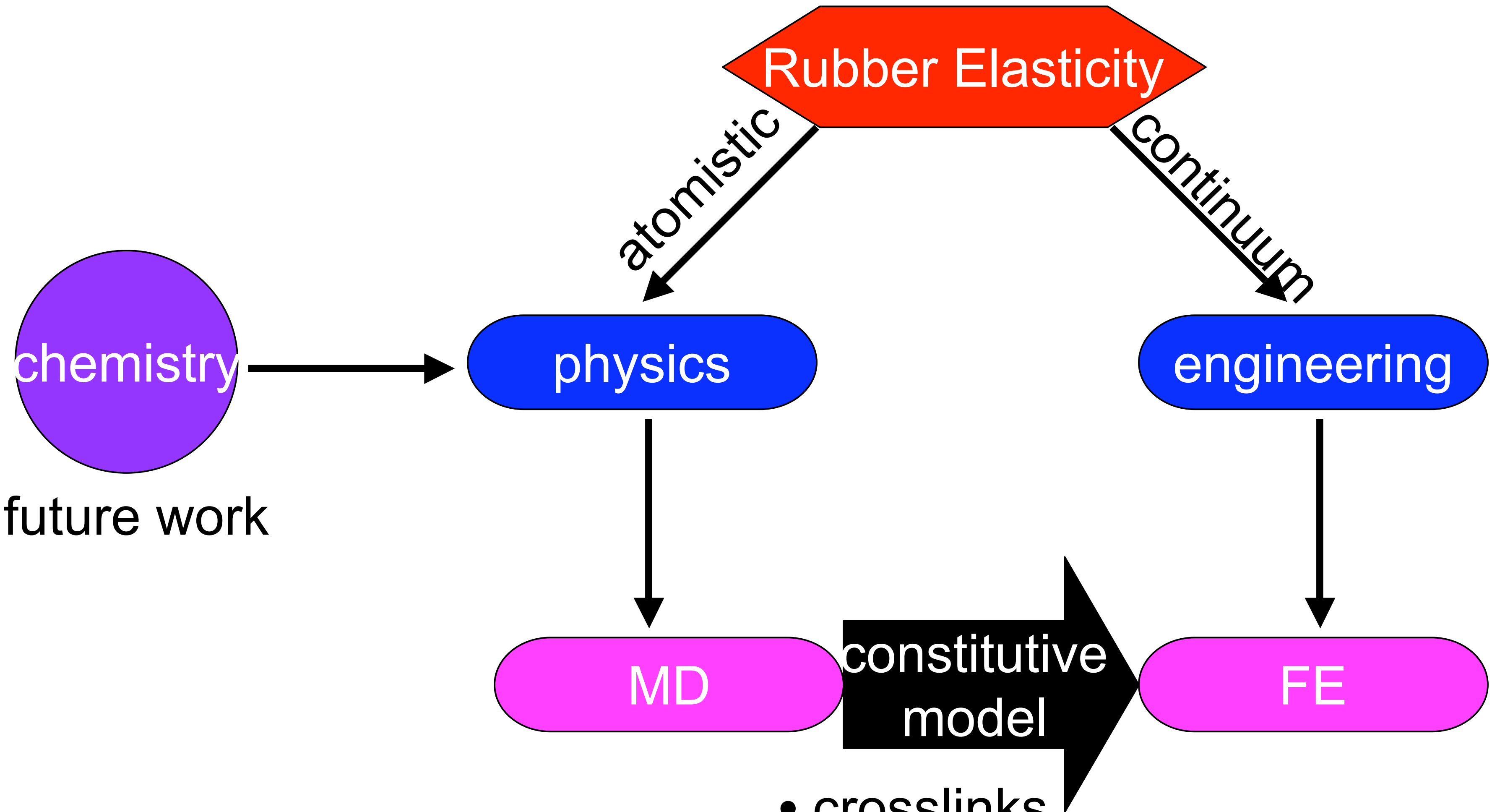
Arrhenius relation changes slope at moderate temperature

Future Work



Kinetic data
experiment
simulation
difficult to obtain
possible With new FF
parameterize with polypropylene
years
Time
10-15
Ångstrom
Distance
Meters
QM
ab initio, DFT, HF
ReaxFF
MD
Empirical force fields
theory
Grains
FEA
Grids
Design

Summary



- crosslinks
- entanglements
- coupled strain-reaction histories