Understanding the Mechanical Behaviour of Glassy Amorphous Polymers through Molecular Dynamics Simulations

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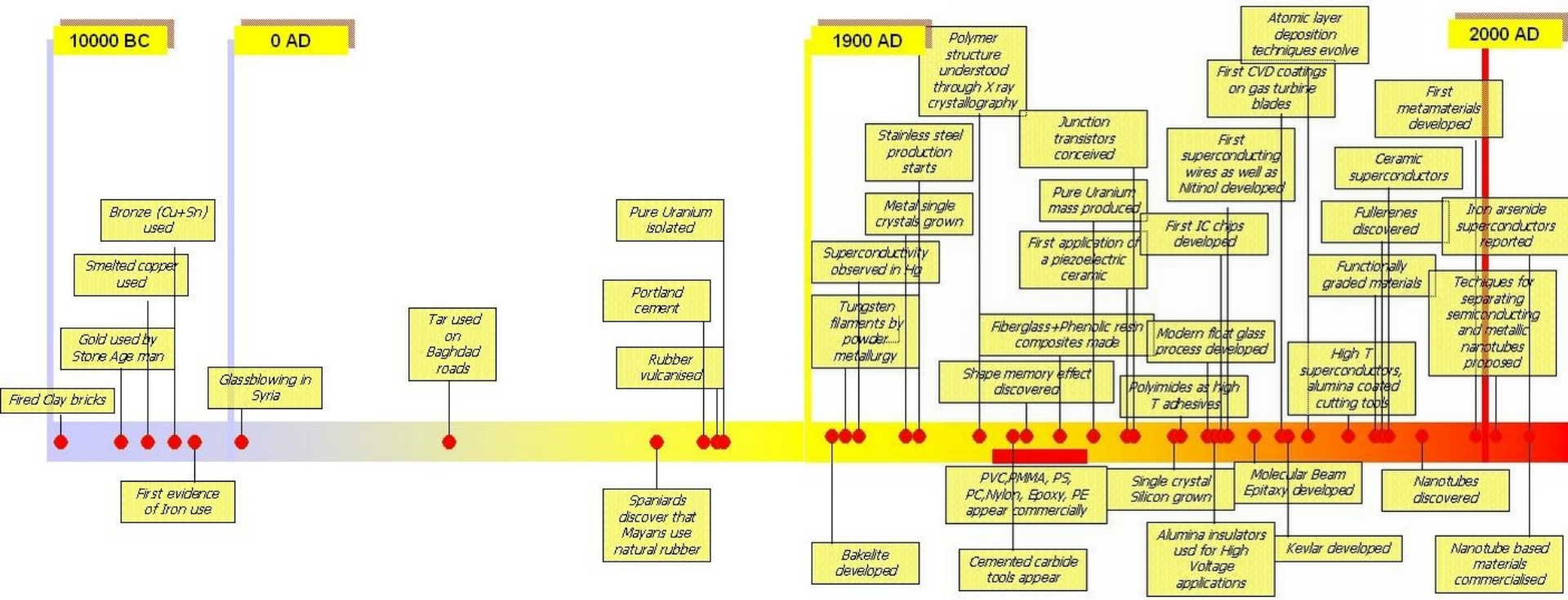
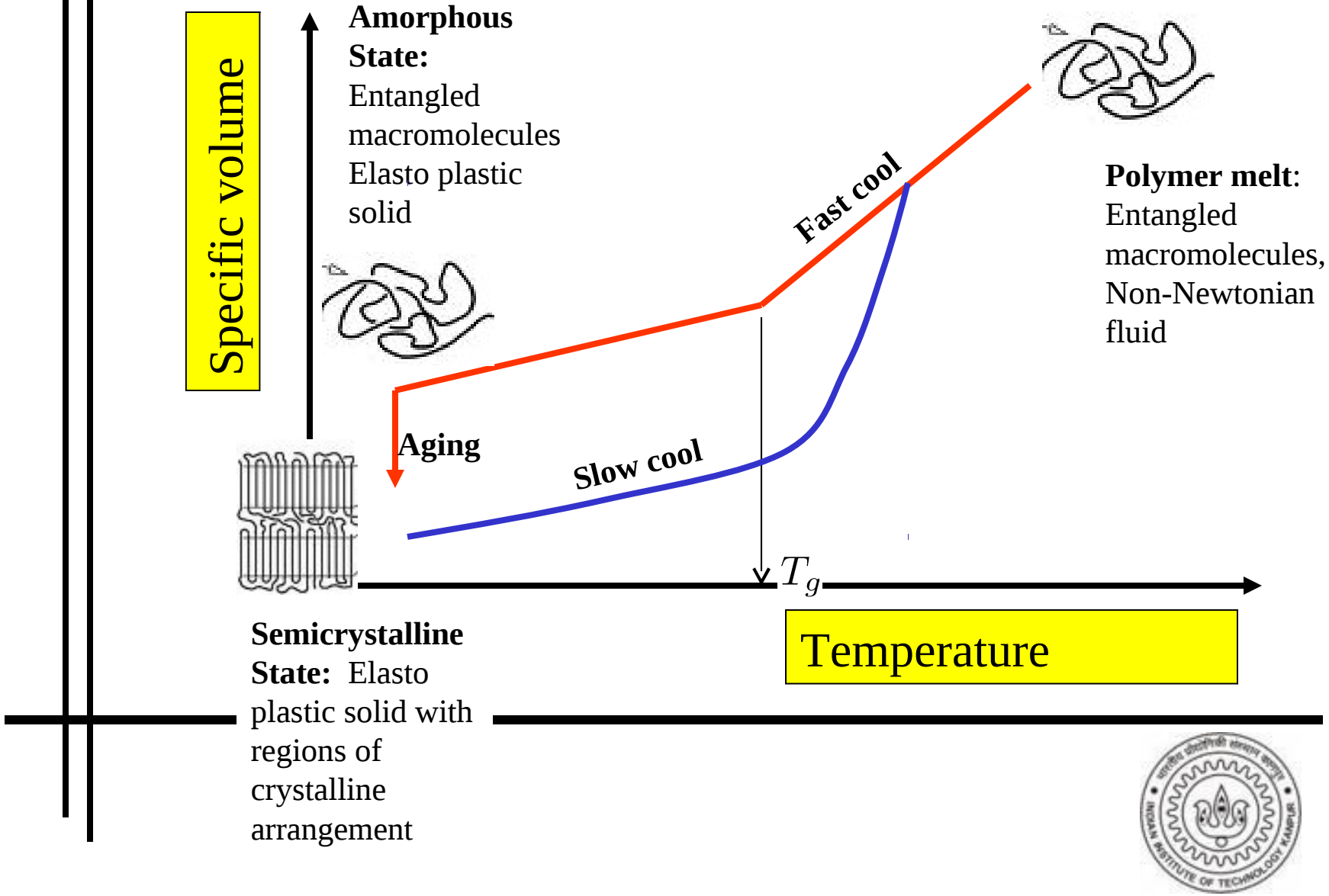
Has he walked into the wrong classroom?


10000 BC
0 AD
1900 AD
2000 AD
Bronze (Cu+Sn) used
Smelted copper used
Gold used by Stone Age man
Fired Clay bricks
First evidence of Iron use
Glassblowing in Syria
Tar used on Baghdad roads
Pure Uranium isolated
Portland cement
Rubber vulcanised
Spaniards discover that Mayans use natural rubber
Polymer structure understood through X ray crystallography
Stainless steel production starts
Metal single crystals grown
Superconductivity observed in Hg
Tungsten filaments by powder metallurgy
Bakelite developed
Junction transistors conceived
Pure Uranium mass produced
First application of a piezoelectric ceramic
Fiberglass+Phenolic resin composites made
Shape memory effect discovered
PVC,PMMA, PS, PC,Nylon, Epoxy, PE appear commercially
Cemented carbide tools appear
First IC chips developed
Modern float glass process developed
Polyimides as high T adhesives
Single crystal Silicon grown
Alumina insulators usd for High Voltage applications
Atomic layer deposition techniques evolve
First CVD coatings on gas turbine blades
First superconducting wires as well as Nitinol developed
Molecular Beam Epitaxy developed
Kevlar developed
First metamaterials developed
Ceramic superconductors
Fullerenes discovered
Functionally graded materials
High T superconductors, alumina coated cutting tools
Iron arsenide superconductors reported
Techniques for separating semiconducting and metallic nanotubes proposed
Nanotubes discovered
Nanotube based materials commercialised

What are glassy amorphous polymers?

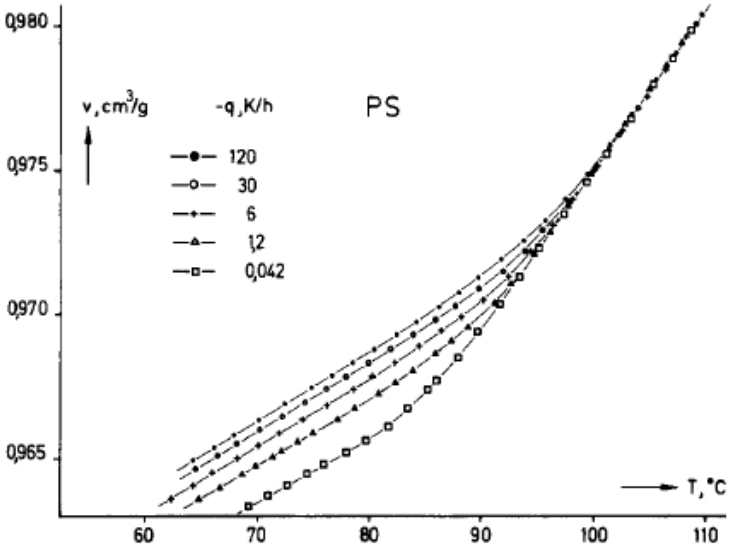


To give you an idea of the numbers involved…

For polystyrene:

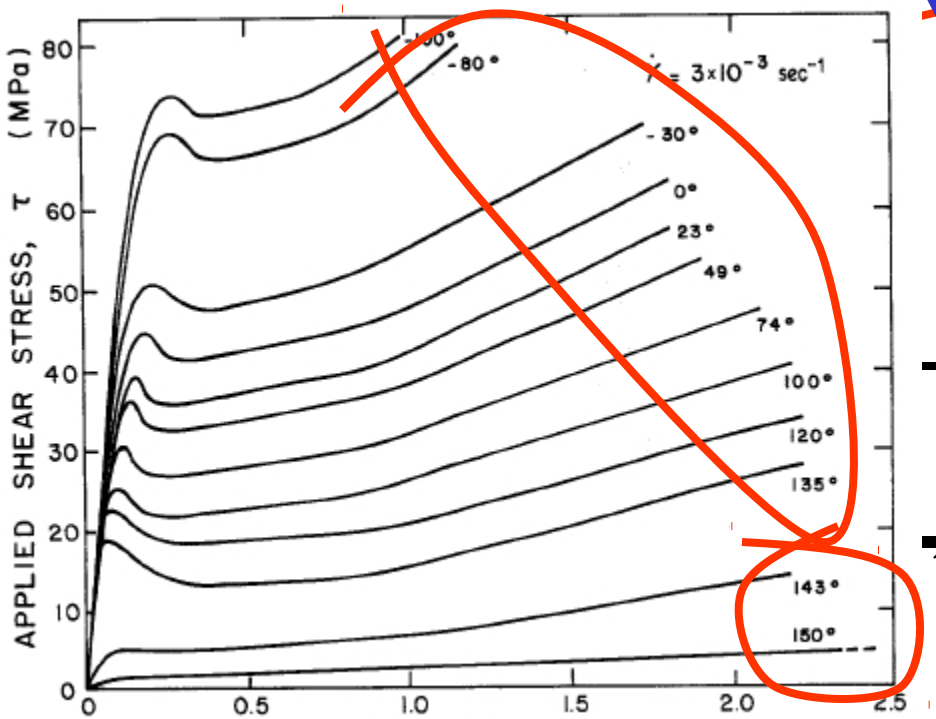
1. Typical values of T_g lie between 85.8 to 95.7 °C
2. Cooling rates between 0.0042 to 120 K/hour yield amorphous structures.

Greiner and Schwarzl, 1984, Rheologica Acta, v23, p378



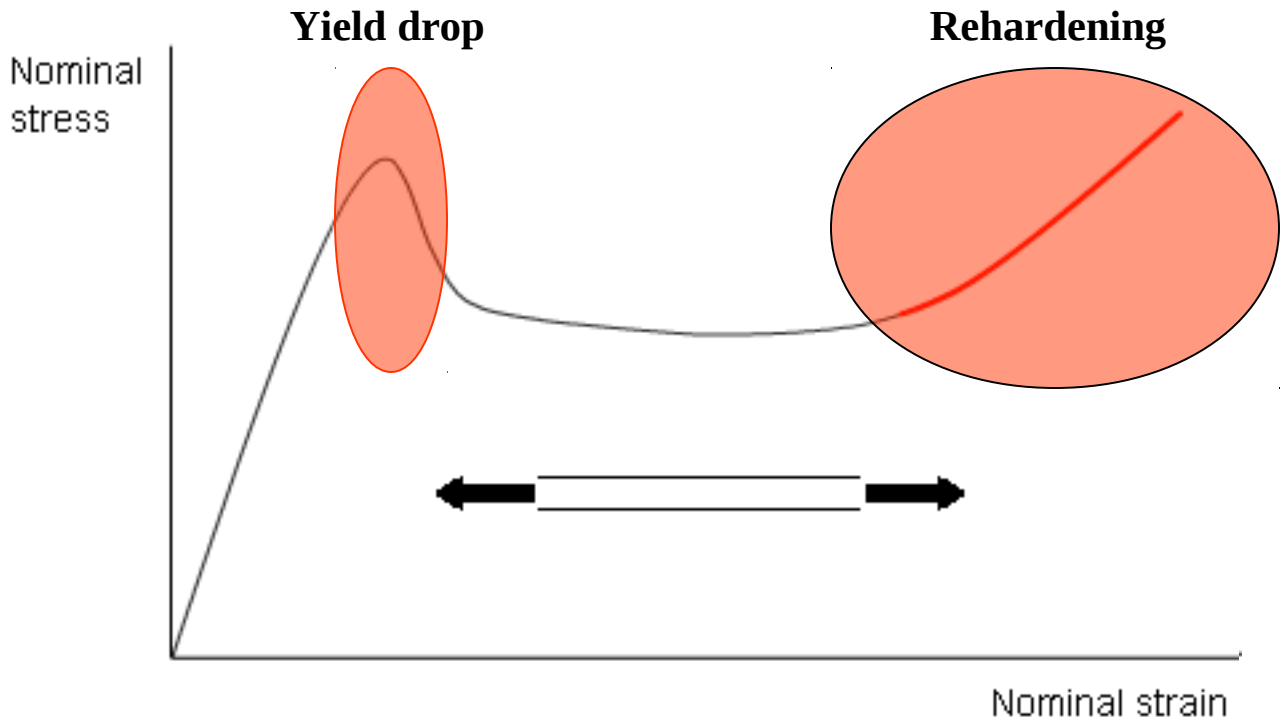
Polymer	T_g
PS	95.7 °C
PMMA	103.7 °C
PVC	71.7 °C
PC	141.3 °C

Glassy polymers have much superior mechanical properties



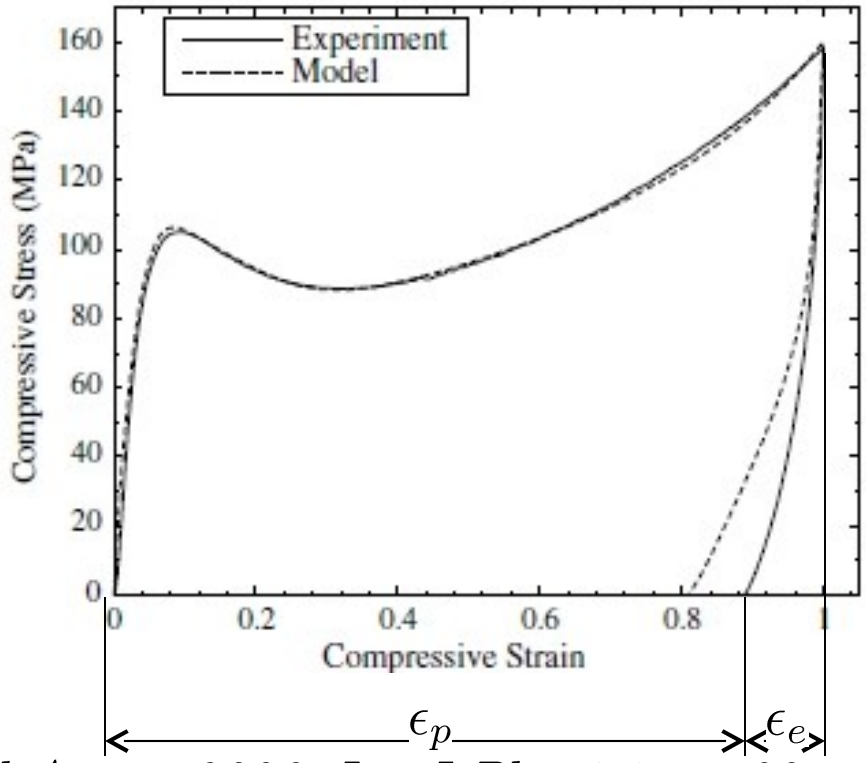
G'Sell and Lopez, 1985, J Mater. Sc, v20, pp3462

The nature of the stress strain curve has enormous technological consequences



The stress strain curve gives amorphous polymers their *formability*

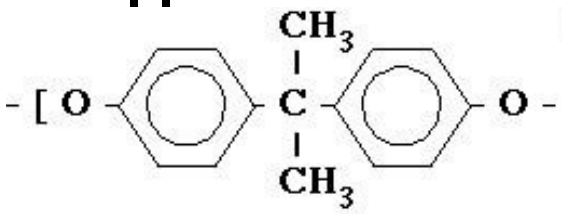
Glassy polymers can undergo large plastic deformation

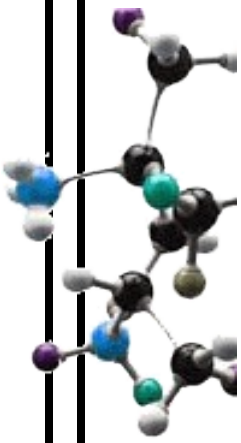


Anand and Ames, 2006, Int J Plasticity, v22, p1123

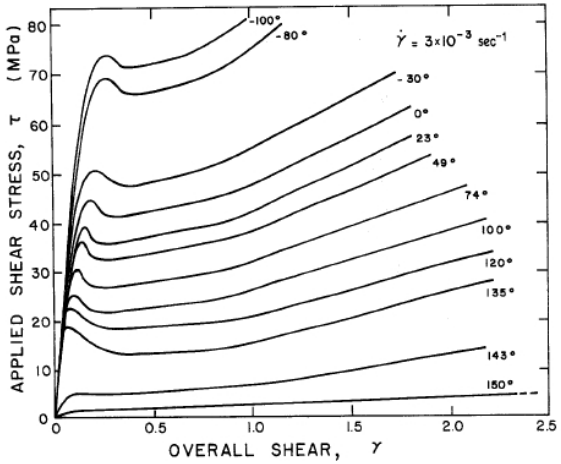
Motivation for doing MD 1:
Understanding mechanical behaviour esp the origins of plasticity.

Motivation for doing MD 2: Mechanical Property prediction



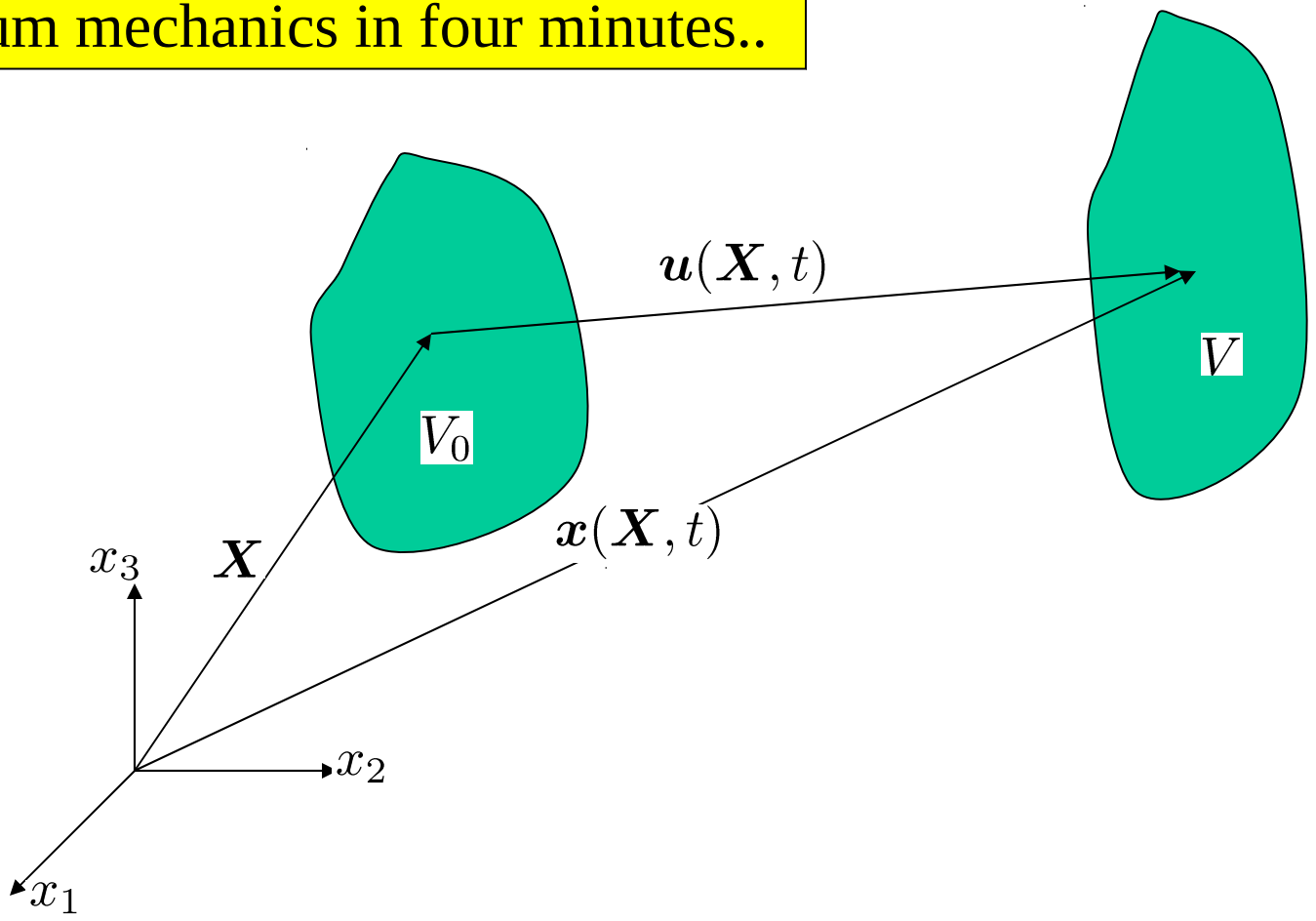


Given a macromolecular architecture



Predict mechanical behaviour in the glassy amorphous state

Continuum mechanics in four minutes..



$$\boldsymbol{x}(\boldsymbol{X}+d\boldsymbol{X}) = \boldsymbol{x} + \boldsymbol{F}d\boldsymbol{X}$$

$\boldsymbol{F}$: *Deformation gradient tensor*

In indicial notation

$$F_{ij} = \frac{\partial x_i}{\partial X_j}$$

Alternately, since

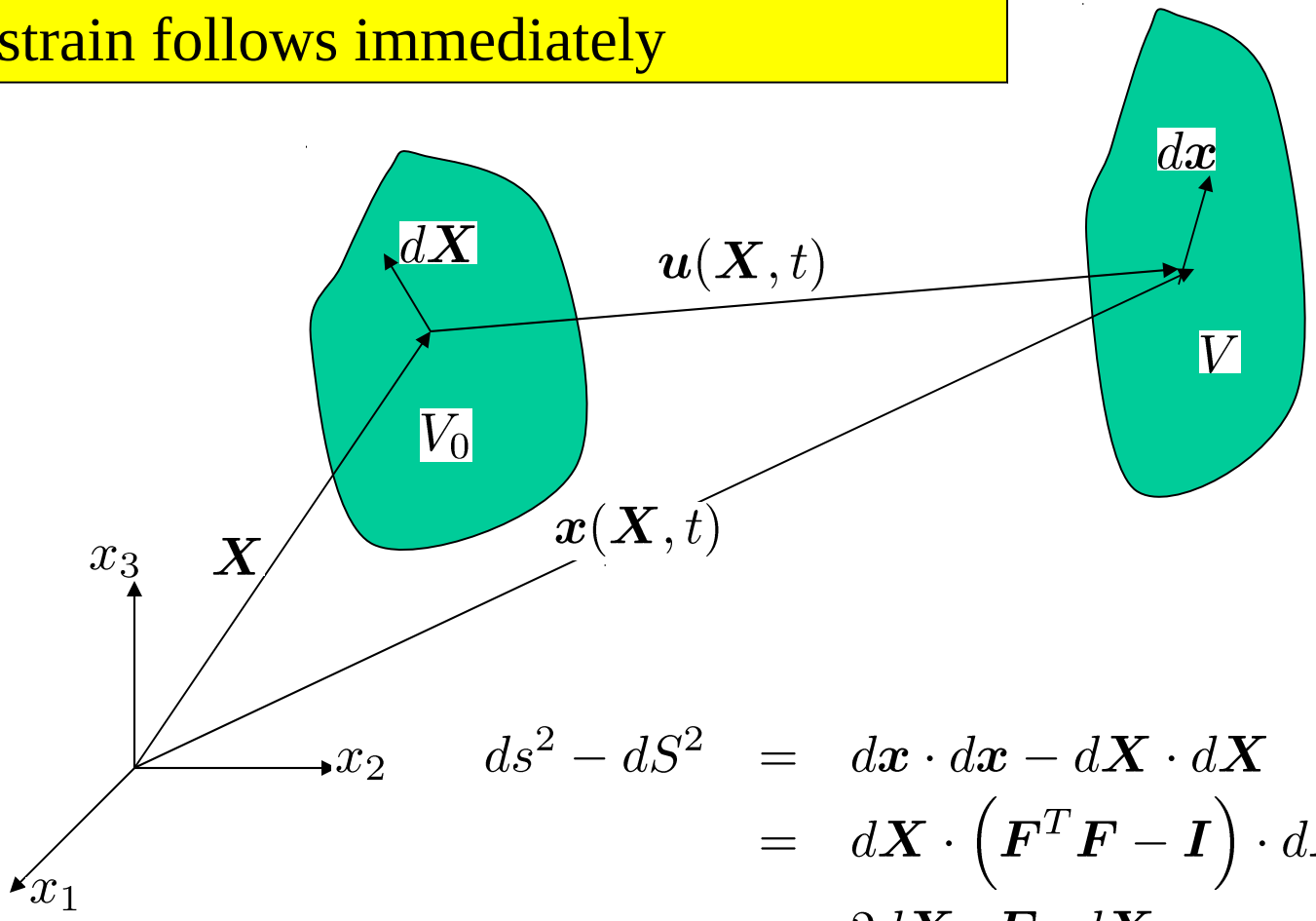
$$\boldsymbol{x} = \boldsymbol{X} + \boldsymbol{u},$$

$$\boldsymbol{F} = \boldsymbol{I} + \nabla \boldsymbol{u}$$

or

$$F_{ij} = \delta_{ij} + u_{i,j}$$

The concept of strain follows immediately



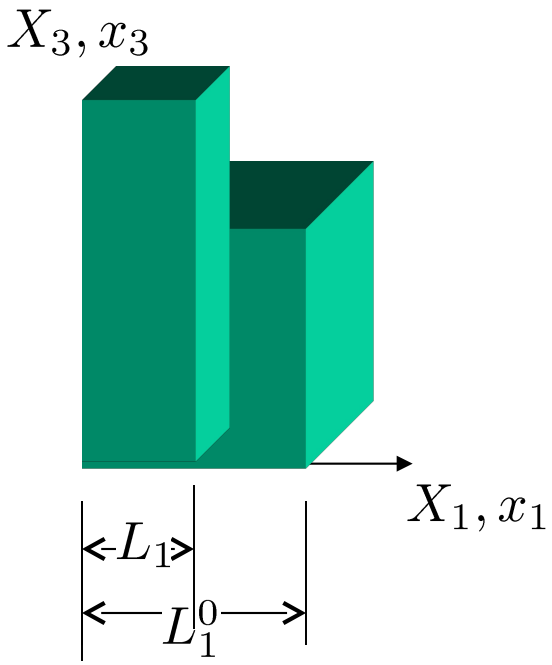
$$
\begin{aligned}
ds^2 - dS^2 &= d\boldsymbol{x}\cdot d\boldsymbol{x} - d\boldsymbol{X}\cdot d\boldsymbol{X} \\
&= d\boldsymbol{X}\cdot\left(\boldsymbol{F}^T\boldsymbol{F} - \boldsymbol{I}\right)\cdot d\boldsymbol{X} \\
&= 2d\boldsymbol{X}\cdot\boldsymbol{E}\cdot d\boldsymbol{X}
\end{aligned}
$$

where

$$
\boldsymbol{E} = \frac{1}{2}\left(\boldsymbol{F}^T\boldsymbol{F} - \boldsymbol{I}\right).
$$

is the *Lagrangian strain tensor*

Example: Pulling a block, uniaxial tension



The motion is given by

$$
\begin{aligned}
x_1 &= \lambda_1 X_1 \\
x_2 &= \lambda_2 X_2 \\
x_3 &= \lambda_3 X_3
\end{aligned}
$$

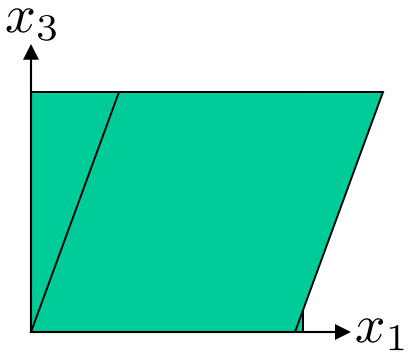
$$
\boldsymbol{F} = \begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{pmatrix}
$$

$$
\boldsymbol{E} = \begin{pmatrix} \lambda_1^2 - 1 & 0 & 0 \\ 0 & \lambda_2^2 - 1 & 0 \\ 0 & 0 & \lambda_3^2 - 1 \end{pmatrix}
$$

where

$$
\lambda_\alpha = \frac{L_\alpha}{L_\alpha^0}
$$

Example: Shearing a block



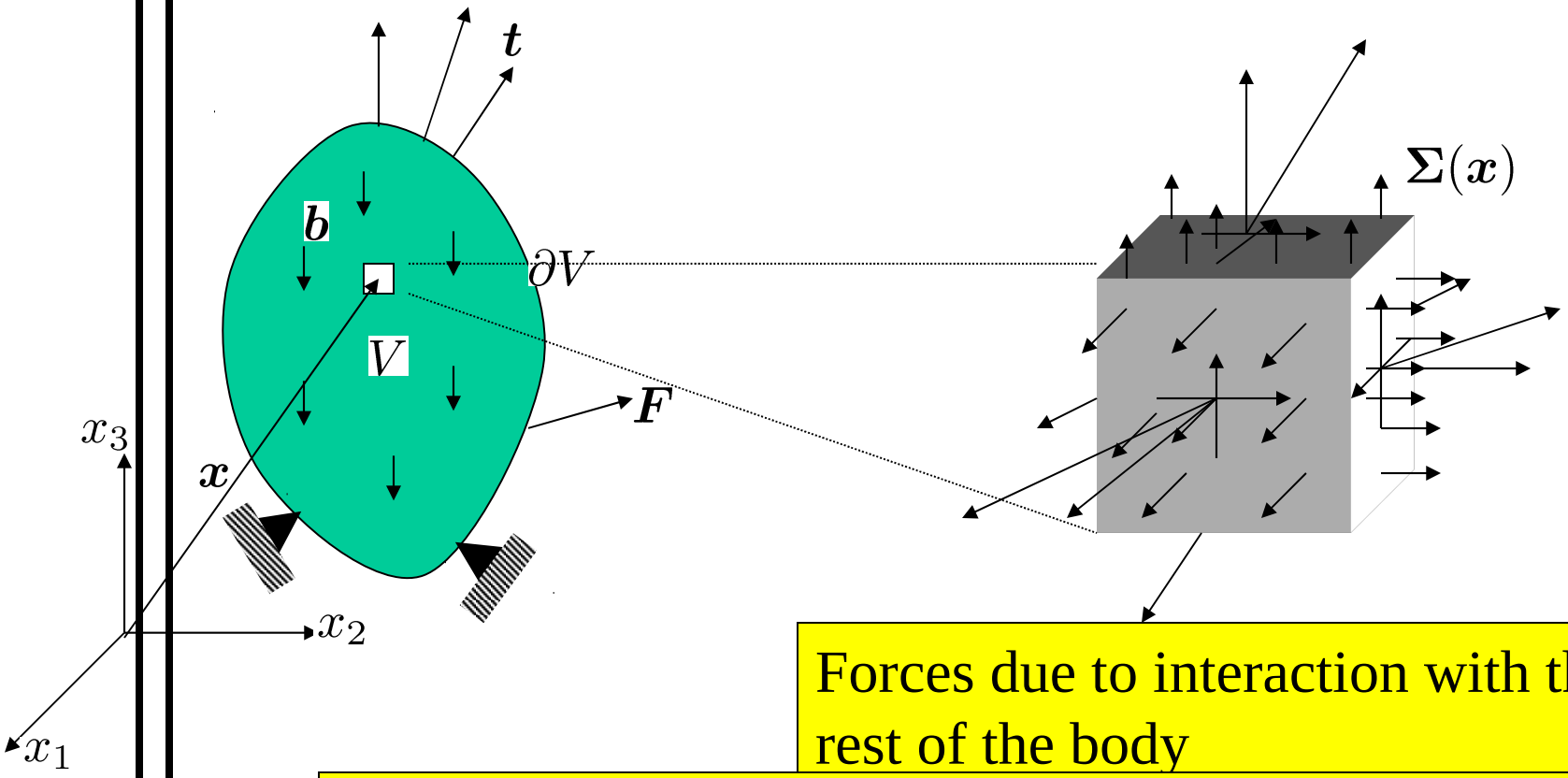
The deformation map is

$$\begin{aligned} x_1 &= X_1 + \gamma X_3 \\ x_2 &= X_2 \\ x_3 &= X_3 \end{aligned}$$

such that

$$\boldsymbol{F} = \begin{pmatrix} 1 & 0 & \gamma \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \boldsymbol{I} + \gamma \boldsymbol{e}_1 \otimes \boldsymbol{e}_3$$

Understanding stress



Forces due to interaction with the rest of the body

Inter-atomic forces that have been cut through can be

The components of the traction on all surfaces together constitute the stress tensor $\boldsymbol{\Sigma}$

Newton's second law: Rate of change of linear momentum equals the applied force:

$$\frac{D}{Dt}\int_V \rho \boldsymbol{v} dv = \int_{\partial V} \boldsymbol{t} da + \int_V \boldsymbol{b} dv$$

leads to

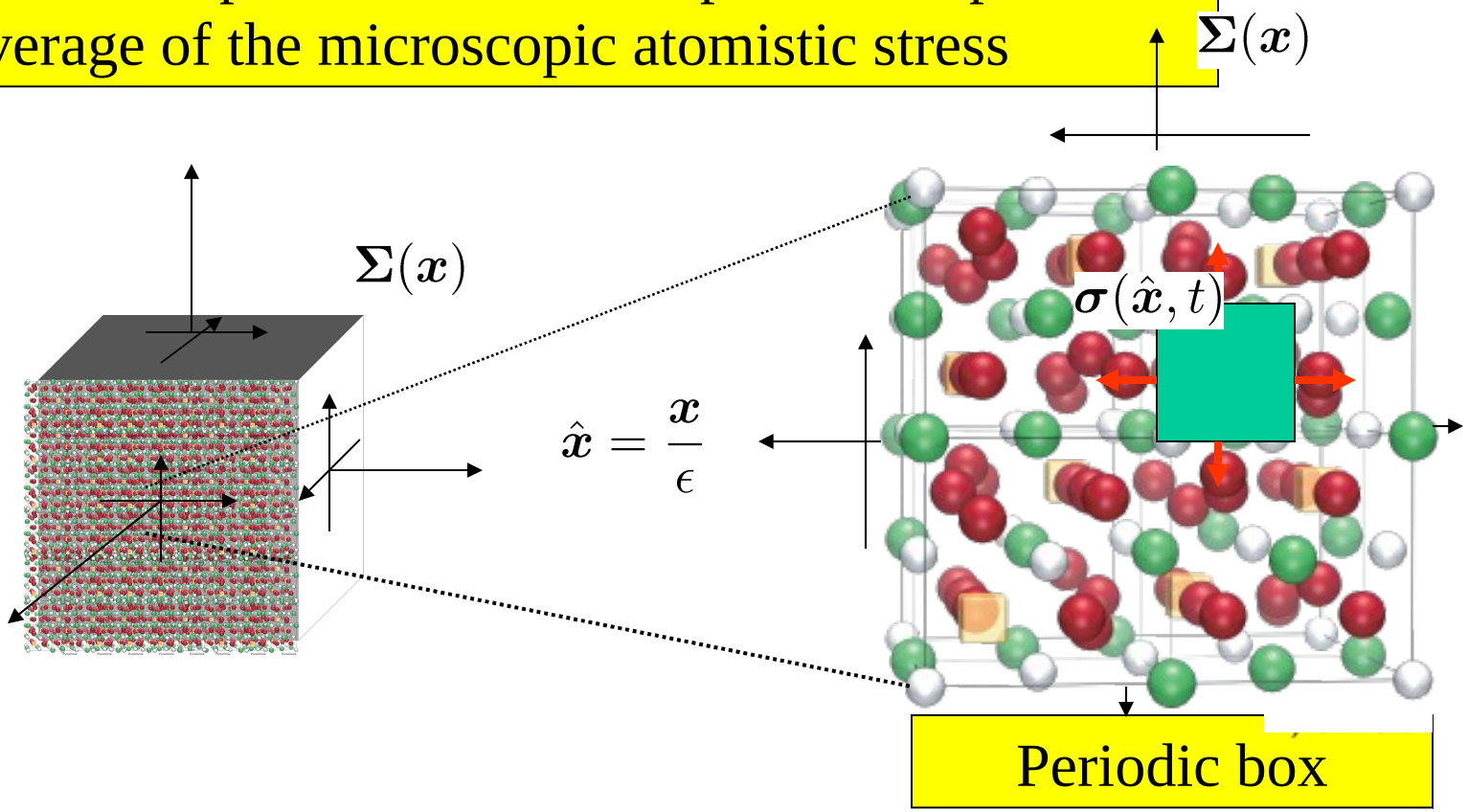
$$\nabla \cdot \boldsymbol{\Sigma} + \boldsymbol{b} = \rho \frac{D\boldsymbol{v}}{Dt}.$$

The material enters into the relation between the stress and the deformation

$$\boldsymbol{\Sigma} = \boldsymbol{C} : \boldsymbol{E},$$

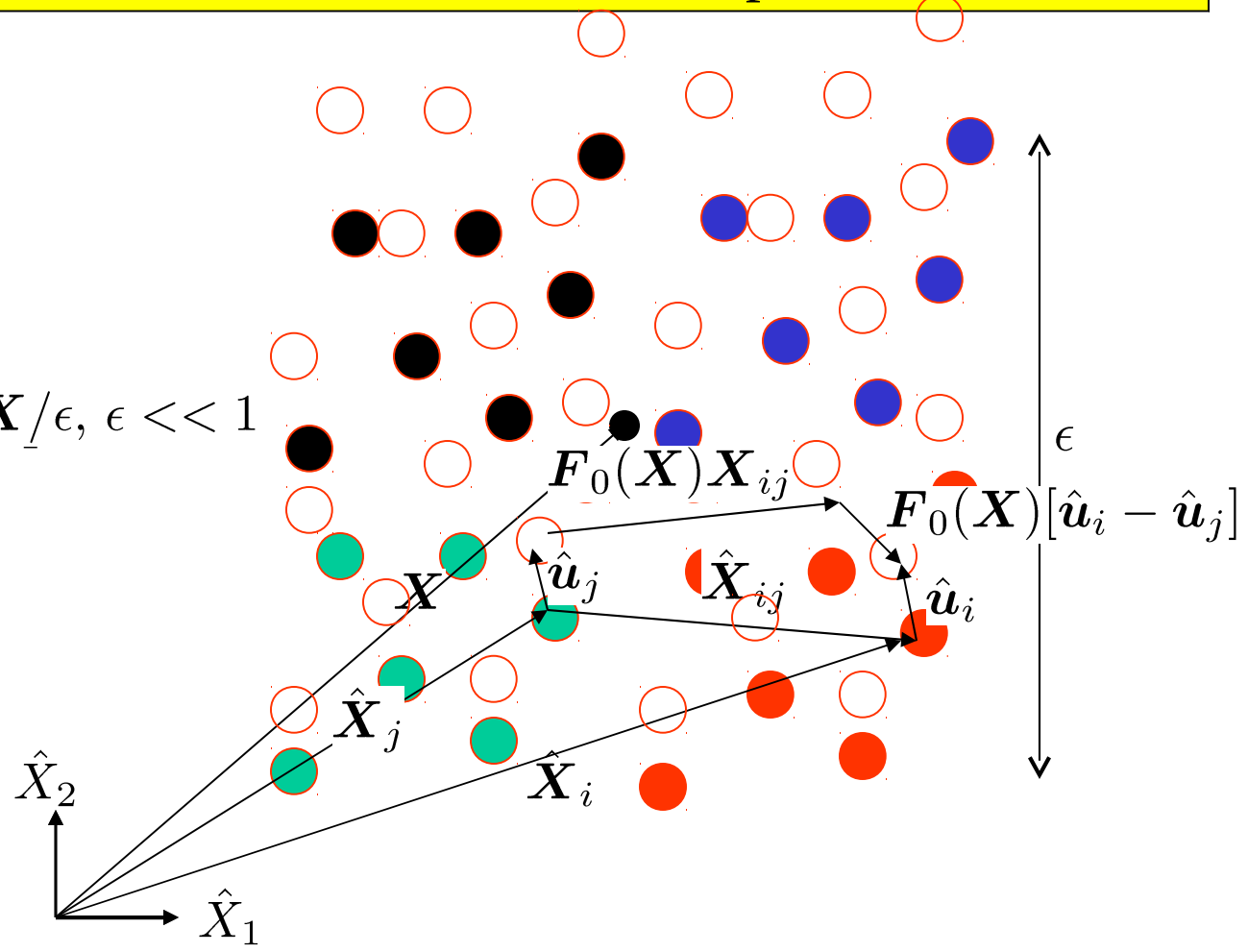
Governs the constitutive response of the continuum

The macroscopic stress is the temporal and spatial average of the microscopic atomistic stress



$$\boldsymbol{\Sigma}(\boldsymbol{x}) = \frac{1}{T}\int_0^T \left\{ \frac{1}{\Omega_{pbc}} \int_{\Omega_{pbc}} \boldsymbol{\sigma}(\hat{\boldsymbol{x}}, t) dV \right\} dt$$

What is $\boldsymbol{\sigma}(\hat{x}, t)$? A 0 K picture.



Chen and Fish, 2006, Int J Numer Method Engng, v67, pp189

The displacement of a point admits a multiscale expansion as:

$$\boldsymbol{u}(\boldsymbol{x}, \hat{\boldsymbol{x}}, t) = \boldsymbol{u}^0(\boldsymbol{x}, t) + \epsilon \boldsymbol{u}^1(\boldsymbol{x}, \hat{\boldsymbol{x}}, t) + \dots$$

Coarse grain displacement

At the coarse scale $\boldsymbol{x}$

$$\nabla \cdot \boldsymbol{\Sigma} = \rho \ddot{\boldsymbol{u}},$$

At the fine scale $\hat{\boldsymbol{x}} = \boldsymbol{x}/\epsilon$

$$\sum_{i \neq j} \boldsymbol{f}_{ij} = m_i \ddot{\boldsymbol{u}}_i.$$

Note that we have considered pairwise forces only but this restriction can be easily removed.

If the continuum deforms homogeneously,

$$\nabla \cdot \boldsymbol{\Sigma} \sim \mathcal{O}(1).$$

Also,

$$\rho \sim \mathcal{O}(1).$$

and

$$\Omega_{pbc} \sim \mathcal{O}(\epsilon^3)$$

$$\frac{1}{\epsilon^3} \sum_{i \neq j} \boldsymbol{f}_{ij} = \rho \ddot{\boldsymbol{u}}_i \sim \nabla \cdot \boldsymbol{\Sigma} \Rightarrow \boldsymbol{f}_{ij} \sim \mathcal{O}(\epsilon^3).$$

With a first order expansion of $\boldsymbol{u}$ (upto order ϵ), and pbc, the stress measure

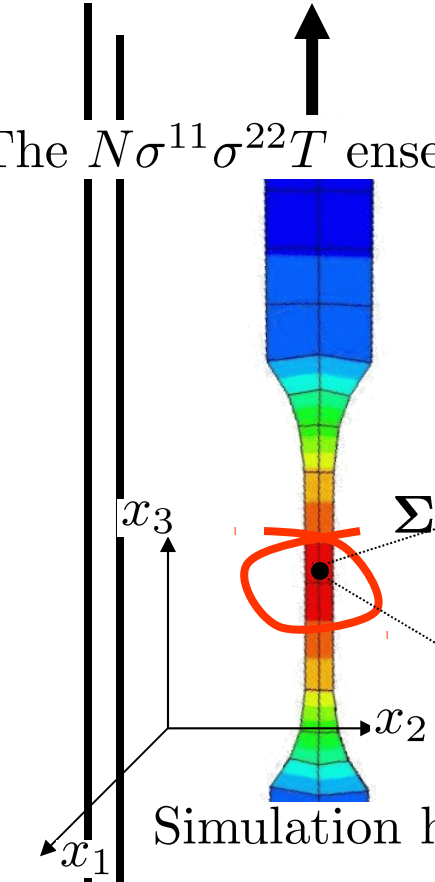
$$\boldsymbol{\Sigma} = \frac{1}{2\Omega_{pbc}} \sum_i \sum_{j \neq i} \boldsymbol{f}_{ij} \otimes \boldsymbol{x}_{ij}.$$

satisfies the continuum equilibrium equation

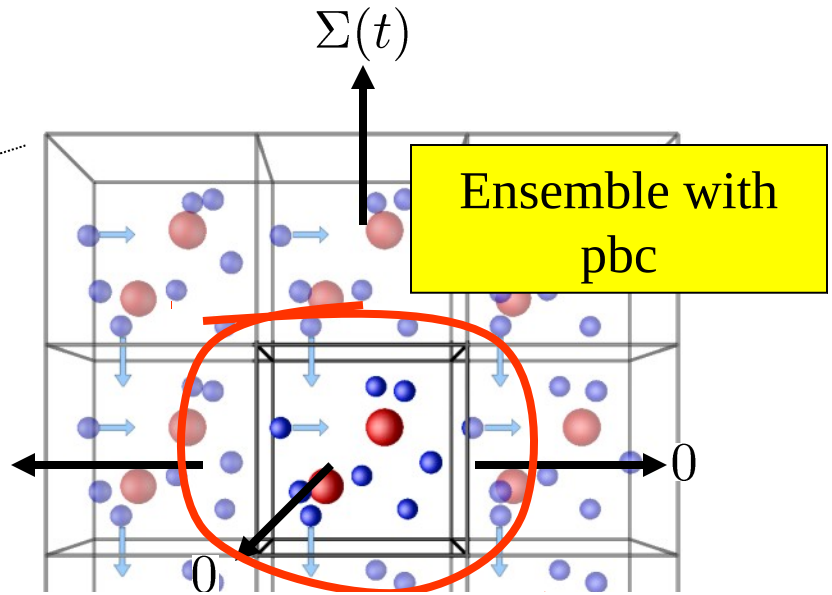
$$\nabla \cdot \boldsymbol{\Sigma} - \rho \ddot{\boldsymbol{u}} = 0.$$

The uniaxial 'experiment'

The $N\sigma^{11}\sigma^{22}T$ ensemble: see *Yang et al., 1997, J. Chem. Phys, v107, pp4396*



$$\boldsymbol{\Sigma} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \Sigma(t) \end{pmatrix}$$



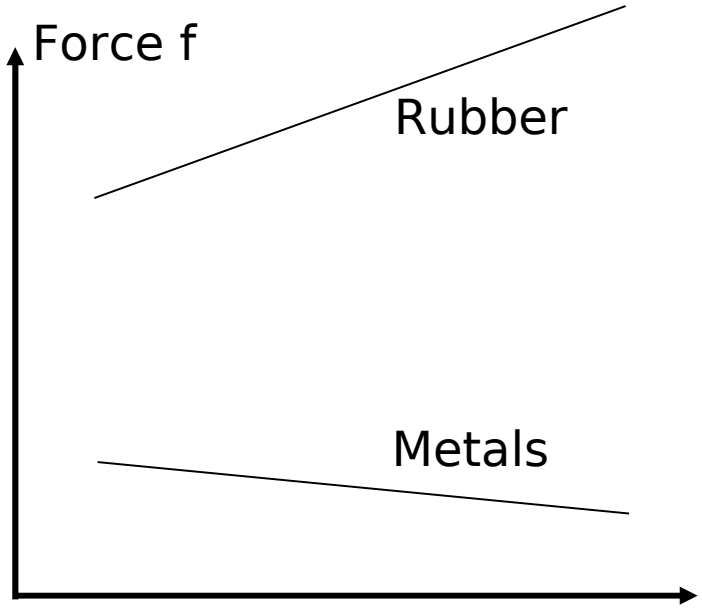
Simulation has to proceed such that:

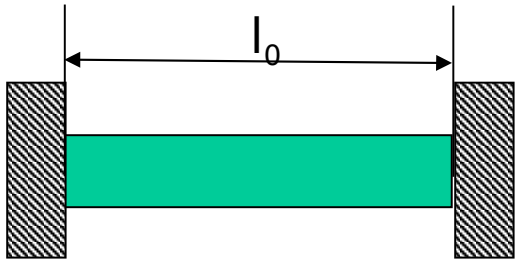
$$\begin{aligned} \Sigma &= \Sigma^{33} = \frac{1}{2\Omega_{pbc}} \sum\sum f_{ij}^3 x_{ij}^3 \\ 0 &= \frac{1}{2\Omega_{pbc}} \sum\sum f_{ij}^1 x_{ij}^1 = \frac{1}{2\Omega_{pbc}} \sum\sum f_{ij}^2 x_{ij}^2 \\ &= \frac{1}{2\Omega_{pbc}} \sum\sum f_{ij}^1 x_{ij}^2 = \ldots \end{aligned}$$

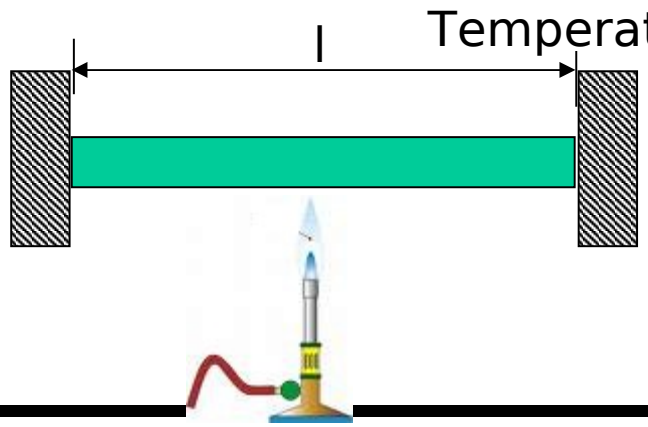
Deformation of long chained molecules: Lessons from rubber elasticity

For rubber $\left(\frac{\partial f}{\partial T}\right)_l > 0$

Kelvin (1857)







For a linear elastic metal

$$\epsilon = \epsilon^e + \epsilon^T$$

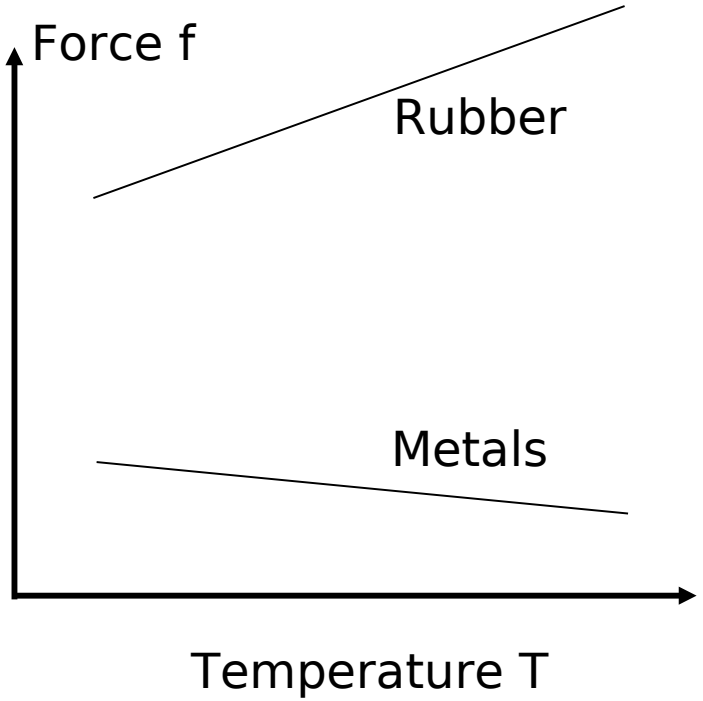
where

$$\epsilon^T = \alpha \Delta T$$

And thus,

$$\sigma = E\epsilon - \alpha E \Delta T$$

Note: $\alpha > 0$



From first law of thermodynamics

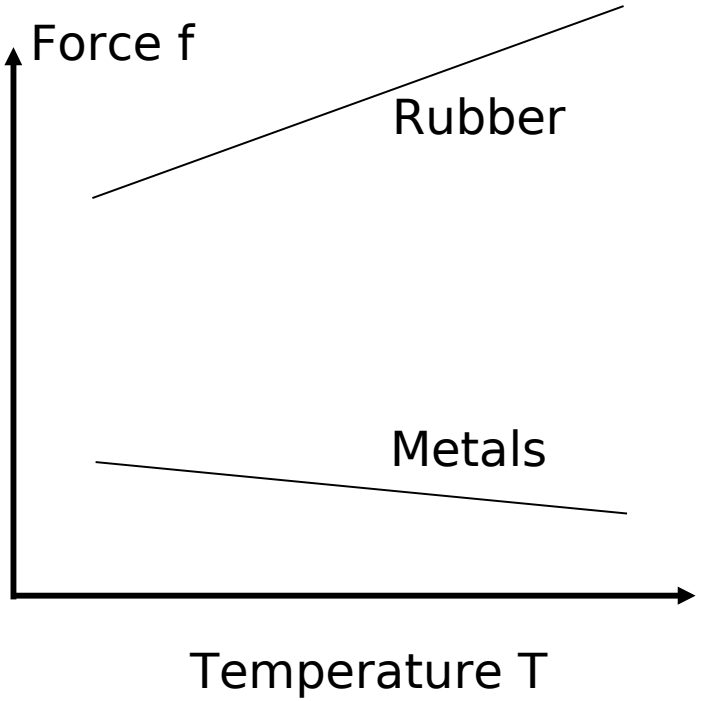
$$dQ = dU + dW$$

or for a reversible, constant volume process

$$0 = dG + SdT - fdl$$

Free energy G=U-TS

Force



As all quantities are point functions

$$\left(\frac{\partial G}{\partial l}\right)_T = f$$

$$\left(\frac{\partial G}{\partial T}\right)_T = -S$$

$\Rightarrow$

$$\left(\frac{\partial S}{\partial l}\right)_T = -\left(\frac{\partial f}{\partial T}\right)_l$$

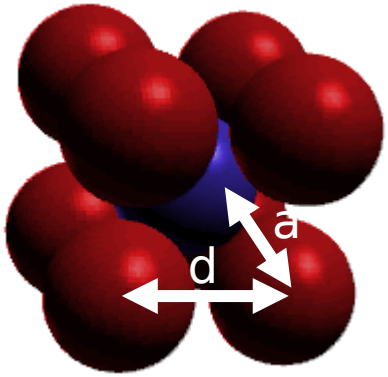
$$\left(\frac{\partial G}{\partial l}\right)_T = \left(\frac{\partial U}{\partial l}\right)_T - T\left(\frac{\partial S}{\partial l}\right)_T, \Rightarrow \boxed{f = \left(\frac{\partial U}{\partial l}\right)_T + T\left(\frac{\partial f}{\partial T}\right)_l}$$

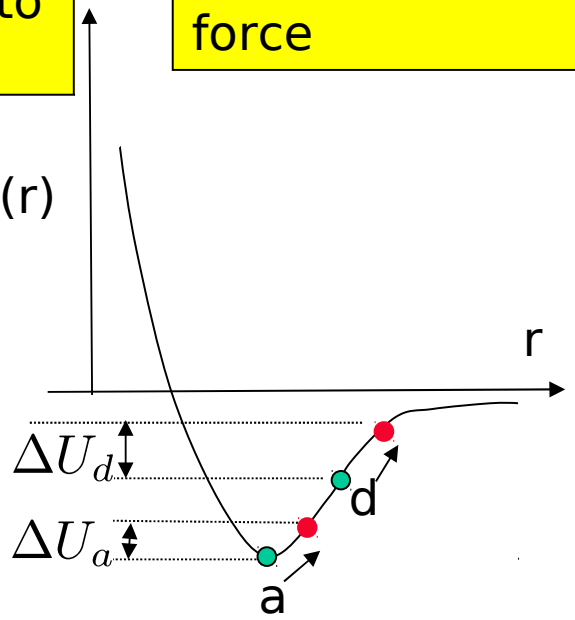
$$f = \left(\frac{\partial U}{\partial l}\right)_T + T\left(\frac{\partial f}{\partial T}\right)_l$$

Energy elastic contribution to force

Entropy elastic contribution to force

?



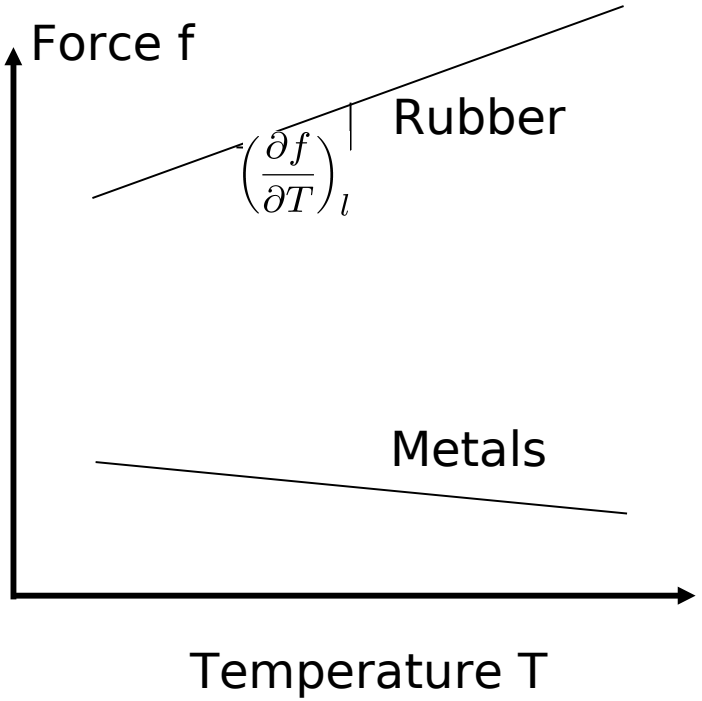


For a entropy elastic material (like rubber)

$$f \simeq -T\left(\frac{\partial S}{\partial l}\right)_T, \quad \Rightarrow \quad f \simeq T\left(\frac{\partial f}{\partial T}\right)_l$$

$$\left(\frac{\partial f}{\partial T}\right)_l > 0 \Rightarrow$$

entropy $\downarrow$ with deformation at a constant temperature.



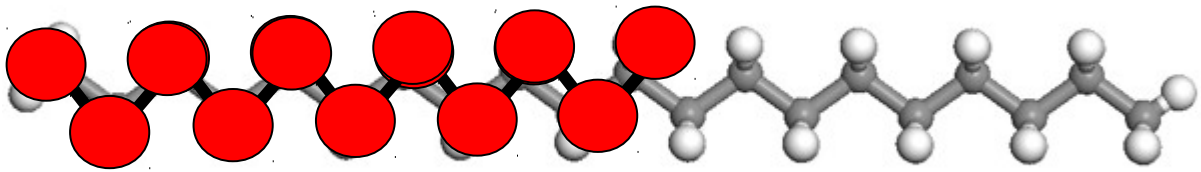
With deformation a more ordered structure emerges from a less ordered one!

Metals: energy elastic

Rubber: entropy elastic

Polymers: energy elastic at small strains. Behave like rubber-elasticity at large strains.

Statistics of long chained molecules: conformations

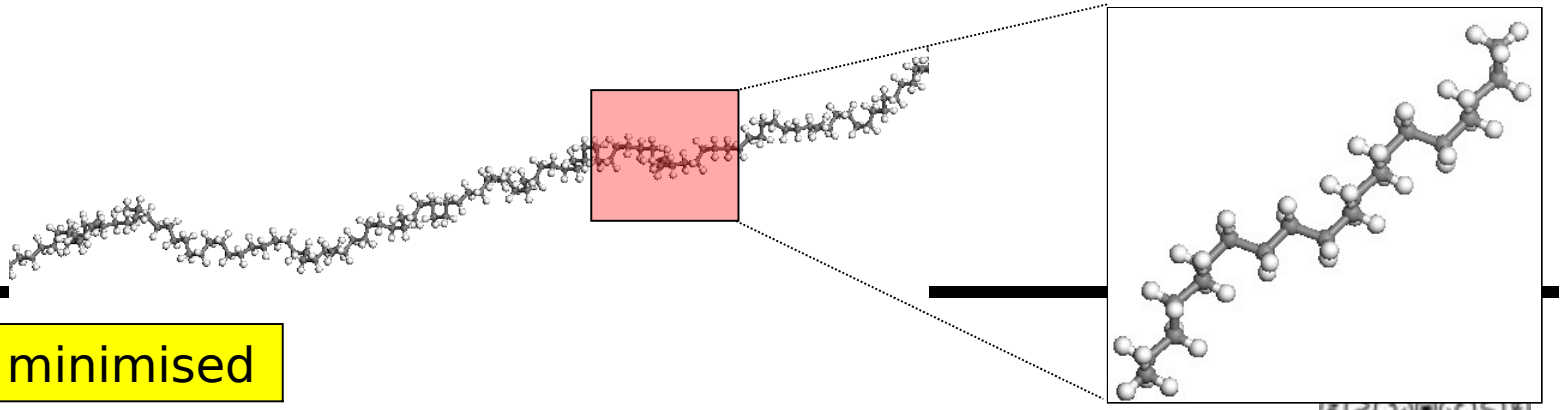


Polyethylene, the simplest of the lot.

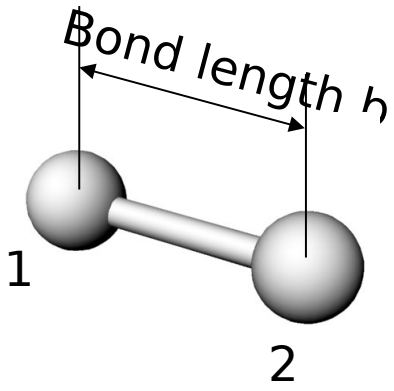
United atom model

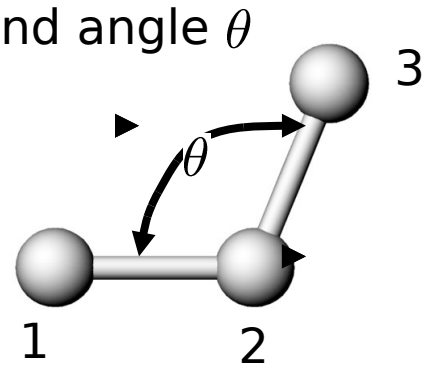
CH_2 → one united atom.

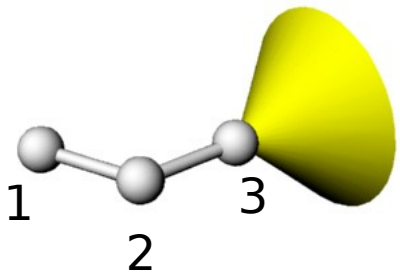
Bonds → a nonlinear spring

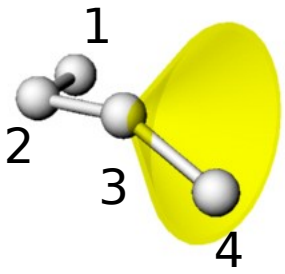


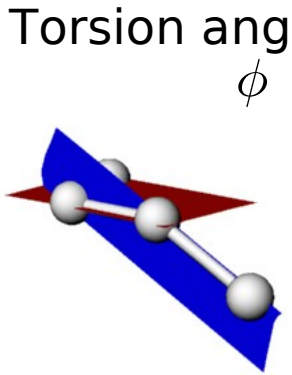
Energy minimised

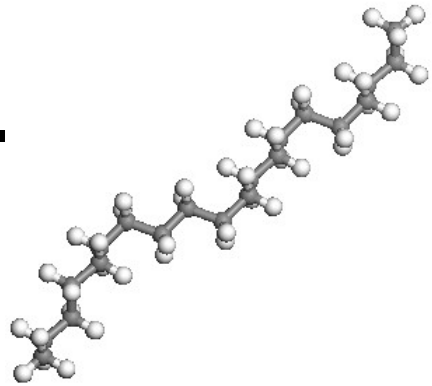

Bond length b
1
2

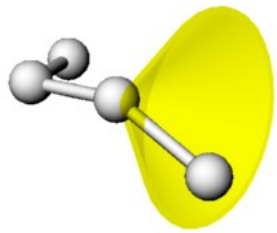

Bond angle θ
3
θ
1
2

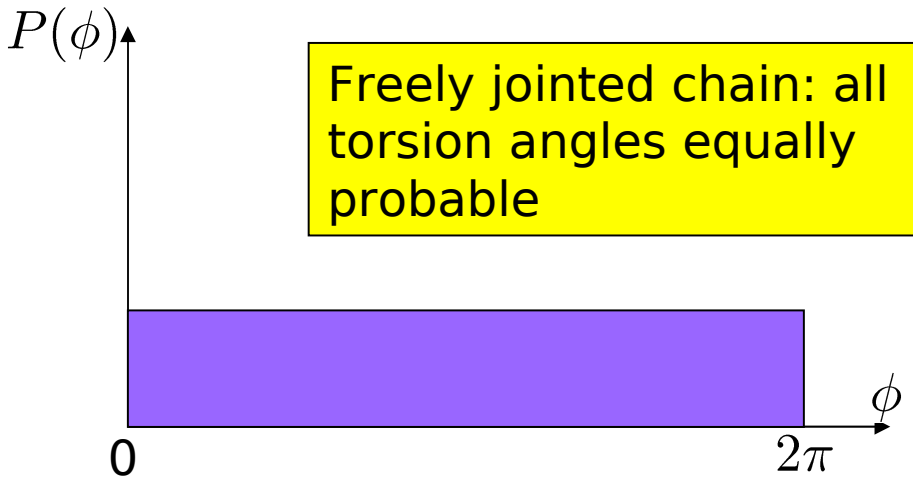

1
2
3


1
2
3
4

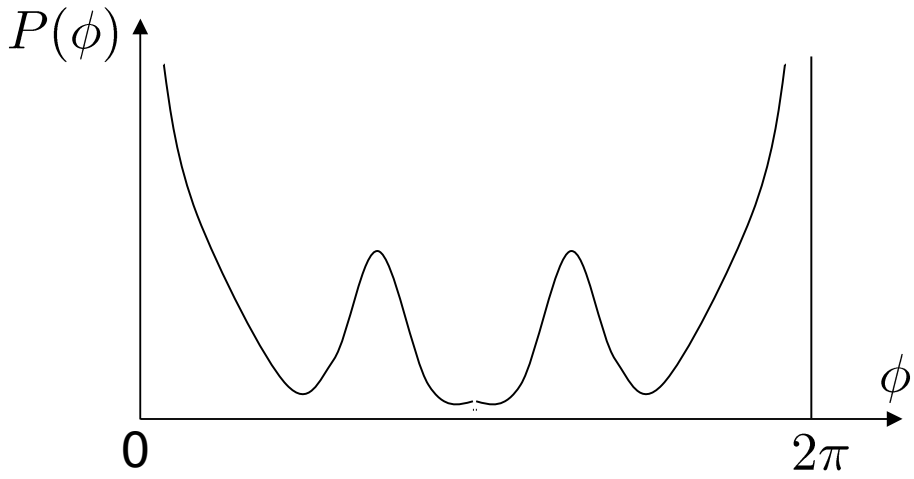

Torsion angle
ϕ







Freely jointed chain: all torsion angles equally probable

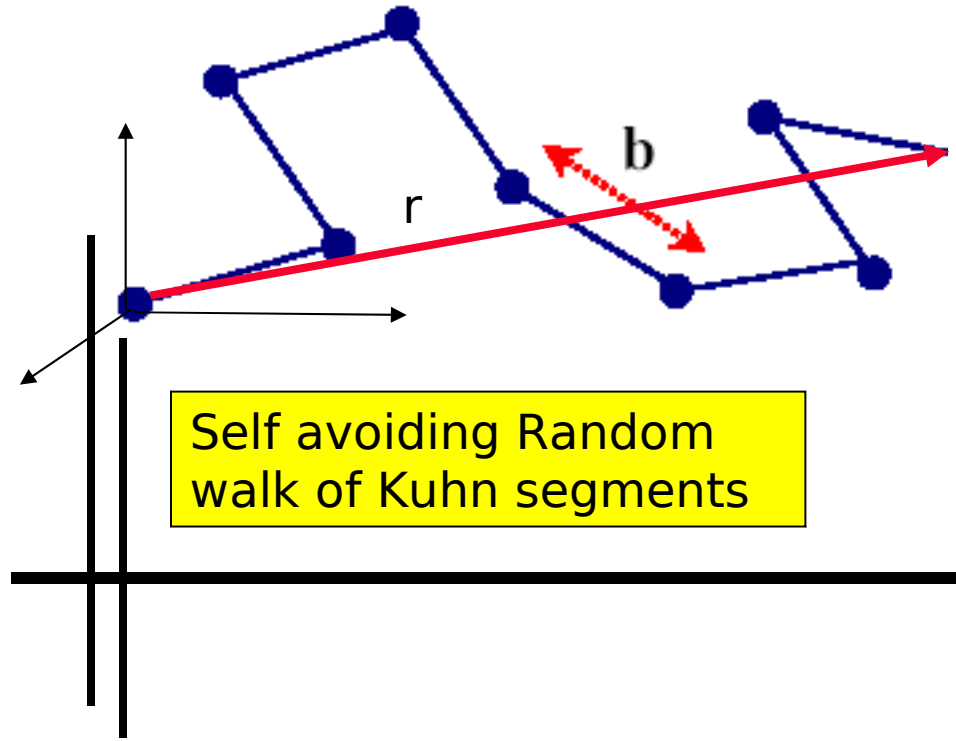


A real polymer chain has preferred torsion angles, is stiffer than a freely jointed one.

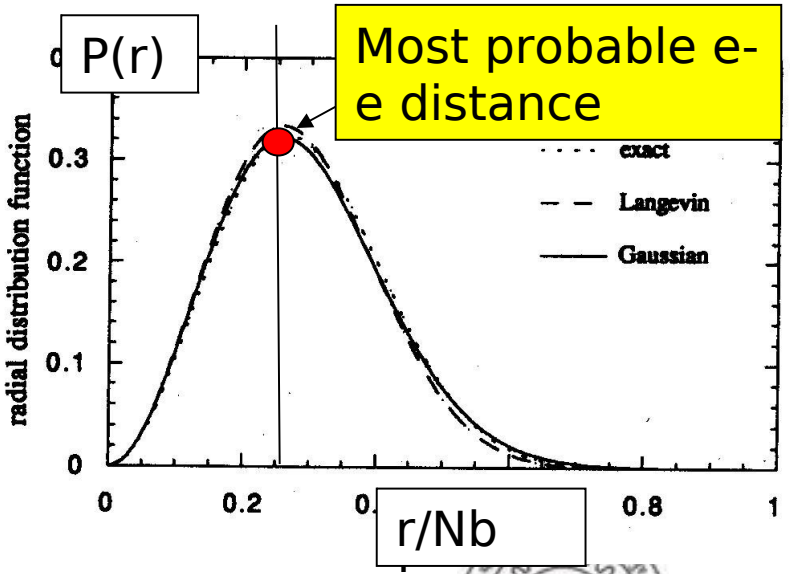
Infinitely long polymer chains qualify as self avoiding random walks. Therefore obey certain statistics even if they are locally not freely jointed.

Freely jointed chain

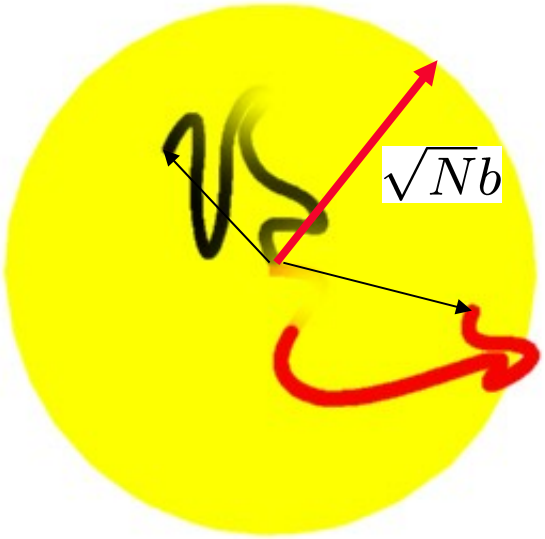
Kuhn segments: a few monomers long



Self avoiding Random walk of Kuhn segments



Gaussian end to end distribution

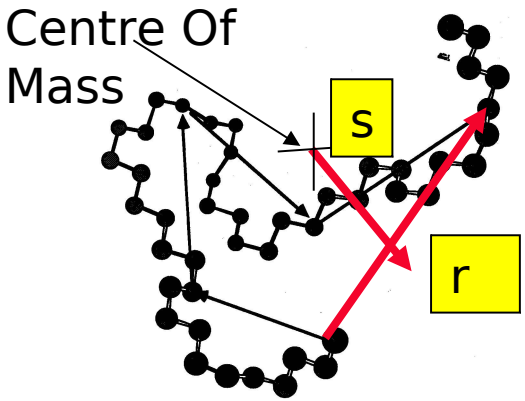


$$\langle r \rangle \propto \sqrt{N} b$$

Radius of gyration

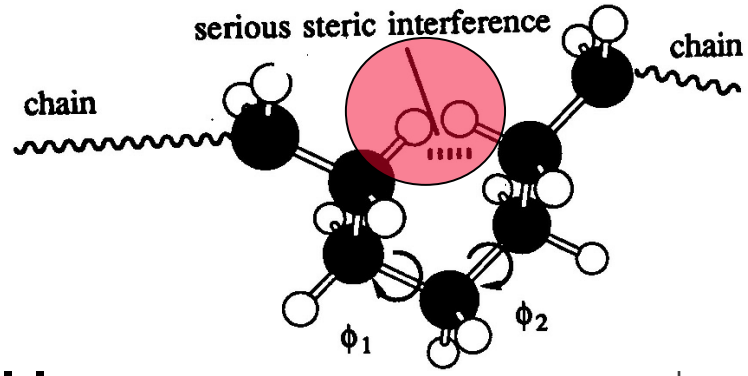
$$\frac{\langle s^2 \rangle}{\langle r^2 \rangle} = \frac{1}{6}$$

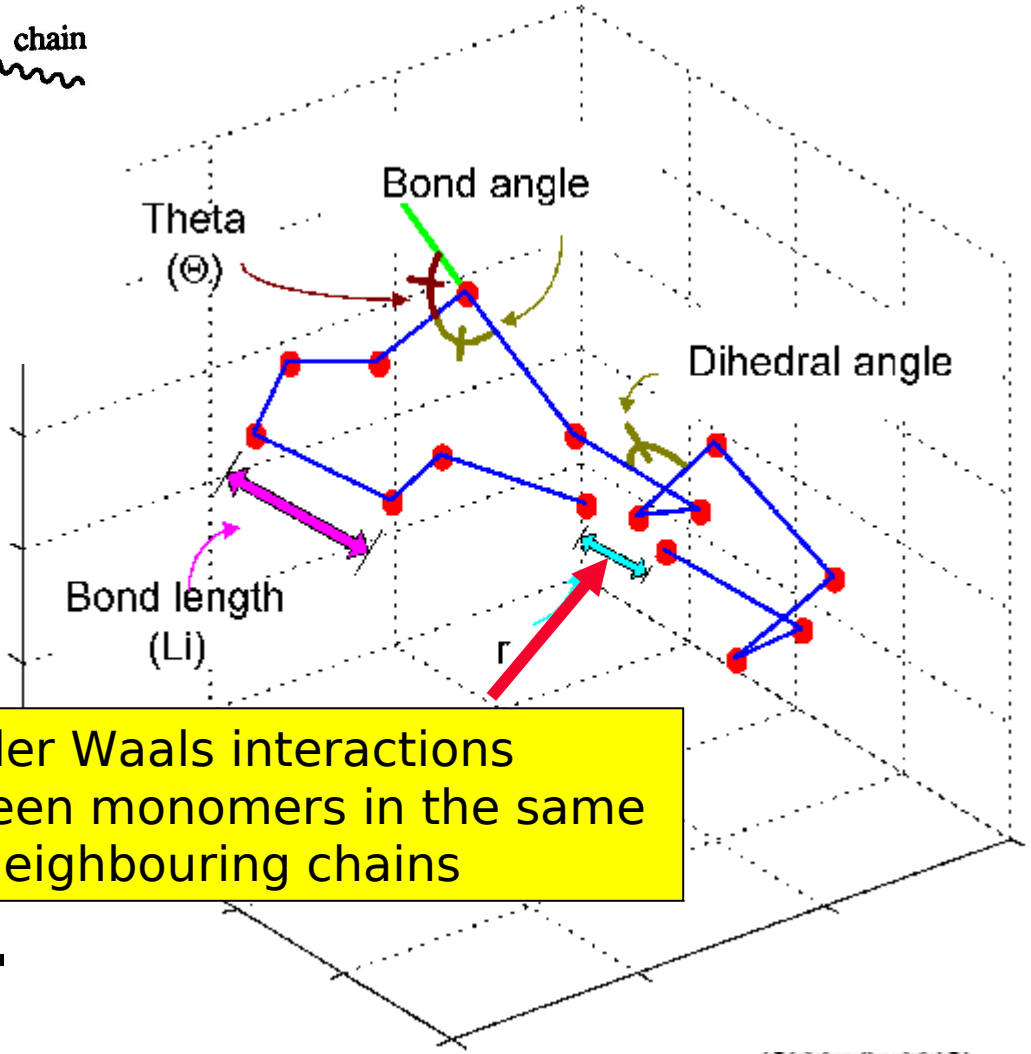
Debye(1946), Flory(1969)



A detailed MD ensemble of long macromolecules should obey these statistics ensuring long range order.

One part of a polymer chain also interacts with another part



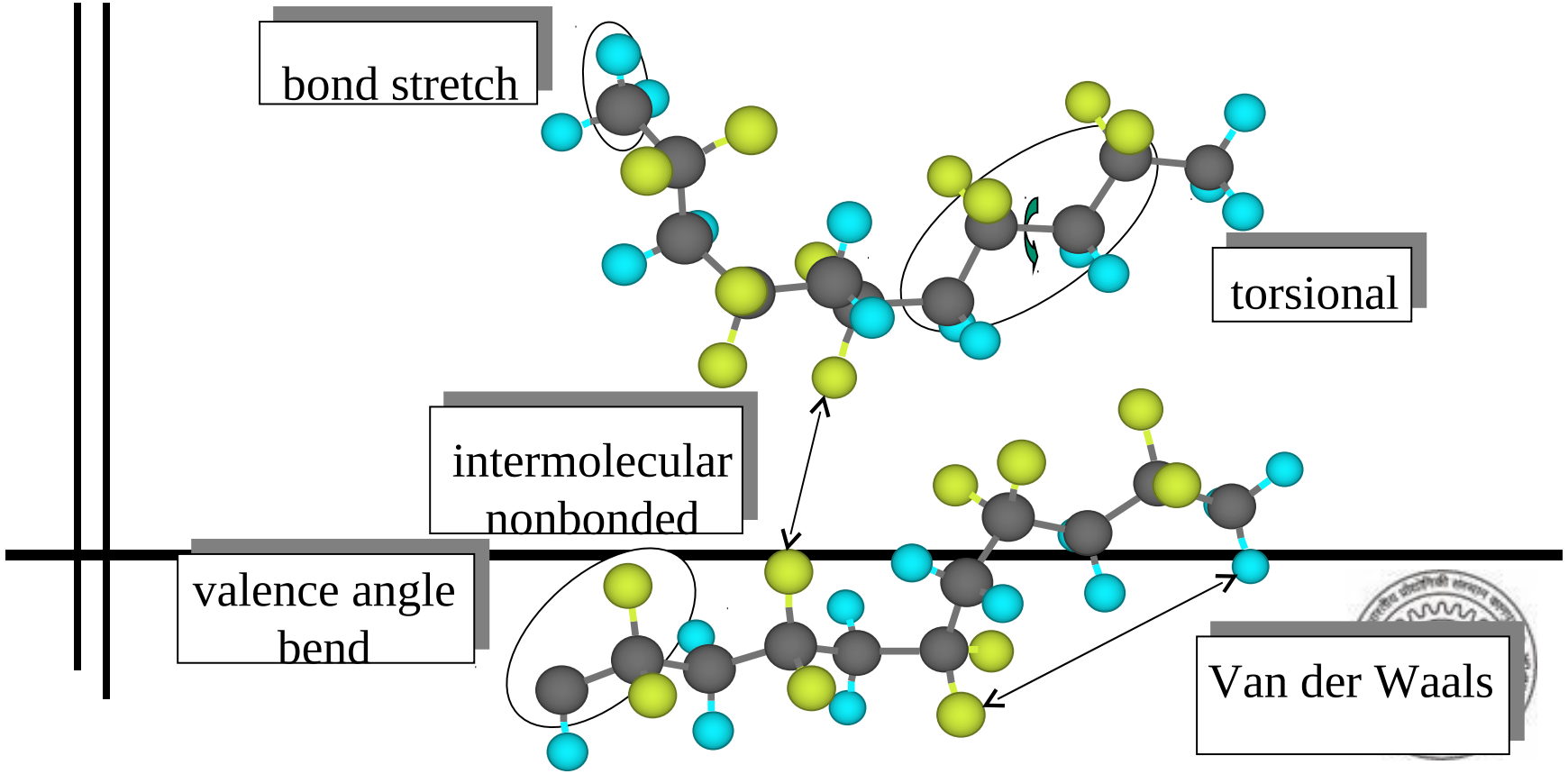


Van der Waals interactions between monomers in the same and neighbouring chains

Essentials of a sample preparation process: ensure equilibriation at short and long length scales

Total energy of an ensemble of macromolecules:

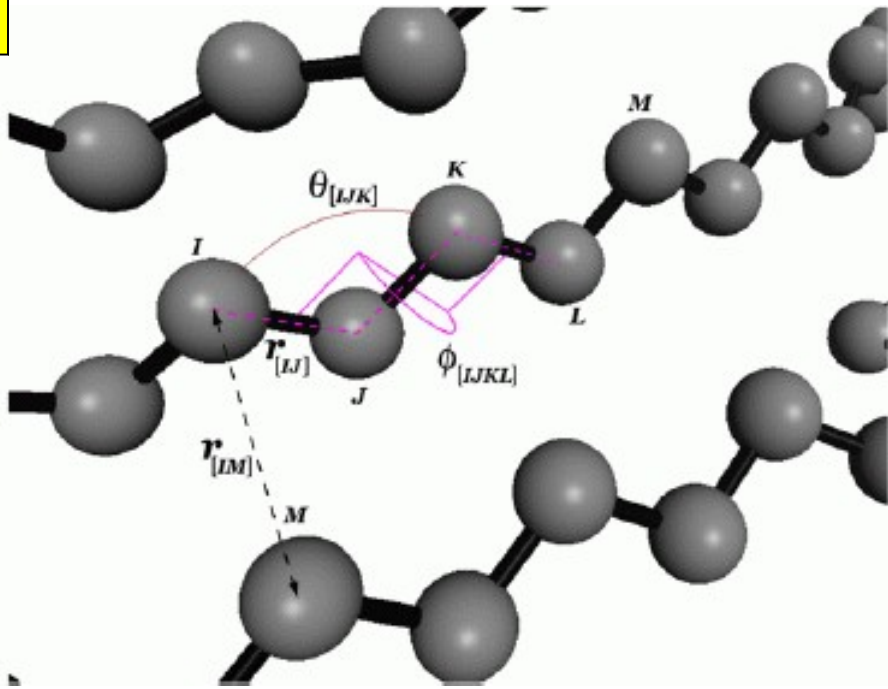
$$\mathcal{U} = \sum_{[IJ]=1}^{n_b} U_b(r_{[IJ]}) + \sum_{[IJK]=1}^{n_\theta} U_\theta(\theta_{[IJK]}) + \sum_{[IJKL]=1}^{n_\phi} U_\phi(\phi_{[IJKL]}) + \sum_{[IM]=1}^{n_{vdW}} U_{vdW}(r_{[IM]}).$$



Typical force fields:

Bond stretching:

$$U_b(r_{[IJ]}) = \frac{1}{2}k_b\left(r_{[IJ]} - b\right)^2$$



Bond bending

$$U_\theta(\theta_{[IJK]}) = \frac{1}{2}k_\theta\left(cos(\theta_{[IJK]}) - cos(\theta_0)\right)$$

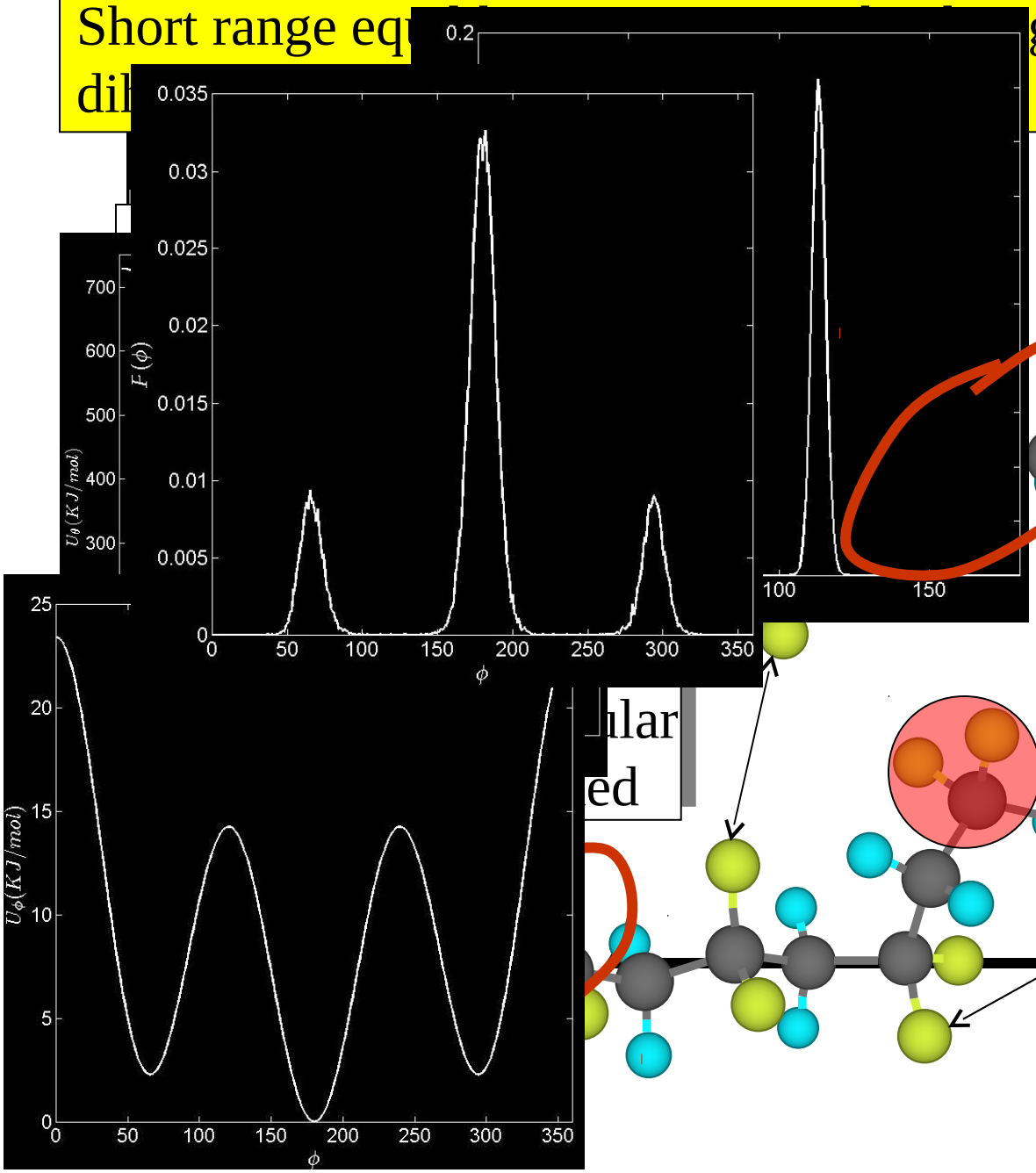
Dihedral:

$$\begin{aligned} U_\phi(\phi_{[IJKL]}) &= \frac{1}{2}A_1(1+\cos(\phi_{[IJKL]})) + \frac{1}{2}A_2(1-\cos(2\phi_{[IJKL]})) \\ &\quad + \frac{1}{2}A_3(1+\cos(3\phi_{[IJKL]})) \end{aligned}$$

Non-bonded

$$U_{vdW}(r_{[IM]}) = 4\epsilon\left[\left(\frac{\sigma}{r_{[IM]}}\right)^{12} - \left(\frac{\sigma}{r_{[IM]}}\right)^{6}\right].$$

Short range eq g lengths, angles and di



Tests for long range equilibriation are based on statistics of long chained molecules in an ensemble

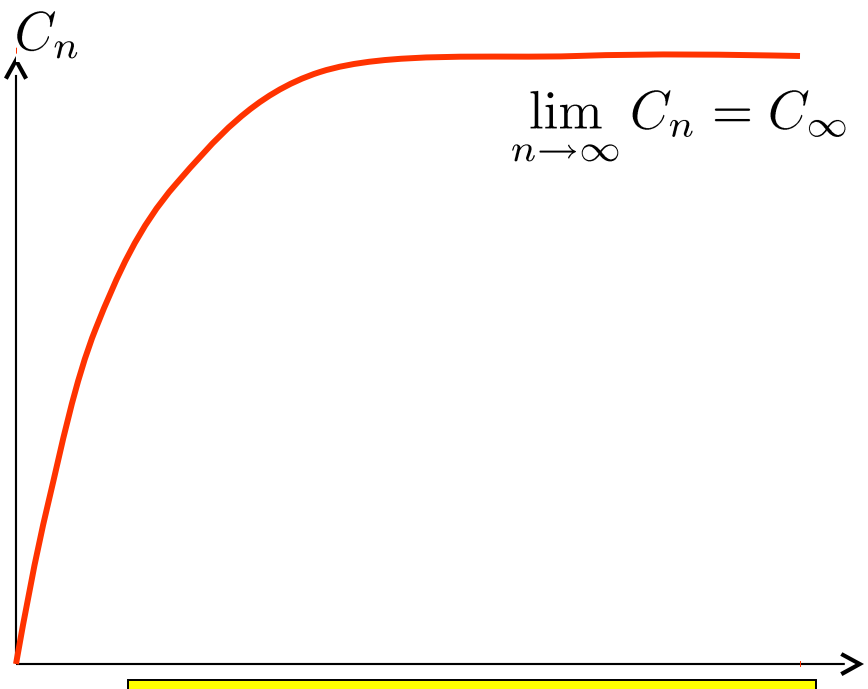
For a freely jointed chain, the squared end-to-end distance of a chain is:

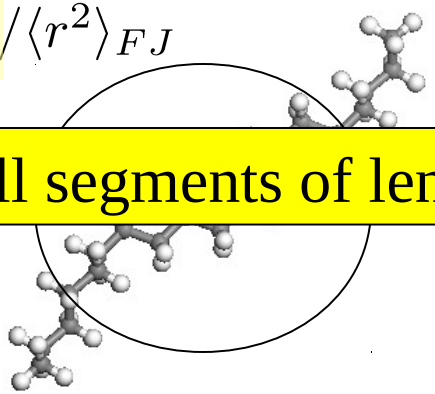
$$\langle r^2 \rangle_{FJ} = Nb^2$$

For a very long real chain, characteristic ratio

$$C_\infty = \frac{\langle r^2 \rangle}{\langle r^2 \rangle_{FJ}}$$

$$C_n = \langle r_n^2 \rangle / \langle r^2 \rangle_{FJ}$$

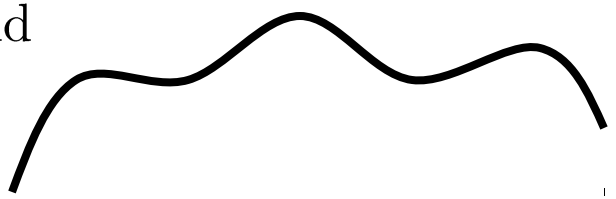




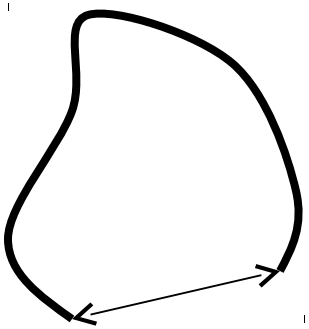
Average over all segments of length n in the ensemble

Steps involved in equilibriation $T > T_g$

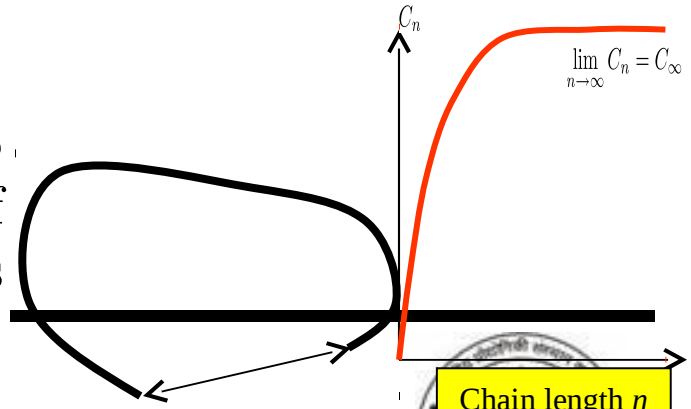
Build a single chain with the equilibrium bond length, angle and dihedral distributions.



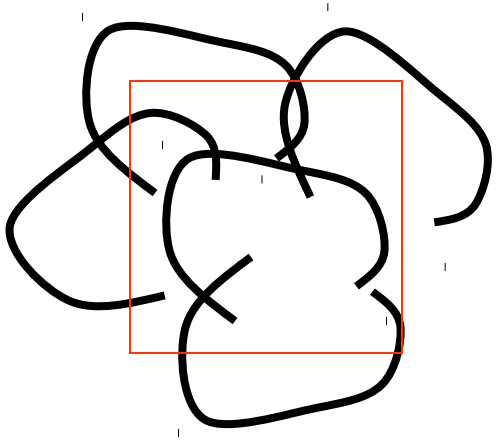
Conjugate gradient based energy minimisation is performed with end to end distance held at $\langle r^2 \rangle = C_\infty n b^2$.



The chain is further equilibriated using only $1-5$ non bonded interactions so that a large number of chain conformations can be sampled. A chain is chosen that is closest to the target structure.



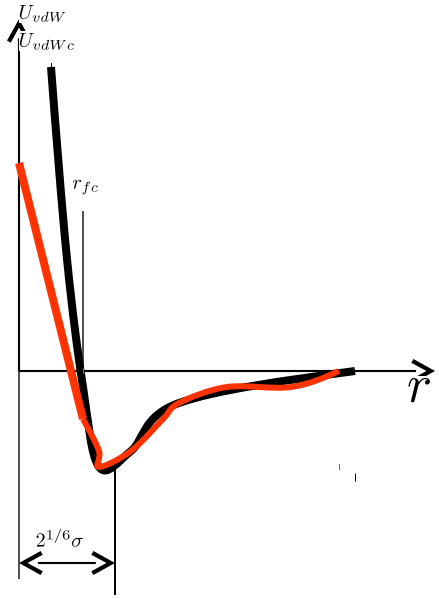
Requisite number of replicas of the selected chain are packed into a box with the box size corresponding to an overall specified density. The chains are then subjected to a zero temperature Monte Carlo optimization whereby they are translated, rotated and reflected with a view to reduce local density fluctuations



A 'slow push off' is performed on the ensemble using a force capped LJ potential U_{vdWc} of the form

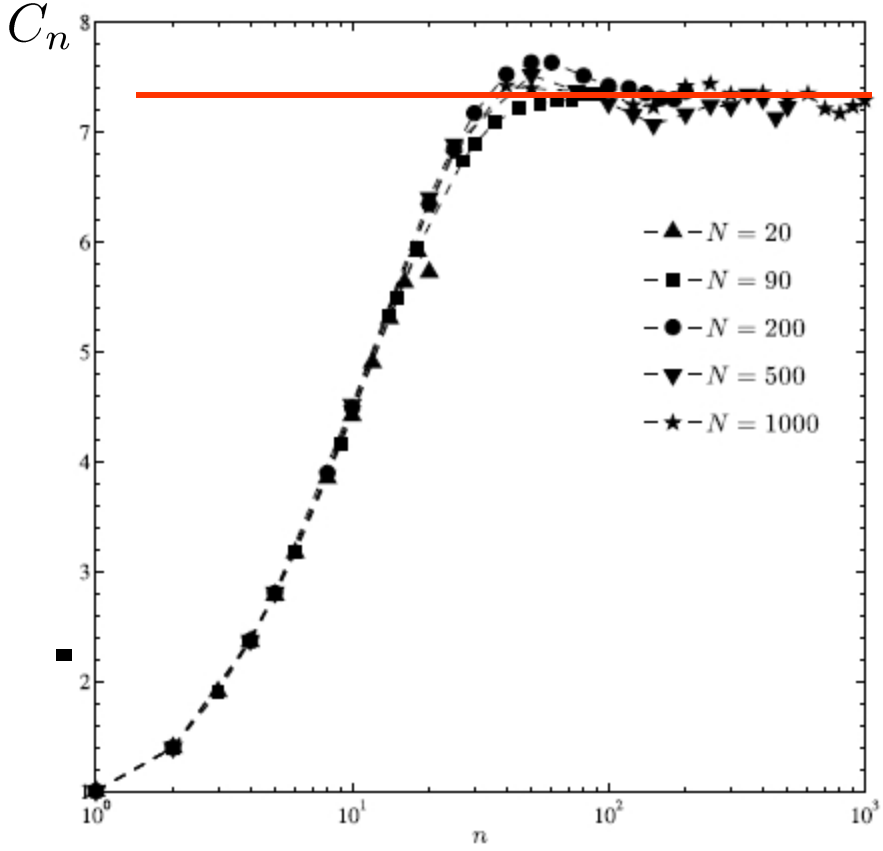
$$U_{vdWc} = \begin{cases} (r - r_{fc})U'_{vdW}(r_{fc}) + U_{vdW}(r_{fc}) & r < r_{fc} \\ U_{vdW}(r) & r \geq r_{fc} \end{cases}$$

typically, we gradually reduce r_{fc} from $2^{1/6}\sigma$ to 0.8σ in 10 stages. Again, only the $1-5$ non-bonded interaction is active.



Finally, slow push off is followed by full MD equilibration for a long time with the full LJ potential switched on.

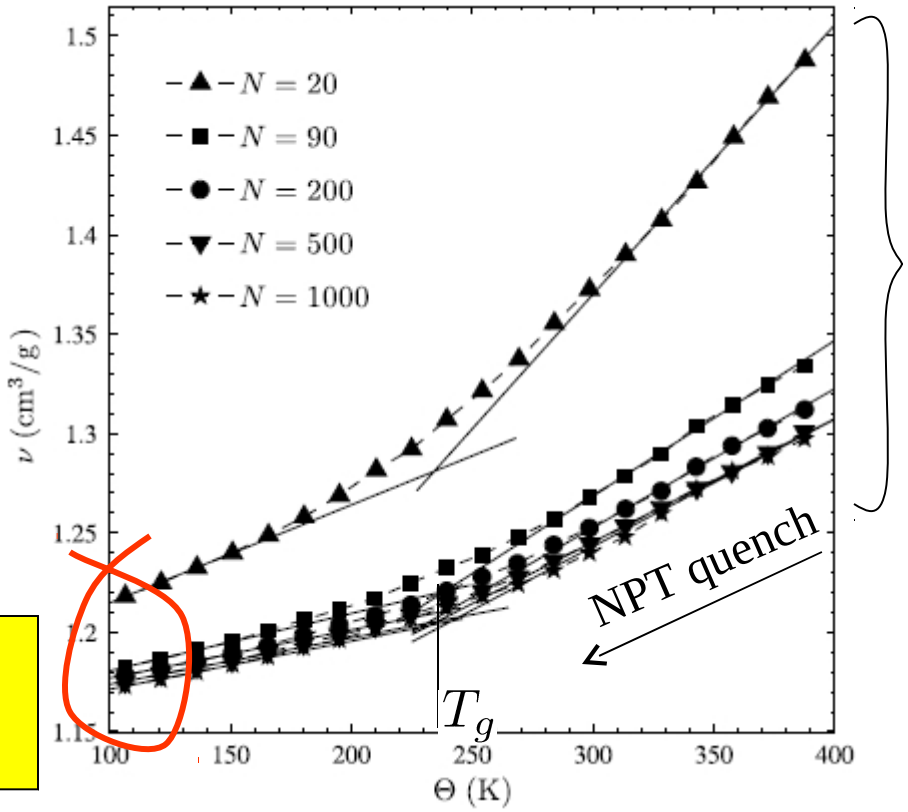
Auhl et al., 2003, J. Chem. Phys., v119, pp12718; Mahajan and Basu, 2010, Model. Simul Mater Sc Engng, v18, pp025001



$C_\infty \simeq 7$

Experimental: $C_\infty = 6.8$ for PE under theta conditions

Quench!



Equilibriated samples

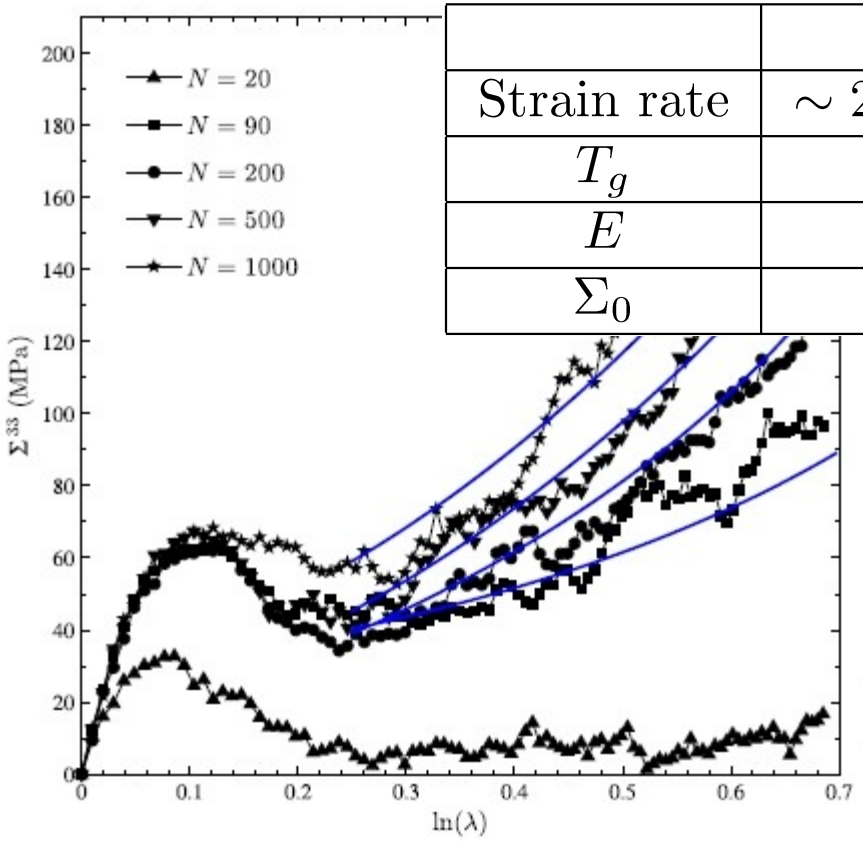
Glassy samples

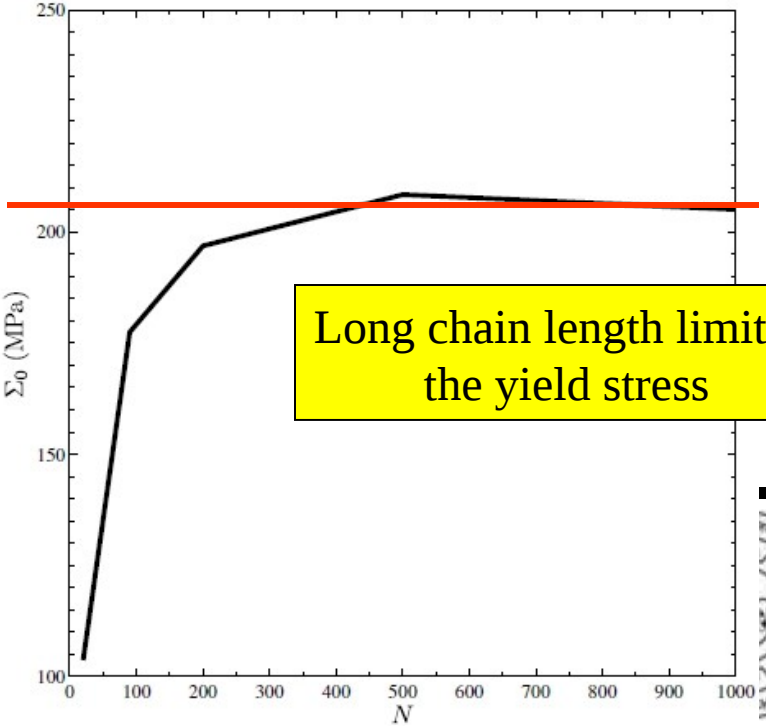
PE is semi-crystalline in reality but can be quenched to an amorphous glass at the high quenching rates used in MD. The equilibriated structure at $T > T_g$ is presered in the glassy sample.

Pull under $N\Sigma^{11}\Sigma^{22}T$

**Gaur and Wunderlich, 1980, Macromolecules, v13, pp445*

	MD	Experiments
Strain rate	$\sim 2 \times 10^{-4}$ ps^{-1}	$1 - 10^{-4}$ s^{-1}
T_g	240 K	$\sim$ 245 K*
E	1.8 GPa	1.5 GPa
Σ_0	200 MPa	120 MPa





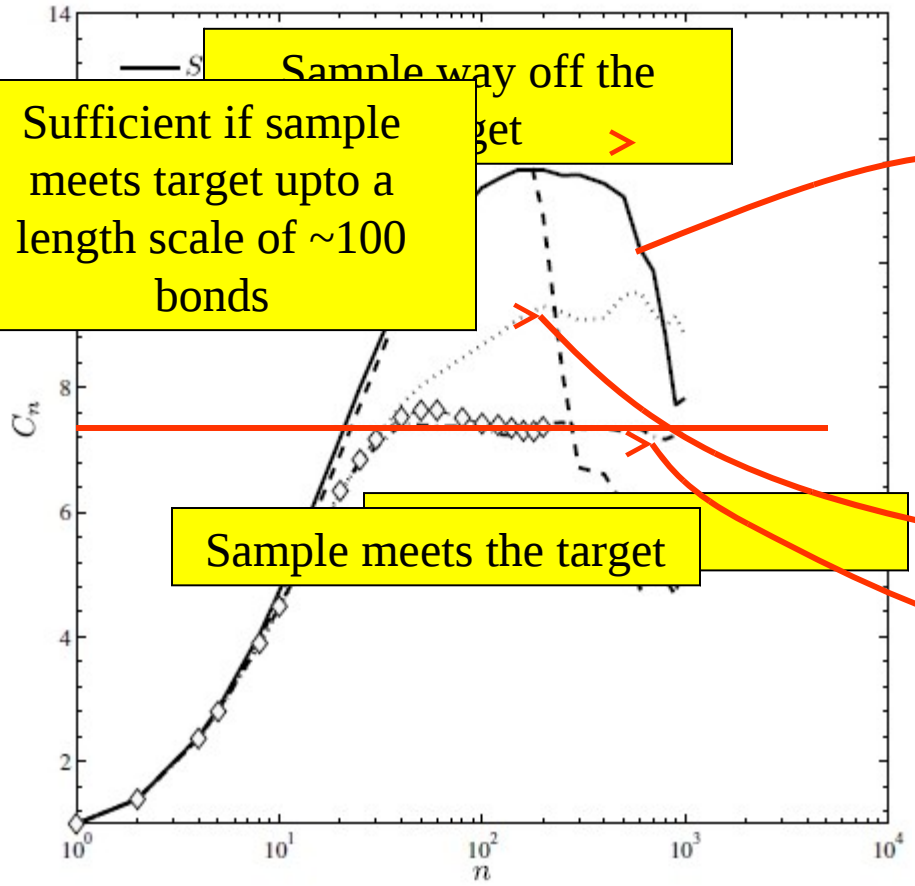
Long chain length limit of the yield stress

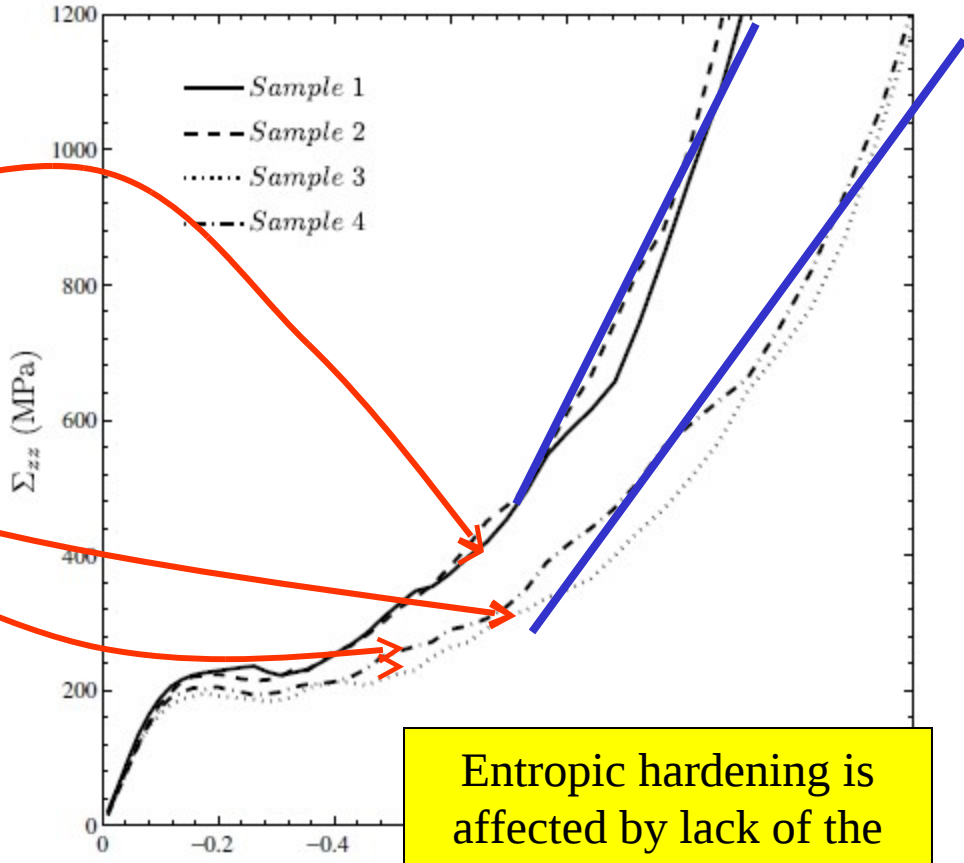
The price of disobeying!

Sufficient if sample meets target upto a length scale of ~100 bonds

Sample way off the get

Sample meets the target





Entropic hardening is affected by lack of the long range equilibriation

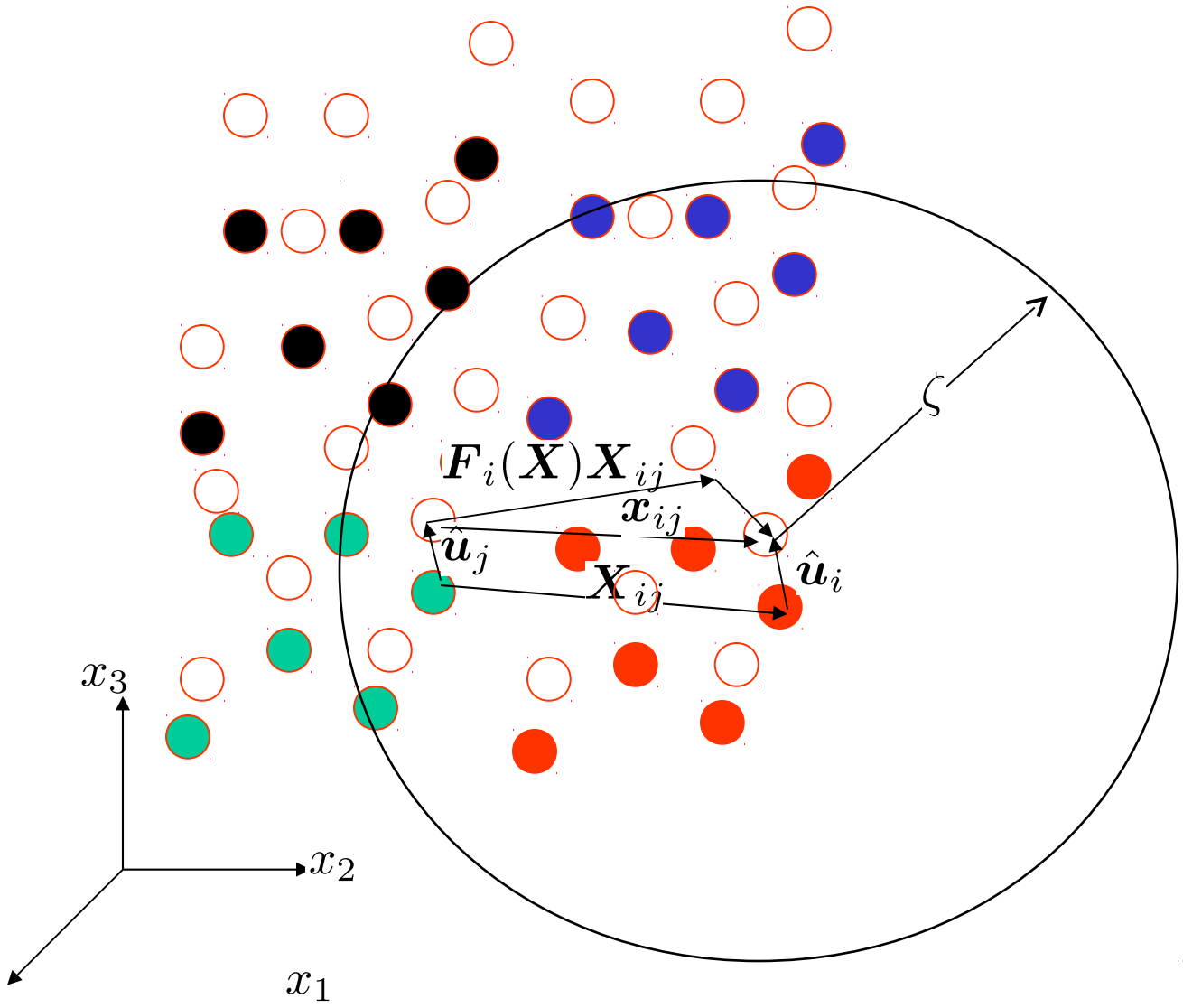
Does the MD ensemble behave like a chunk of continuum?

Recall that the underlying continuum deformation is *homogeneous* and is given by

$$\begin{aligned} x_1 &= \lambda_1 X_1 \\ x_2 &= \lambda_2 X_2 \\ x_3 &= \lambda X_3 \end{aligned}$$

such that

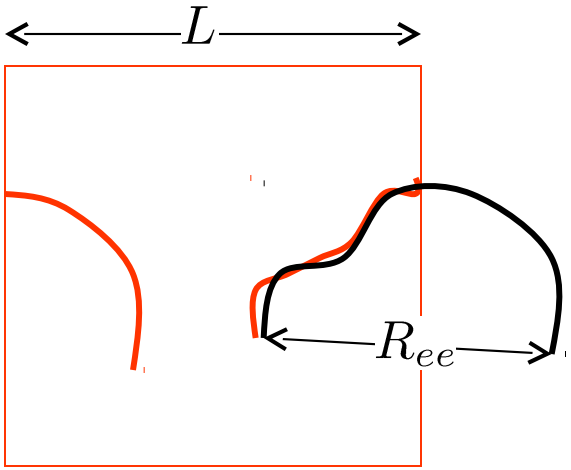
$$E^{33} = \lambda^2 - 1.$$



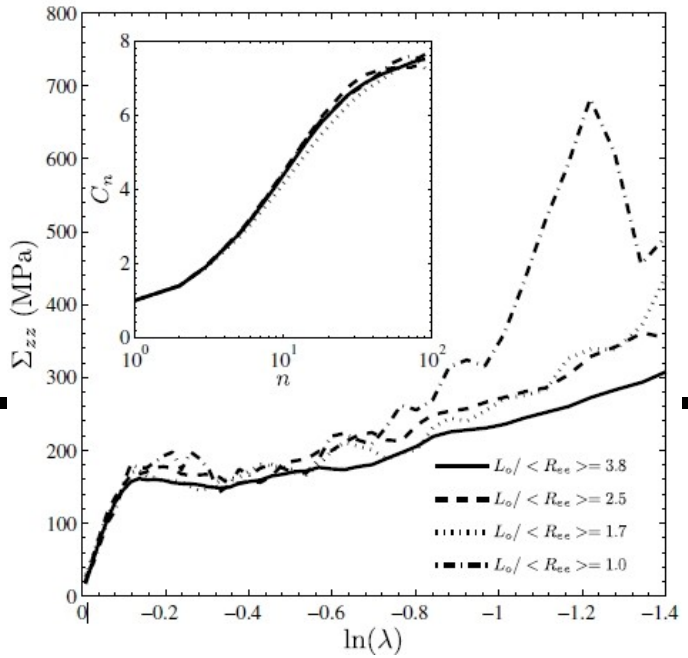
The local deformation gradient $\boldsymbol{F}_i$ is determined by minimising

$$\Pi = \sum_{j \in \Omega(\zeta)} \left| \boldsymbol{F}_i \boldsymbol{X}_{ij} - \boldsymbol{x}_{ij} \right| .$$

How big a sample to take ?

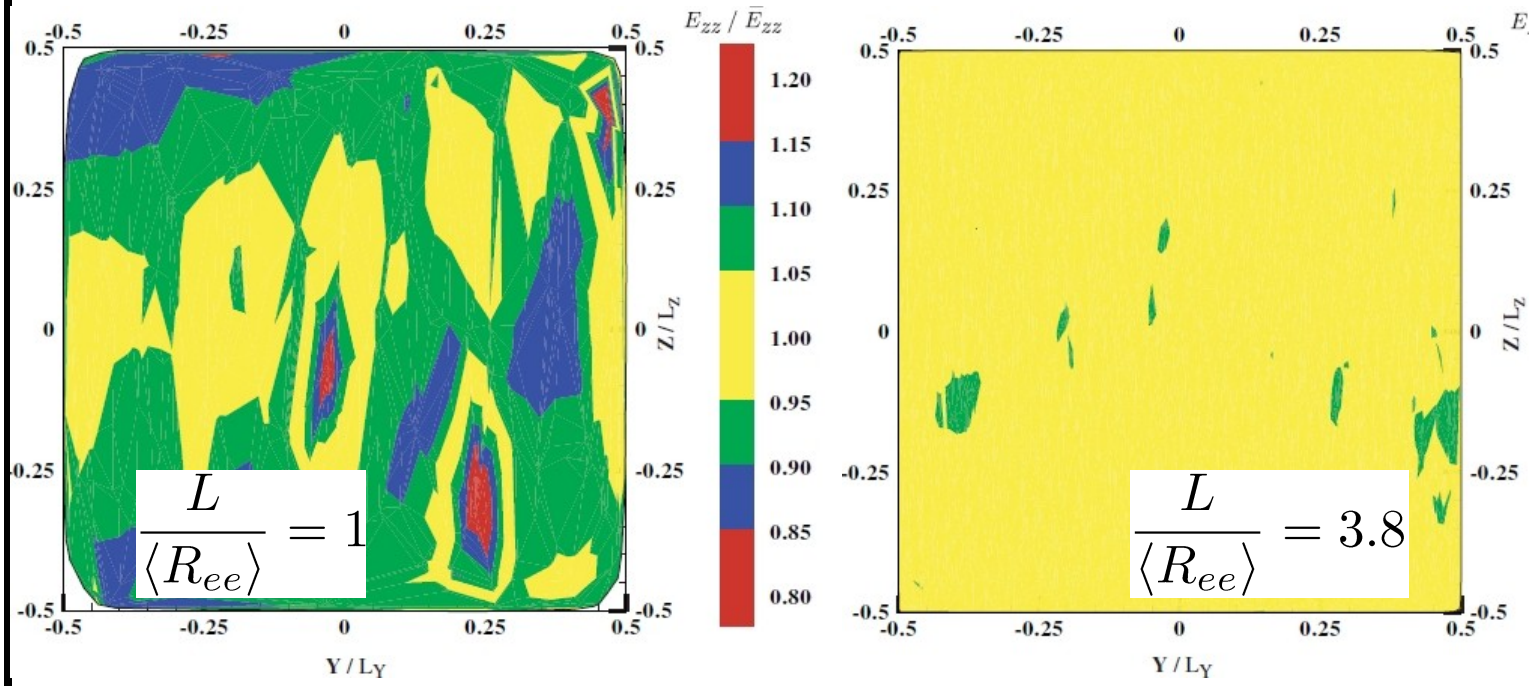


We check if, all things remaining equal, the mechanical response depends on $L/\langle R_{ee}\rangle$.



$L/\langle R_{ee}\rangle \sim 3$ is needed for a smooth stress strain response $\Rightarrow$ ensembles with longer chains need bigger boxes, more monomers and hence more expensive simulations.

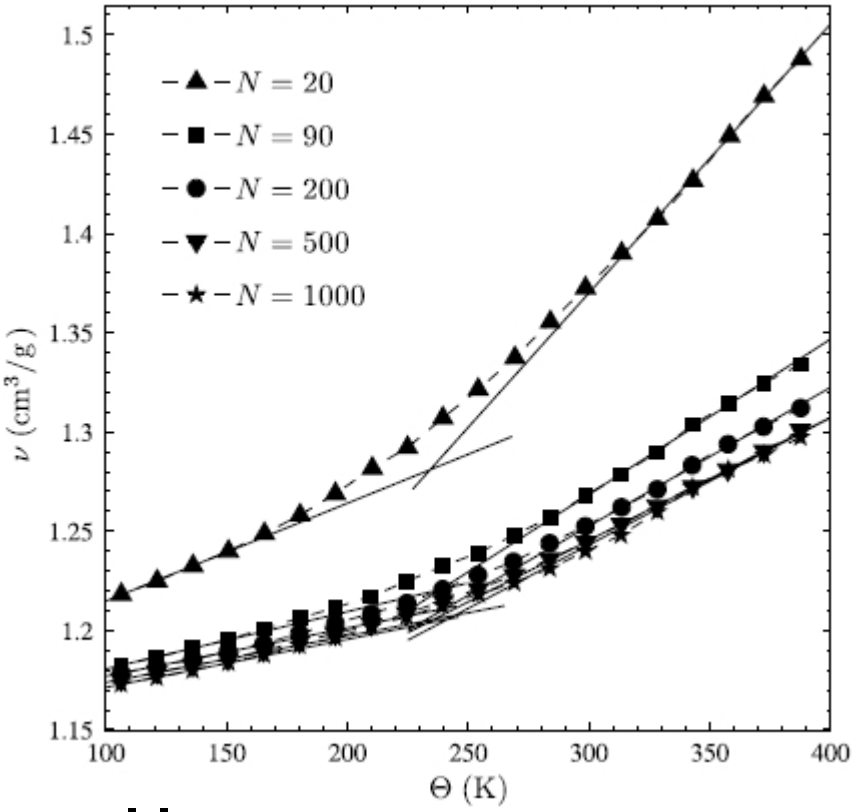
Sample sizes > 3 times the average end to end distance attains an almost homogeneous strain distribution

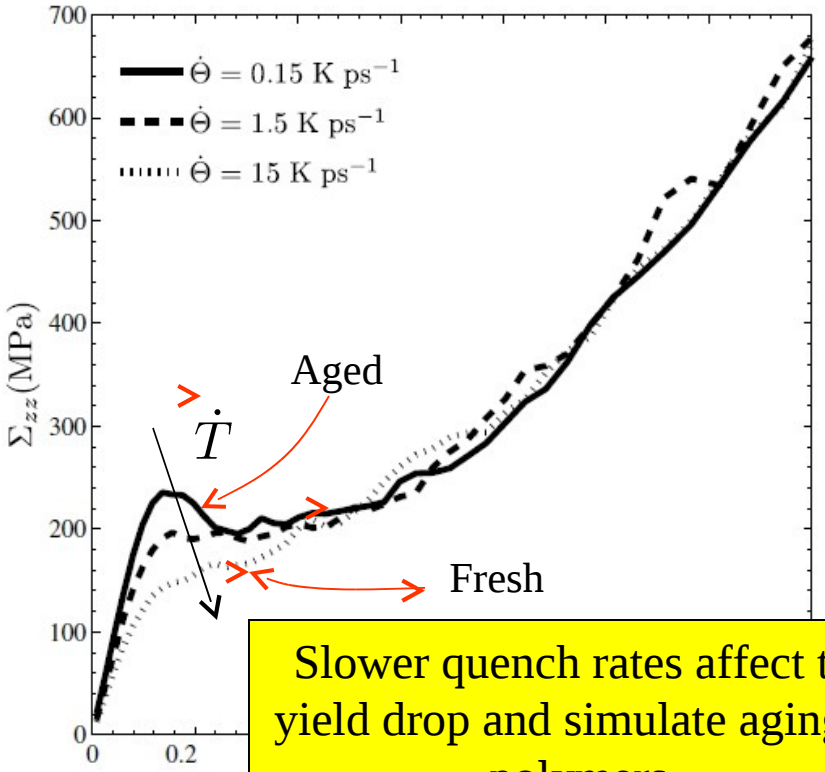


A larger sample is more continuum-like.

How fast should we quench and pull?

Real life quench rates are about $0.3\ \mathrm{K/s} = 0.3 \times 10^{-12}\ \mathrm{K/ps}$

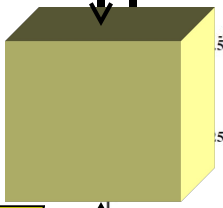




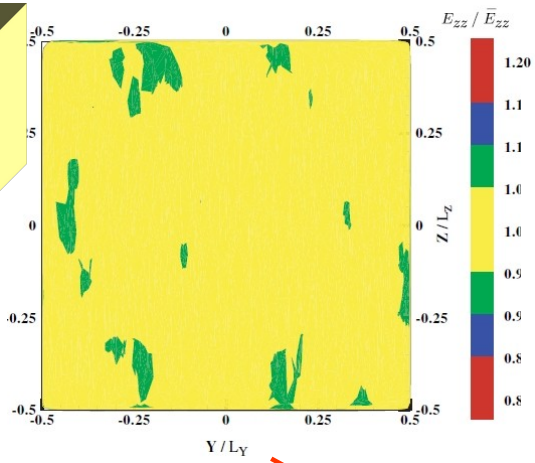
Slower quench rates affect the yield drop and simulate aging in polymers.

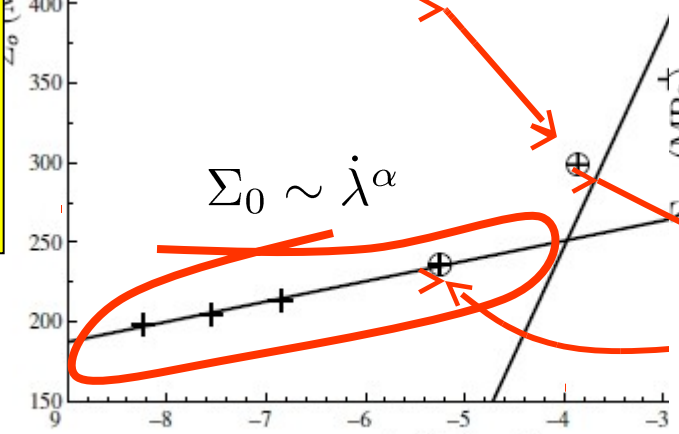
Rate of pulling has a significant effect on the yield stress.

$\dot{\lambda}$



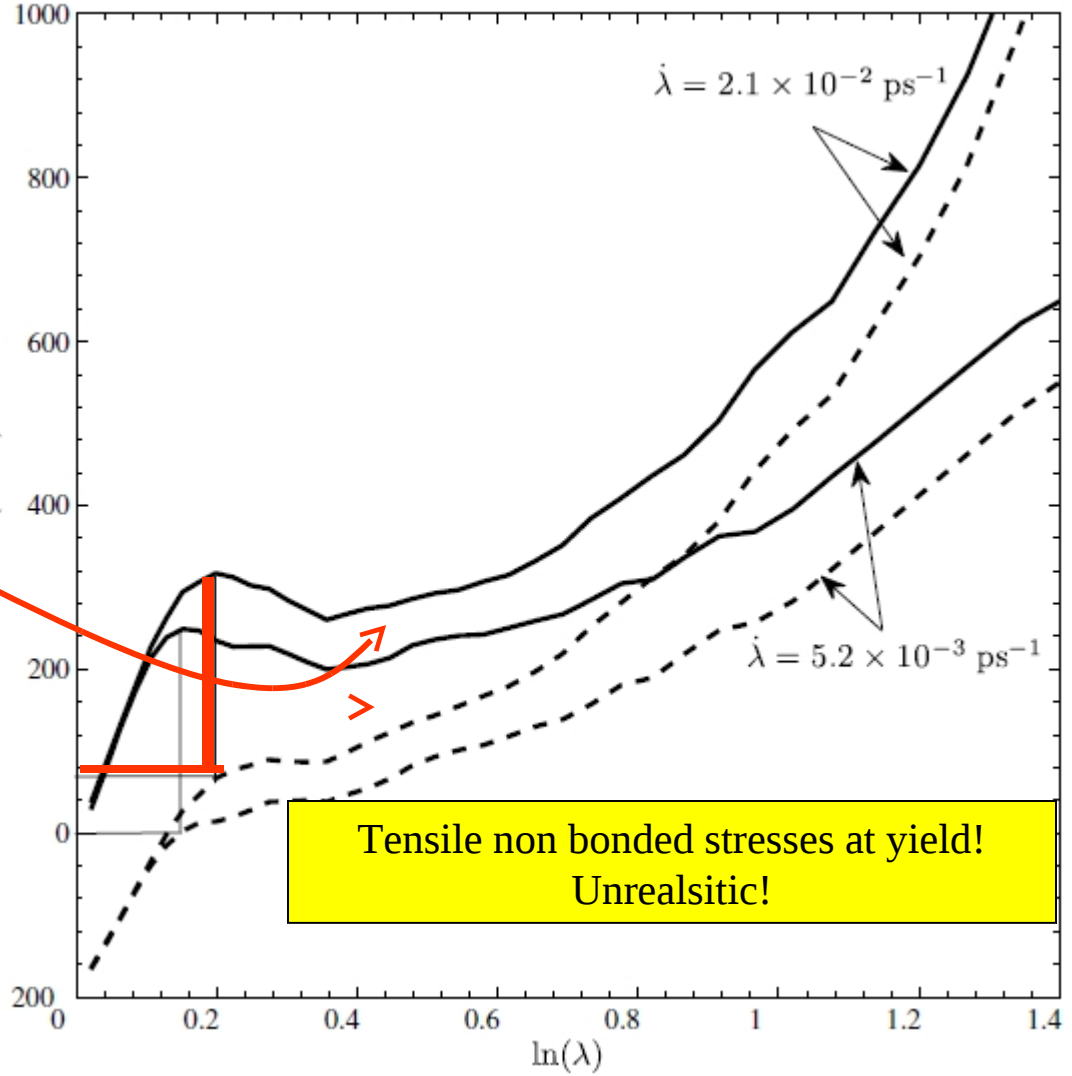
Yield stress





Rate of deformation

Polymers are rate sensitive in re-



Tensile non bonded stresses at yield!
Unrealsitic!

Conclusions: Now we can pull out numbers!

Suppose you wish to simulate a linear polymer of density 1000 kg/m^3. Chain length 1000 monomers, weight of each united atom 14 g/mol $= 2.3 \times 10^{-26}$ kg. Main chain bond length $b = 1.53$ angstrom

Expected end to end distance is $\langle R_{ee} \rangle = \sqrt{N} b^2$ or 48.4 angstrom

Size of periodic box required $3 \times \langle R_{ee} \rangle \simeq 144$ angstrom

Number of chains of 1000 united atoms/chain required is about 129, i.e an ensemble with 129000 united atoms.

Safe strain rates $\dot{\lambda} \sim e^{-7}$ ps^{-1}.

Time required to impart a stretch of 2, i.e doubling of the box size, 2200 ps.

What we did not talk about …

Coarse graining: the art and science of reducing complicated linear architectures (PS, PC, PVC etc) to polyethylene-like chains.

Primitive path analysis: Characterisation of the entanglement network

Constitutive modelling: Extracting parameters of continuum constitutive models from MD simulations