BROWN UNIVERSITY
PROVIDENCE, RHODE ISLAND

Division of Engineering
Brown University

Atomic scale mechanisms of stress production in elastomers

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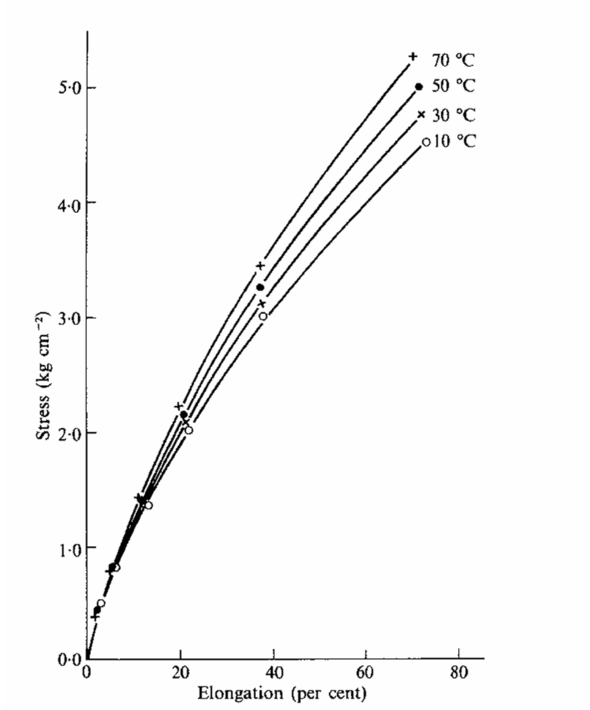
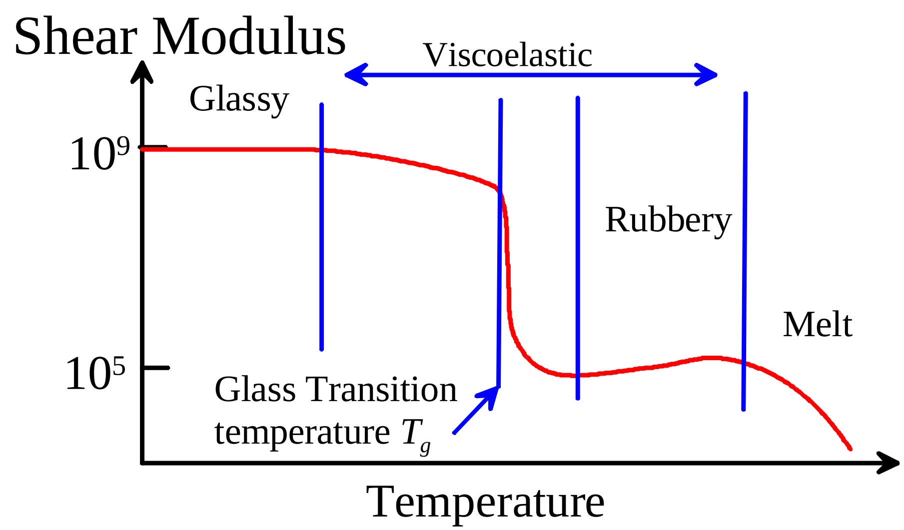
NSF Nanomechanics Workshop

July 2004

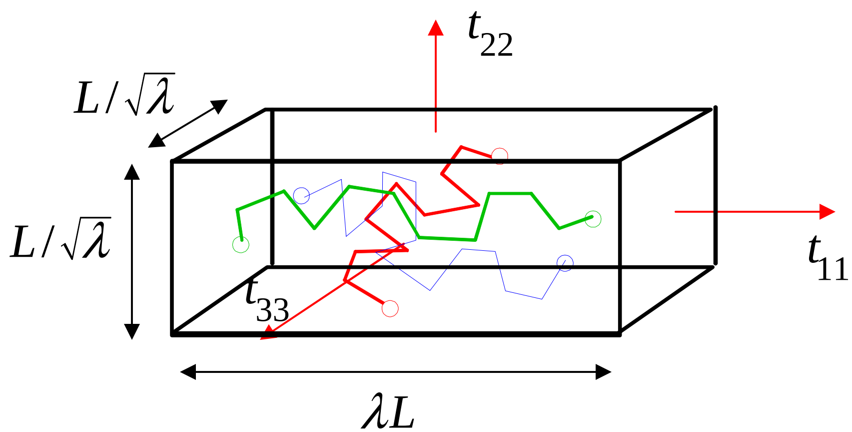
Constitutive response of elastomers

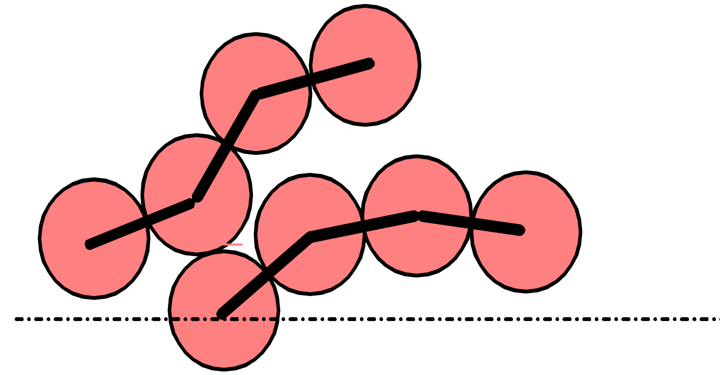




- Rubbers strongly resist volume changes. Bulk modulus comparable to metals or covalently bonded solids;
- Rubbers are very compliant in shear – shear modulus is several orders of magnitude lower than metals or covalently bonded solids
- Shear response is strongly temperature dependent: the material becomes stiffer as it is heated, in sharp contrast to metals;
- When stretched, rubber gives off heat.

Classical theory of rubber elasticity





Mean stress: $p = (t_{11} + t_{22} + t_{33})/3$ due to repulsive excluded volume interactions (fluid-like response)

Deviatoric stress: $\sigma_{11} = t_{11} - p$ due to entropy of chain network

Affine Network Model (freely jointed chains without EV)

Helmholtz free energy $dW = dU - TdS = \sigma_{11} \dfrac{d\lambda}{\lambda}$

Entropy of Gaussian chain network $S = S_0 - k\dfrac{N_c}{2v}(\lambda^2 + 2/\lambda)$

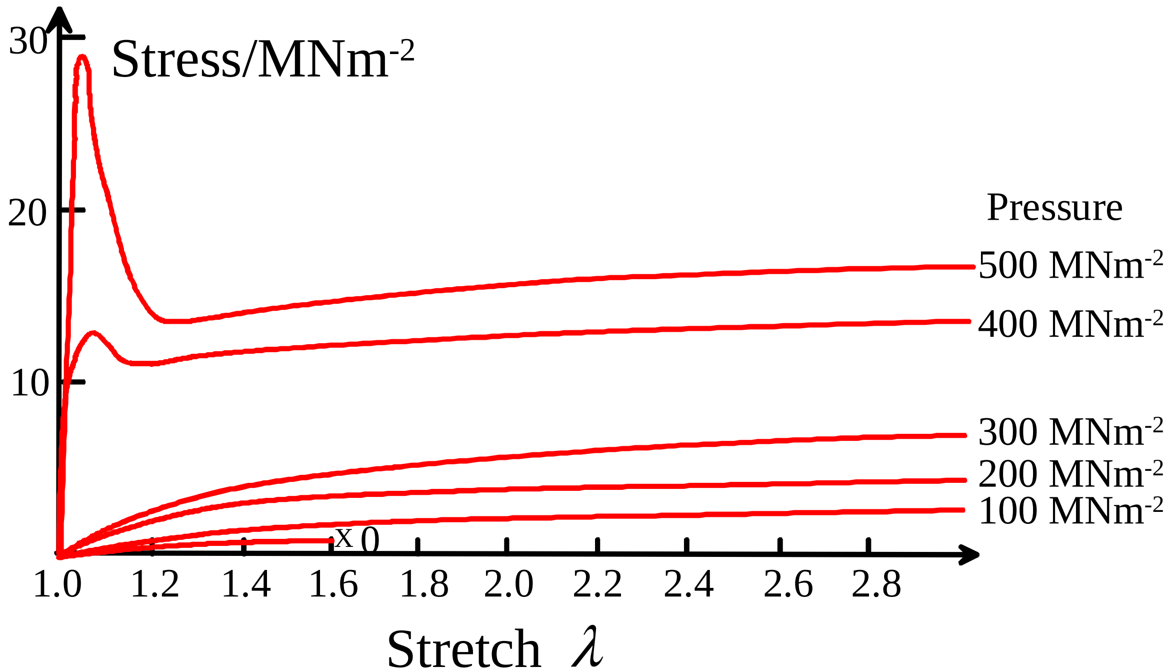
Deviatoric stress: $\sigma_{11} = kT\dfrac{N_c}{v}(\lambda^2 - 1/\lambda)$

Chain force: $f_i = \dfrac{3kT}{N_b a^2} r_i$

The influence of pressure on deviatoric stress

D.L. Quested, K.D. Pae, J.L. Sheinbein and B.A. Newman,
J. Appl. Phys, **52,** (10), 5977 (1981)

Uniaxial deformation of solithane under confining pressure



Pressure dependence cannot be explained using classical theory of rubber elasticity

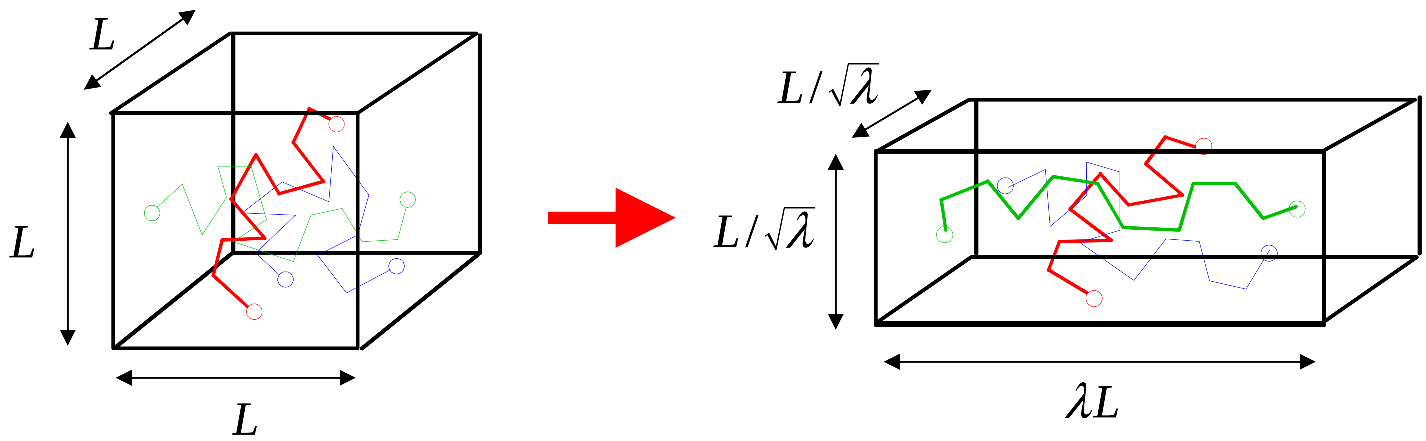
Outline

- Re-examine atomic scale deformation of elastomers using a model that includes Excluded Volume (EV) interactions

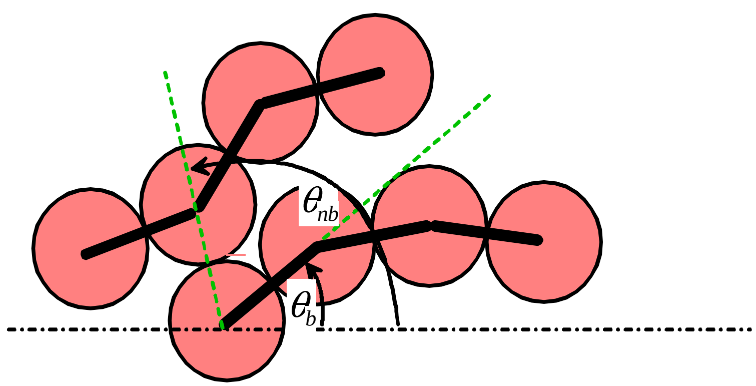
- Deviatoric stress is caused by deformation induced anisotropy of chain network
- Repulsive EV interactions give the dominant contribution to both deviatoric and mean stress
- Pressure and deviatoric stress are intimately connected at atomic scale
- Pressure-deviatoric stress relation

$$\sigma \approx \sigma_b + \sigma_{nbr} = \left(D\Pi_b - AB\Pi_{nbr} \right) \frac{F}{N_b} (\lambda^2 - \lambda^{-1})$$

Molecular model of atomic-scale stress generation



Reduced density $\rho^{*} = N\sigma_{LJ}^{3} / L^{3}$



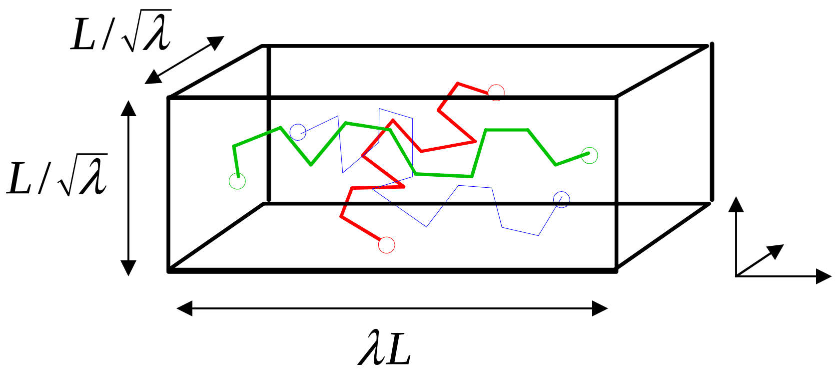
Covalent bonds

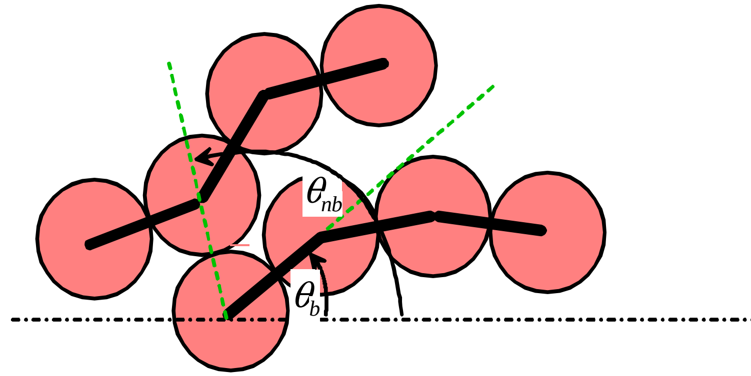
$$u_b(r) = \frac{1}{2}\kappa(r-a)^2$$

Noncovalent interactions

$$u_{nb}(r) = 4\epsilon_{LJ}\left[\left(\frac{\sigma_{LJ}}{r}\right)^{12} - \left(\frac{\sigma_{LJ}}{r}\right)^{6}\right]$$

Stress computations



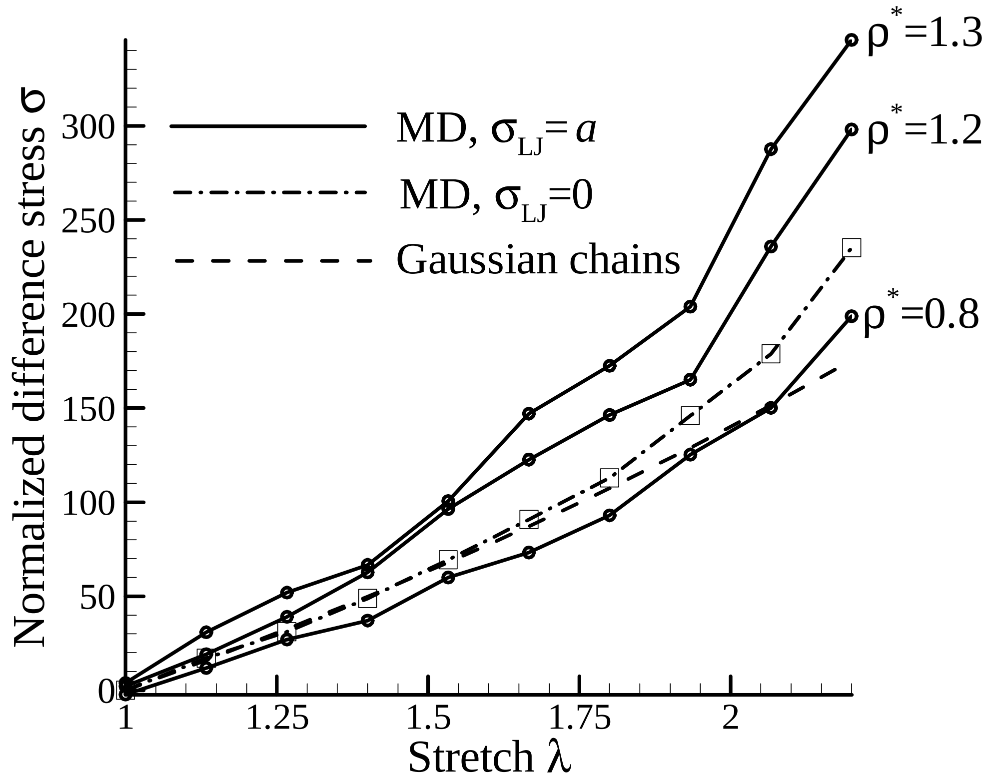


Virial Theorem $$vt_{ij} = -NkT\delta_{ij} + \sum_{\alpha} \left\langle f_i^{\alpha} r_j^{\alpha} \right\rangle$$

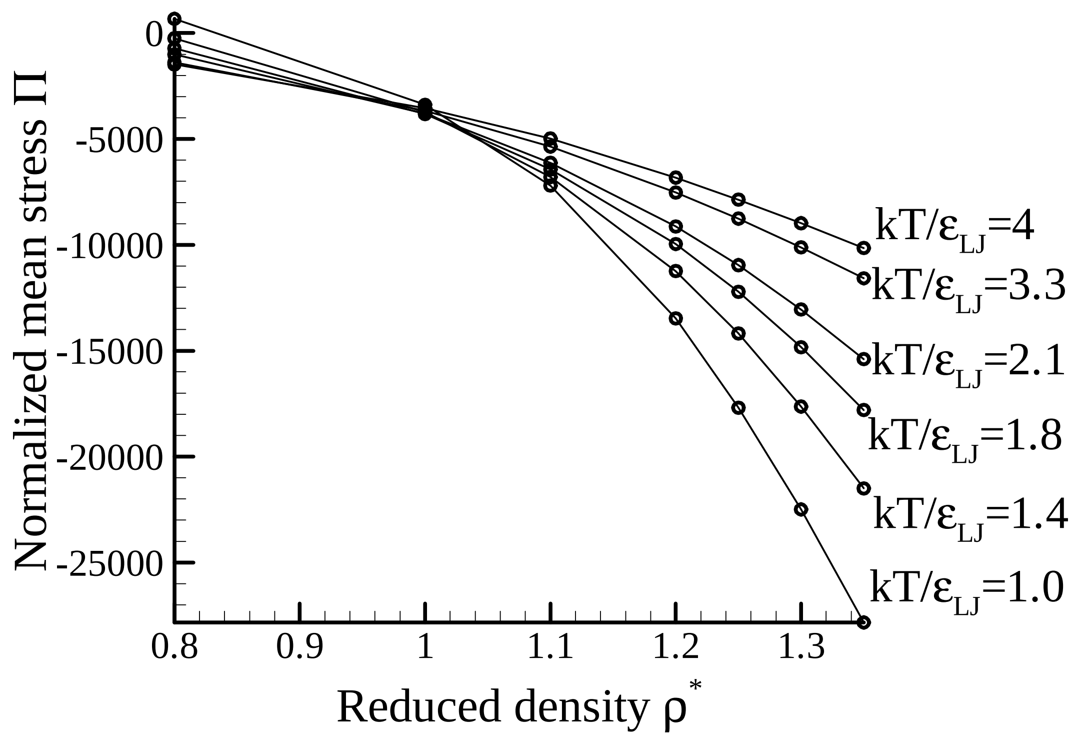
Normalized difference stress $$\sigma = \frac{v}{kT}\{t_{11} - (t_{22} + t_{33})/2\} = \frac{1}{kT}\sum_{\alpha}\left\langle f_1^{\alpha} r_1^{\alpha} - (f_2^{\alpha} r_2^{\alpha} + f_3^{\alpha} r_3^{\alpha})/2 \right\rangle$$

Normalized mean stress $$\Pi = \frac{v}{kT}\{t_{11} + t_{22} + t_{33}\}/3 = -N + \frac{1}{3kT}\sum_{\alpha}\left\langle f_i^{\alpha} r_i^{\alpha} \right\rangle$$

Difference Stress-stretch relations

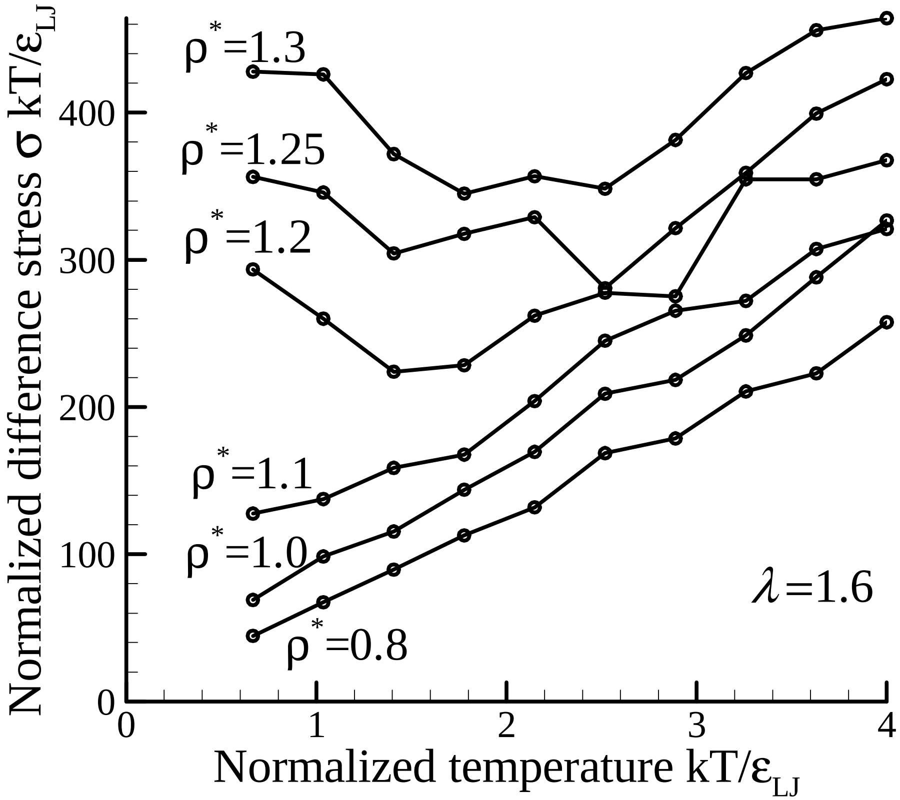


Mean Stress – reduced density relations



Temperature dependence of stress

$$\frac{\sigma kT}{\epsilon_{LJ}} = \frac{v}{\epsilon_{LJ}}\{t_{11} - (t_{22} + t_{33})/2\}$$



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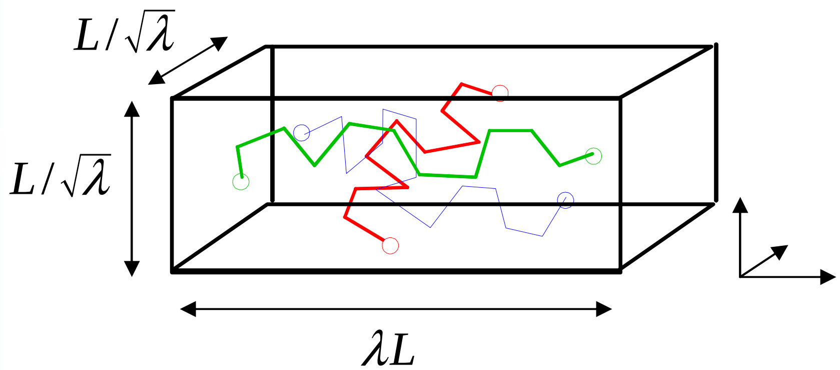
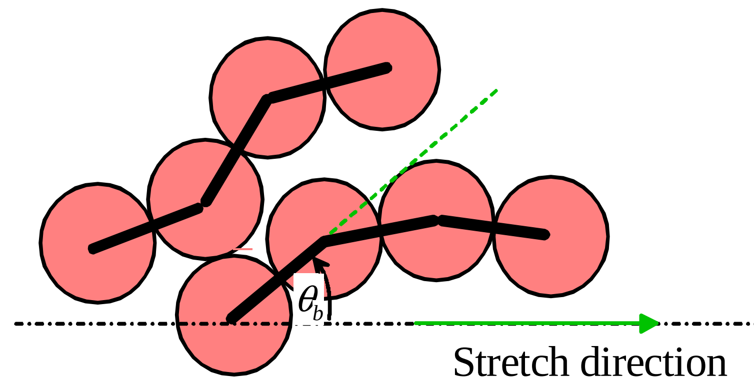
Relation between stress and bond anisotropy





Bond orientation anisotropy measure

$$\langle P_2(\theta_b)\rangle = \frac{1}{N_c N_b}\sum_{\alpha\in b}\left\langle (3\cos^2\theta_\alpha - 1)/2\right\rangle$$

$\langle P_2(\theta_b)\rangle = 0$ for undeformed (isotropic) system.

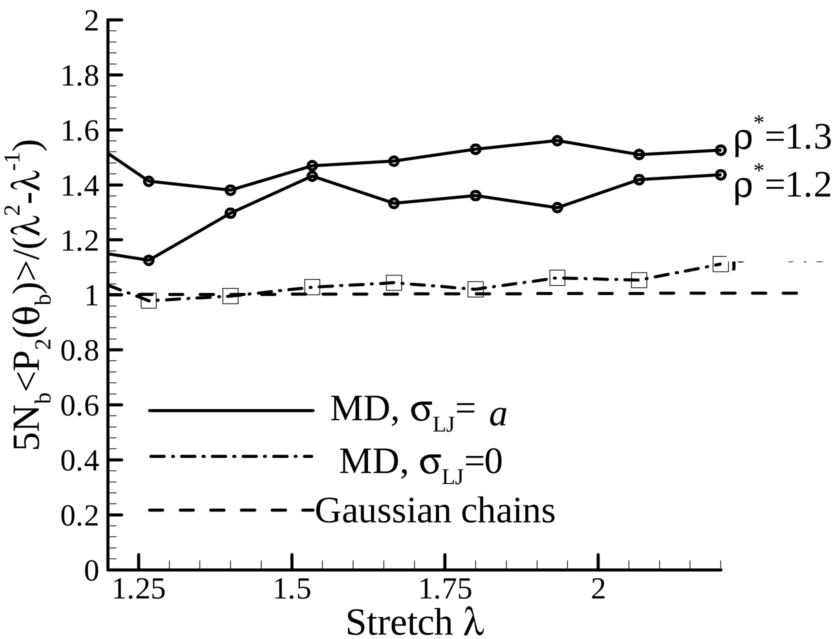
$\langle P_2(\theta_b)\rangle > 0$ (tension) $\quad\quad \langle P_2(\theta_b)\rangle < 0$ (compression)

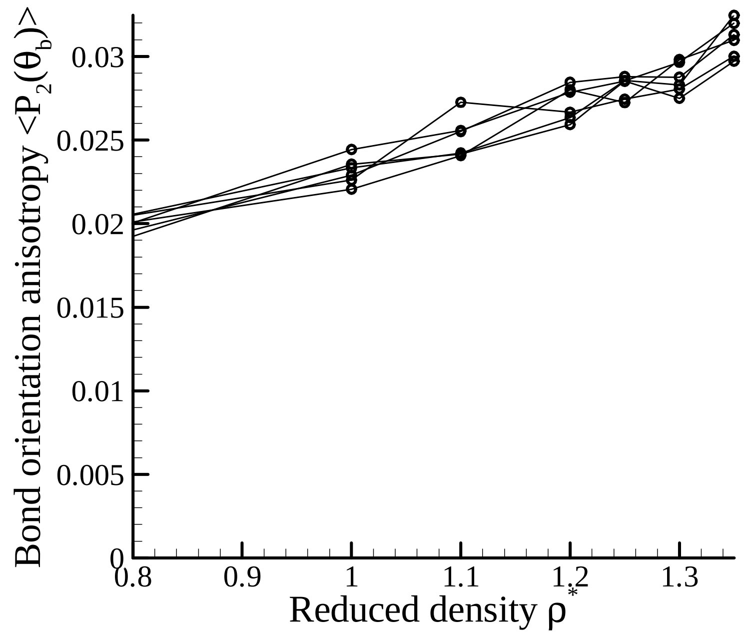
For ideal chain network

$\langle P_2(\theta_b)\rangle = \frac{1}{5N_b}(\lambda^2 - \lambda^{-1})$ Difference stress per atom. $\frac{\sigma}{N} = \frac{1}{(N_b+1)}(\lambda^2 - \lambda^{-1})$

$$\frac{\sigma}{N\langle P_2(\theta_b)\rangle} = \frac{5N_b}{(N_b+1)} = C$$

Relation between stress and bond anisotropy

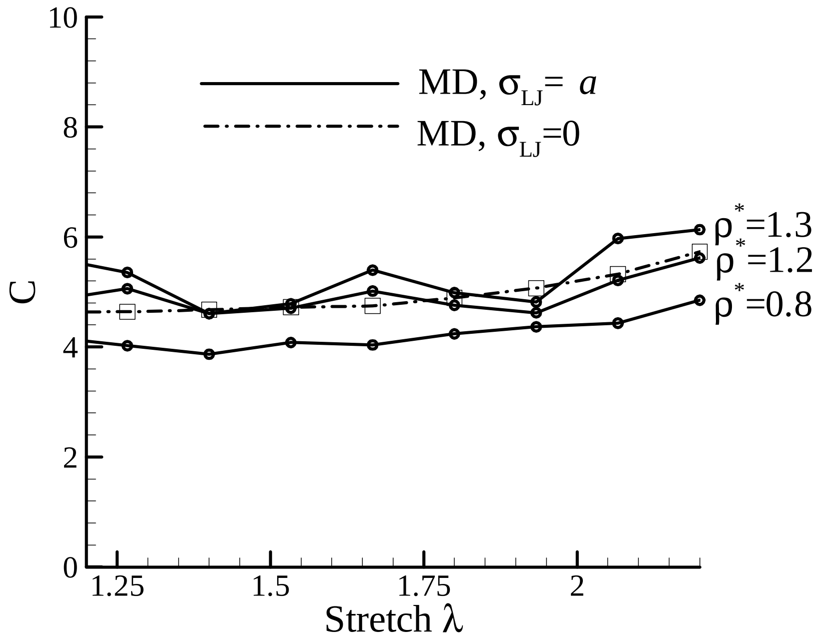


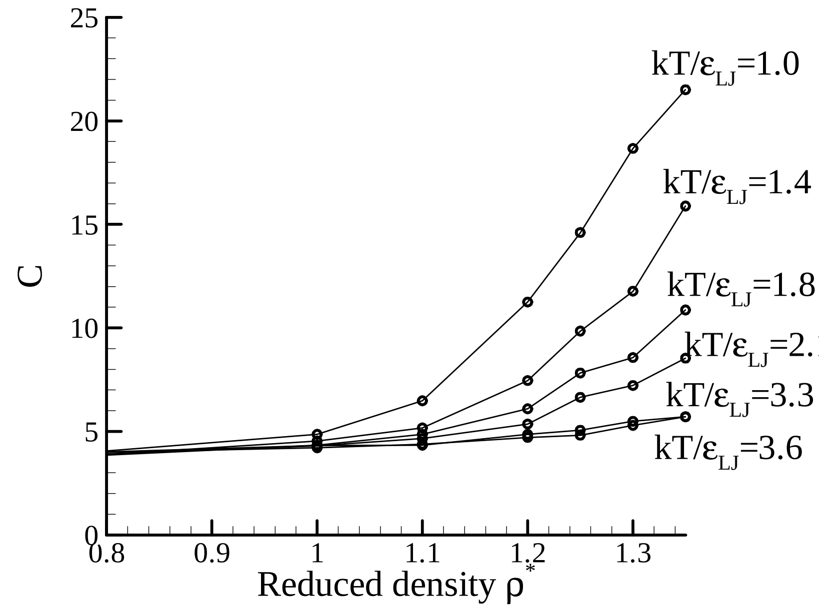


For system that includes EV interactions $\langle P_2(\theta_b)\rangle = \frac{F(\rho)}{N_b}(\lambda^2 - \lambda^{-1})$

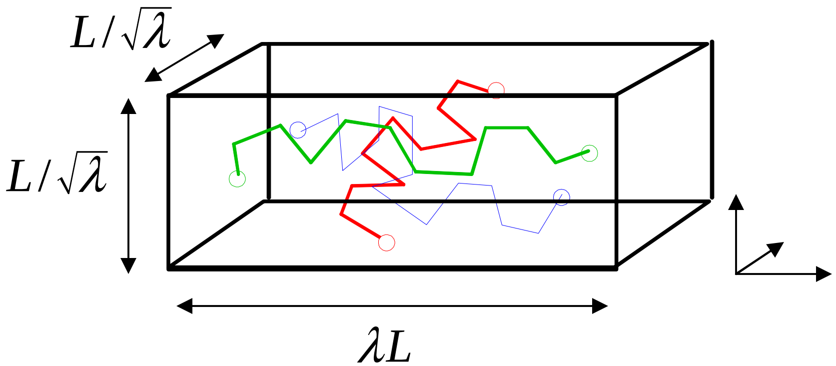
Relation between stress and bond anisotropy

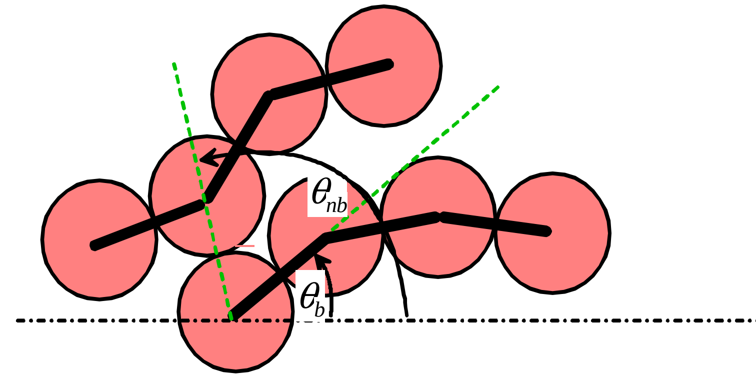
$$C = \frac{\sigma}{N\left\langle P_2(\theta_b)\right\rangle}$$





Atomic scale contributions to stress





Virial Theorem $$vt_{ij} = -NkT\delta_{ij} + \sum_{\alpha} \left\langle f_i^{\alpha} r_j^{\alpha} \right\rangle$$

Stress due to covalent bonds $$\sigma_{ij}^{b} = \frac{1}{kT} \sum_{\alpha \in b} \left\langle f_i^{\alpha} r_j^{\alpha} \right\rangle$$

Stress due to nonbonded interactions

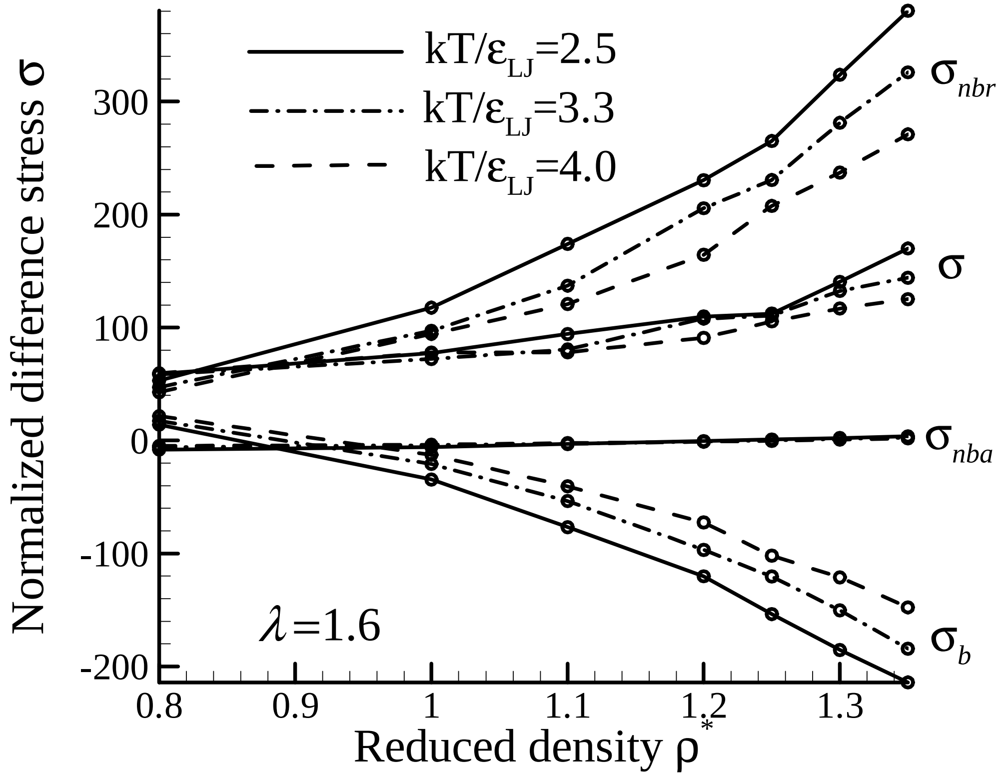
$$\sigma_{ij}^{nbr} = \frac{1}{kT} \sum_{\alpha \in nbr} \left\langle f_i^{\alpha} r_j^{\alpha} \right\rangle$$

$$\sigma_{ij}^{nba} = \frac{1}{kT} \sum_{\alpha \in nba} \left\langle f_i^{\alpha} r_j^{\alpha} \right\rangle$$

$$\sigma^{b} = \sigma_{11}^{b} - [\sigma_{22}^{b} + \sigma_{33}^{b}]/2 \qquad \Pi^{b} = \left\{ \sigma_{11}^{b}(\beta) + \sigma_{22}^{b}(\beta) + \sigma_{33}^{b}(\beta) \right\}/3$$

etc

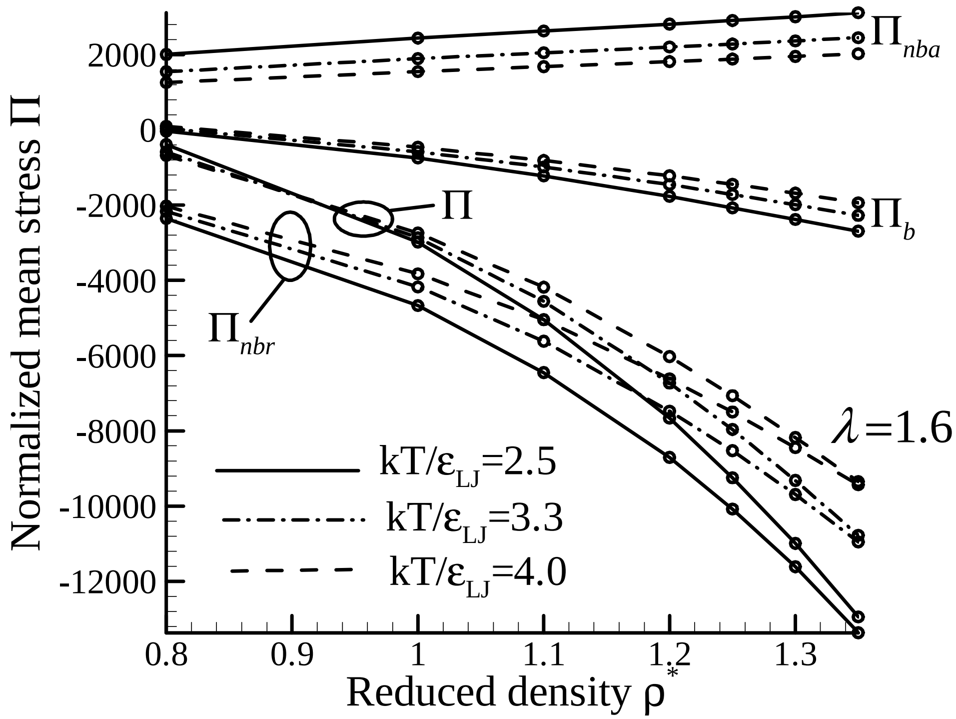
Atomic scale contributions to difference stress



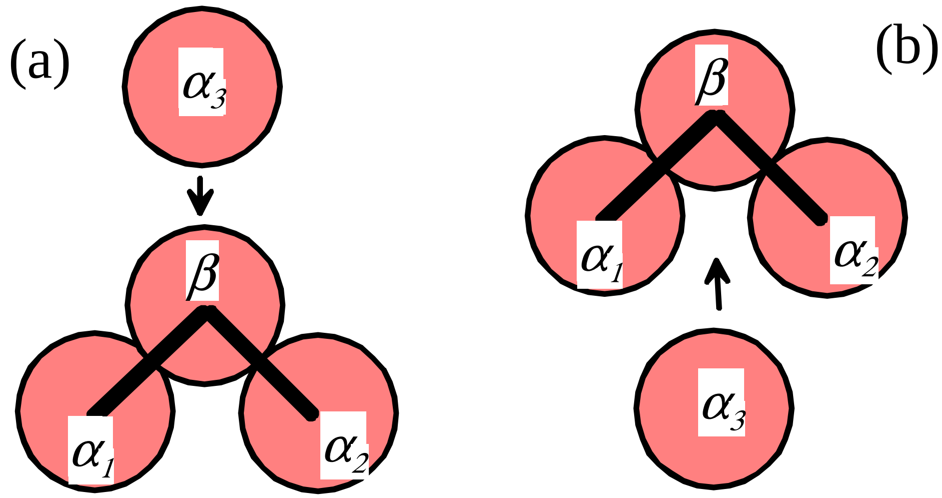
Covalent bonds are in compression, and therefore give a *negative* contribution to difference stress

Dominant contribution to difference stress is from EV interactions

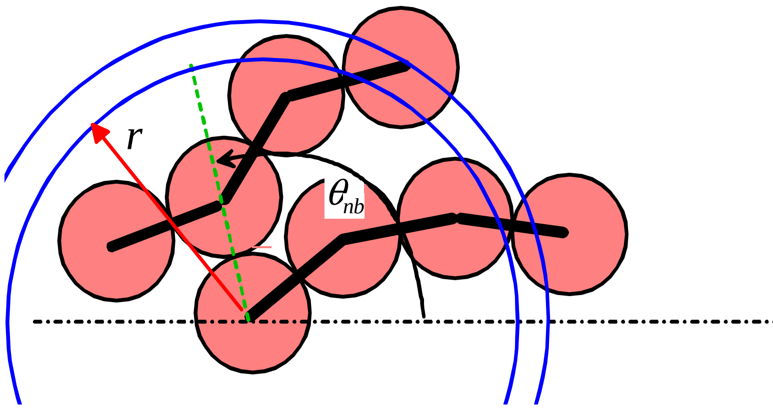
Atomic scale contributions to mean stress



Steric shielding induces compressive bond forces



Stress due to repulsive EV interactions



$$dn = \rho g(r) 4\pi r^2 dr$$

$$S_{ij}(r) = \left\langle \frac{r_i r_j}{r^2} \right\rangle$$

$$\langle P_2(\theta_{nbr}) \rangle = \frac{1}{2dn} \sum_{\alpha \in S_r} \left\langle \left\langle (3\cos^2\theta_\alpha - 1)/2 \right\rangle \right\rangle$$

$$\sigma_{ij}^{nbr} = \frac{1}{kT} \sum_{\alpha \in nb} \left\langle f_i^\alpha r_j^\alpha \right\rangle = \frac{2\pi\rho^2 v}{kT} \int_0^\infty u'_{nb}(r) g(r) S_{ij}(r) r^3 dr$$

$$\sigma_{nbr} = \sigma_{11}^{nbr} - [\sigma_{22}^{nbr} + \sigma_{33}^{nbr}]/2 = \frac{3\pi\rho^2 v}{kT} \int_0^{R_c} u'_{nb}(r) g(r) \langle P_2(\theta_{nbr}) \rangle r^3 dr$$

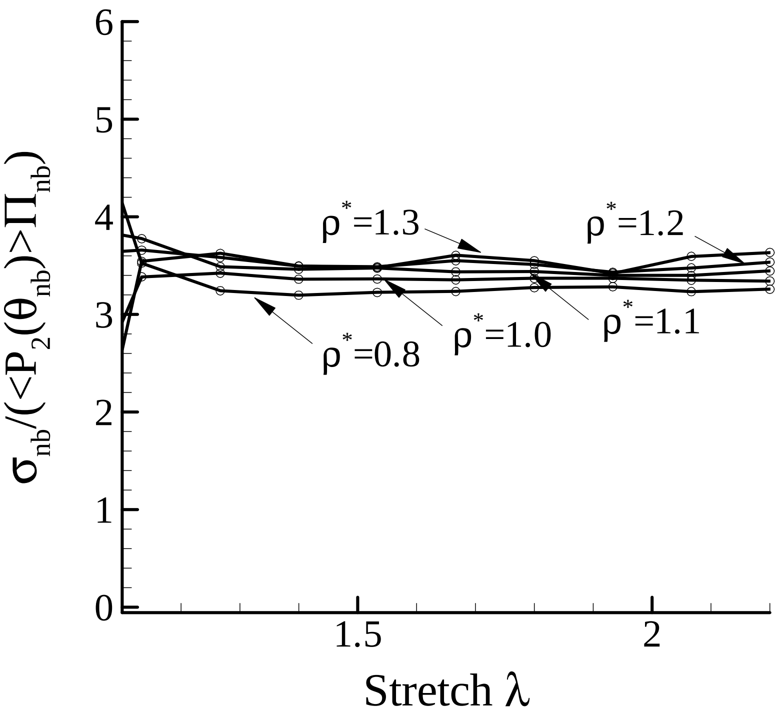
$$\Pi_{nbr} = [\sigma_{11}^{nbr} + \sigma_{22}^{nbr} + \sigma_{33}^{nbr}]/3 = \frac{2\pi\rho^2 v}{3kT} \int_0^{R_c} u'_{nb}(r) g(r) r^3 dr$$

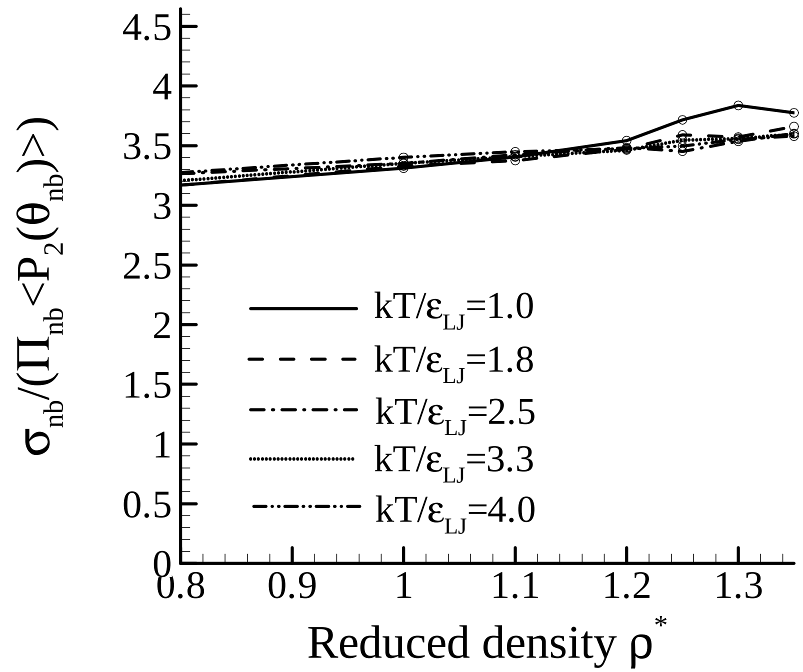
Hard sphere limit

$$\sigma_{nbr} = -3\pi\rho^2 v d^3 g(d) \langle P_2(\theta_{nbr}) \rangle \qquad \Pi_{nb} = -\frac{2}{3}\pi\rho^2 v d^3 g(d)$$

$$\sigma_{nbr} = \frac{9}{2} \Pi_{nbr} \langle P_2(\theta_{nbr}) \rangle$$

Stress due to repulsive EV interactions

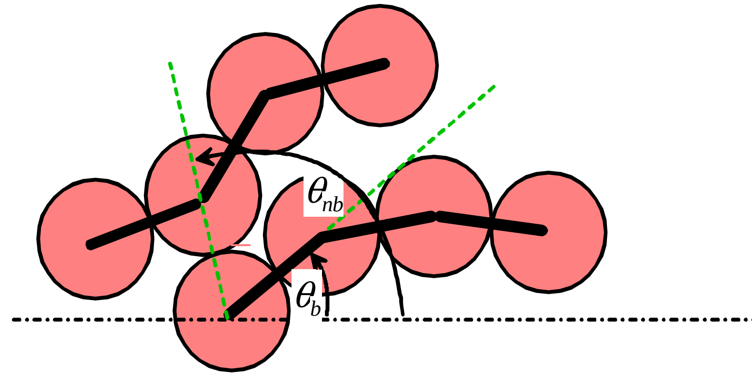


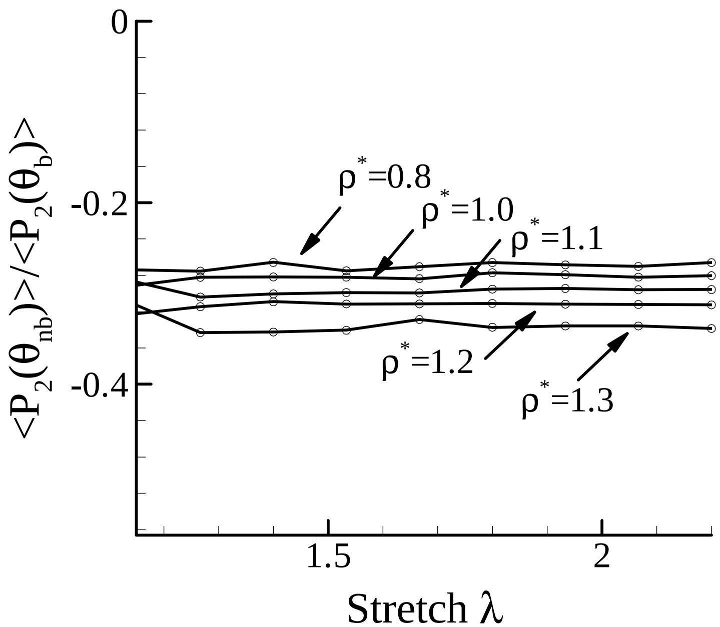


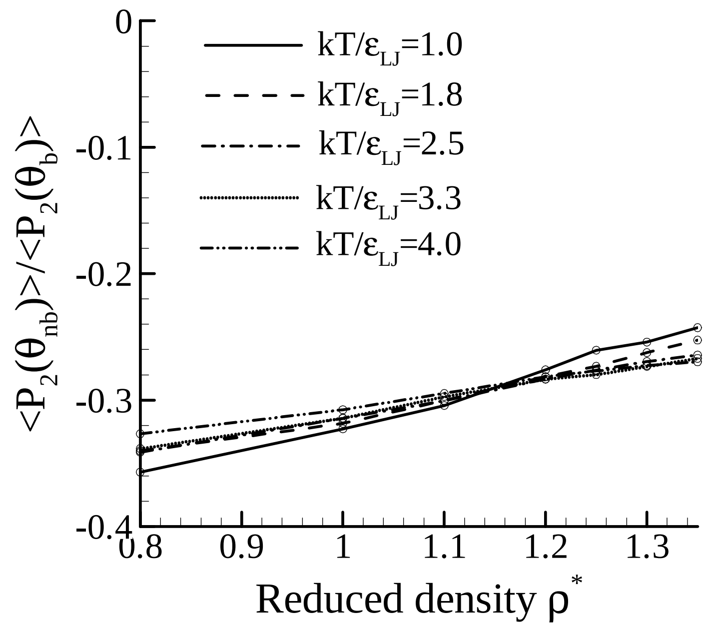
$$\sigma_{nbr} = A\Pi_{nbr}\left\langle P_2(\theta_{nbr})\right\rangle$$

$$A \approx 3.5$$

Orientation of repulsive EV interactions

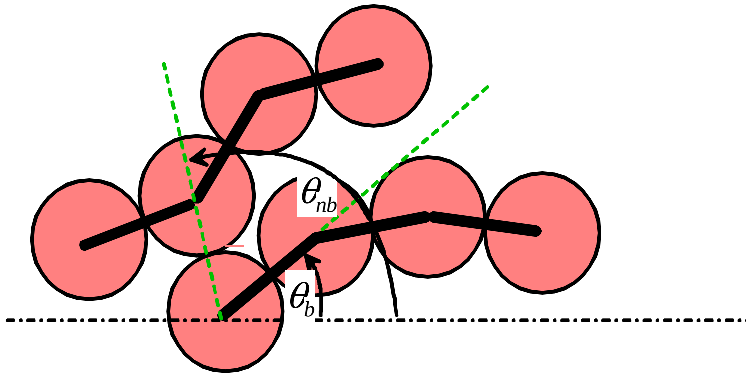






$$\left\langle P_2\left(\theta_{nb}\right)\right\rangle = -B\left\langle P_2\left(\theta_b\right)\right\rangle$$

Stress due to covalent bonds



$$u_b(r) = \frac{1}{2}\kappa(r-a)^2$$

$$S_{ij}(r) = \left\langle \frac{r_i r_j}{r^2} \right\rangle$$

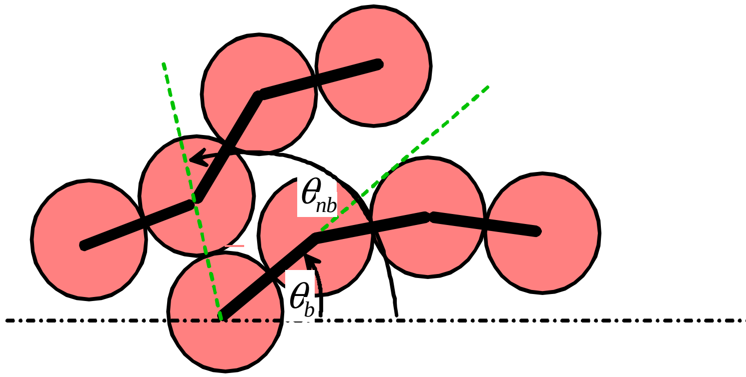
$$\sigma_{ij}^b = \frac{1}{kT}\sum_{\alpha\in b}\left\langle f_i^\alpha r_j^\alpha \right\rangle = \frac{1}{kT}\sum_{\alpha\in b}\left\langle r u_b'(r)\frac{r_i^\alpha r_j^\alpha}{r^2} \right\rangle \approx \frac{1}{kT}\sum_{\alpha\in b}\left\langle r u_b'(r) \right\rangle S_{ij}(r)$$

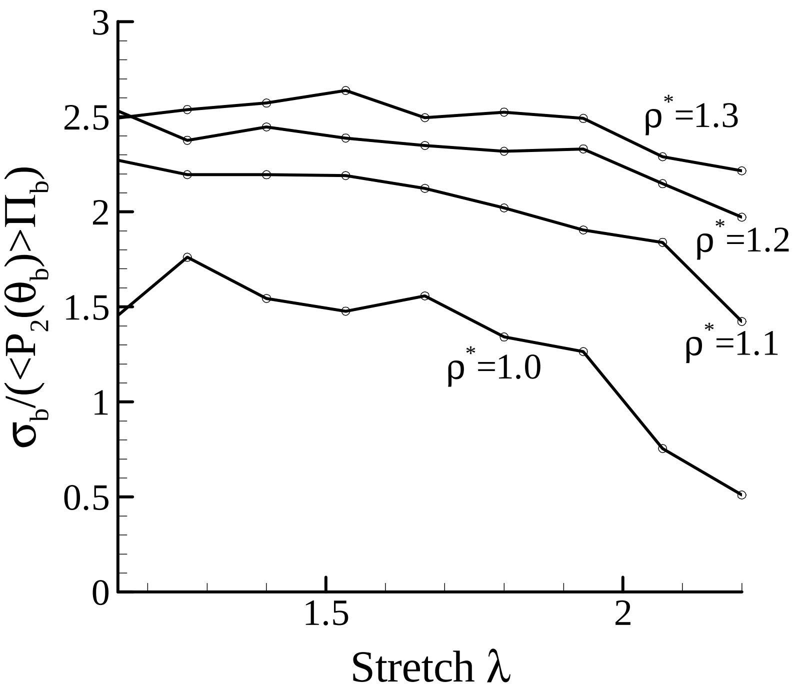
$$\left\langle r u_b'(r) \right\rangle = \left\langle r\kappa(r-a) \right\rangle = \left\langle \kappa(r-a)^2 + a\kappa(r-a) \right\rangle = kT + a\left\langle f \right\rangle$$

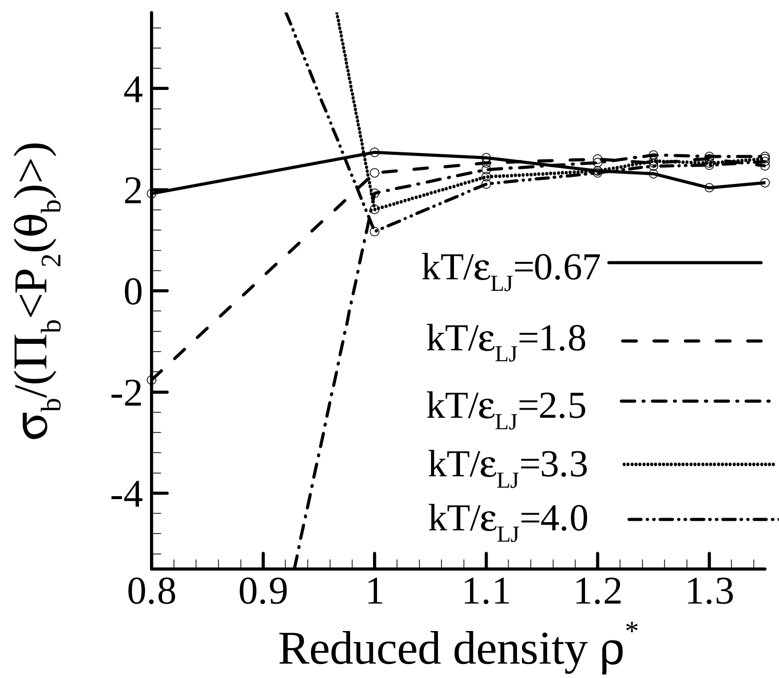
$$\sigma_b = \sigma_{11}^b - [\sigma_{22}^b + \sigma_{33}^b]/2 = \left(1 + \frac{a\left\langle f \right\rangle}{kT}\right)\left\langle P_2(\theta_b) \right\rangle \qquad \Pi_b(\gamma) = \frac{1}{3}\left(1 + \frac{a\left\langle f \right\rangle}{kT}\right)$$

$$\sigma_b = 3\Pi_b\left\langle P_2(\theta_b) \right\rangle$$

Stress due to covalent bonds



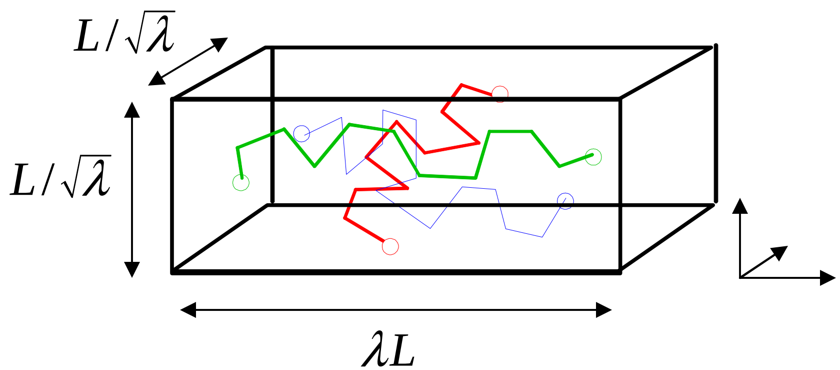


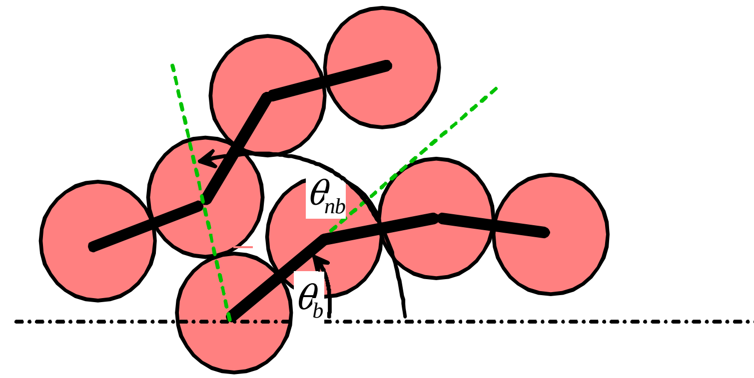


$$\sigma_b = D\Pi_b \left\langle P_2(\theta_b) \right\rangle$$

$$D \approx 2.5$$

Summary





Covalent bond anisotropy $\langle P_2(\theta_b)\rangle = \frac{F}{N_b}(\lambda^2 - \lambda^{-1})$

Repulsive EV anisotropy $\langle P_2(\theta_{nbr})\rangle = -B\langle P_2(\theta_b)\rangle$

Difference stress $\sigma = \sigma_{nbr} + \sigma_{nba} + \sigma_b$

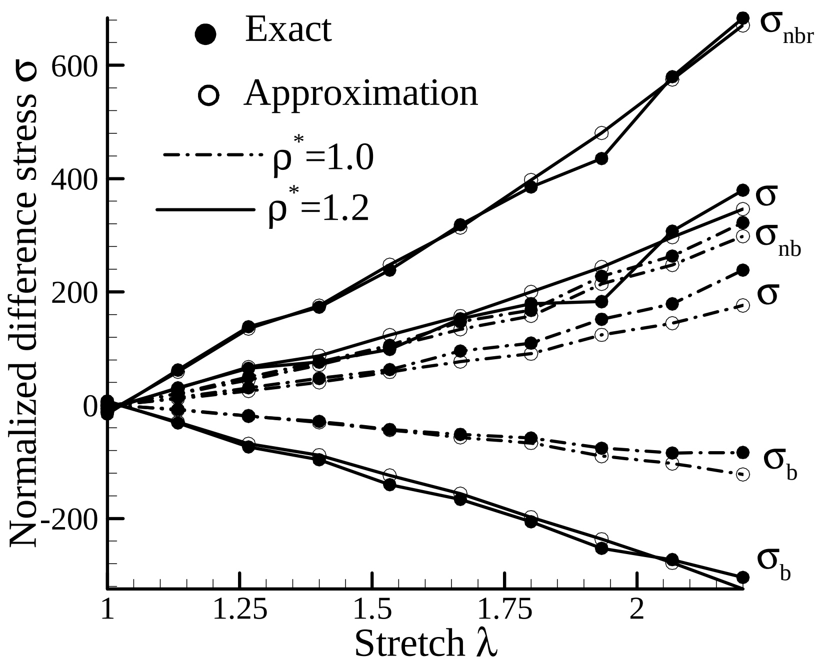
Mean stress $\Pi = -1 + \Pi_{nbr} + \Pi_{nba} + \Pi_b$

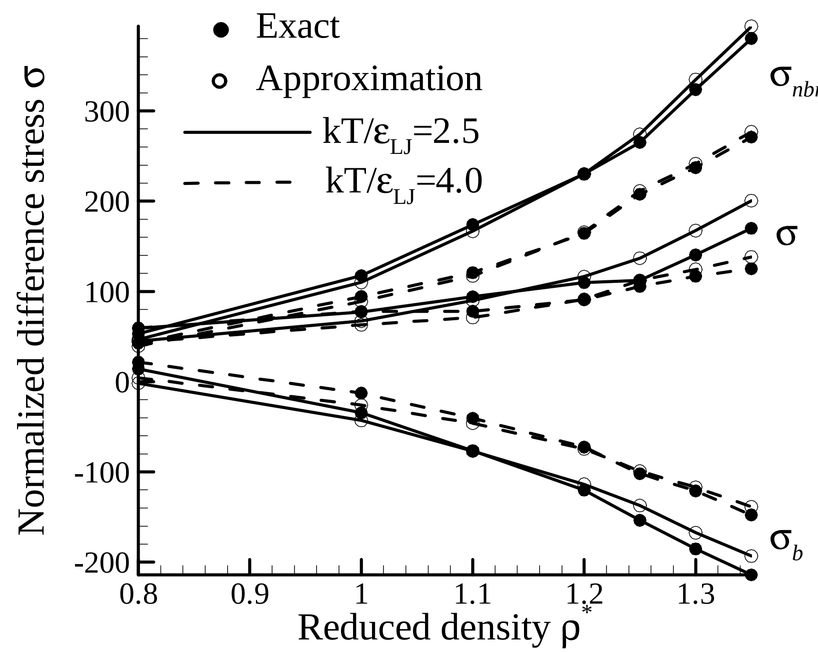
Stress due to covalent bonds $\sigma_b = D\Pi_b \langle P_2(\theta_b)\rangle$

Stress due to EV interactions $\sigma_{nba} = 0 \qquad \sigma_{nbr} = A\Pi_{nbr}\langle P_2(\theta_{nbr})\rangle$

Conclusion $\sigma \approx \sigma_b + \sigma_{nbr} = \left(D\Pi_b - 3AB\Pi_{nbr}\right)\frac{F}{N_b}(\lambda^2 - \lambda^{-1})$

Comparison of analytical and numerical results





$$\sigma \approx \sigma_b + \sigma_{nbr} = \left(D\Pi_b - AB\Pi_{nbr}\right)\frac{F}{N_b}(\lambda^2 - \lambda^{-1})$$

Conclusions

- Re-examine atomic scale deformation of elastomers using a model that includes Excluded Volume (EV) interactions
- Deviatoric stress is caused by deformation induced anisotropy of chain network
- Repulsive EV interactions give the dominant contribution to both deviatoric and mean stress
- Pressure and deviatoric stress are intimately connected at atomic scale
- Pressure-deviatoric stress relation $\sigma \approx \sigma_b + \sigma_{nbr} = \left(D\Pi_b - AB\Pi_{nbr} \right) \frac{F}{N_b} (\lambda^2 - \lambda^{-1})$

Outstanding issues

- Atomic scale origin of entropic response
- Tension/compression asymmetry
- Role of cross links and junctions
- Glass transition
- Dilation under tensile loading