Statistical mechanics and related constitutive theory for polymer networks

Mechanics Student Seminar (first instance)

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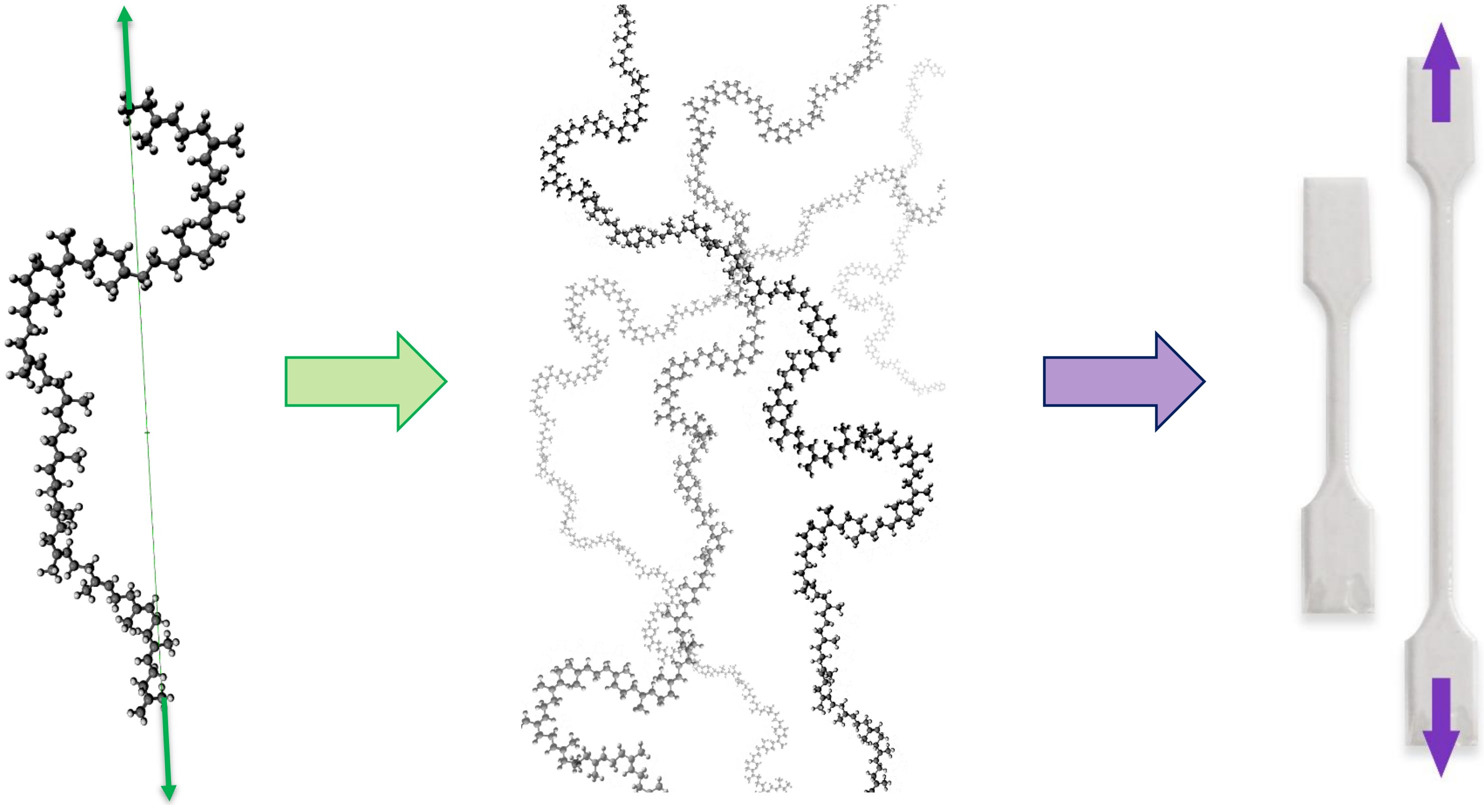
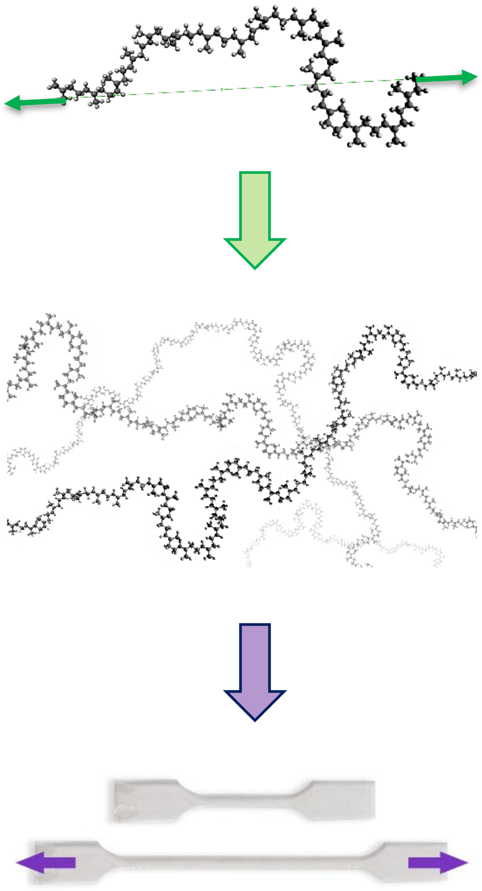
2/21/2020

Range of Mechanics



Overview

- Statistical mechanics
- Single polymer chain statistics
- Many chain statistics
- Connecting micro to macro
- Macroscopic constitutive theory
- Continuum mechanical response



Classical Statistical Mechanics

- How to turn 6N variables into a few macroscopic variables?
- Thermal equilibrium – thermodynamic state variables
  - Postulate of equal a priori probabilities
  - Maximum (Gibbs) entropy requirement

$$S = k \ln \Omega$$

$$P = 1/\Omega$$

$$\Omega(E, \Delta E) = \frac{1}{N! h^{3N}} \underbrace{\int \cdots \int}_{E - \Delta E \leq E_{\text{sys}} \leq E} \prod_{i=1}^{N} d^3\mathbf{p}_i \, d^3\mathbf{q}_i$$

  - Varying energy levels

$$P = e^{-E/kT} / \mathfrak{Q}$$

$$\mathfrak{Q}(N, V, T) = \int \Omega(N, V, E) \, e^{-E/kT} \, dE$$

$$A = -kT \ln \mathfrak{Q}$$

D. A. McQuarrie, *Statistical Mechanics* (University Science Books, 2000).

Symbols and Things

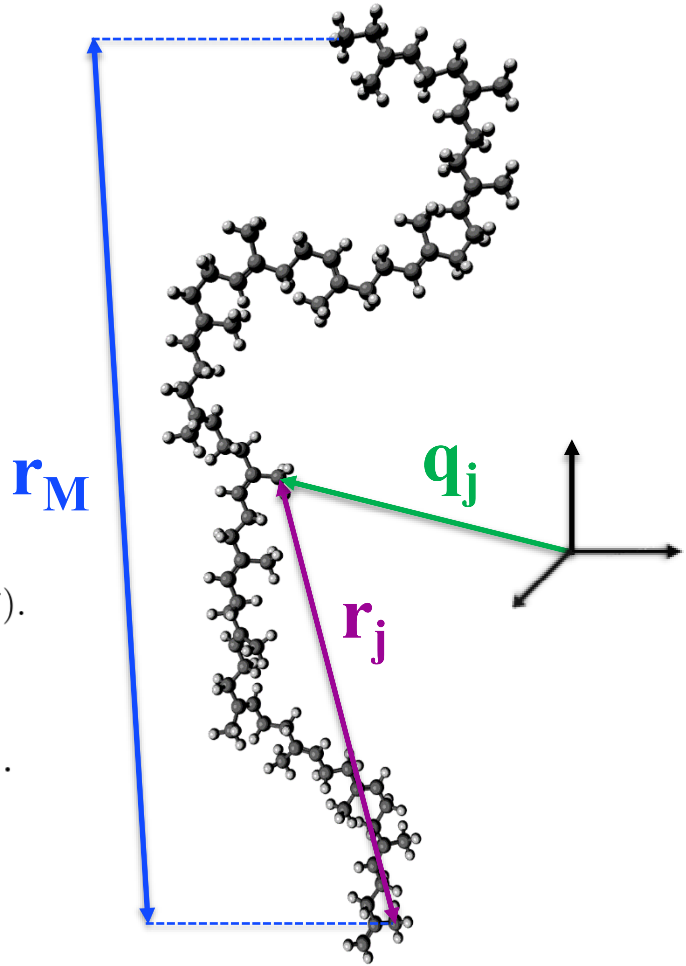
Partition function $\mathfrak{q}$, atomic coordinates $\mathbf{q}_j$, relative coordinates $\mathbf{r}_j = \mathbf{q}_j - \mathbf{q}_1$, end-to-end vector $\boldsymbol{\xi} = \mathbf{r}_M$.

Probability P, pressure p, atomic momenta $\mathbf{p}_j$.

Total Helmholtz free energy A, density $a = A/V$, single chain $\psi^*(\boldsymbol{\xi})$.

Deformation gradient $\mathbf{F}$, with $J = \det(\mathbf{F})$ and $\mathbf{L} = \dot{\mathbf{F}} \cdot \mathbf{F}^{-1}$.

$\beta = 1/kT$ $\qquad$ $n = N/V$



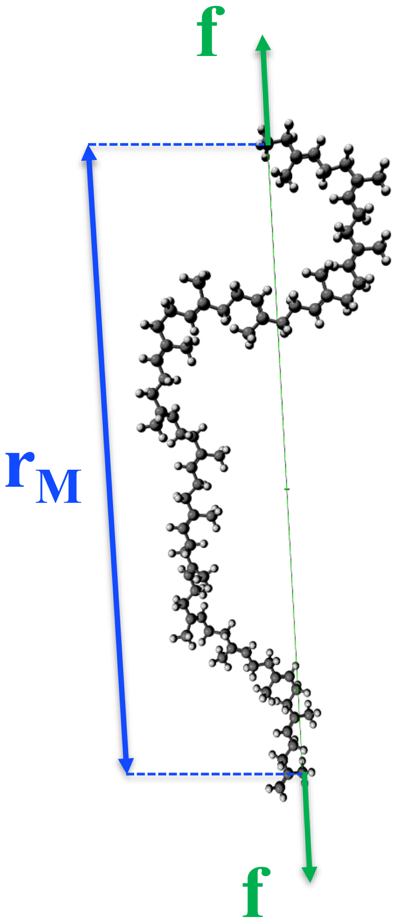
Single chain statistical mechanics

$$\mathfrak{q} = \frac{1}{h^{3M}} \int \cdots \int e^{-\beta\varepsilon} \prod_{j=1}^{M} d^3\mathbf{p}_j \, d^3\mathbf{q}_j \qquad \varepsilon = u(\mathbf{q}_1, \ldots, \mathbf{q}_M) + \sum_{j=1}^{M} \frac{p_j^2}{2m_j}$$

$$\mathfrak{q} = \mathfrak{q}_{\mathrm{con}} \mathfrak{q}_{\mathrm{mom}} V \qquad \mathfrak{q}_{\mathrm{mom}} = \prod_{j=1}^{M} \left(\frac{2\pi m_j kT}{h^2} \right)^{3/2}$$

$$\mathfrak{q}_{\mathrm{con}} = \int \cdots \int e^{-\beta u} \prod_{j=2}^{M} d^3\mathbf{r}_j = \iiint \mathfrak{q}^*(\tilde{\boldsymbol{\xi}}) \, d^3\tilde{\boldsymbol{\xi}}$$

$$\mathfrak{q}^*(\boldsymbol{\xi}) = \int \cdots \int e^{-\beta u(\mathbf{r}_M = \boldsymbol{\xi})} \prod_{j=2}^{M-1} d^3\mathbf{r}_j$$



Buche and Silberstein, Physical Review E, 102, 012501 (2020).

Single chain statistical mechanics

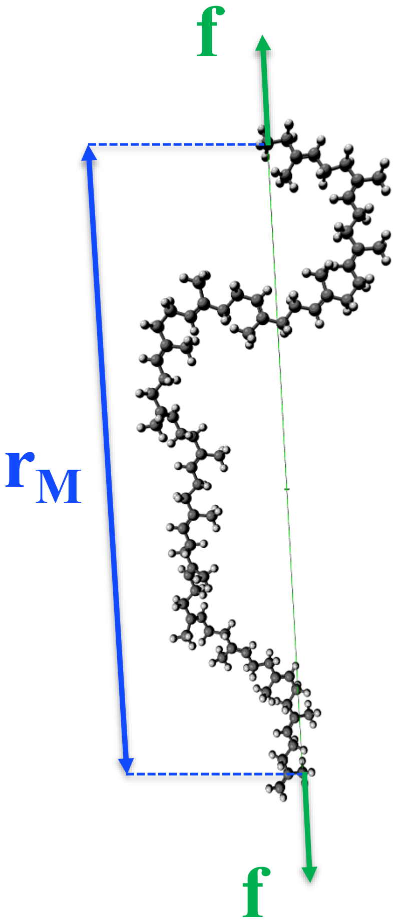
$$\mathrm{q}^*(\boldsymbol{\xi}) = \int \cdots \int e^{-\beta u(\mathbf{r}_M = \boldsymbol{\xi})} \prod_{j=2}^{M-1} d^3\mathbf{r}_j$$

$$\psi^*(\boldsymbol{\xi}) = -kT \ln \mathrm{q}^*(\boldsymbol{\xi})$$

$$\mathbf{f} = \frac{\partial \psi^*}{\partial \boldsymbol{\xi}}$$

$$P^{\mathrm{eq}}(\boldsymbol{\xi}) = \frac{\mathrm{q}^*(\boldsymbol{\xi})}{\iiint \mathrm{q}^*(\tilde{\boldsymbol{\xi}})\, d^3\tilde{\boldsymbol{\xi}}}$$

Ensemble choice matters!



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Many identical chains

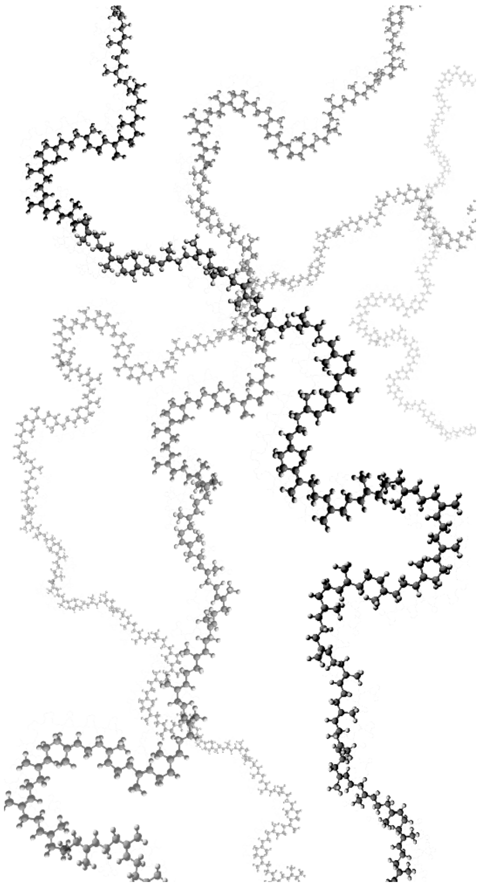
$$P^{\mathrm{eq}}(\boldsymbol{\xi}) = \frac{e^{-\beta\psi^*(\boldsymbol{\xi})}}{\iiint e^{-\beta\psi^*(\tilde{\boldsymbol{\xi}})}\, d^3\tilde{\boldsymbol{\xi}}}$$

$$\psi^*(\boldsymbol{\xi}) = \psi^*_{\mathrm{ref}} - kT \ln\left[\frac{P^{\mathrm{eq}}(\boldsymbol{\xi})}{P^{\mathrm{eq}}(\boldsymbol{\xi}_{\mathrm{ref}})}\right]$$

Distribution-behavior correspondence

A rule to follow!

Specify one, solve for the other



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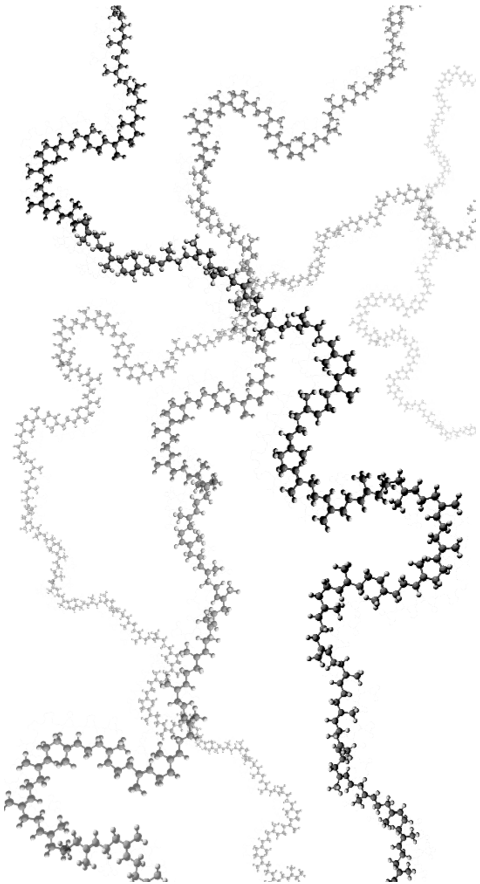
Many identical chains

$$\mathfrak{Q} = \frac{\mathfrak{q}^N}{N!} \qquad A = -kT\ln\mathfrak{Q}$$

$$a = n\iiint P(\boldsymbol{\xi},t)\psi^*(\boldsymbol{\xi})\,d^3\boldsymbol{\xi} - nkT\ln\left(\frac{\mathfrak{q}_{\mathrm{mom}}e}{n}\right) - p(J-1)$$

$$\frac{\partial f}{\partial t} = -\sum_{j=1}^{M}\left(\frac{\partial f}{\partial \mathbf{q}_j}\cdot\dot{\mathbf{q}}_j + \frac{\partial f}{\partial \mathbf{p}_j}\cdot\dot{\mathbf{p}}_j\right)$$ (just calculus!)

$$\frac{\partial P}{\partial t} = -\frac{\partial P}{\partial \boldsymbol{\xi}}\cdot\dot{\boldsymbol{\xi}}$$



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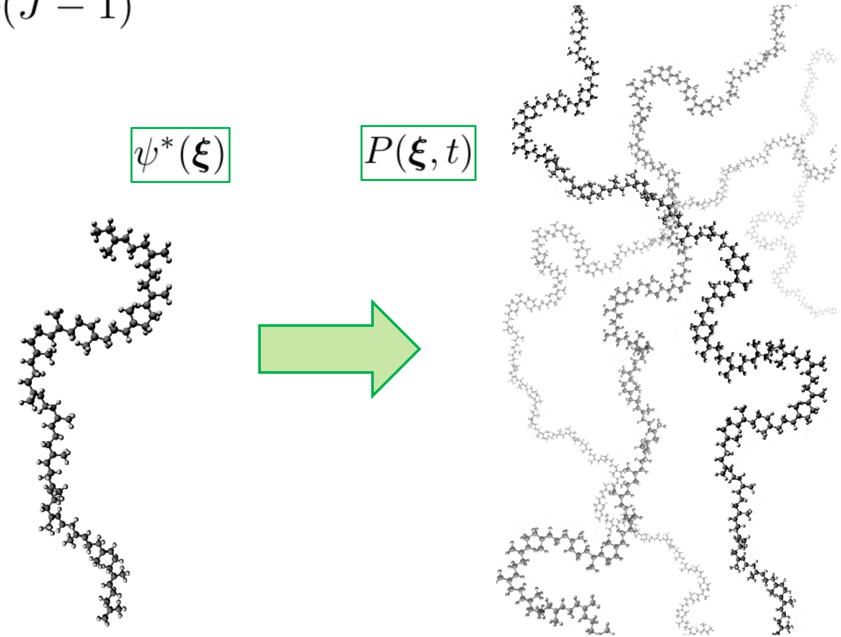
Statistical mechanics summary

$$a = n \iiint P(\boldsymbol{\xi}, t)\psi^*(\boldsymbol{\xi})\, d^3\boldsymbol{\xi} - nkT \ln\left(\frac{\mathfrak{q}_{\mathrm{mom}} e}{n}\right) - p(J-1)$$

$$\frac{\partial P}{\partial t} = -\frac{\partial P}{\partial \boldsymbol{\xi}} \cdot \dot{\boldsymbol{\xi}}$$

$$P^{\mathrm{eq}}(\boldsymbol{\xi}) = \frac{e^{-\beta\psi^*(\boldsymbol{\xi})}}{\iiint e^{-\beta\psi^*(\tilde{\boldsymbol{\xi}})}\, d^3\tilde{\boldsymbol{\xi}}}$$

$$\psi^*(\boldsymbol{\xi}) = \psi^*_{\mathrm{ref}} - kT \ln\left[\frac{P^{\mathrm{eq}}(\boldsymbol{\xi})}{P^{\mathrm{eq}}(\boldsymbol{\xi}_{\mathrm{ref}})}\right]$$



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Connecting Macro to Micro

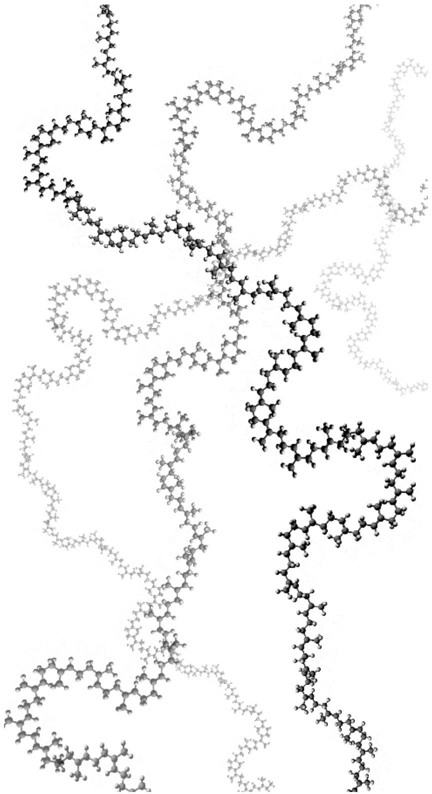
$$\frac{\partial P}{\partial t} = -\frac{\partial P}{\partial \boldsymbol{\xi}} \cdot \dot{\boldsymbol{\xi}}$$

Pick some $\dot{\xi} = \dot{\xi}(\mathbf{F})$

$$\dot{\boldsymbol{\xi}} = \mathbf{L} \cdot \boldsymbol{\xi}$$

$$\frac{\partial P}{\partial t} = -\left(\frac{\partial P}{\partial \boldsymbol{\xi}}\right) \cdot \mathbf{L} \cdot \boldsymbol{\xi}$$

$$P(\boldsymbol{\xi}, t) = P^{\mathrm{eq}}\left[\mathbf{F}^{-1}(t) \cdot \boldsymbol{\xi}\right]$$



$\dot{\xi} = \dot{\xi}(\mathbf{F})$

Buche and Silberstein, Physical Review E, 102, 012501 (2020).

Macroscopic Constitutive Theory

- Coleman-Noll procedure (or Müller-Liu if masochist, or worse*)

$$\dot{a} + s\dot{T} - \boldsymbol{\sigma} : \mathbf{L} \leq 0 + \ldots$$

- Complete set of independent state variables (just calculus!)
  - Including **F** but not its derivatives (**L**, etc.)

$$\boldsymbol{\sigma} = \frac{1}{J}\left(\frac{\partial a}{\partial \mathbf{F}}\right)_{\mathcal{I}} \cdot \mathbf{F}^T$$

S. Paolucci, *Continuum Mechanics and Thermodynamics of Matter* (Cambridge University Press, 2016).
*I. Müller and T. Ruggeri, *Rational Extended Thermodynamics, 2nd Ed.* (Springer, 1998).

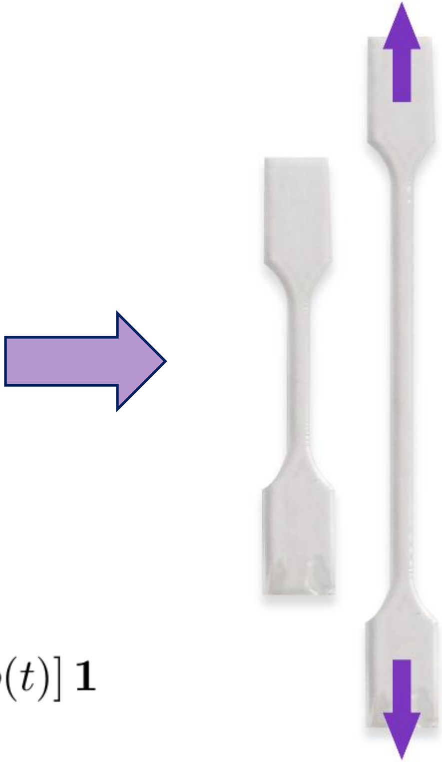
Macroscopic Constitutive Theory

- 2nd Law analysis stress

$$\boldsymbol{\sigma} = -n \iiint \left(\frac{\partial P}{\partial \boldsymbol{\xi}}\right) \psi^* \boldsymbol{\xi}\, d^3\boldsymbol{\xi} - p\mathbf{1}$$

- Stress after a lot more math (fun)

$$\boldsymbol{\sigma}(t) = n \iiint P^{\mathrm{eq}} \left[\mathbf{F}^{-1}(t) \cdot \boldsymbol{\xi}\right] \left(\frac{\partial \psi^*}{\partial \xi}\right) \left(\frac{\boldsymbol{\xi}\boldsymbol{\xi}}{\xi}\right) d^3\boldsymbol{\xi} - \left[p^{\mathrm{eq}} + \Delta p(t)\right] \mathbf{1}$$



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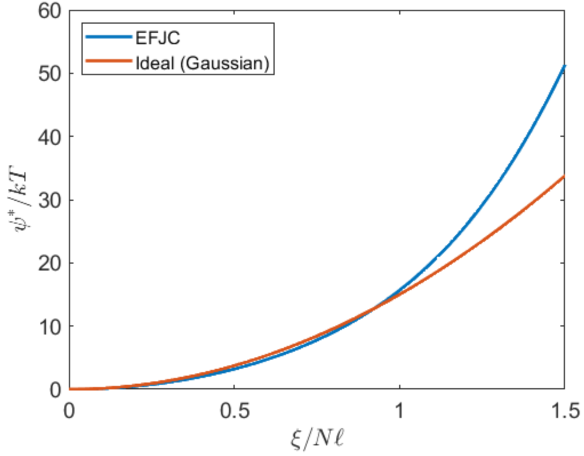
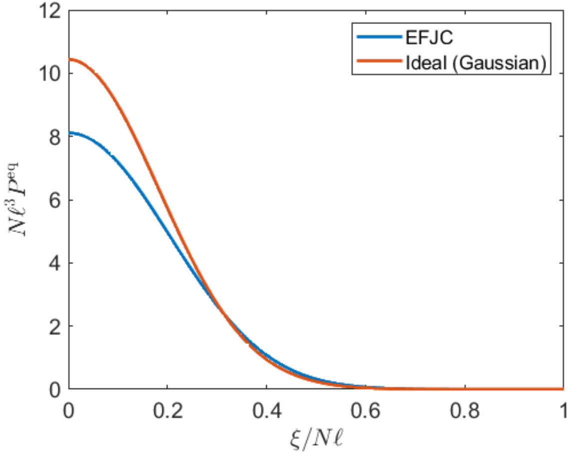
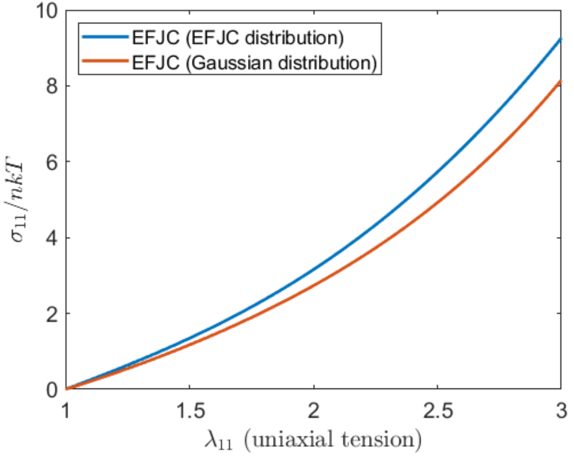
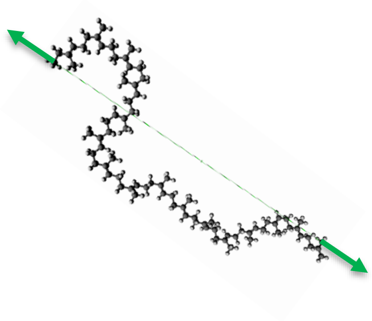
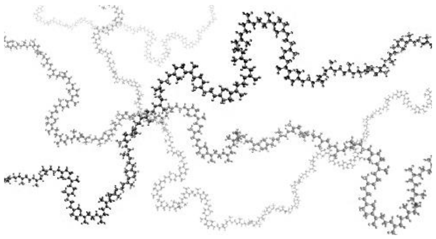
Some results











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Looking ahead

- Network relaxation
- Breaking/reforming chains

- Reversible crosslinking (between chains)

- Interacting chains