Proposing: Fundamental Theories for the Mechanics of Polymer Chains and Networks

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Chair and Advisor: Meredith N. Silberstein

Minor Committee: Steven H. Strogatz

Alan T. Zehnder

5/20/2020

Outline

Fundamental Theories for the Mechanics of Polymer Chains and Networks

Introduction

Part I – completed

- Theoretical study of metal-ligand crosslinking in a polymer
- Statistical mechanical constitutive theory of polymer networks

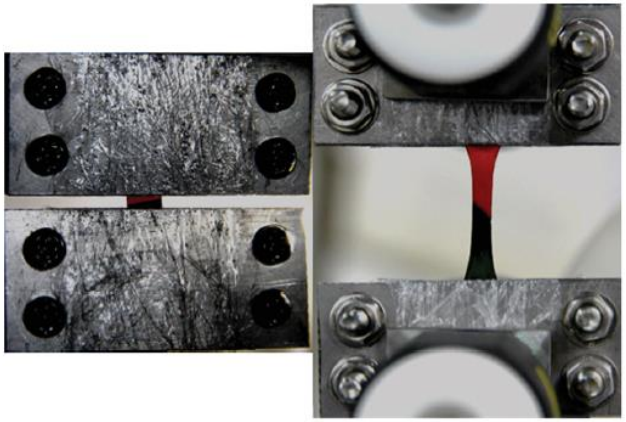
Part II – in progress

- Statistical mechanics with stiff degrees of freedom
- Mechanics of polymers with reversible crosslinks

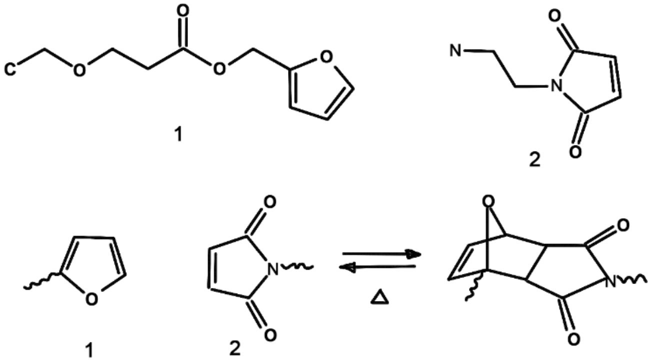
Closing/Summary

Polymers with Reversible Linkages

- Self-healing, plus things such as
  - Highly stretchable
  - High stiffness
- Great dissipation, while avoiding
  - Defect creation and growth
  - Microscopic damage
- General property modulation
  - Range in chemical interaction strengths
    - Each might be tunable (spoiler)
- Theoretical approaches are essential
  - Predictive power
  - Fundamental physical understanding



Jin-Feng, et al., *Macromol. Rapid Commun.*, **37**, p. 1667, 2016.



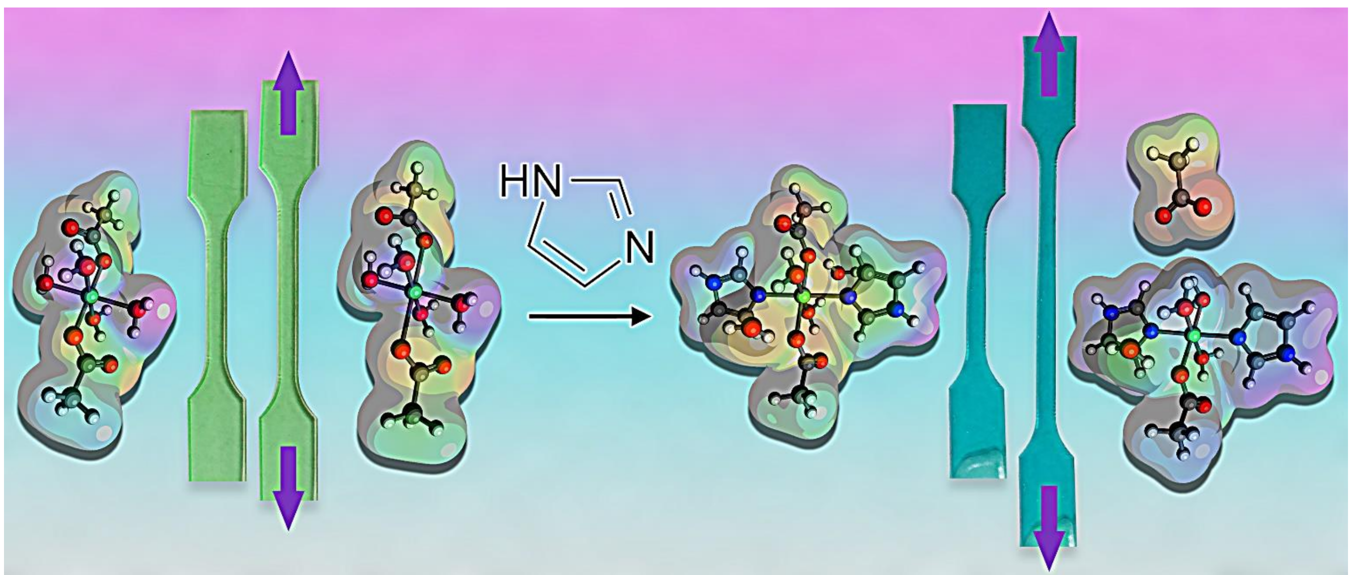
Xiangxu, et al., *Science*, **295**, p. 1698, 2002.

Macromolecules

pubs.acs.org/Macromolecules Article

Tuning the Mechanical Properties of Metallopolymers via Ligand Interactions: A Combined Experimental and Theoretical Study

Yuval Vidavsky, Michael R. Buche, Zachary M. Sparrow, Xinyue Zhang, Steven J. Yang, Robert A. DiStasio Jr.,* and Meredith N. Silberstein*



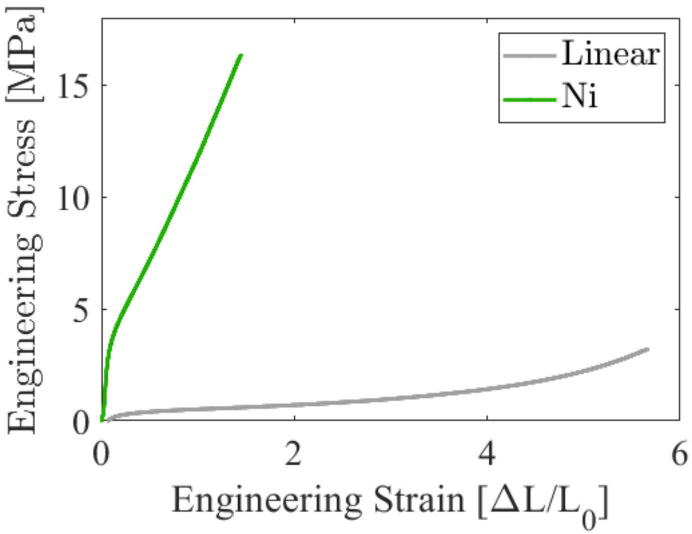
Vidavsky†, Buche†, Sparrow, Zhang, Yang, DiStasio, Silberstein, Macromolecules, 53, p. 2021 (2020).

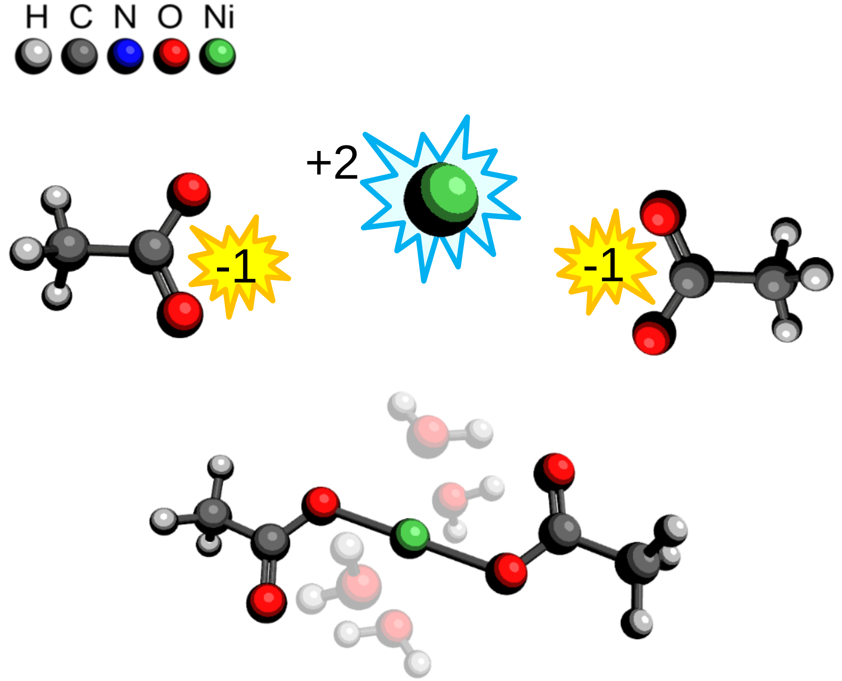
Background

- Crosslinking changes mechanical properties
  - Can we finely tune them?

- Metal-ligand bonds
  - Lone pair donation
    - Electron density

- Add neutral ligands
  - Modify crosslinks
    - Modify bulk mechanical properties
  - Investigate using theory





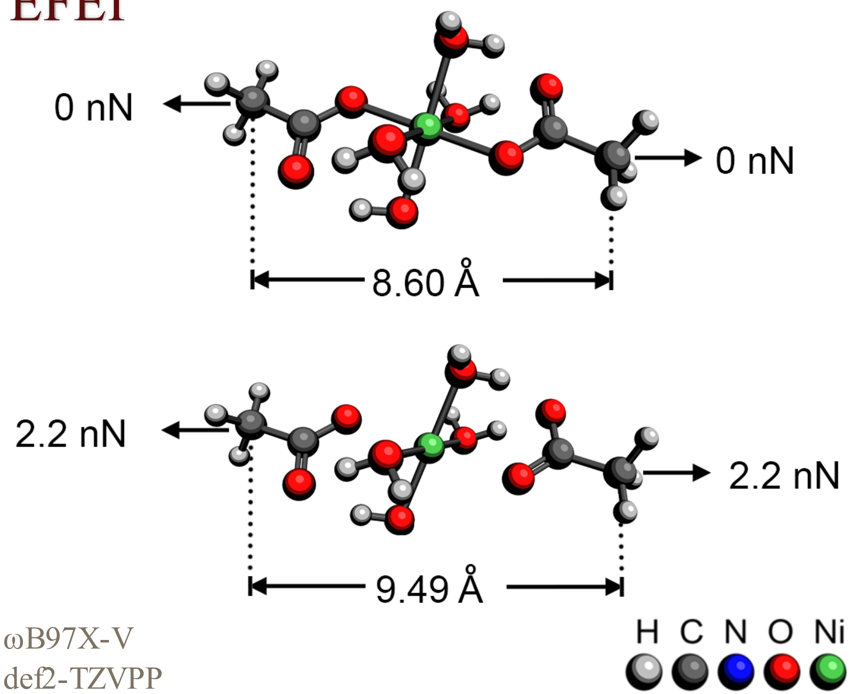
Vidavsky†, Buche†, Sparrow, Zhang, Yang, DiStasio, Silberstein, Macromolecules, 53, p. 2021 (2020).

DFT Calculation Overview

Mechanics

- Minima search (OPT)
- Diagonalize Hessian (FREQ)
- Apply external forces (EFEI)

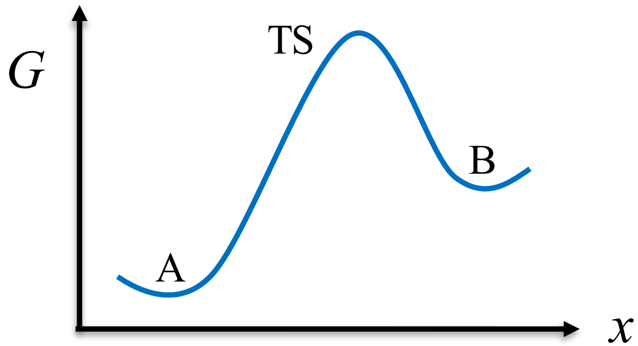
EFEI



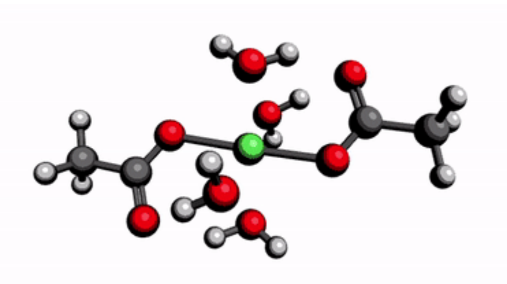
ωB97X-V
def2-TZVPP

Thermodynamics

- EFEI-informed "product" (OPT)
- Approximate reaction path (FSM)
- Transition state search (TS)

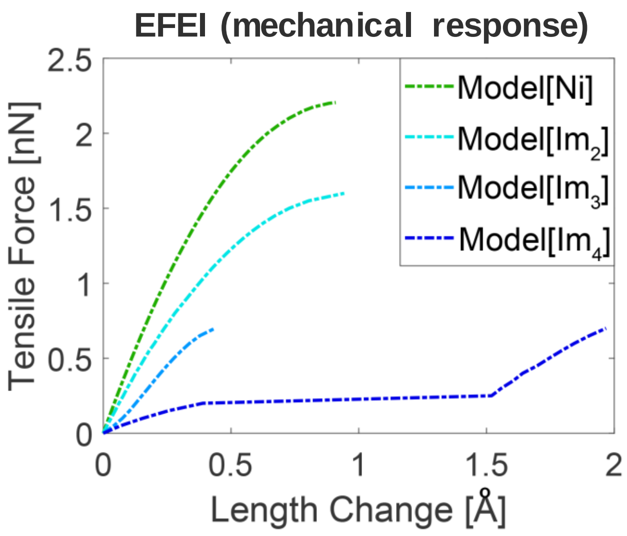


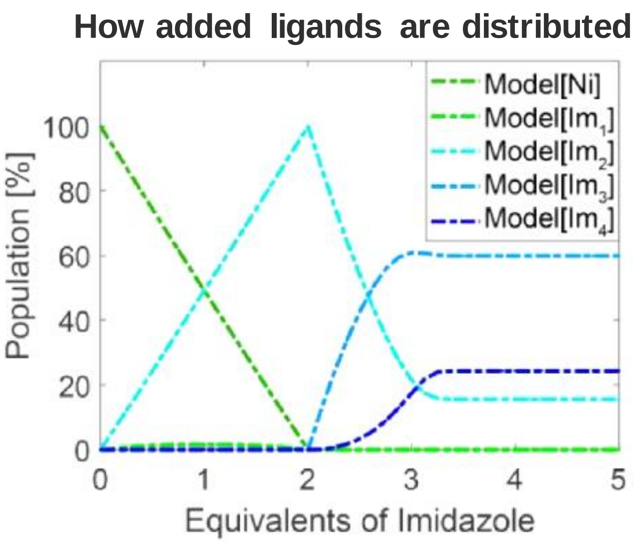
FSM

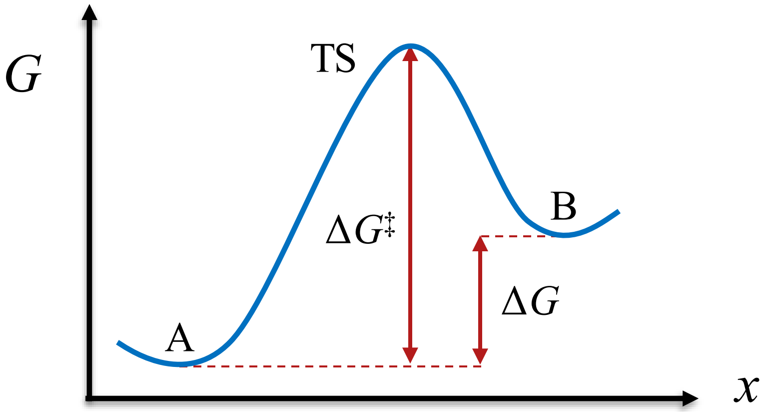


Vidavsky†, Buche†, Sparrow, Zhang, Yang, DiStasio, Silberstein, Macromolecules, 53, p. 2021 (2020).

Theoretical Results







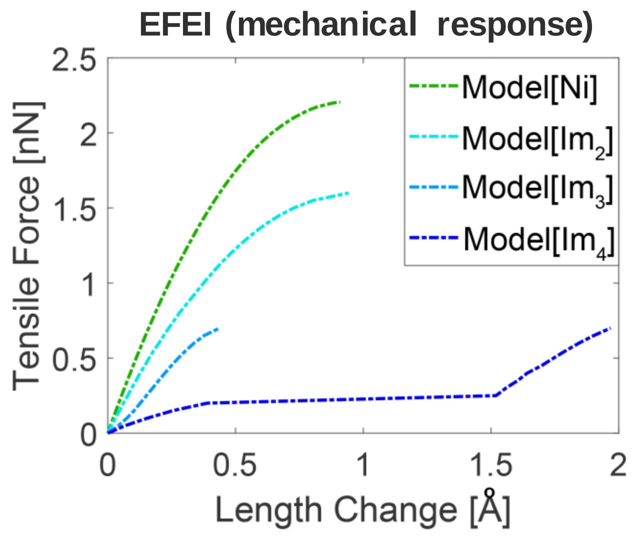
Model	[Ni]	$[Im_2]$	$[Im_3]$
ΔG (kcal/mol)	5.06	6.29	2.12
$\Delta G^{\ddagger}$(kcal/mol)	18.13	15.60	11.57

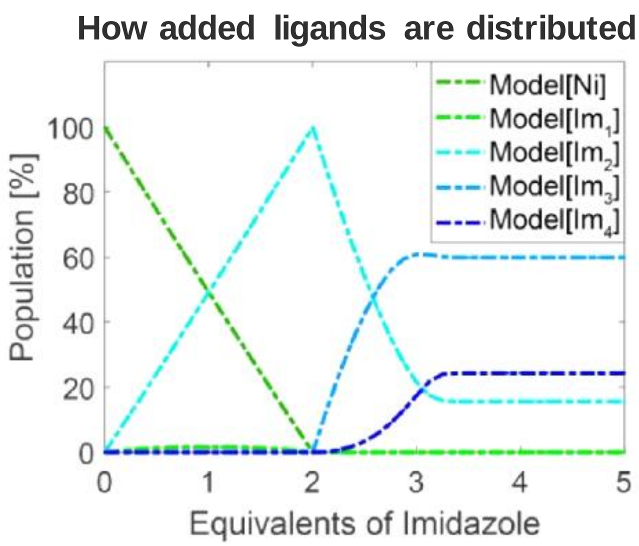
kT: 0.592 kcal/mol

- More ligands = less stiff, smaller barrier
- Ligands distributed unevenly

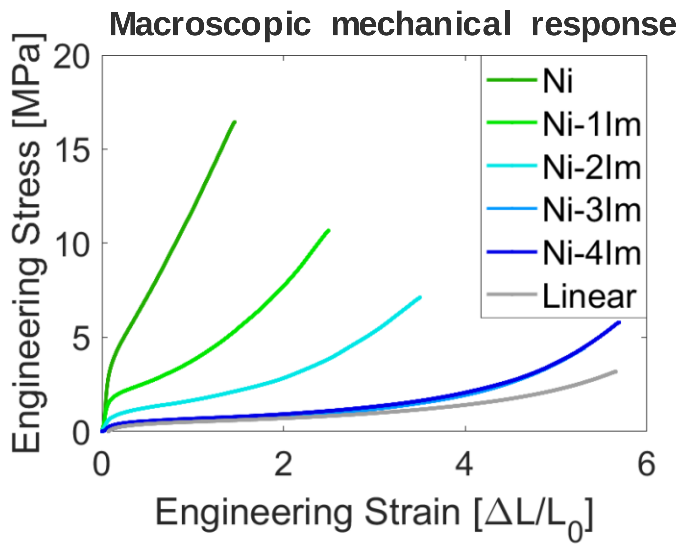
Vidavsky†, Buche†, Sparrow, Zhang, Yang, DiStasio, Silberstein, Macromolecules, 53, p. 2021 (2020).

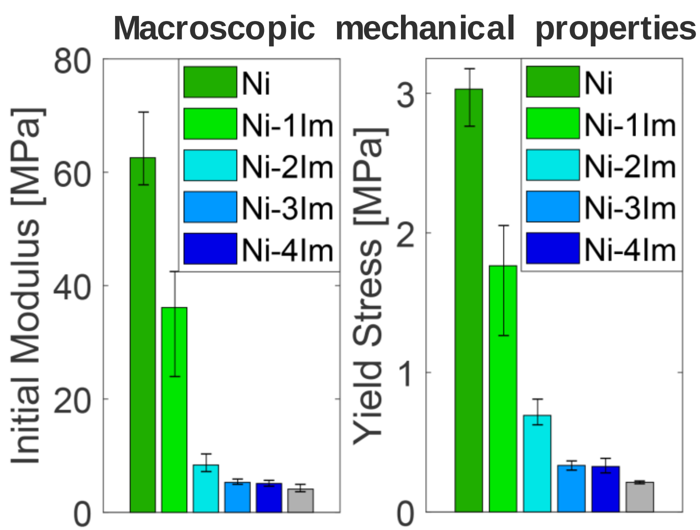
Theory





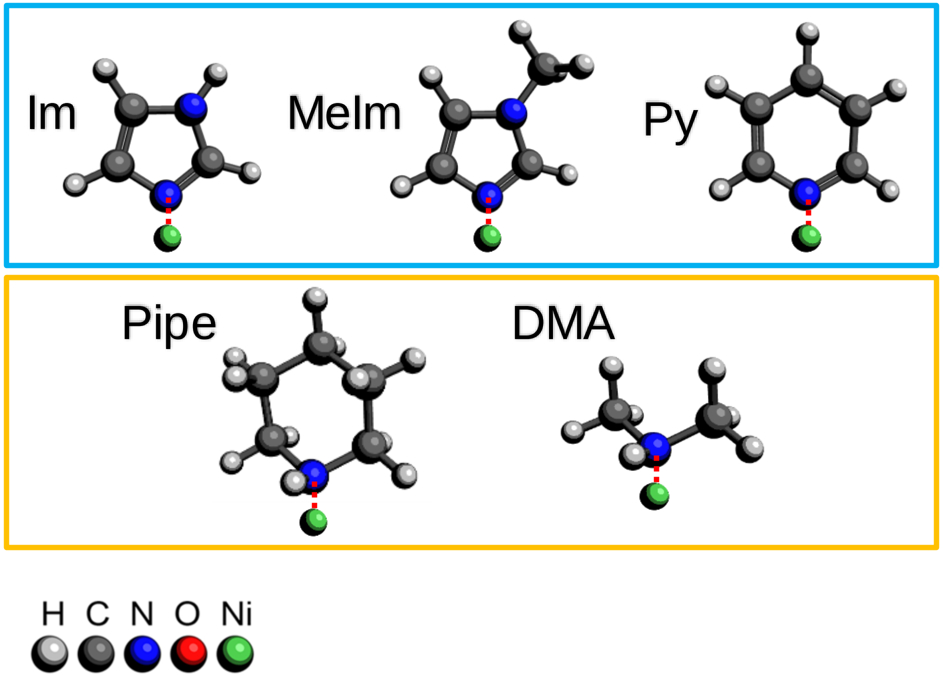
Experiment

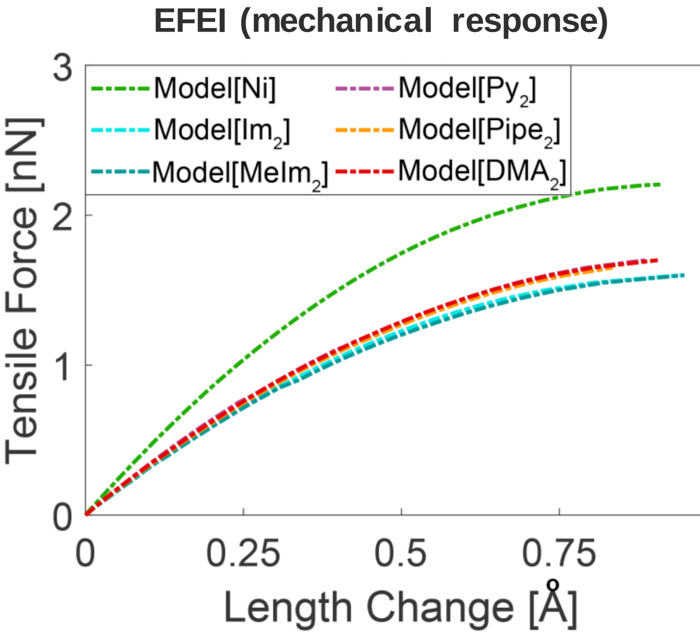




Vidavsky†, Buche†, Sparrow, Zhang, Yang, DiStasio, Silberstein, Macromolecules, 53, p. 2021 (2020).

Changing Ligand Type (Theory)

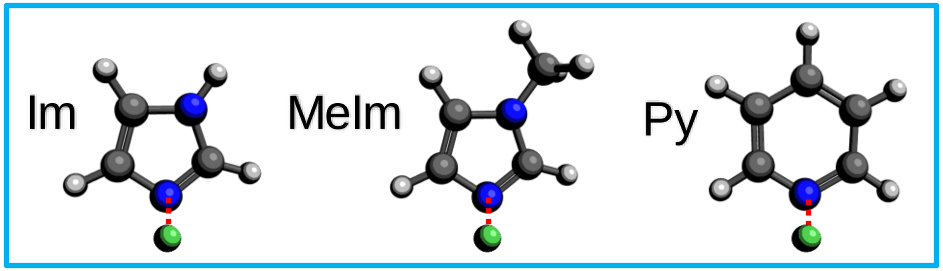


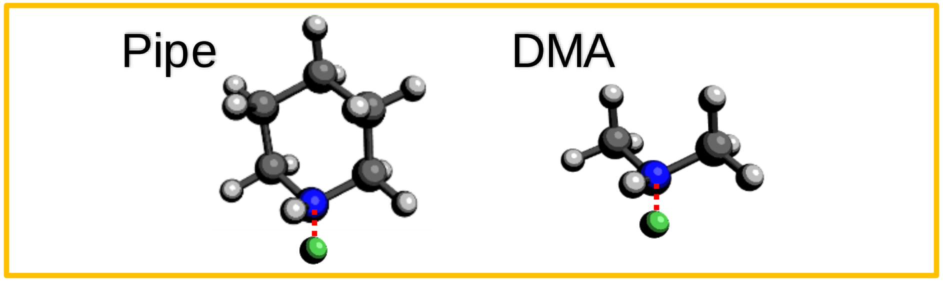


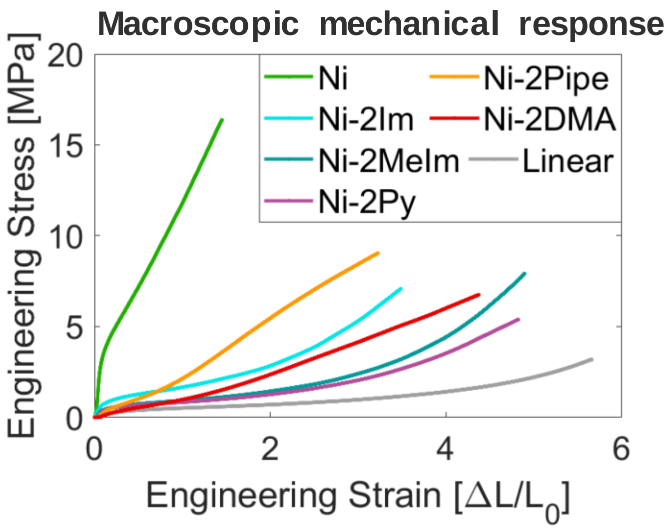
Model	[MeIm$_2$]	[Py$_2$]	[Pipe$_2$]	[DMA$_2$]
ΔG (kcal/mol)	4.68	5.21	5.95	6.51
ΔG‡ (kcal/mol)	15.36	16.63	16.33	16.66

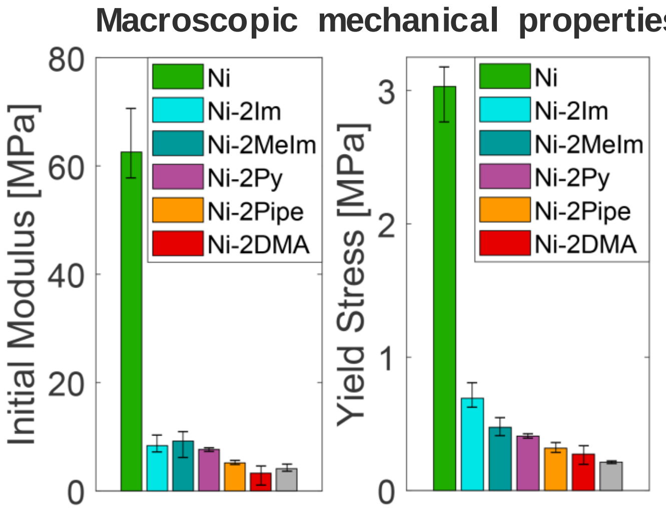
Vidavsky†, Buche†, Sparrow, Zhang, Yang, DiStasio, Silberstein, Macromolecules, 53, p. 2021 (2020).

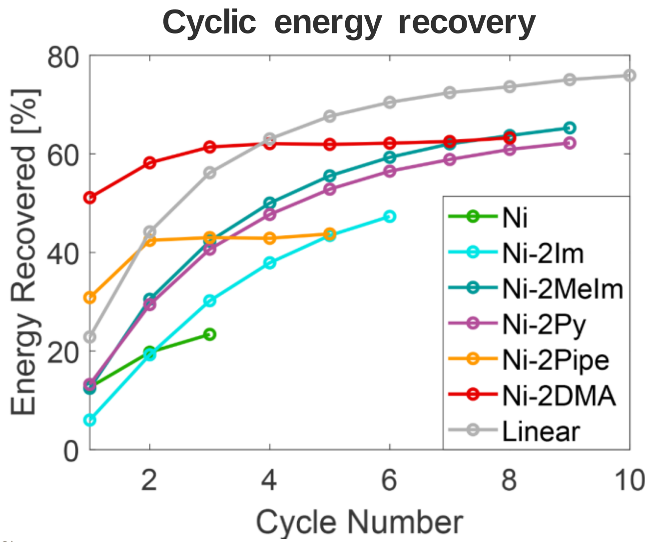
Changing Ligand Type (Experiment)











Vidavsky†, Buche†, Sparrow, Zhang, Yang, DiStasio, Silberstein, Macromolecules, 53, p. 2021 (2020).

PHYSICAL REVIEW E
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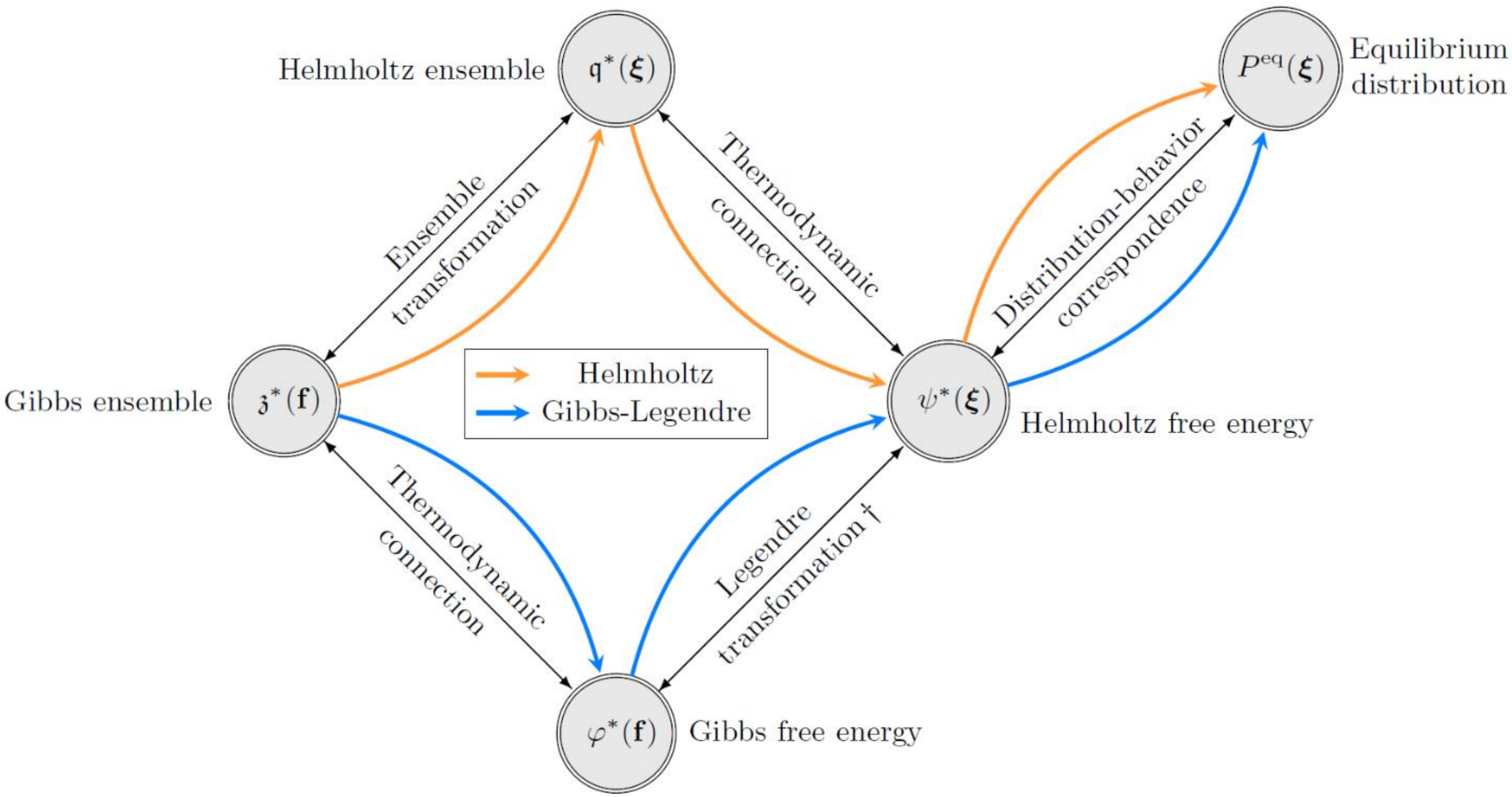
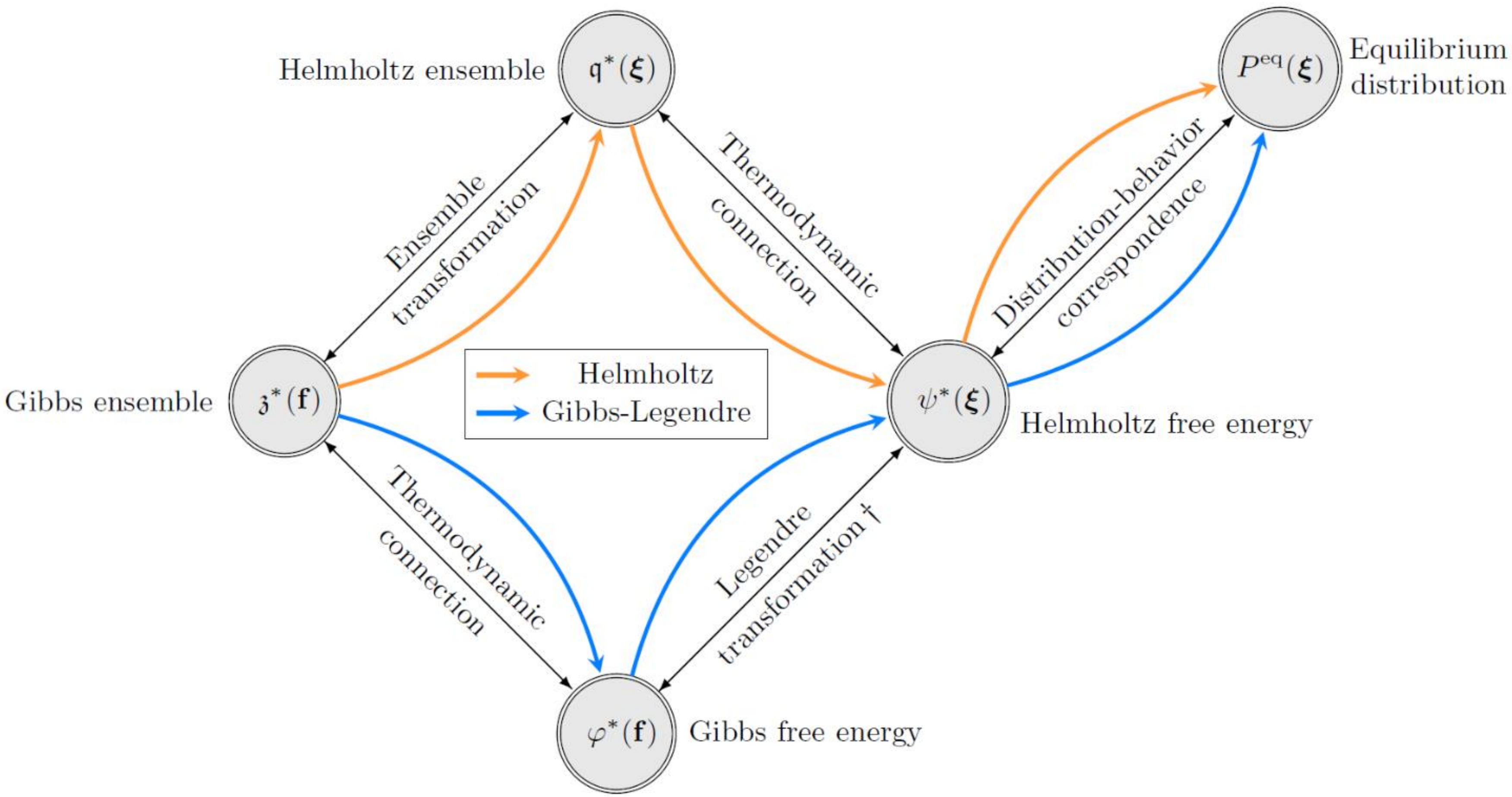
Statistical mechanical constitutive theory of polymer networks: The inextricable links between distribution, behavior, and ensemble

Michael R. Buche and Meredith N. Silberstein
Phys. Rev. E **102**, 012501 – Published 2 July 2020



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

Inextricable links



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

Single Chain Statistical Mechanics

Configuration integral

$$\mathfrak{q}_{\mathrm{con}} = \int \cdots \int e^{-\beta u} \prod_{j=2}^{M} d^3\mathbf{r}_j$$

$$= \iiint \mathfrak{q}^*(\tilde{\boldsymbol{\xi}})\, d^3\tilde{\boldsymbol{\xi}}$$

Relative configuration integral

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

Boltzmann distribution

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

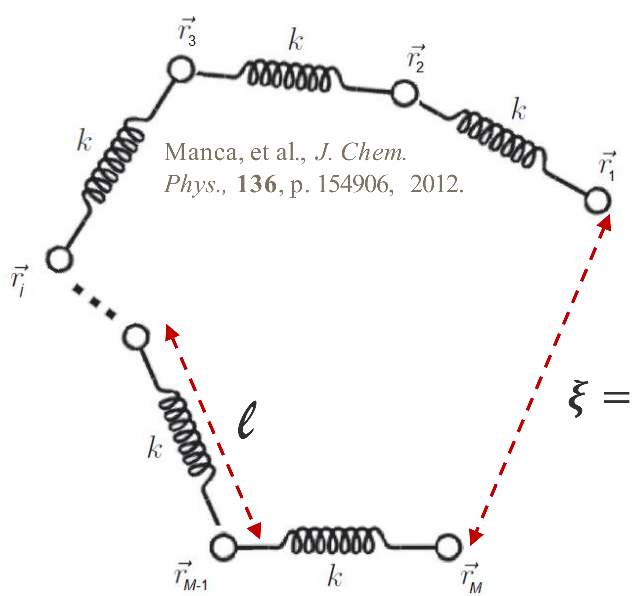
Helmholtz free energy

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

Mechanical response

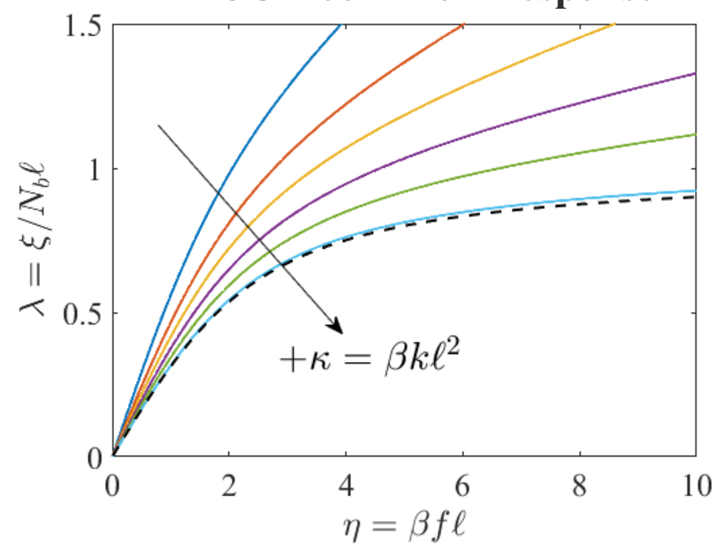
$$\mathbf{f} = \frac{\partial \psi^*}{\partial \boldsymbol{\xi}}$$

EFJC model



$$\boldsymbol{\xi} = \mathbf{r}_M - \mathbf{r}_1$$

EFJC mechanical response



McQuarrie, *Statistical Mechanics* (University Science Books, 2000).
Buche and Silberstein, Physical Review E, **102**, 012501 (2020).

Natural Statistical Correspondences

Distribution-behavior correspondence

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

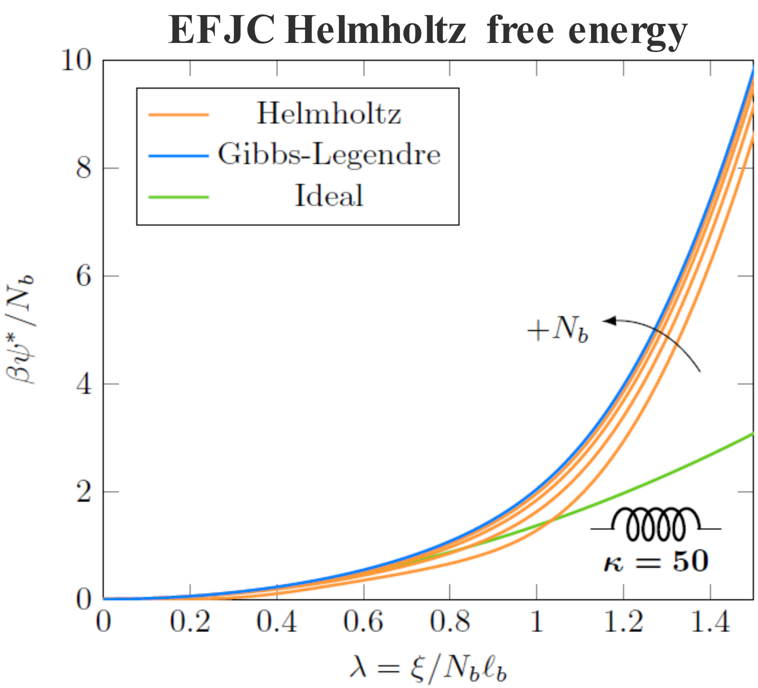
$$\psi^*(\boldsymbol{\xi}) = \psi^*_{\mathrm{ref}} - kT\ln\left[\frac{P^{\mathrm{eq}}(\boldsymbol{\xi})}{P^{\mathrm{eq}}(\boldsymbol{\xi}_{\mathrm{ref}})}\right]$$

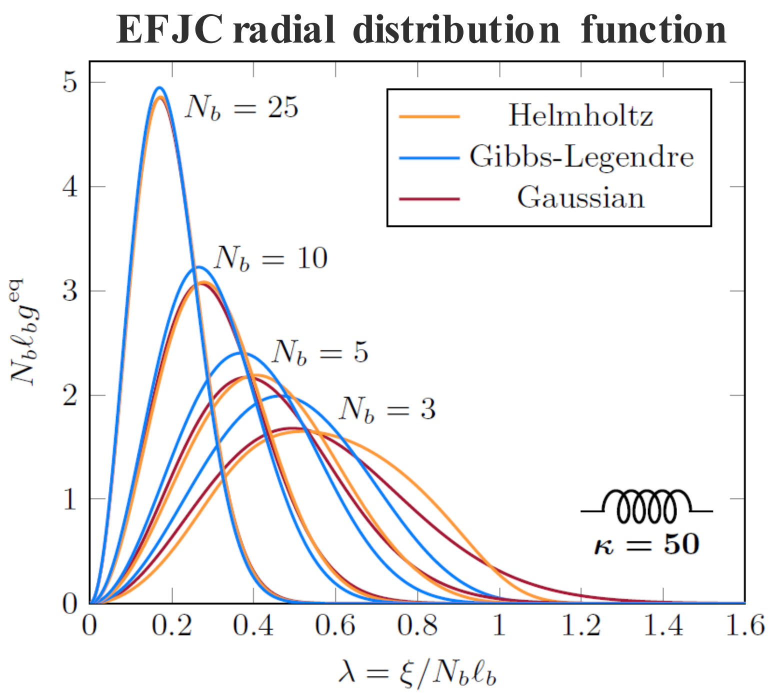
Ensemble transformation

$$\mathfrak{z}^*(\mathbf{f}) = \iiint \mathfrak{q}^*(\boldsymbol{\xi})e^{\beta\mathbf{f}\cdot\boldsymbol{\xi}}\,d^3\boldsymbol{\xi}$$

$$\mathfrak{q}^*(\boldsymbol{\xi}) = \left(\frac{\beta}{2\pi}\right)^3 \iiint \mathfrak{z}^*(i\mathbf{f})e^{-i\beta\mathbf{f}\cdot\boldsymbol{\xi}}\,d^3\mathbf{f}$$

Manca, et al., *J. Chem. Phys.*, **136**, p. 154906, 2012.

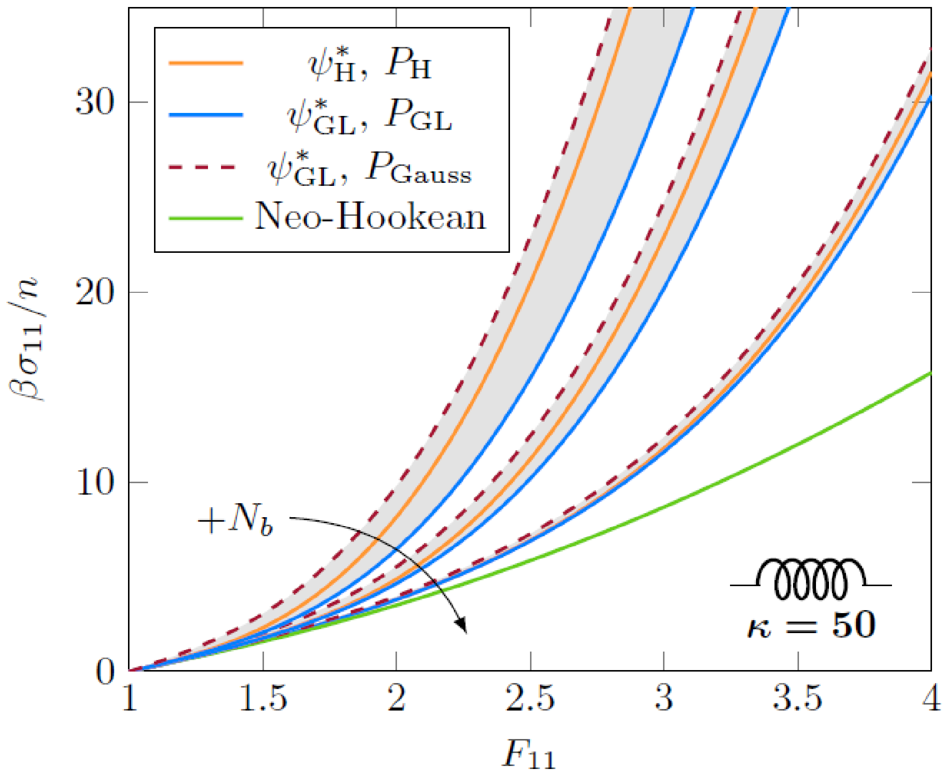




Buche and Silberstein, Physical Review E, **102**, 012501 (2020).

Macroscopic Mechanical Response

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



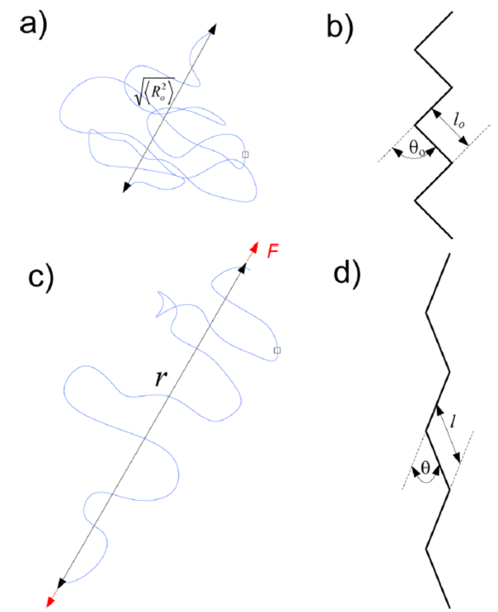
- Distinctions in the statistical description persist to play an important role in the macroscopic mechanics
- Approximation method performance depends on the regime of deformation
- Future models will be affected in a similar matter

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

Statistical Mechanics with Stiff Degrees of Freedom

- Simple (i.e. decoupled) models for stiff systems have become attractive
  - Resorting to improper models that violate basic statistical mechanics
- Multiple gaps in the literature
  - No recognized general approach
- We can obtain the proper approximation (and more)
  - Analogous to high temperature perturbation expansion

1) Hüsnü, and Kaliske, *J. Mech. Phys. Solids*, **57**, 2009.
2) Mao, et al., *Extr. Mech. Lett.*, **13**, 2017.
3) Mao et al., *J. Mech. Phys. Solids*, **85**, 2018.
4) Talamini, et al., *J. Mech. Phys. Solids*, **111**, 2018.
5) Mao, et al., *J. Mech. Phys. Solids*, **115**, 2018.
6) Lavoie, et al., *J. Phys. Chem. B*, **124**, 2019.
7) Li and Bouklas, *Int. J. Solids. Struc.*, **182**, 2020.
8) Lu, et al., *J. Mech. Phys. Solids*, **137**, 2020.



Zwanzig, Robert W. "High-temperature equation of state by a perturbation method. I. Nonpolar gases." The Journal of Chemical Physics 22, (1954): 1420-1426.

Lavoie, Shawn Ryan, Rong Long, and Tian Tang. "Modeling the Mechanics of Polymer Chains with Deformable and Active Bonds." *The Journal of Physical Chemistry B* (2019).

Statistical Mechanics with Stiff Degrees of Freedom

- Asymptotic approximations
  - u is minimized
    - Only a true decoupling at first order
    - Statistical mechanics near the ground state (low temperature limit)
  - General cases difficult

Bleistein, Norman, and Richard A. Handelsman. *Asymptotic Expansions of Integrals* (Courier Corporation, 1986).

- Current method
  - ψ is minimized
    - Idea of chemical equilibrium?
    - Idea of macroscopic mechanics?

Integration over energy levels

$$\mathfrak{q} = \int_{\hat{u}}^{\infty} \omega(\tilde{u}) e^{-\beta \tilde{u}} \, d\tilde{u}$$

Helmholtz free energy

$$\begin{aligned}\psi &= -kT \ln \mathfrak{q} \\ &\sim \hat{u} - (kT) \ln \left[\omega(\hat{u}) + (kT) \left. \frac{\partial \omega}{\partial u} \right|_{u=\hat{u}} + \cdots \right]\end{aligned}$$

First order approximations

$$\begin{aligned}\psi &\sim \hat{u} - kT \ln [\omega(\hat{u})] \\ &= \hat{u} - T\hat{s}\end{aligned}$$

Statistical Mechanics with Stiff Degrees of Freedom

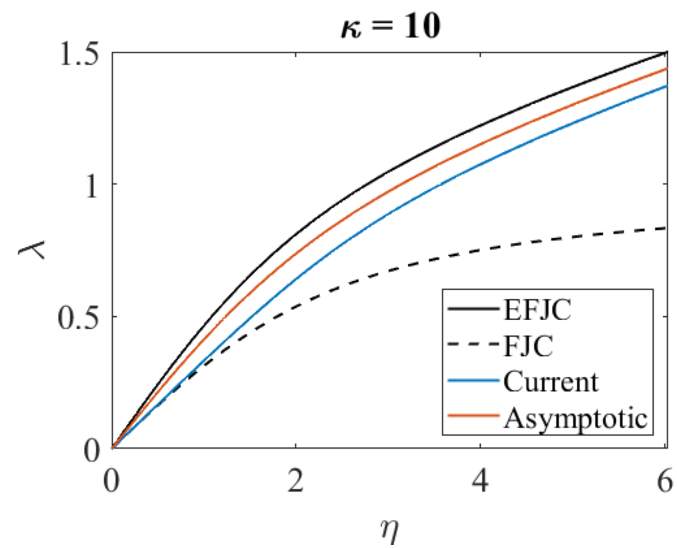
EFJC asymptotic approximation (first order)

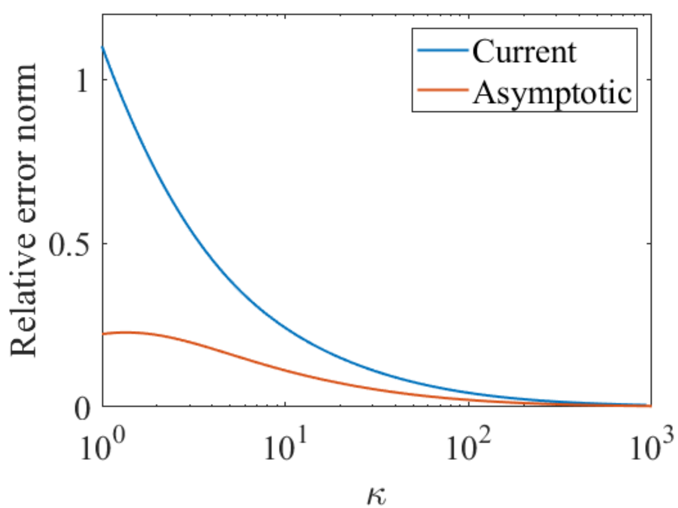
$$\lambda \sim \frac{\eta}{\kappa} + \mathcal{L}(\eta)$$

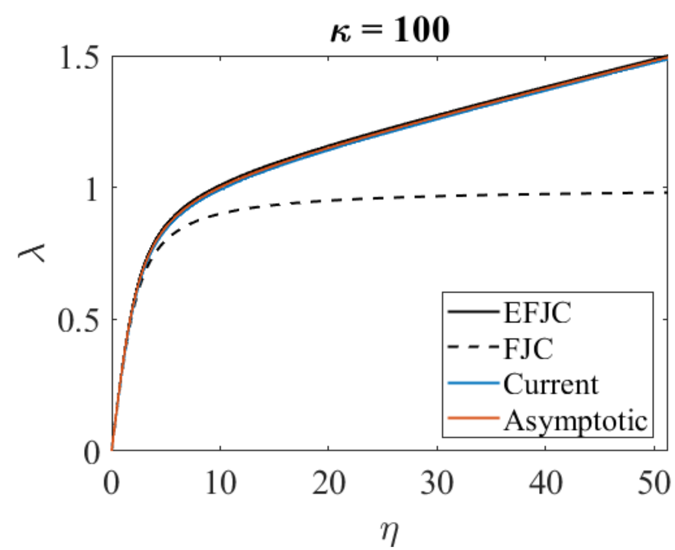
EFJC current method approximation

$$\lambda \approx \lambda_b \mathcal{L}(\eta), \text{ where } \frac{\lambda}{\lambda_b} = \mathcal{L}\left[\frac{\lambda_b^2}{\lambda}(\lambda_b - 1)\,\kappa\right]$$

Mao, Yunwei, Brandon Talamini, and Lallit Anand. "Rupture of polymers by chain scission." Extreme Mechanics Letters 13 (2017): 17-24.



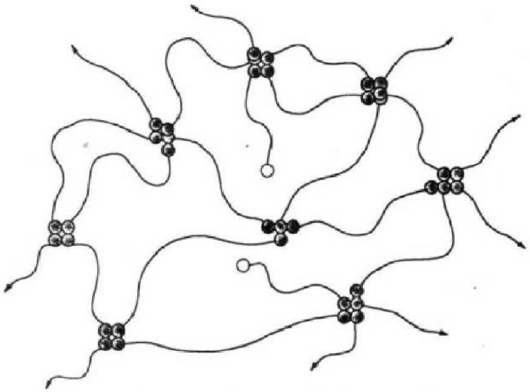




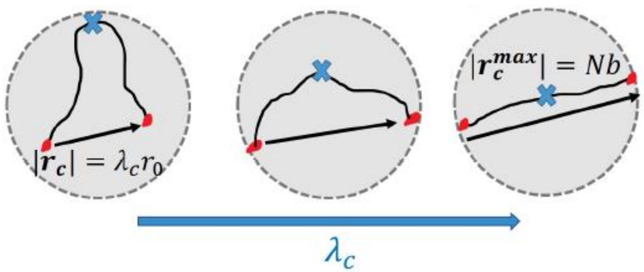
Mechanics of polymers with reversible crosslinks

- **Physical-motivated network models**
  - Continuous distribution of dynamic chains[1,2,3,4]
  - Force- or stretch-driven kinetics[2,4]
  - Distribution of contour lengths[5,6,7]
  - Non-affine deformation of distribution[7,8]
  - General, meticulous treatment of static network[9]

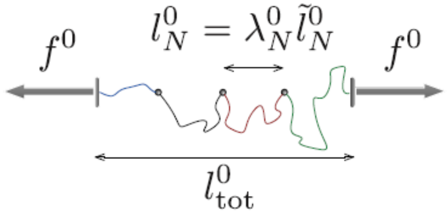
What about a more complicated picture?



1) Tanaka and Edwards, *Macromolecules*, **25**, p. 1516, 1992.



4) Lalitha Sridhar and Vernerey, *Polymers*, **10**, 2018.

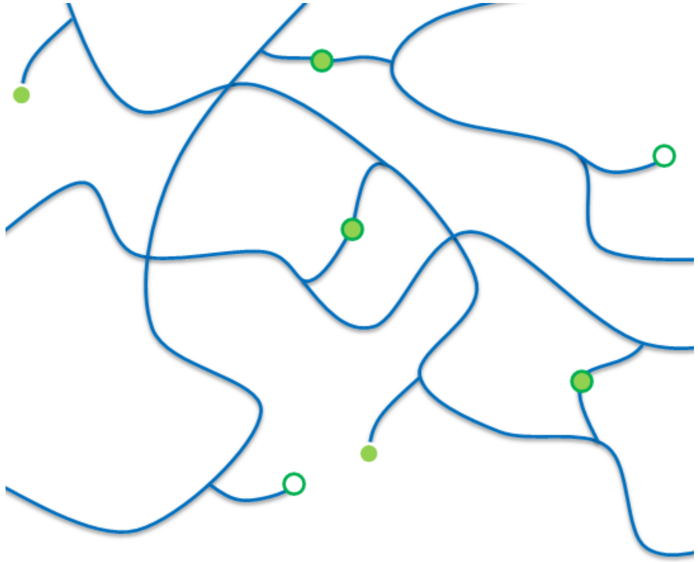


7) Verron and Gros, *J. Mech. Phys. Solids*, **106**, p. 176, 2017.

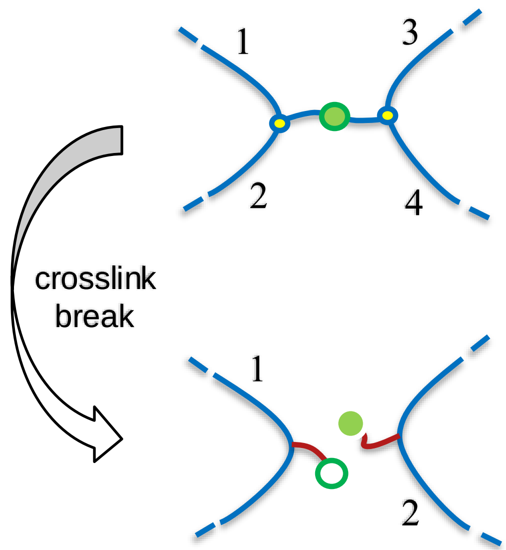
2) Vernerey, et al., *J. Mech. Phys.* Solids, **107**, p. 1, 2017.
3) Long, et al., *Macromolecules*, **47**, p. 7243, 2014.
5) Wang, et al., *J. Mech. Phys. Solids,* **82**, p. 320, 2015.
6) Tehrani, et al., *Physical Biology*, **15**, 2018.
8) Miehe et al., *J. Mech. Phys.* Solids, **52**, p. 2617, 2004.
9) Buche and Silberstein, *arXiv.org*, 2004.07874, 2020.

Mechanics of polymers with reversible crosslinks

- Complicated physics
  - Crosslinks contribute to stiffness
  - Polydispersity from chains, crosslinking
  - Strong dependence on rate of reformation
  - Non-affinity due to polydispersity, crosslinks



- Extensive data available
  - Many ligand cases; varying strain rate, cyclic, stress-relaxation
  - DFT work can inform physical parameters, functions
- Maintain model power
  - Statistical mechanical derivation, analogous to previous work
  - Ensure all proposed mechanisms satisfy physical conditions



Mechanics of polymers with reversible crosslinks

- Equilibrium statistical mechanics
  - Pick your interactions/restrictions, let it rip

- PDEs governing network evolution
  - Analytical solution unwieldy, likely not guaranteed
    - Robust numerical scheme, coordinate transformations
  - Chemical restrictions are clear, explicit forms are not
    - Probabilistic approaches
    - Effective chain length method
  - Affinity of deformation-induced evolution
    - Choices to be made (constraints): average stretch, equal force, etc.
  - Previous mathematical manipulations may not be possible
    - More numerical methods, computational expense

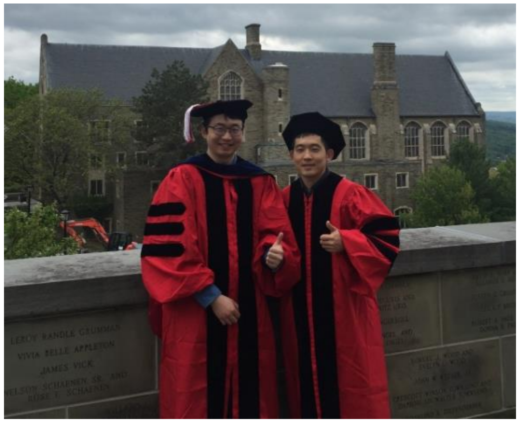
Past Accomplishments

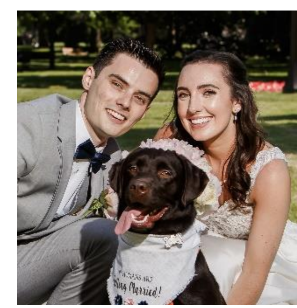
- Papers
  - “Tuning the mechanical properties of metallopolymers…”
  - “Statistical mechanical constitutive…”
- Talks
  - APS March Meeting 2019
  - Society of Engineering Science 2019
  - (internal) Mechanics Student Seminar
- Posters
  - MechanoChemBio 2019

Plan to Complete Before Graduation

- Research
  - "Statistical mechanics with stiff…" (November 2020)
  - "Mechanics of polymers with reversible…" (February 2021)
- Talks
  - ~~Multiscale Materials Modeling (October 2020)~~
- Potential Courses
  - MATH (Probability Theory, Lie Algebra, Fourier Analysis)
  - ORIE (Stochastic Processes)
  - PHYS (Quantum Field Theory)
- B Exam (May 2021)

Acknowledgements





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This research is funded by the National Science Foundation (CMMI-1653059) and the Office of Naval Research (N00014-17-1-2989).