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

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6/7/2021

Outline

Fundamental Theories for the Mechanics of Polymer Chains and Networks

Introduction

Part I – statistical mechanical constitutive theory, no bond breaking

- Focus: distribution-behavior connection, thermodynamic ensemble
- Highlight: approximation method performance in macroscale

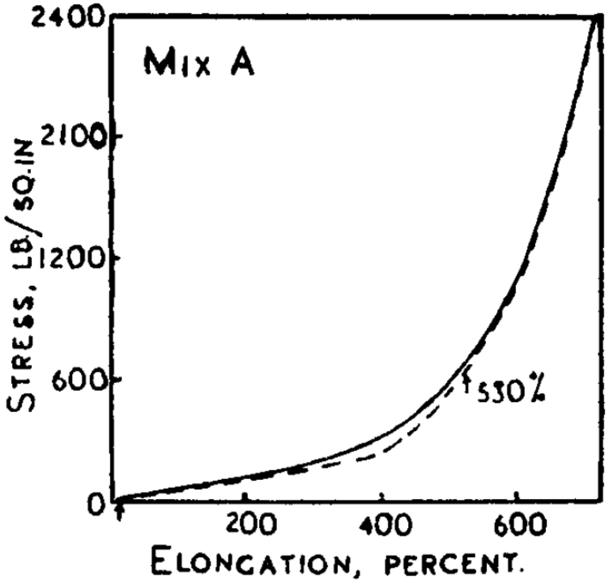
Part II – statistical mechanical constitutive theory, with bond breaking

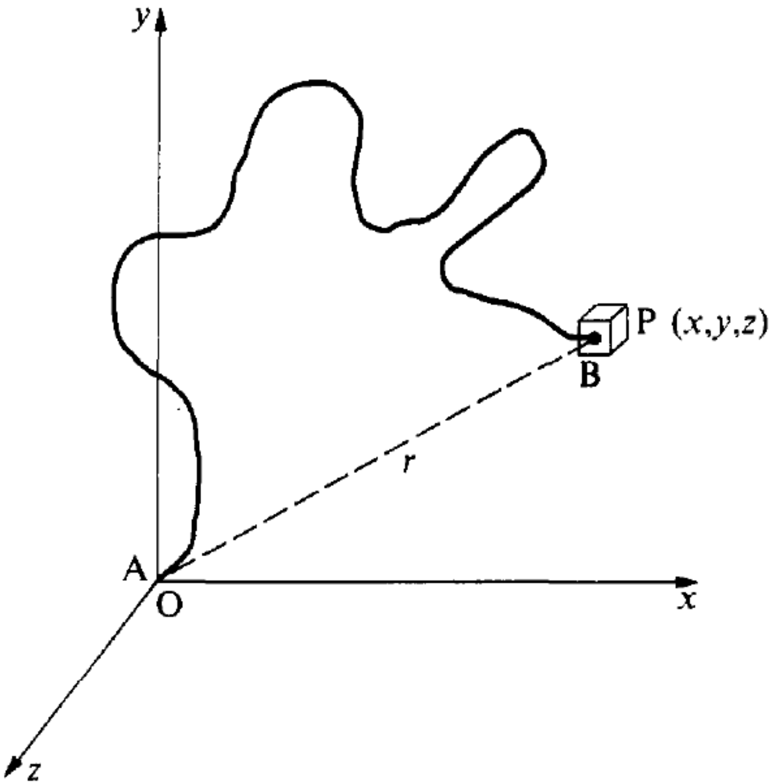
- Focus: general derivation, IPDE solution, single-chain mechanical response
- Highlight: modeling mechanical experiments of polymers

Closing/Summary

Elastomers and rubber elasticity

Elastomers consist of many single polymer chains forming a network



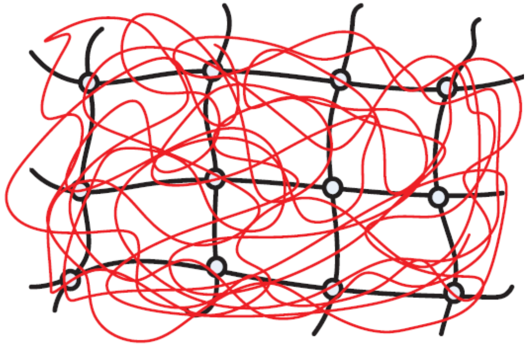


1. Long polymer chains
2. Weak intermolecular forces (above Tg)
3. Crosslinking

L. R. G. Treloar. The Physics of Rubber Elasticity. Clarendon Press, Cambridge, UK, 1949.
L. Mullins. Rubber Chem. Technol. **21**, 2 (1948).

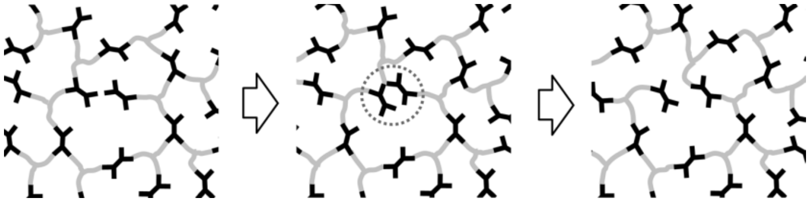
Elastomers designed to break (bonds)

Emerging elastomers are often designed to benefit from bond breaking while being deformed



Lavoie, Millereau, Creton, Long, Tang, J. Mech. Phys. Solids, 125, p. 523 (2019).

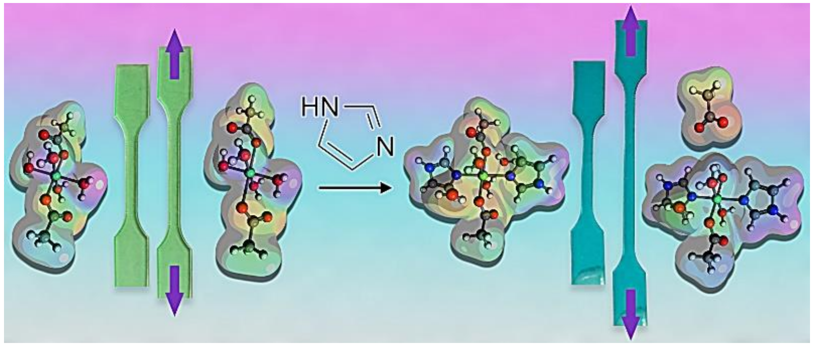
1. Irreversible bond breaking
2. Transient bond breaking
3. Force-driven reversible breaking



Montarnal, Capelot, Tournilhac, Leibler, Science, **334**, p. 965 (2011).

Physically-founded constitutive models are essential

- Predictive power
- Fundamental understanding



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

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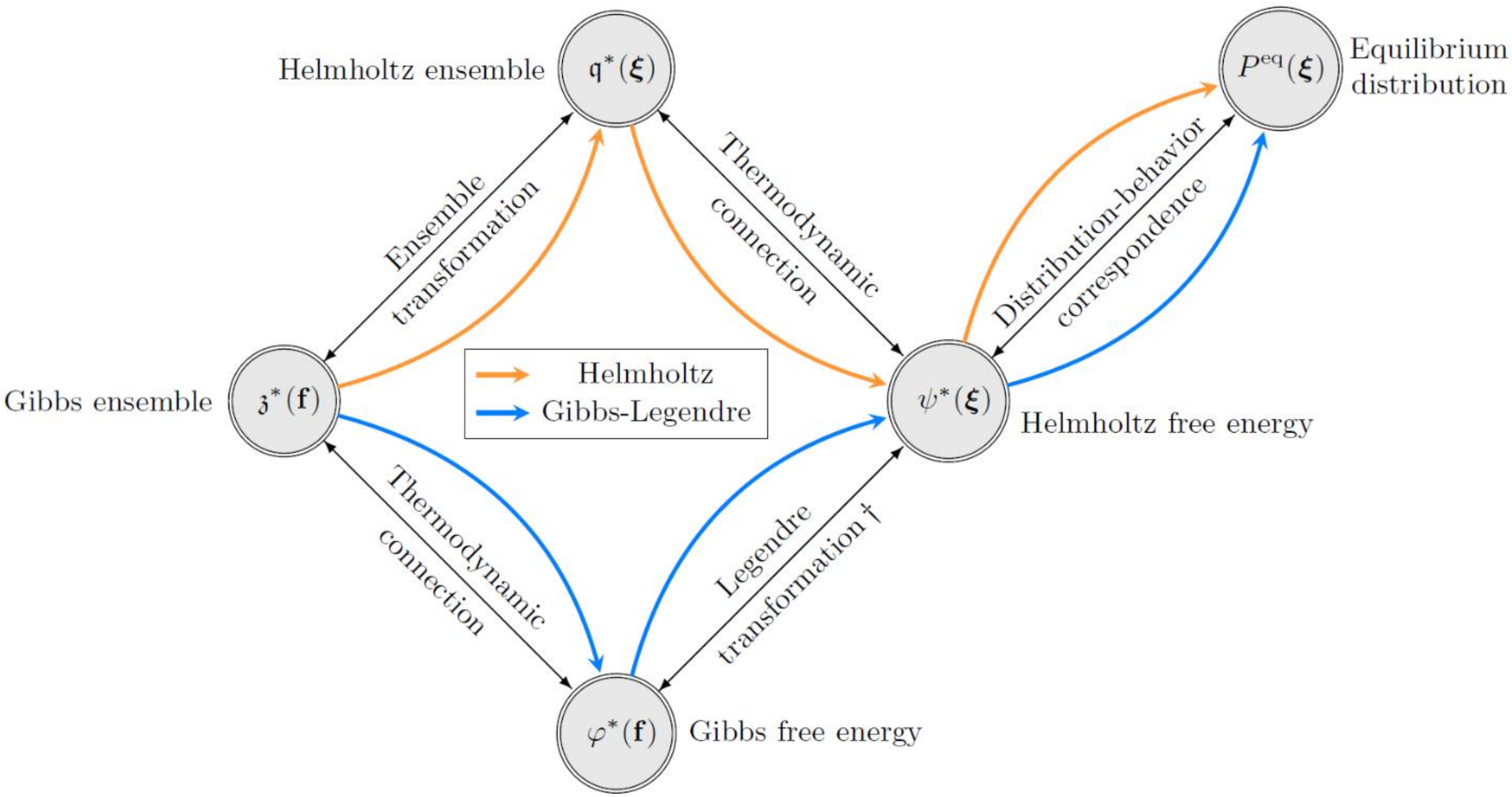
Statistical mechanical constitutive theory of polymer networks: The inextricable links between distribution, behavior, and ensemble

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



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

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

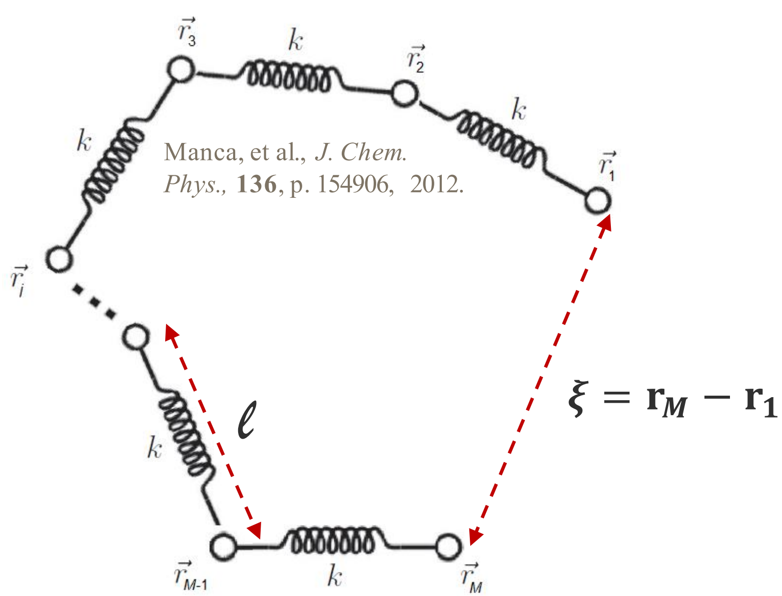
Helmholtz free energy

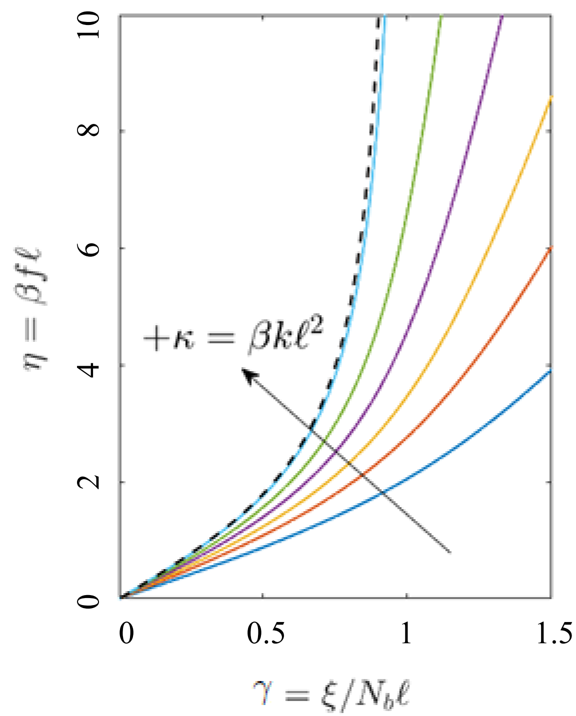
$$\psi^*(\boldsymbol{\xi}) = -kT \ln \mathfrak{q}^*(\boldsymbol{\xi})$$

Mechanical response

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

EFJC model





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

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

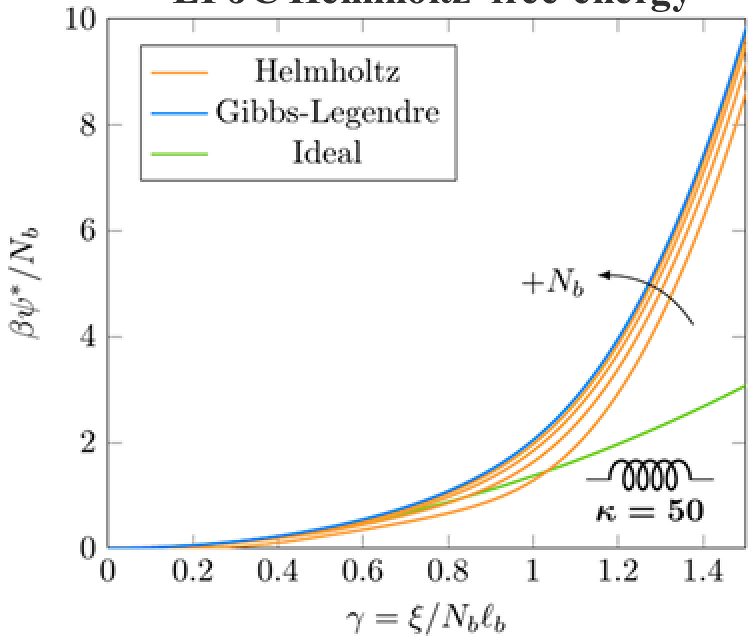
$$\mathfrak{q}^*(\boldsymbol{\xi}) = \left(\frac{\beta}{2\pi}\right)^3 \iiint \mathfrak{z}^*(i\mathbf{f}) e^{-i\beta\mathbf{f}\cdot\boldsymbol{\xi}}\, d^3\mathbf{f}$$

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

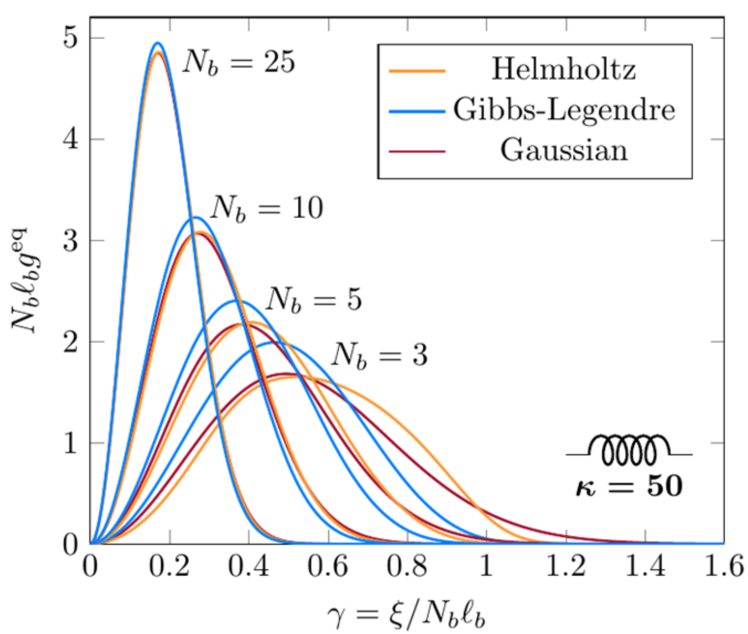
Legendre transformation

$$\varphi^*(\mathbf{f}) = \psi^*(\boldsymbol{\xi}) - \mathbf{f}\cdot\boldsymbol{\xi}$$

EFJC Helmholtz free energy



EFJC radial distribution function

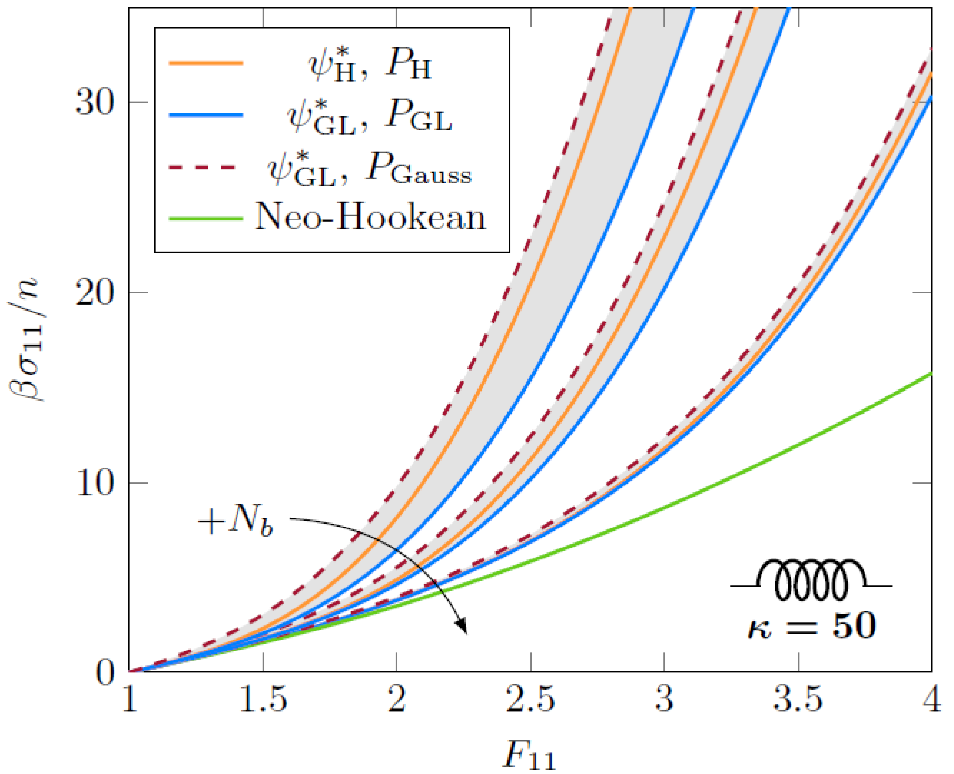


Buche and Silberstein, Physical Review E, **102**, 012501 (2020).

Macroscopic Mechanical Response

Cauchy stress obtained using constitutive theory

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



- Distinctions in the statistical description persist to play an important role in the macroscopic mechanics
- Approximation method performance may depend on the regime of deformation
- In any case, a physically-based hyperelastic constitutive model

$$\boldsymbol{\sigma} = \left(\frac{\partial a}{\partial \mathbf{F}}\right)_T \cdot \mathbf{F}^T$$

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

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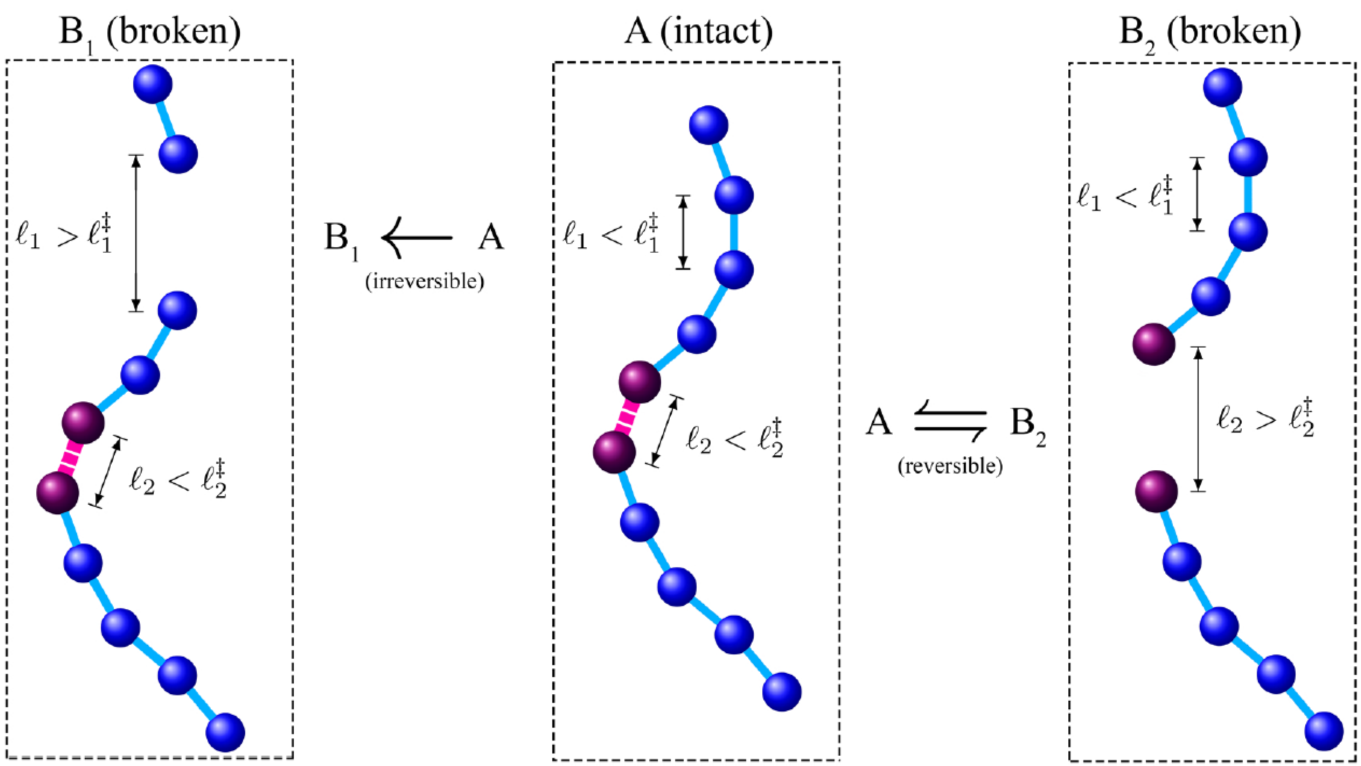
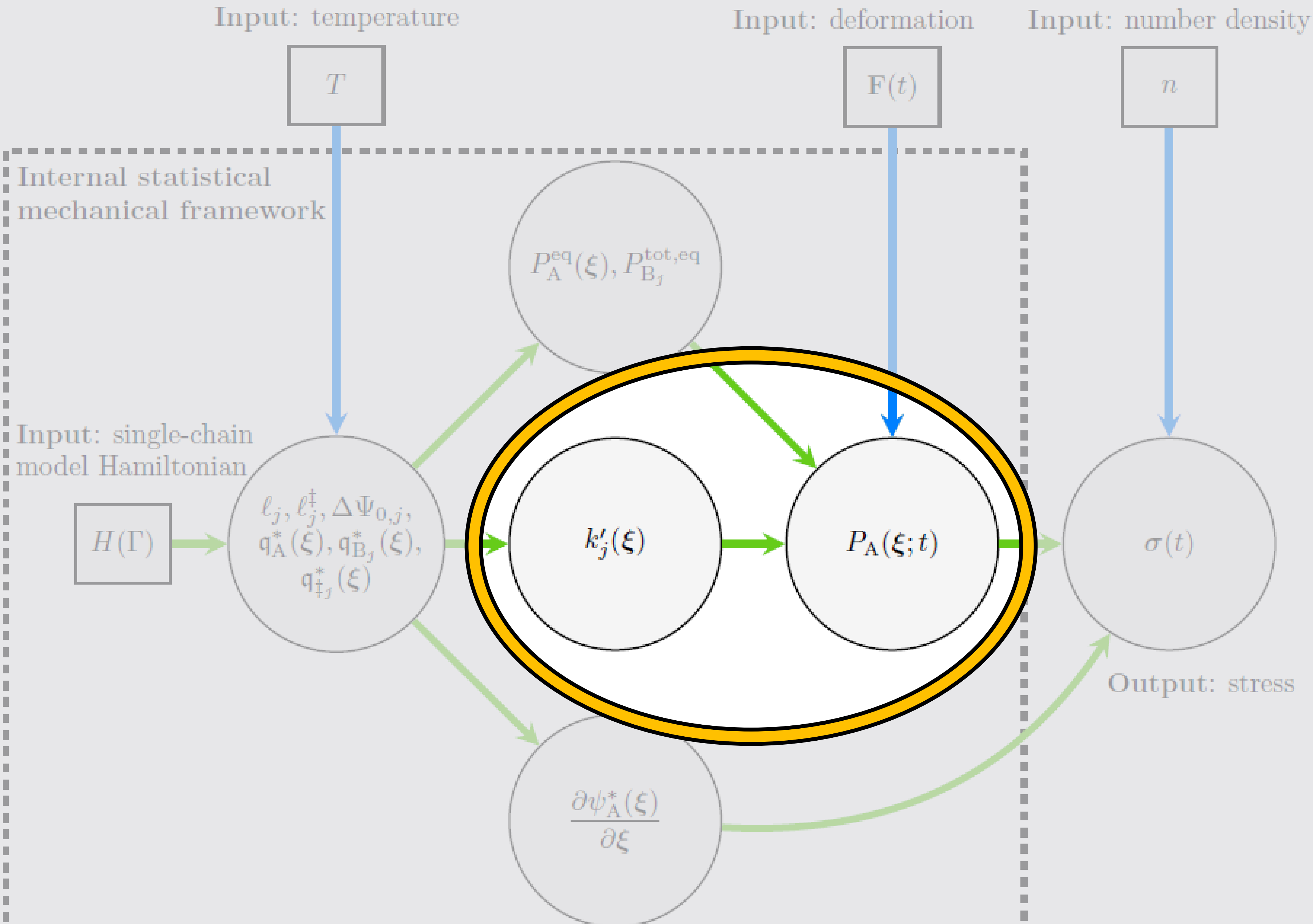
Volume 156, November 2021, 104593

Chain breaking in the statistical mechanical constitutive theory of polymer networks

Michael R. Buche, Meredith N. Silberstein





Buche and Silberstein, J. Mech. Phys. Solids 156, 104593 (2021).

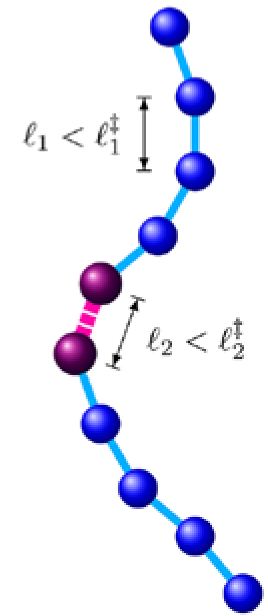
Nonequilibrium statistical mechanics

Nonequilibrium ensemble average

$$\Phi(t) = \langle \phi \rangle \equiv \int \cdots \int f(\Gamma; t)\phi(\Gamma)\, d\Gamma.$$

Probability distribution for intact chains

$$P_{\mathrm{A}}(\xi; t) = \left\langle \delta^3 \left[\mathbf{R}(\Gamma) - \xi\right] \prod_{i=1}^{M} \Theta\left(\ell_i^\ddagger - \ell_i\right) \right\rangle$$



Liouville equation

$$\frac{\partial f}{\partial t} = (-\mathscr{L})\, f = \left(\frac{\partial H}{\partial \mathbf{q}} \cdot \frac{\partial}{\partial \mathbf{p}} - \frac{\partial H}{\partial \mathbf{p}} \cdot \frac{\partial}{\partial \mathbf{q}}\right) f$$

Evolution equation using $\frac{d}{dt}\langle \phi \rangle = \langle \mathscr{L} \phi \rangle$

$$\frac{\partial P_{\mathrm{A}}(\xi; t)}{\partial t} = \sum_{j=1}^{M} \mathcal{R}_j''(\xi; t) - \sum_{j=1}^{M} \mathcal{R}_j'(\xi; t) - \frac{\partial}{\partial \xi} \cdot \left[\dot{\xi}_{\mathrm{A}}(\xi; t) P_{\mathrm{A}}(\xi; t)\right]$$

Affine assumption

$$\dot{\xi}_{\mathrm{A}}(\xi; t) = \mathbf{L}(t) \cdot \xi$$

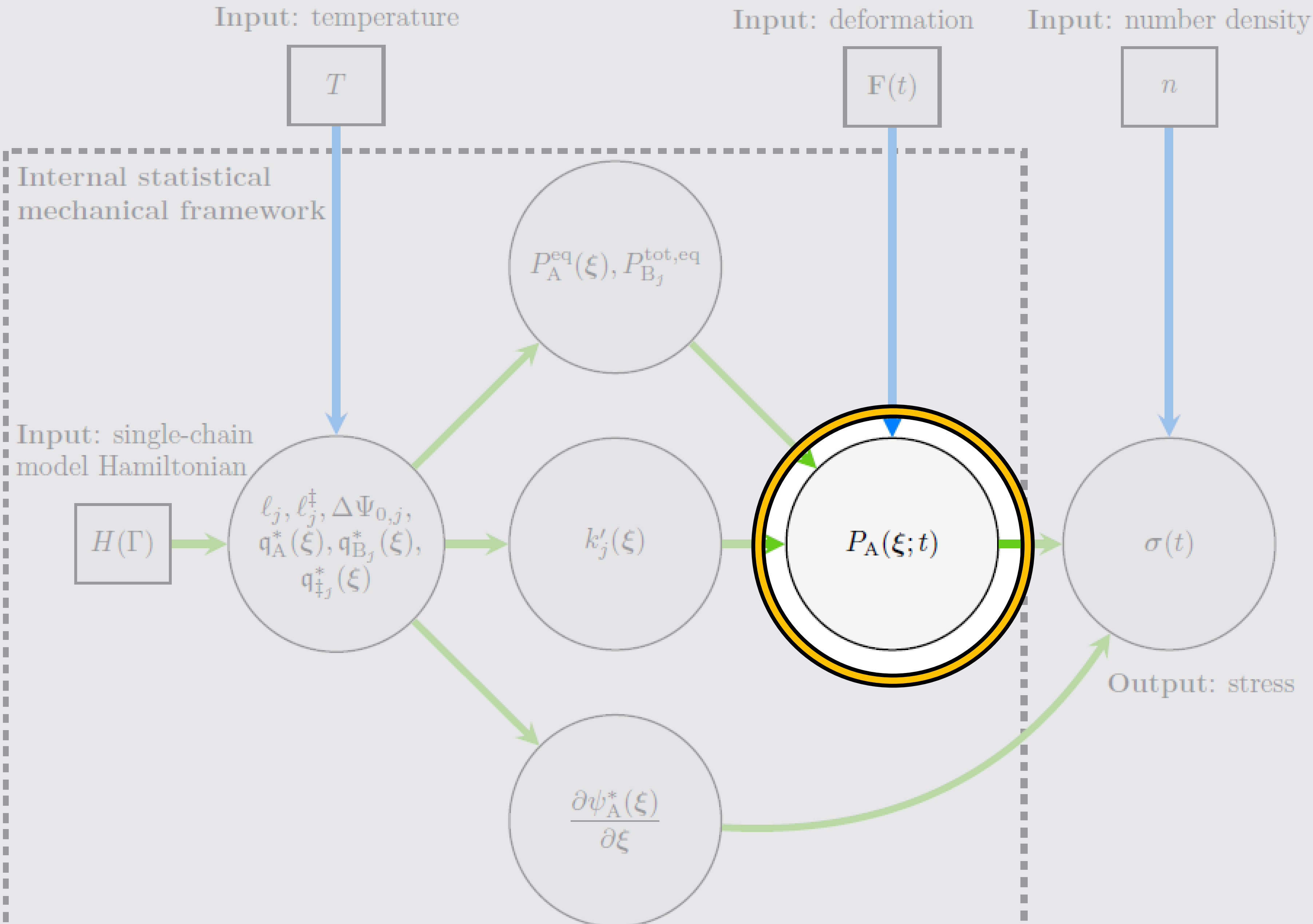
Transition state theory assumption

$$\mathcal{R}_j'(\xi; t) = k_j'(\xi) P_{\mathrm{A}}(\xi; t)$$
$$\mathcal{R}_j''(\xi; t) = k_j''(\xi) P_{\mathrm{B}_j}(\xi; t)$$

Reaction rate coefficient functions

$$k_j'(\xi) = \frac{1}{\beta} \frac{\mathfrak{q}^*_{\ddagger_j}(\xi)}{\mathfrak{q}^*_{\mathrm{A}}(\xi)}$$
$$k_j''(\xi) = \frac{1}{\beta} \frac{\mathfrak{q}^*_{\ddagger_j}(\xi)}{\mathfrak{q}^*_{\mathrm{B}_j}(\xi)}$$

Zwanzig, Nonequilibrium Statistical Mechanics, Oxford University Press, 2001.
Zwanzig, Physical Review **124**, 983 (1961).
Buche and Silberstein, J. Mech. Phys. Solids **156**, 104593 (2021).



Buche and Silberstein, J. Mech. Phys. Solids 156, 104593 (2021).

Exactly solving governing IPDE

Simplified evolution equation

$$\frac{\partial P_{\mathrm{A}}(\boldsymbol{\xi};t)}{\partial t} = -\left[\frac{\partial P_{\mathrm{A}}(\boldsymbol{\xi};t)}{\partial \boldsymbol{\xi}}\,\boldsymbol{\xi}\right] : \mathbf{L}(t) - k(\boldsymbol{\xi})\left\{P_{\mathrm{A}}(\boldsymbol{\xi};t) - \frac{P_{\mathrm{A}}^{\mathrm{eq}}(\boldsymbol{\xi})}{P_{\mathrm{B}}^{\mathrm{tot,eq}}}\left[1 - \iiint P_{\mathrm{A}}(\tilde{\boldsymbol{\xi}};t)\,d^3\tilde{\boldsymbol{\xi}}\right]\right\}$$

Conservation requirement (built-in)

$$\rho(t) \equiv \frac{P_{\mathrm{B}}^{\mathrm{tot}}(t)}{P_{\mathrm{B}}^{\mathrm{tot,eq}}} = \frac{1 - \iiint P_{\mathrm{A}}(\boldsymbol{\xi};t)\,d^3\boldsymbol{\xi}}{1 - \iiint P_{\mathrm{A}}^{\mathrm{eq}}(\boldsymbol{\xi})\,d^3\boldsymbol{\xi}}$$

Change of variables (flavor: method of characteristics)

$$H(\boldsymbol{\xi};t) \equiv P_{\mathrm{A}}\left[\mathbf{F}(t)\cdot\boldsymbol{\xi};t\right] e^{\int_0^t k[\mathbf{F}(s)\cdot\boldsymbol{\xi}]\,ds}$$

Rearrange, RHS only function of time

$$\frac{\partial H(\boldsymbol{\xi};t)}{\partial t}\,e^{-\int_0^t k[\mathbf{F}(s)\cdot\boldsymbol{\xi}]\,ds} = \frac{k\left[\mathbf{F}(t)\cdot\boldsymbol{\xi}\right] P_{\mathrm{A}}^{\mathrm{eq}}\left[\mathbf{F}(t)\cdot\boldsymbol{\xi}\right]}{P_{\mathrm{B}}^{\mathrm{tot,eq}}}\left\{1 - \iiint H(\tilde{\boldsymbol{\xi}};t)\,e^{-\int_0^t k\left[\mathbf{F}(s)\cdot\tilde{\boldsymbol{\xi}}\right]\,ds}\,d^3\tilde{\boldsymbol{\xi}}\right\}$$

$$\frac{\partial H(\boldsymbol{\xi};t)}{\partial t}\,\frac{e^{-\int_0^t k[\mathbf{F}(s)\cdot\boldsymbol{\xi}]\,ds}}{k\left[\mathbf{F}(t)\cdot\boldsymbol{\xi}\right] P_{\mathrm{A}}^{\mathrm{eq}}\left[\mathbf{F}(t)\cdot\boldsymbol{\xi}\right]} = \underbrace{\frac{1}{P_{\mathrm{B}}^{\mathrm{tot,eq}}}\left\{1 - \iiint H(\tilde{\boldsymbol{\xi}};t)\,e^{-\int_0^t k\left[\mathbf{F}(s)\cdot\tilde{\boldsymbol{\xi}}\right]\,ds}\,d^3\tilde{\boldsymbol{\xi}}\right\}}_{\equiv\rho(t)}$$

Integrate, now need (consistent) solution for ρ

$$H(\boldsymbol{\xi};t) = H(\boldsymbol{\xi};0) + \int_0^t \frac{k\left[\mathbf{F}(\tau)\cdot\boldsymbol{\xi}\right] P_{\mathrm{A}}^{\mathrm{eq}}\left[\mathbf{F}(\tau)\cdot\boldsymbol{\xi}\right]}{e^{-\int_0^\tau k[\mathbf{F}(s)\cdot\boldsymbol{\xi}]\,ds}}\,\rho(\tau)\,d\tau$$

Exactly solving governing IPDE

Tentative solution

$$H(\boldsymbol{\xi};t) = H(\boldsymbol{\xi};0) + \int_0^t \frac{k\left[\mathbf{F}(\tau)\cdot\boldsymbol{\xi}\right] P_{\mathrm{A}}^{\mathrm{eq}}\left[\mathbf{F}(\tau)\cdot\boldsymbol{\xi}\right]}{e^{-\int_0^\tau k[\mathbf{F}(s)\cdot\boldsymbol{\xi}]\,ds}}\,\rho(\tau)\,d\tau \qquad H(\boldsymbol{\xi};t) \equiv P_{\mathrm{A}}\left[\mathbf{F}(t)\cdot\boldsymbol{\xi};t\right] e^{\int_0^t k[\mathbf{F}(s)\cdot\boldsymbol{\xi}]\,ds}$$

Substitution into the conservation requirement retrieves a Volterra integral equation:

$$\rho(t) \equiv \frac{P_{\mathrm{B}}^{\mathrm{tot}}(t)}{P_{\mathrm{B}}^{\mathrm{tot,eq}}} = \frac{1-\iiint P_{\mathrm{A}}(\boldsymbol{\xi};t)\,d^3\boldsymbol{\xi}}{1-\iiint P_{\mathrm{A}}^{\mathrm{eq}}(\boldsymbol{\xi})\,d^3\boldsymbol{\xi}} \qquad \rho(t) + \int_0^t K(t,\tau)\rho(\tau)\,d\tau = b(t)$$

where the kernel and right-hand-side function are

$$K(t,\tau) = \frac{1}{P_{\mathrm{B}}^{\mathrm{tot,eq}}}\iiint P_{\mathrm{A}}^{\mathrm{eq}}\left[{}_{(t)}\mathbf{F}(\tau)\cdot\boldsymbol{\xi}\right]\frac{\partial\Xi(\boldsymbol{\xi};t,\tau)}{\partial\tau}\,d^3\boldsymbol{\xi} \qquad b(t) = \frac{1}{P_{\mathrm{B}}^{\mathrm{tot,eq}}}\left\{1-\iiint P_{\mathrm{A}}\left[\mathbf{F}^{-1}(t)\cdot\boldsymbol{\xi};0\right]\,\Xi(\boldsymbol{\xi};t,0)\,d^3\boldsymbol{\xi}\right\}$$

where the relative deformation is

$${}_{(t)}\mathbf{F}(\tau) \equiv \mathbf{F}(\tau)\cdot\mathbf{F}^{-1}(t)$$

and where we define the reaction propagator as

$$\Xi(\boldsymbol{\xi};t,\tau) \equiv \exp\left\{-\int_\tau^t k\left[{}_{(t)}\mathbf{F}(s)\cdot\boldsymbol{\xi}\right]\,ds\right\}$$

Buche and Silberstein, J. Mech. Phys. Solids 156, 104593 (2021).

Exactly solving governing IPDE

Liouville-Newmann series solution:

$$\rho(t) = b(t) + \sum_{m=1}^{\infty} (-1)^m \int_0^t K_m(t,\tau) b(\tau)\, d\tau$$

$$K_m(t,\tau) \equiv \int_\tau^t K(t,s) K_{m-1}(s,\tau)\, ds$$

Solution converges if kernel square-integrable

$$\|K\|^2 \equiv \int_0^T \int_0^t \left|K(t,\tau)\right|^2 d\tau\, dt < \infty$$

Since $0 \leq \Xi(\boldsymbol{\xi}; t, \tau) \leq 1$ we have $K \leq \hat{K}$ and thus $\|K\|^2 \leq \|\hat{K}\|^2$, where

$$\hat{K}(t,\tau) \equiv \frac{1}{P_{\mathrm{B}}^{\mathrm{tot,eq}}} \iiint k\left[{}_{(t)}\mathbf{F}(\tau)\cdot\boldsymbol{\xi}\right] P_{\mathrm{A}}^{\mathrm{eq}}\left[{}_{(t)}\mathbf{F}(\tau)\cdot\boldsymbol{\xi}\right] d^3\boldsymbol{\xi}$$

$$= \frac{1}{P_{\mathrm{B}}^{\mathrm{tot,eq}}} \iiint k(\boldsymbol{\xi}) P_{\mathrm{A}}^{\mathrm{eq}}(\boldsymbol{\xi})\, d^3\boldsymbol{\xi}$$

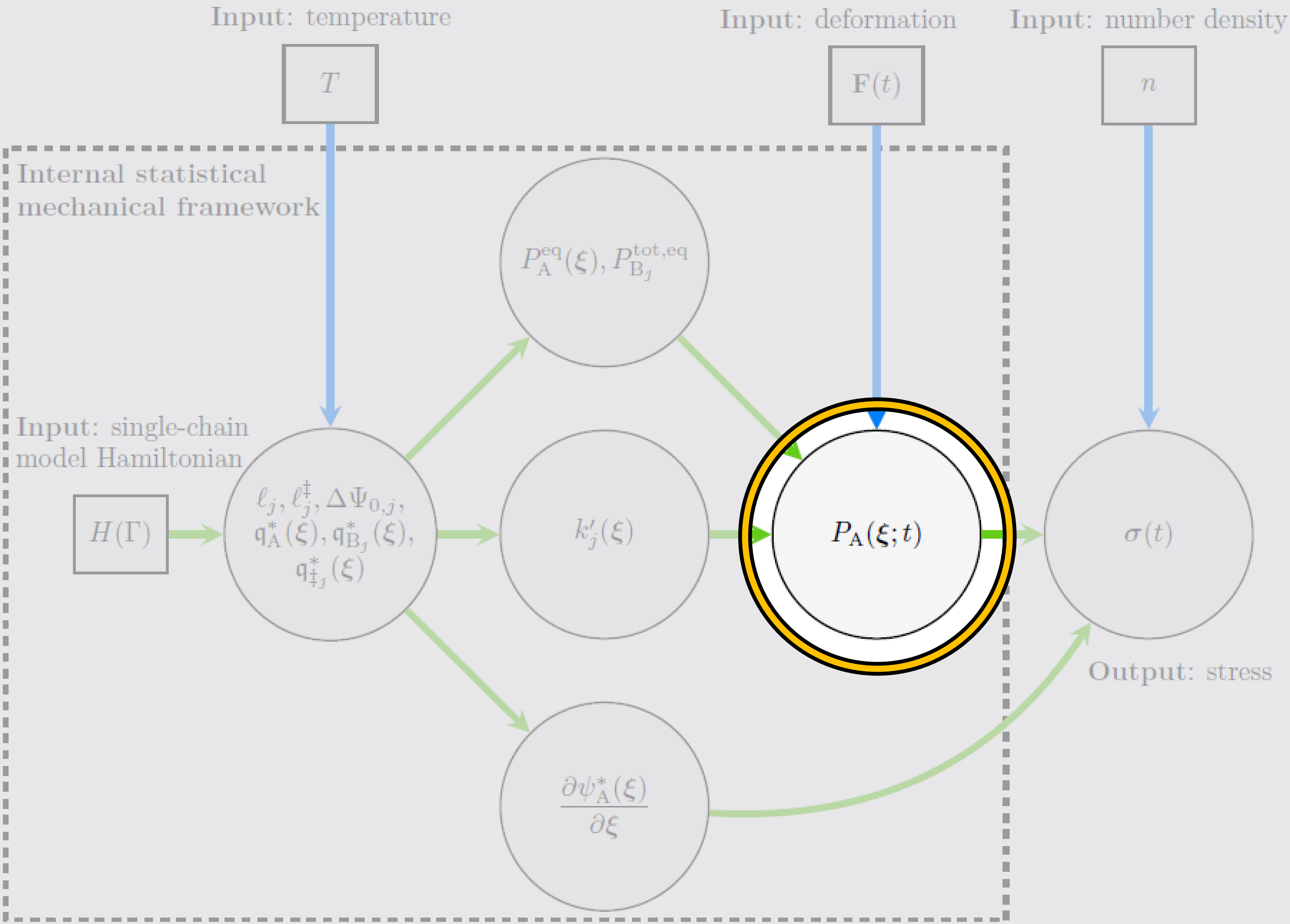
since $d^3\boldsymbol{\xi}$ is invariant under ${}_{(t)}\mathbf{F}(\tau)\cdot\boldsymbol{\xi} \rightarrow \boldsymbol{\xi}$ due to incompressibility

If we follow the framework, this is $\mathfrak{b}T\mathfrak{q}_{\ddagger}/\mathfrak{q}_{\mathrm{B}} < \infty$ (true)
Otherwise, acts as a rule.

$$P_{\mathrm{A}}(\boldsymbol{\xi};t) = P_{\mathrm{A}}\left[\mathbf{F}^{-1}(t)\cdot\boldsymbol{\xi};0\right] \Xi(\boldsymbol{\xi};t,0) + \int_0^t P_{\mathrm{A}}^{\mathrm{eq}}\left[{}_{(t)}\mathbf{F}(\tau)\cdot\boldsymbol{\xi}\right] \frac{\partial \Xi(\boldsymbol{\xi};t,\tau)}{\partial\tau}\rho(\tau)\, d\tau$$

$$\boldsymbol{\sigma}(t) = n \iiint P_{\mathrm{A}}(\boldsymbol{\xi};t) \frac{\partial \psi_{\mathrm{A}}^*(\boldsymbol{\xi})}{\partial\boldsymbol{\xi}} \boldsymbol{\xi}\, d^3\boldsymbol{\xi} - p(t)\mathbf{1}$$

R. P. Kanwal. Linear Integral Equations. Springer Science & Business Media, New York, 2013.
M. Rahman. Integral Equations and Their Applications. WIT press, Boston, MA, 2007.
J. A. Cochran. The Analysis of Linear Integral Equations. McGraw-Hill, New York, 1972.
Buche and Silberstein, J. Mech. Phys. Solids 156, 104593 (2021).



Buche and Silberstein, J. Mech. Phys. Solids 156, 104593 (2021).

Single-chain model

uFJC model, with Hamiltonian

$$H(\Gamma) = \sum_{i=1}^{N_b+1} \frac{p_i^2}{2m} + \sum_{i=1}^{N_b} u(\ell_i)$$

Nondimensional variables

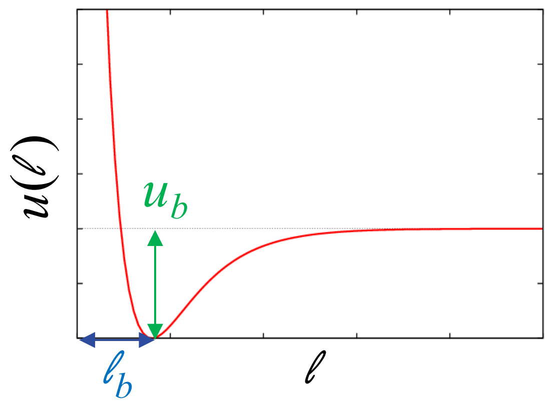
$$\eta \equiv \beta f \ell_b \qquad \kappa \equiv \beta \ell_b^2 \left.\frac{\partial^2 u(\ell)}{\partial \ell^2}\right|_{\ell=\ell_b}$$

$$\gamma \equiv \xi / N_b \ell_b$$

Langevin function

$$\mathcal{L}(\eta) = \coth(\eta) - 1/\eta$$

Morse potential



Low forces, stiff bonds

Harmonic potential mechanical response

$$\gamma_{\mathrm{EFJC}}(\eta) = \mathcal{L}(\eta) + \frac{\eta}{\kappa}\left[1 + \frac{1 - \mathcal{L}(\eta)\coth(\eta)}{1 + (\eta/\kappa)\coth(\eta)}\right]$$

Fiasconaro and Falo, *Physica A*, **532**, p. 121929 (2019).

First-order asymptotic approximation (stiff bonds)

$$\gamma_{\mathrm{EFJC}}(\eta) \sim \mathcal{L}(\eta) + \frac{\eta}{\kappa}\left[2 - \mathcal{L}(\eta)\coth(\eta)\right] \quad \text{for } \kappa \gg 1.$$

For small forces and stiff bonds, uFJC has the same

$$\gamma(\eta) \sim \mathcal{L}(\eta) + \frac{\eta}{\kappa}\left[2 - \mathcal{L}(\eta)\coth(\eta)\right] \quad \text{for } \kappa \gg 1 \text{ and } \eta \ll 1.$$

High forces, stiff bonds

For large forces, direct bond stretching

$$\gamma(\eta) \sim \lambda(\eta) \quad \text{for } \kappa \gg 1 \text{ and } \eta \gg 1,$$

$$\eta = \beta \ell_b \left.\frac{\partial u(\ell)}{\partial \ell}\right|_{\ell=\ell_b\lambda(\eta)}$$

Buche and Silberstein, J. Mech. Phys. Solids 156, 104593 (2021).

Single-chain model

Asymptotic matching (Prandtl's method)

$$\lim_{\eta\to\infty} \gamma_{\eta\ll 1}(\eta) = \lim_{\eta\to 0} \gamma_{\eta\gg 1}(\eta).$$

First-order approximation

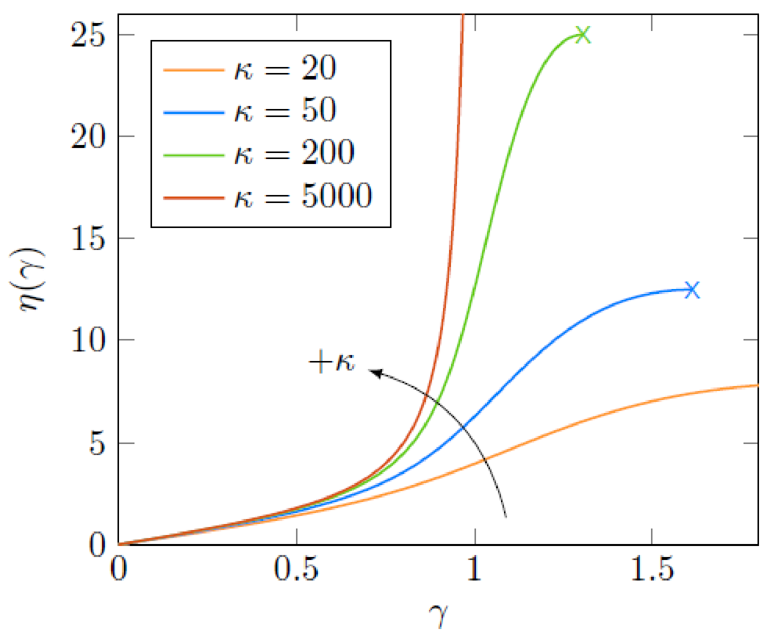
$$\gamma_1(\eta) \sim \mathcal{L}(\eta) + \frac{\eta}{\kappa}\left[1 - \mathcal{L}(\eta)\coth(\eta)\right] + \lambda(\eta) - 1 \quad \text{for } \kappa \gg 1.$$

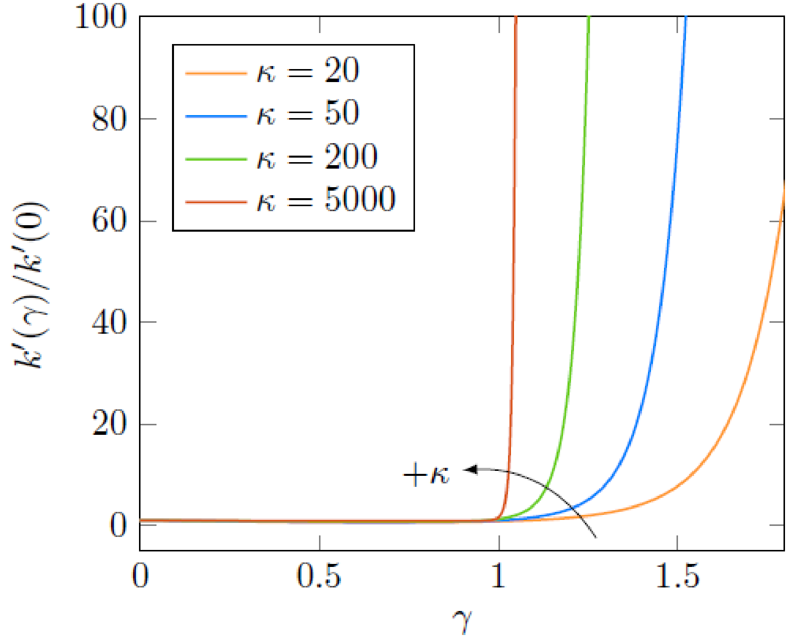
For sufficiently large stiffness, insignificant term

$$\Big|\eta[1 - \mathcal{L}(\eta)\coth(\eta)]\Big| \leq 1 \quad \text{for all } \eta,$$

Simplest approximation

$$\boxed{\gamma(\eta) \sim \mathcal{L}(\eta) + \lambda(\eta) - 1 \quad \text{for } \kappa \gg 1,}$$





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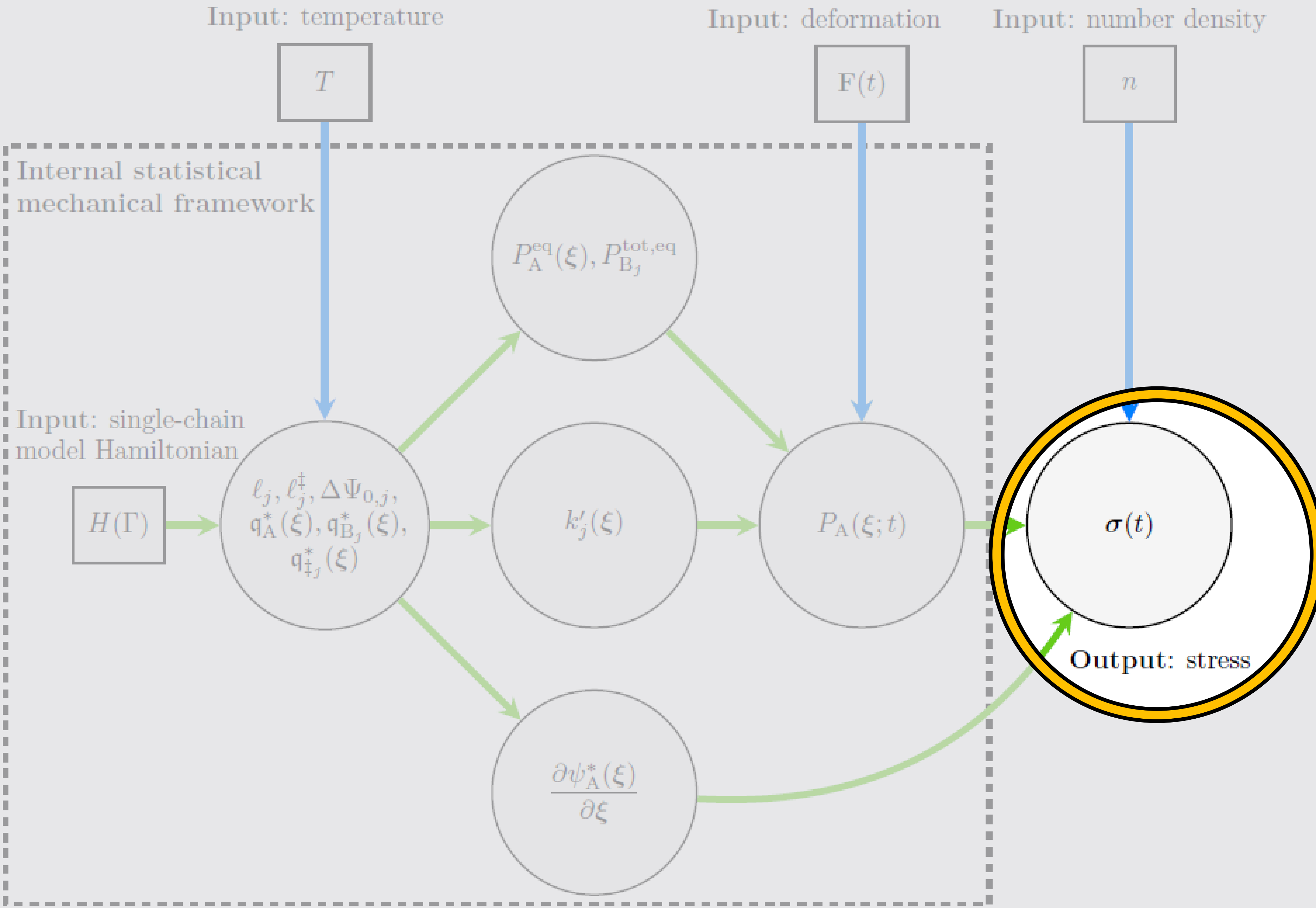
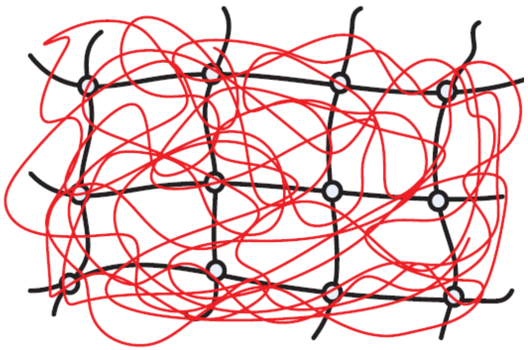


Buche and Silberstein, J. Mech. Phys. Solids 156, 104593 (2021).

Modeling multinetwork elastomer



Lavoie, Millereau, Creton, Long, Tang,
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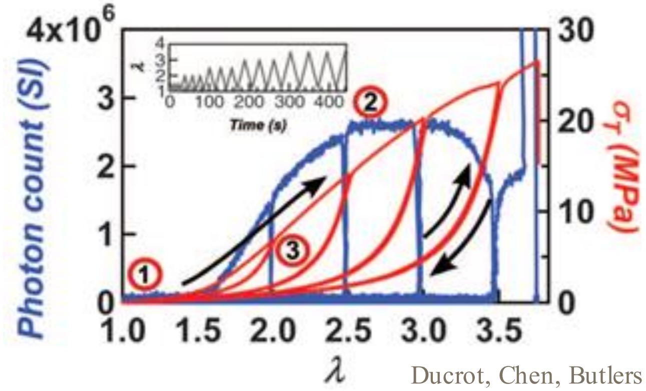
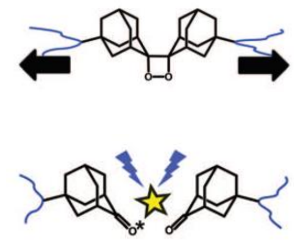




Ducrot, Chen, Butlers, Sijbesma, Creton, Science, **344**, p. 186, 2014.

Rate-independent irreversible breaking

Specialized solution

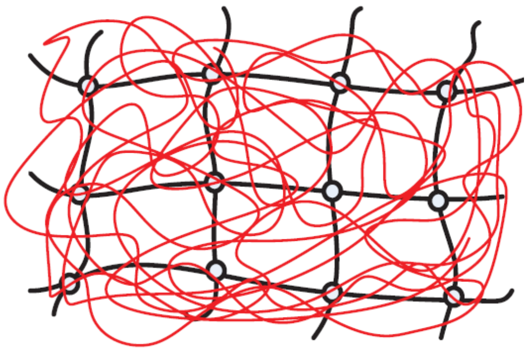
$$P_{\mathrm{A}}(\xi;t) = P_{\mathrm{A}}^{\mathrm{eq}}\left[\mathbf{F}^{-1}(t)\cdot\xi\right]\Theta(\xi;t,0)$$

Reaction propagator becomes yield function

$$\Theta(\xi;t,\tau) \equiv \begin{cases} 1, & \left\|{}_{(t)}\mathbf{F}(s)\cdot\xi\right\|_2 \leq \xi_c \quad \forall s\in[\tau,t], \\ 0, & \text{otherwise.} \end{cases}$$

Ducrot, Chen, Butlers, Sijbesma, Creton, Science, **344**, p. 186, 2014.
Buche and Silberstein, J. Mech. Phys. Solids 156, 104593 (2021).

Modeling multinetwork elastomer



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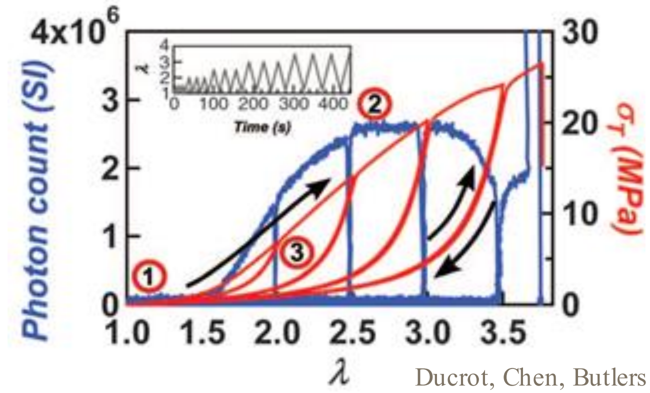

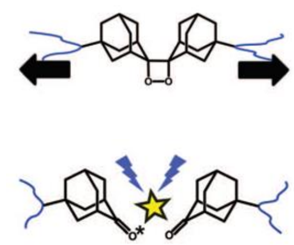

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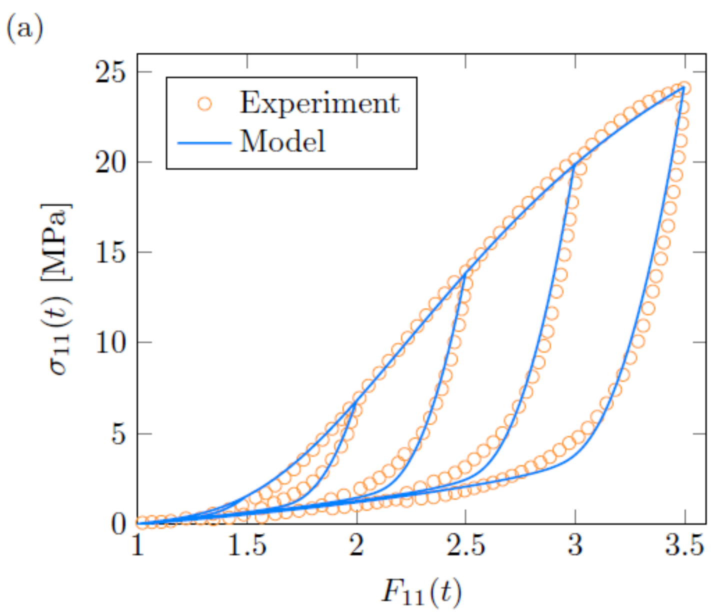

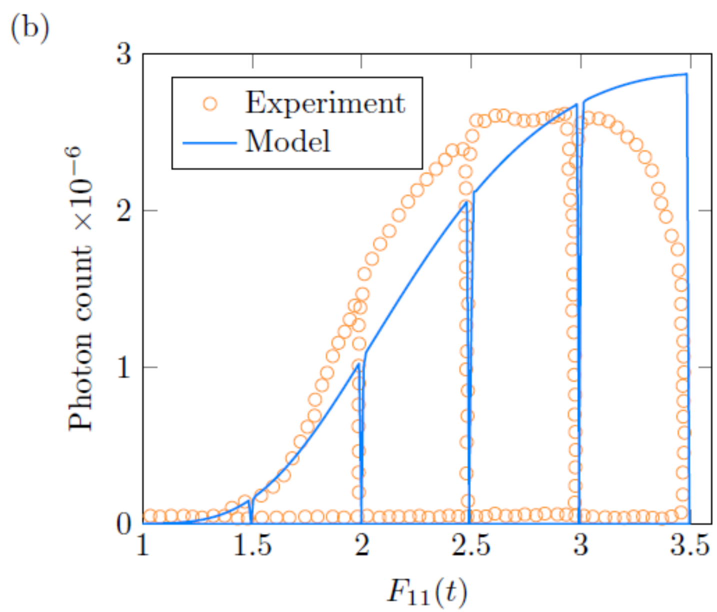

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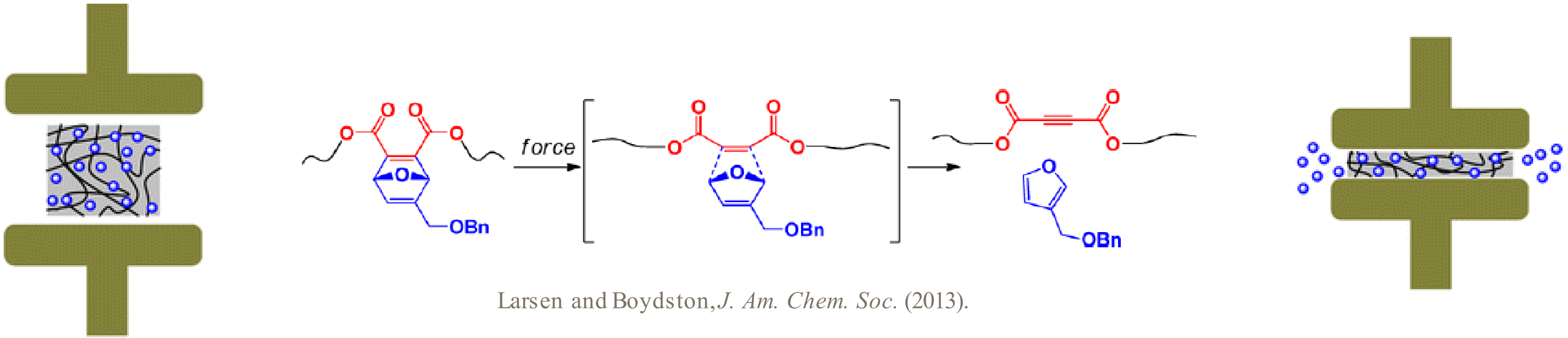
Modeling molecular release in a gel



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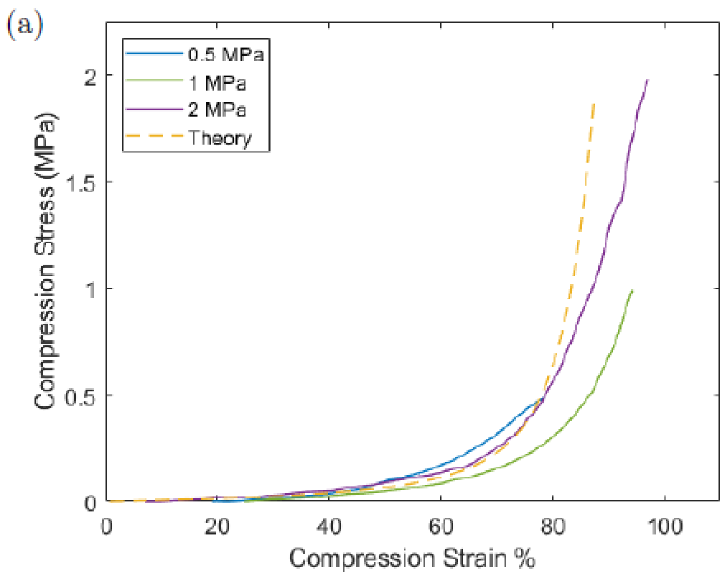

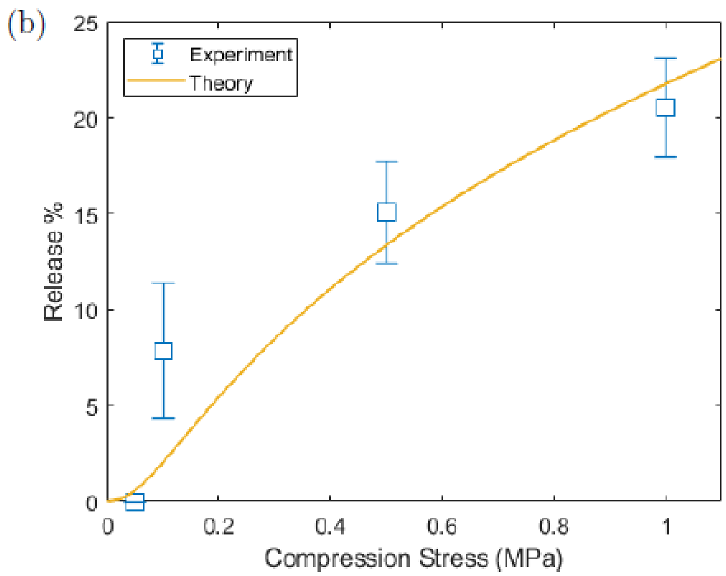

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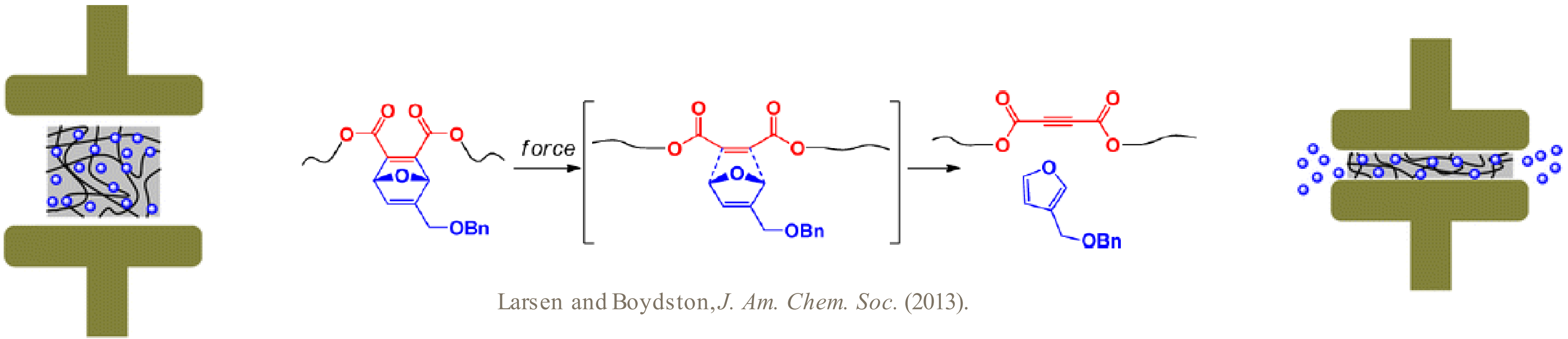

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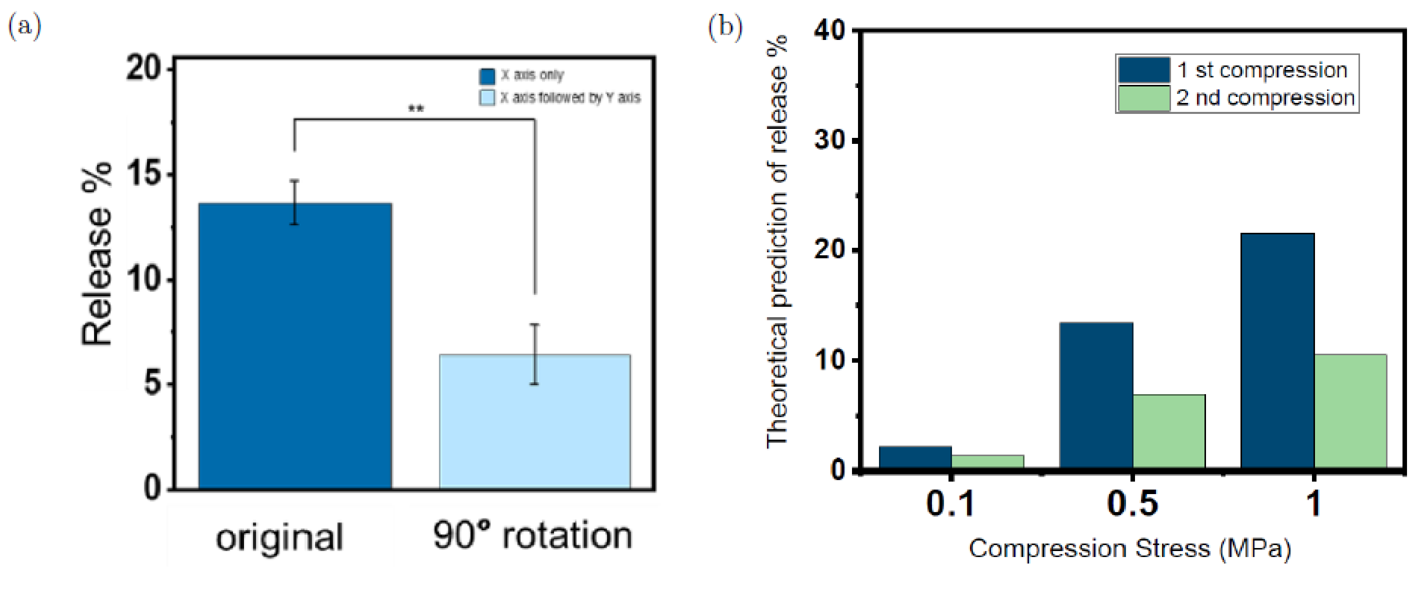

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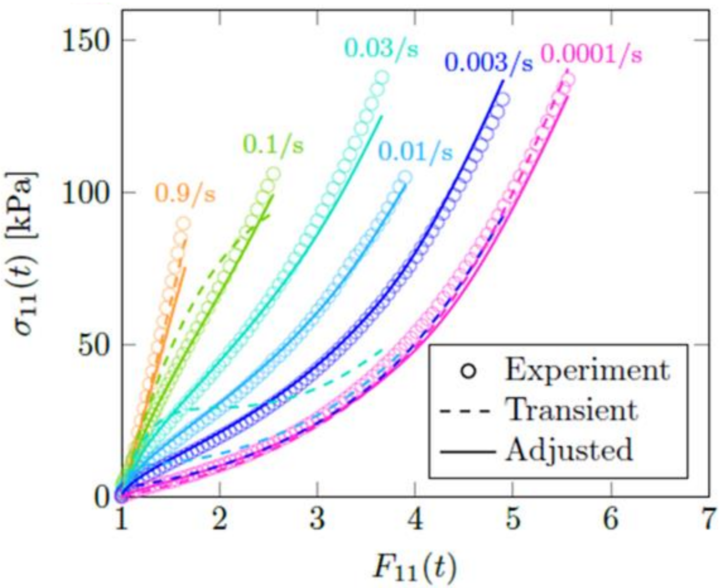
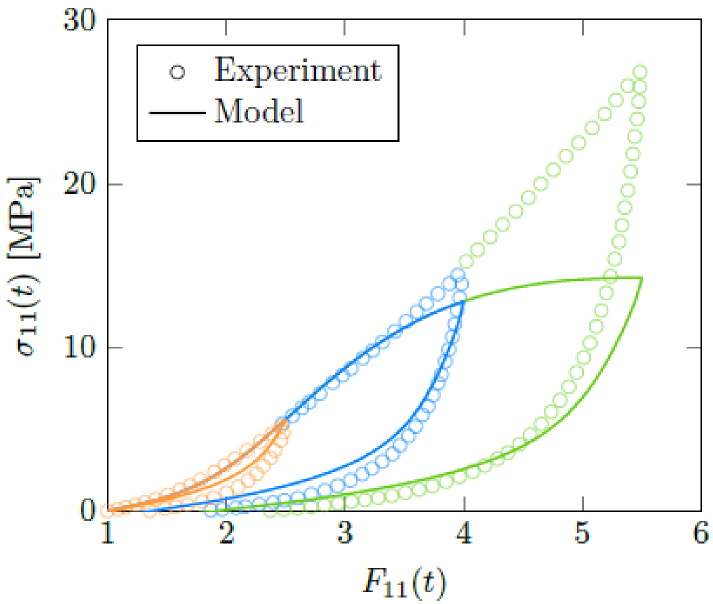
Outlook

- Single linear timescale of transient breaking
  - Sufficient in a limited capacity
  - **Future:** many timescales, and/or revisiting TST
- Dissipation not from bond breaking
  - Sometimes significant. Distinction: lack of droop.
  - **Future:** viscous stresses (chain slippage, etc.)
- Other important future avenues
  - Breaking-induced network alteration
  - Non-trivial reforming
  - Non-affine swelling/deformation

Overall, the approach is a robust method for macroscale constitutive models in terms of molecular functions and parameters





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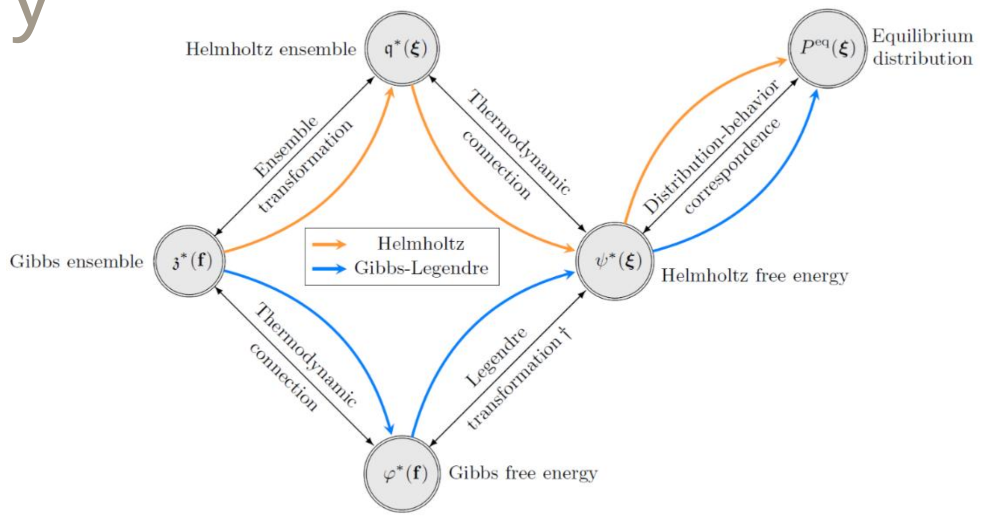
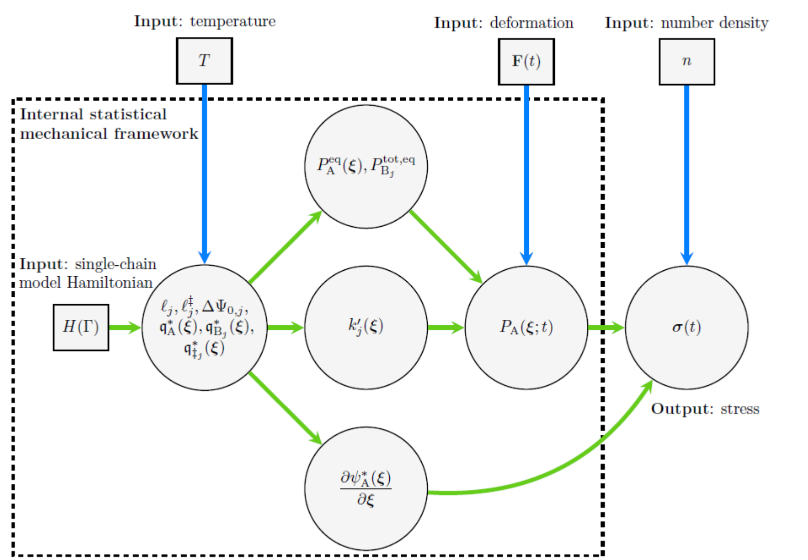
Presentation summary

- **Single polymer chain mechanics**
  - Single-chain mechanical response
  - Equilibrium distribution of chains
  - Extension-dependent reaction rates

- **Polymer network mechanics**
  - Exactly-solved evolution equations
  - Constitutive theory (stress, dissipation inequality)
  - Informed almost entirely by single-chain model

- **Elastomer constitutive models**
  - General (force-driven reversible breaking)
  - Special cases
    - Absence of bond breaking
    - Irreversible bond breaking
    - Transient bond breaking
    - Intact after reaction





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Publications

Primary

1. Vidavsky, Yuval*, **Michael R. Buche***, Zachary M. Sparrow, Xinyue Zhang, Steven J. Yang, Robert A. DiStasio, Meredith N. Silberstein. Tuning the mechanical properties of metallopolymers via ligand interactions: a combined experimental and theoretical study. *Macromolecules*, **53**, 2021-2030 (2020). *Denotes equal contribution.
2. **Buche, Michael R.**, and Meredith N. Silberstein. Statistical mechanical constitutive theory of polymer networks: the inextricable links between distribution, behavior, and ensemble. *Physical Review E*, **102**, 012501 (2020).
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Secondary

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2. P. B. Jayathilaka, T. G. Molley, Y. Haung, M. S. Islam, **M. R. Buche**, M. N. Silberstein, J. J. Kruzic, and K. A. Kilian. Force-mediated molecule release from double network hydrogels. Submitted to *Chemical Communications* (2021).

Presentations

Conferences

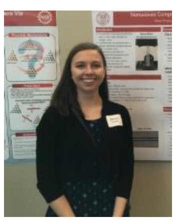
1. APS March Meeting 2019
2. MechanoChemBio (poster)
3. Society of Engineering Science 2019

Other seminars

1. Cornell mechanics colloquium
2. A Exam
3. Sandia job interviews (x2)

Acknowledgements

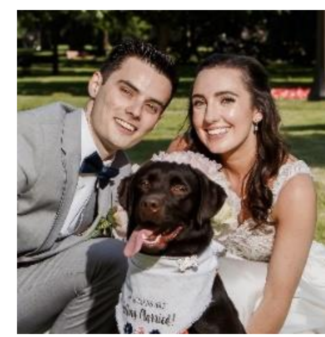








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