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An asymptotic approach for the statistical thermodynamics of certain model systems

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Abstract

Configuration integrals

- Vital for analytic modeling in statistical thermodynamics
- Difficult, if not impossible to obtain in most cases

Certain model systems

- Approximated by replacing steep potentials with athermal rigid constraints
  - Often inadequate, especially when modeling molecular stretching

An asymptotic approach

- Systematically builds upon the approximation provided by the (rigid) reference system
  - Low-temperature analog of Zwanzig's high-temperature perturbation theory [1]
- Here, the asymptotic theory [2] and several successful applications [3-8] are reviewed

[1] Zwanzig, Robert W. High-temperature equation of state by a perturbation method. I. Nonpolar gases. J. Chem. Phys. **22**, 1420 (1954).
[2] Buche, Michael R. *Fundamental Theories for the Mechanics of Polymer Chains and Networks*. Cornell University (2021).

Outline

- Theoretical background
  - General asymptotic theory
  - Three-dimensional harmonic oscillator
- Applications and results
  - Freely jointed chain models with extensible links
  - A statistical mechanical model for crack growth
  - Modeling single-molecule stretching experiments
- Conclusion
- Acknowledgements

General asymptotic theory

Canonical partition function (full system)

$$Q = \int d\Gamma_0 \int dX \; e^{-\beta H_0(\Gamma_0;X)} \; e^{-\beta U_1(X)}$$

Canonical partition function (reference system)

$$Q_0(X) = \int d\Gamma_0 \; e^{-\beta H_0(\Gamma_0;X)}$$

Rewrite canonical partition function (full system)

$$Q = \int dX \; Q_0(X) \; e^{-\beta U_1(X)}$$

Steep potentials ($|\varepsilon_j| \gg 1, \; \kappa_j \gg 1$) minimized at $\hat{x}_j$

$$U_1(X) = \sum_{i=1}^{M} u_i(x_i) \qquad \varepsilon_j \equiv \beta u_j(\hat{x}_j) \qquad \kappa_j \equiv \beta u_j''(\hat{x}_j)$$

Asymptotic approximation via Laplace's method [2]

Reference system

$$Q \sim \underbrace{Q_0(\hat{X}) \left(\prod_{j=1}^{M} \sqrt{\frac{2\pi}{\kappa_j}} \, e^{-\varepsilon_j} \right)}_{\text{Leading order approximation}} \underbrace{\left[1 + \sum_{j=1}^{M} \frac{h_j}{\kappa_j} + \text{ord}\left(\kappa_j^2\right) \right]}_{\text{Corrections}}$$

$$h_j = \frac{1}{2Q_0} \left[\frac{\partial^2 Q_0}{\partial x_j^2} - \frac{\kappa_j'}{\kappa_j} \frac{\partial Q_0}{\partial x_j} \right] - \frac{1}{8} \frac{\kappa_j''}{\kappa_j} + \frac{5}{24} \left(\frac{\kappa_j'}{\kappa_j} \right)^2$$

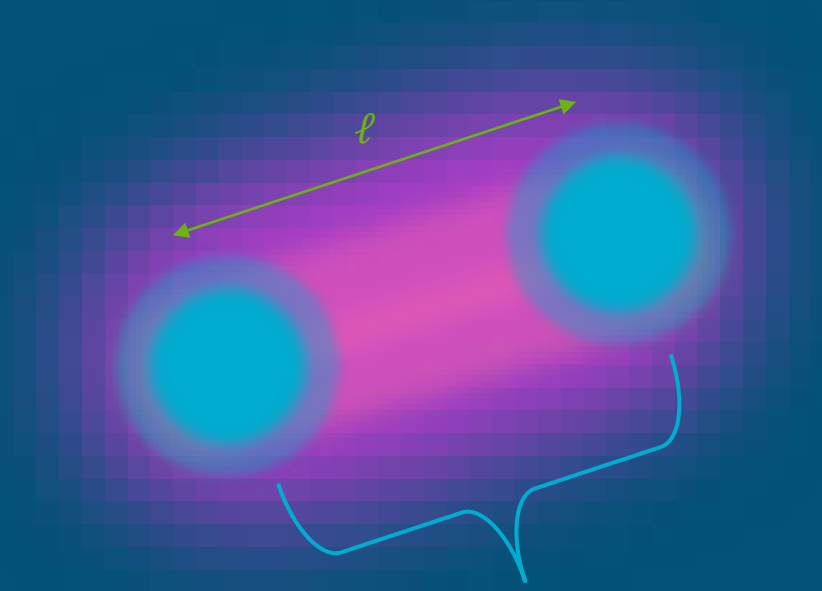
[2] Buche, Michael R. *Fundamental Theories for the Mechanics of Polymer Chains and Networks*. Cornell University (2021).

Three-dimensional harmonic oscillator

Asymptotic approximation, valid for $\kappa \gg 1$

Reference system (rigid rotor) $q_0(\ell) = 4\pi\ell^2$

$$q \sim \underbrace{q_0(\ell_b)\,\ell_b\sqrt{\frac{2\pi}{\kappa}}}_{\text{Leading order approximation (rigid-rotor-harmonic-oscillator)}}\underbrace{\left[1+\frac{1}{\kappa}\right]}_{\text{First order correction (rotation-vibration coupling)}}$$



Compare to the exact result

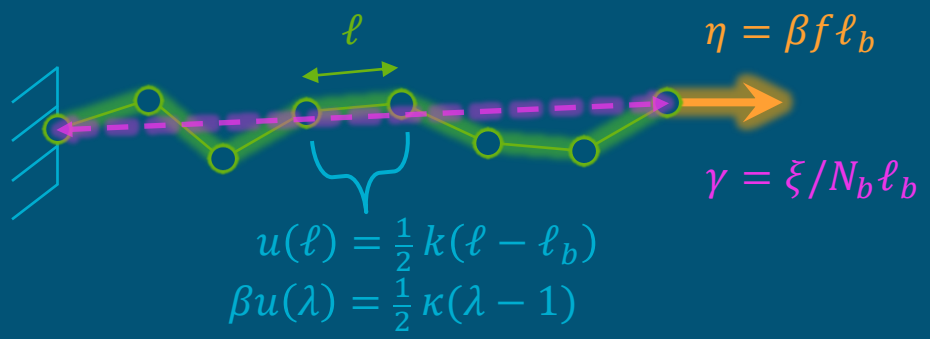
$$q = 4\pi\ell_b^3\left\{\frac{e^{-\kappa/2}}{\kappa} + \sqrt{\frac{\pi}{2\kappa}}\left(1+\frac{1}{\kappa}\right)\left[2-\operatorname{erfc}\left(\sqrt{\frac{\kappa}{2}}\right)\right]\right\}$$

$$= q_0(\ell_b)\,\ell_b\sqrt{\frac{2\pi}{\kappa}}\left[1+\frac{1}{\kappa}+\underbrace{\operatorname{ord}\left(e^{-\kappa/2}\right)}_{\text{Additional corrections are transcendentally small in this case}}\right]$$

For some anharmonic potential
- Same leading order approximation
- Anharmonic vibration corrections at first order
- Additional terms not transcendentally small

[2] Buche, Michael R. *Fundamental Theories for the Mechanics of Polymer Chains and Networks*. Cornell University (2021).

Freely jointed chain models with extensible links



uFJC partition function, expected mechanical response

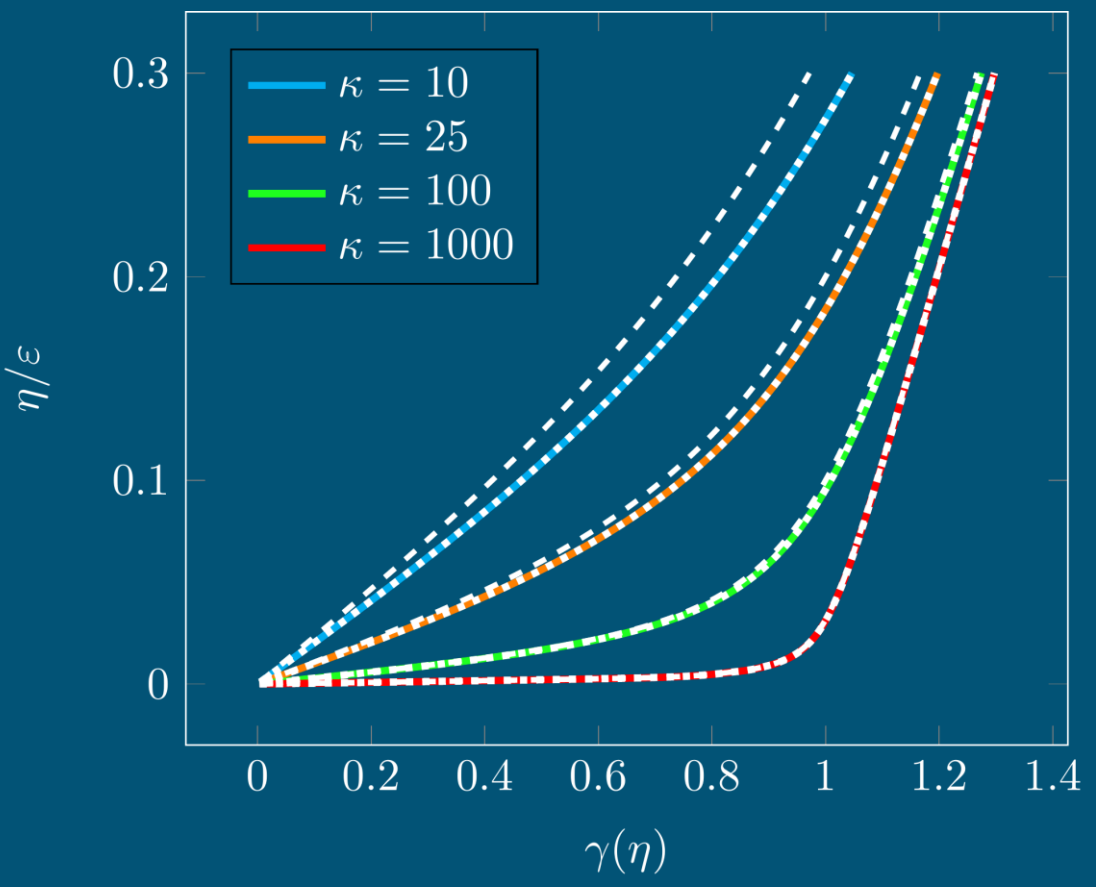
$$z(\eta) = \ell_b \int z_0(\eta, \lambda)\, e^{-\beta u(\lambda)}\, d\lambda, \qquad \gamma(\eta) = \frac{\partial \ln z}{\partial \eta}$$

FJC partition function

$$\gamma(\eta) \sim \mathcal{L}(\eta) + \frac{\eta}{\kappa}\left[\frac{1 - \mathcal{L}(\eta)\coth(\eta)}{c + (\eta/\kappa)\coth(\eta)}\right] + \Delta\lambda(\eta)$$

FJC mechanical response

η/κ



[3] Buche, Michael R., Silberstein, Meredith N., and Grutzik, Scott J. Freely jointed chain models with flexible links. Physical Review E **106**, 024502 (2022).
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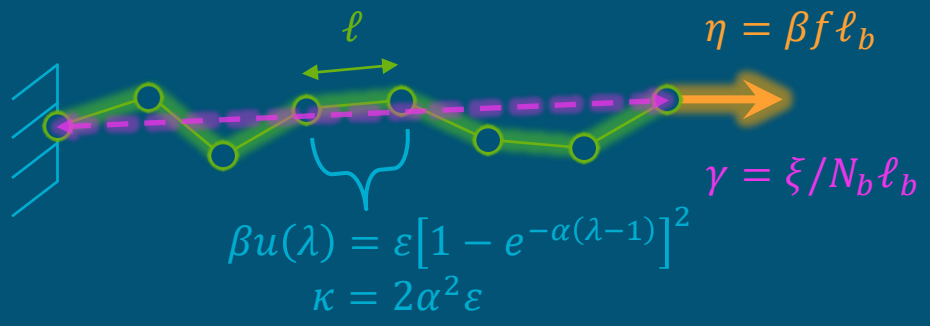
Freely jointed chain models with extensible links



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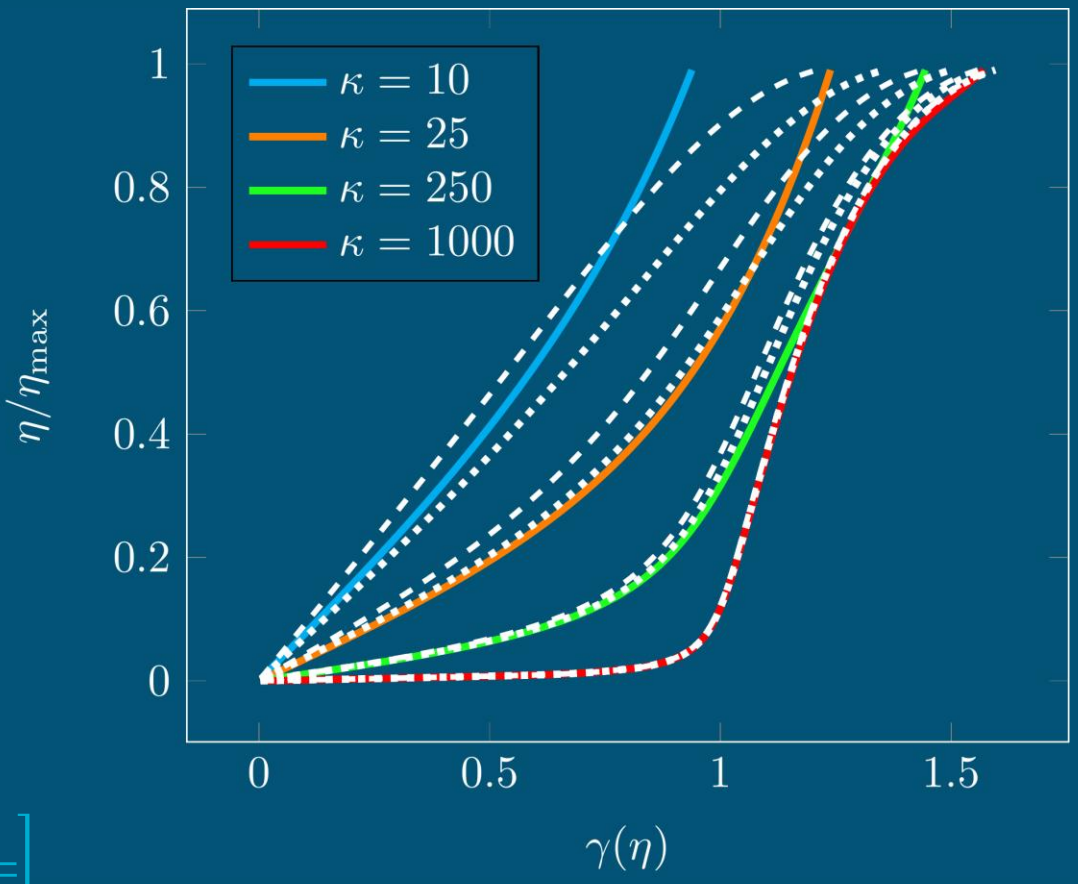
FJC mechanical response

$$\frac{1}{\alpha}\ln\left[\frac{2}{1 + \sqrt{1 - \frac{2\eta}{\alpha\varepsilon}}}\right]$$



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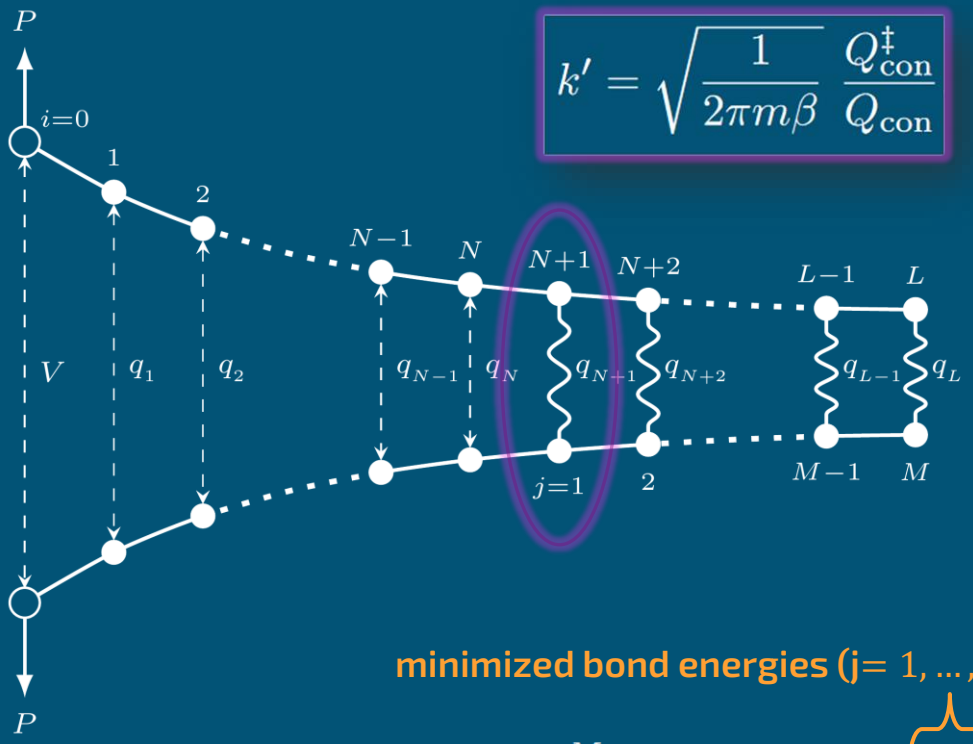
A statistical mechanical model for crack growth

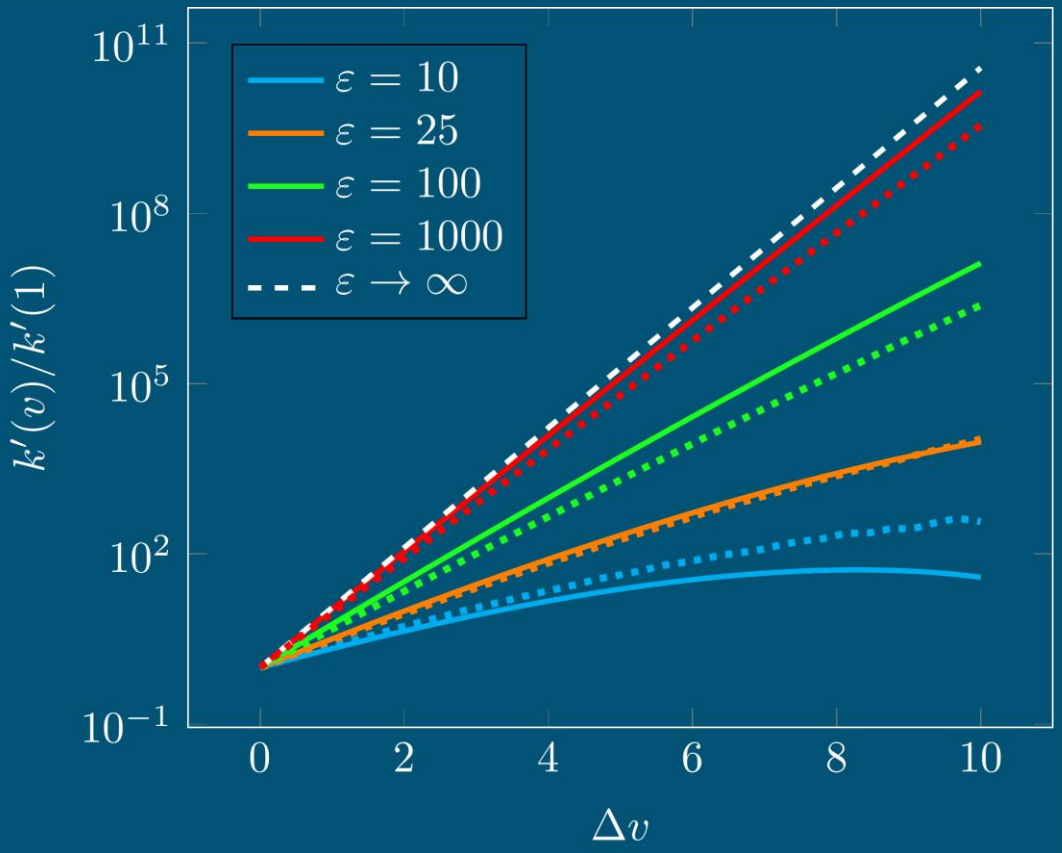


$$k' = \sqrt{\frac{1}{2\pi m\beta}}\,\frac{Q^{\ddagger}_{\mathrm{con}}}{Q_{\mathrm{con}}}$$

minimized bond energies (j= 1, … , M)

$$Q_{\mathrm{con}}(v) \sim Q_{0,\mathrm{con}}(v,\hat{\lambda}) \prod_{j=1}^{M} \sqrt{\frac{2\pi}{\beta u''(\hat{\lambda}_j)}}\, e^{-\beta u(\hat{\lambda}_j)}$$

bending crack faces ($i = 1, \dots, N$)



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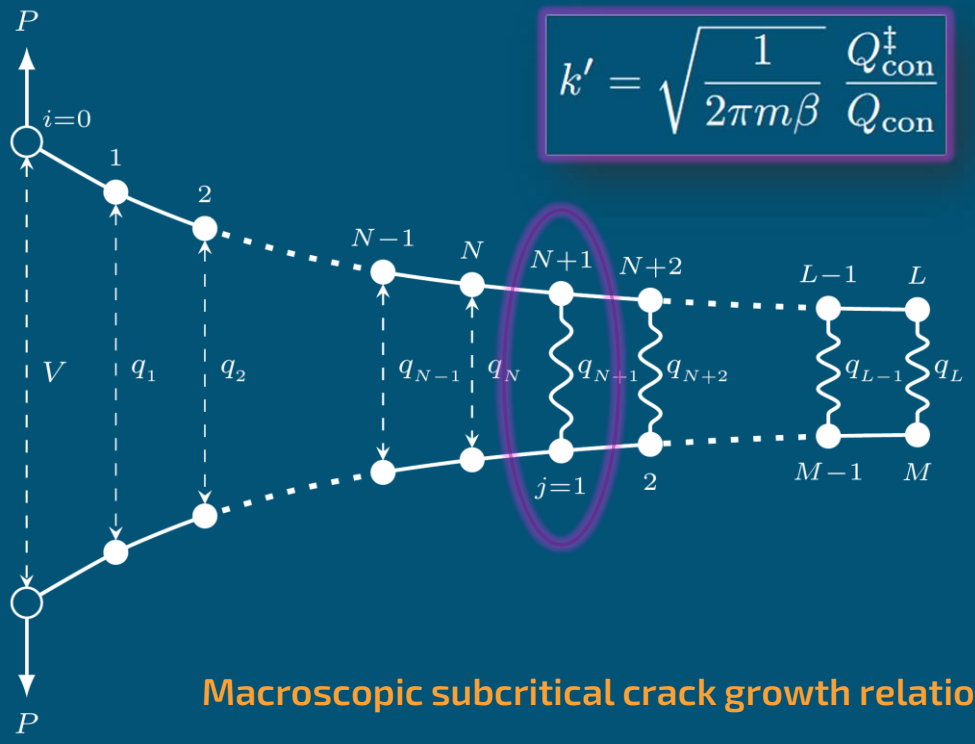
A statistical mechanical model for crack growth

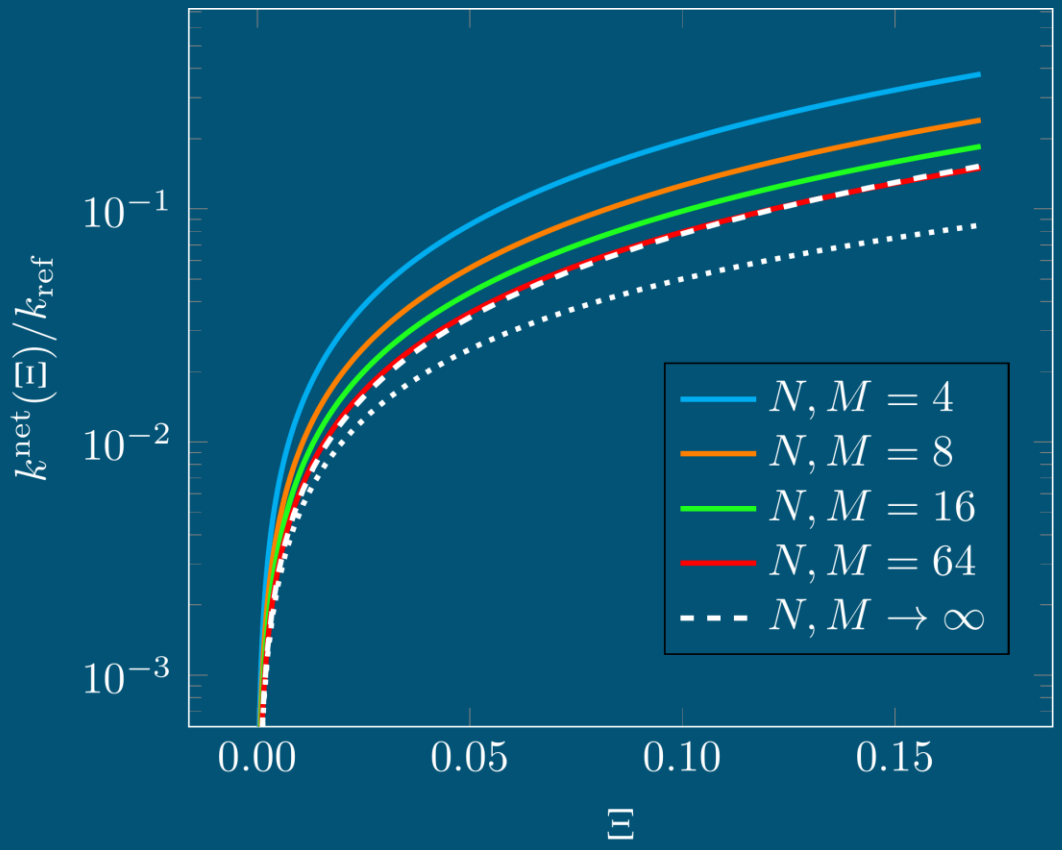


$$k' = \sqrt{\frac{1}{2\pi m\beta}}\,\frac{Q^{\ddagger}_{\mathrm{con}}}{Q_{\mathrm{con}}}$$

Macroscopic subcritical crack growth relation

$$k^{\mathrm{net}} \sim \frac{\omega_0}{\pi}\exp\left(\frac{f\Delta x^{\ddagger} - \Delta u^{\ddagger}}{kT}\right)\sinh\left(\frac{Rb^2}{2kT}\right)$$

$$f \equiv \sqrt{REb^3}$$



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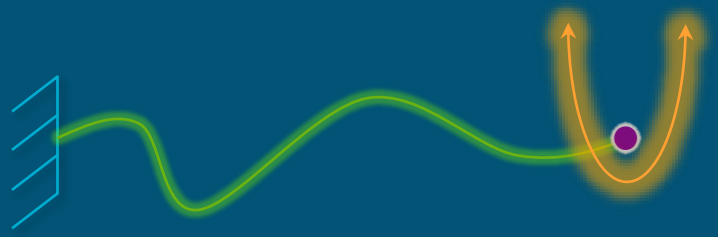
Modeling single-molecule stretching experiments

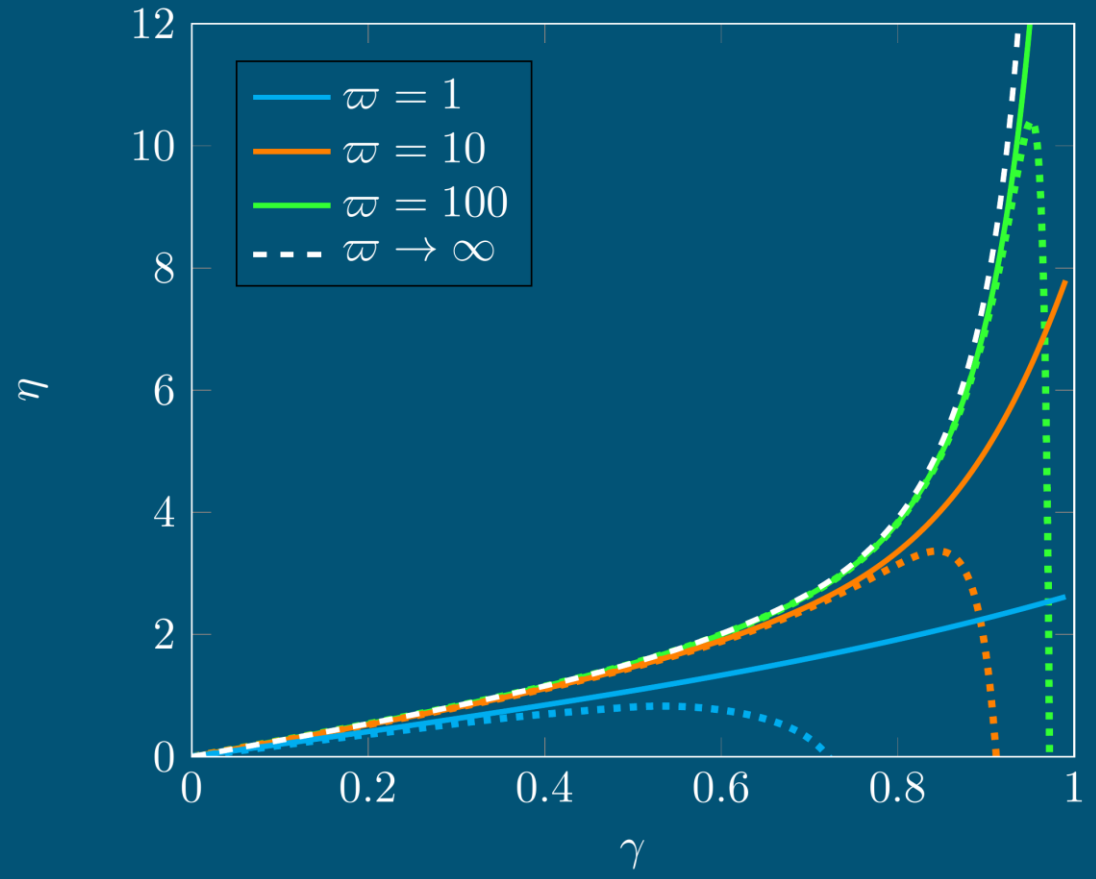


applied potential

$$Q(\gamma) = \iiint \underbrace{Q_0(\gamma')}_{\text{isometric partition function}} e^{-\overbrace{\frac{\varpi}{2} N_b^2 (\gamma - \gamma')^2}} d^3\gamma'$$

FJC model under strong potential

$$\eta(\gamma) \sim \underbrace{\eta_0(\gamma)}_{\text{isometric mechanical response}} - \frac{1}{N_b \varpi}\left[\eta_0(\gamma)\eta_0'(\gamma) - \frac{\eta_0''(\gamma)}{2N_b}\right]$$



[7] Buche, Michael R. and Jessica, Rimsza M. Modeling single-molecule stretching experiments using statistical thermodynamics. *In Preparation* (2023).
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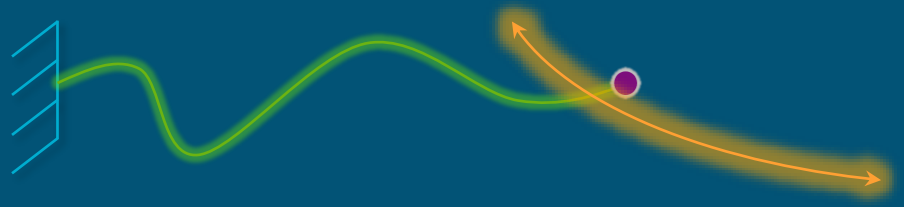
Modeling single-molecule stretching experiments

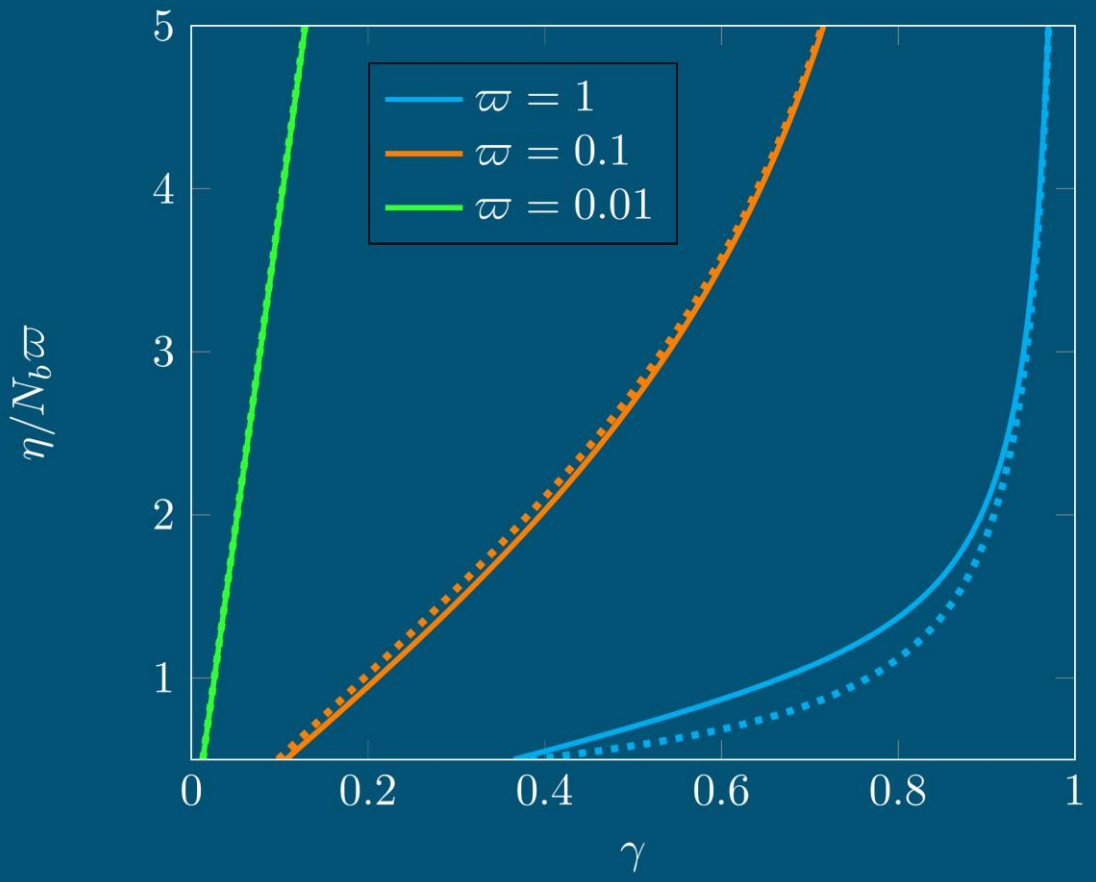


applied potential

$$Q(\gamma) = \iiint \underbrace{Q_0(\gamma')}_{\text{isometric partition function}} e^{-\frac{\varpi}{2} N_b^2 (\gamma - \gamma')^2} d^3\gamma'$$

FJC model under weak potential

$$\gamma(\eta) \sim \underbrace{\gamma_0(\eta)}_{\text{isotensional mechanical response}} \left[1 - N_b \varpi \gamma_0'(\eta)\right]$$



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Conclusion

- An asymptotic approach for statistical thermodynamics
  - Steep potentials (low temperatures)
  - Build upon a more easily solvable reference system
- Successful applications
  - Freely jointed chain models with extensible links
  - A statistical mechanical model for crack growth
  - Modeling single-molecule stretching experiments
- Future work
  - Many more model systems
  - Quantum statistical thermodynamics

Acknowledgements

Sibley School of Mechanical and Aerospace Engineering

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