# 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
  - 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]

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

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

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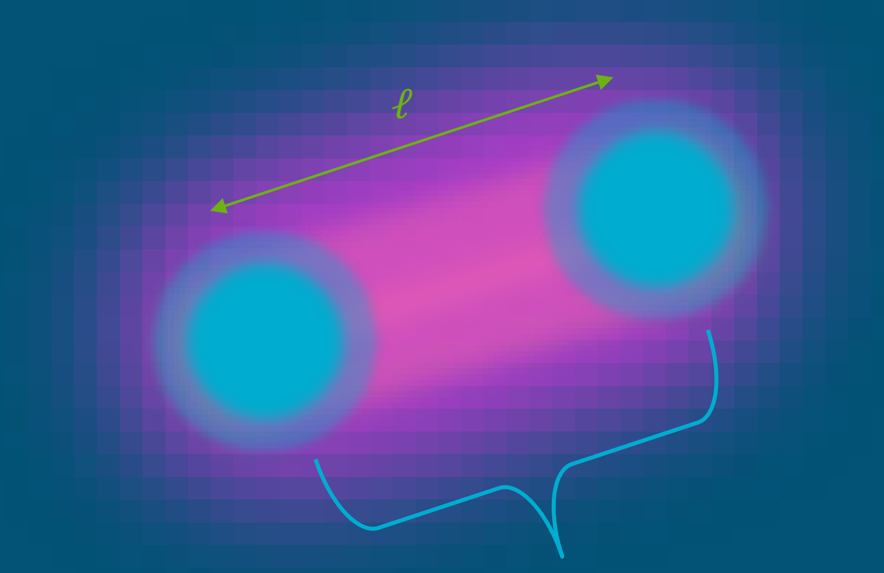
# Three-dimensional harmonic oscillator




$$u(\ell) = \tfrac{1}{2}k(\ell-\ell_b)$$
$$\beta u(\lambda) = \tfrac{1}{2}\kappa(\lambda-1)$$

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

$$q \sim \underbrace{\overbrace{q_0(\ell_b)}^{\text{Reference system (rigid rotor)}\quad q_0(\ell)=4\pi\ell^2}\,\ell_b\sqrt{\frac{2\pi}{\kappa}}}_{\text{Leading order approximation (rigid-rotor-harmonic-oscillator)}}\;\underbrace{\left[1+\frac{1}{\kappa}\right]}_{\text{First order correction (rotation-vibration coupling)}}$$

### 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

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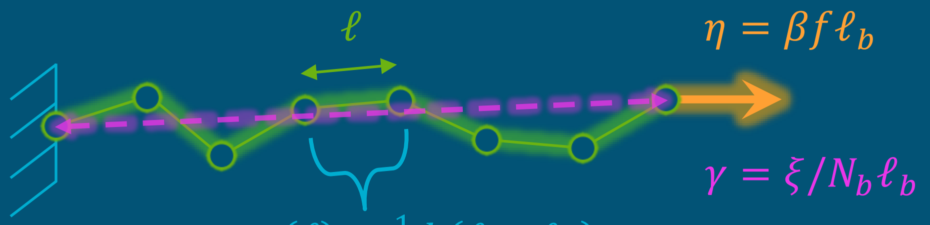
# Freely jointed chain models with extensible links

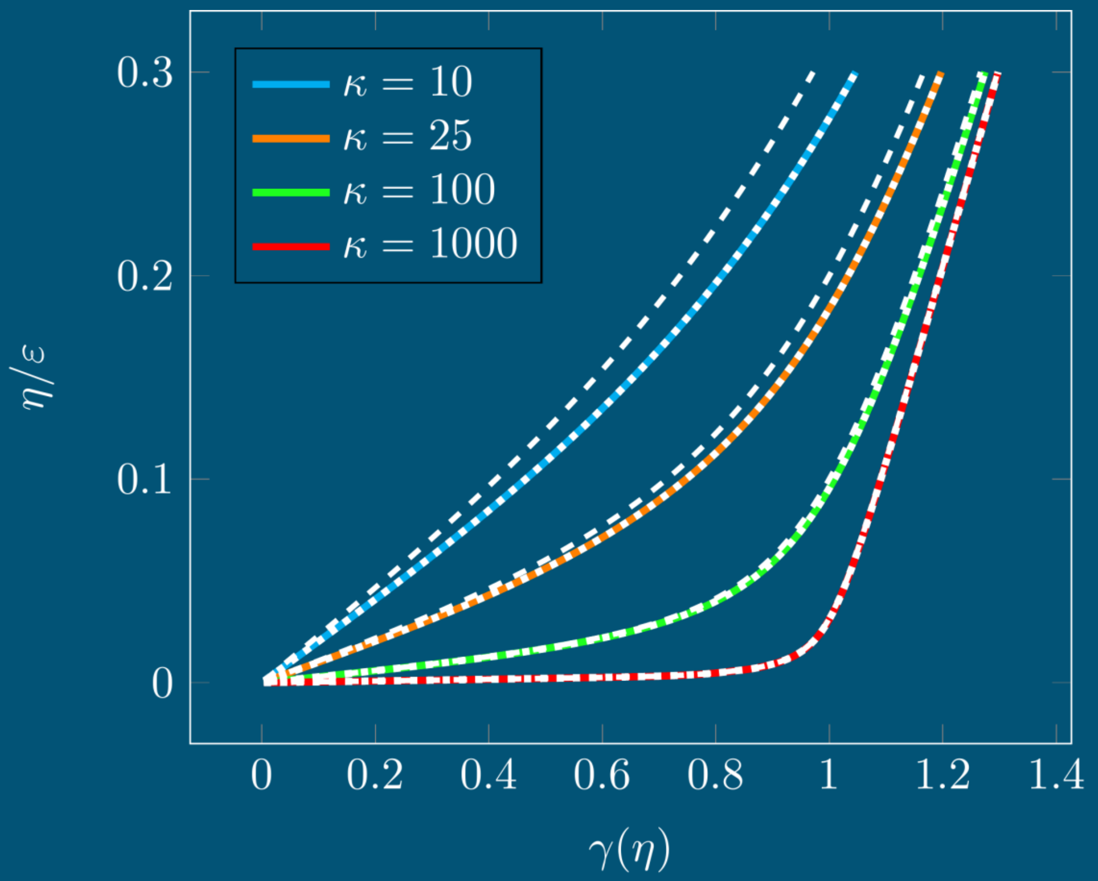



$$u(\ell) = \frac{1}{2} k(\ell - \ell_b)$$
$$\beta u(\lambda) = \frac{1}{2} \kappa(\lambda - 1)$$

**uFJC partition function, expected mechanical response**

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

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

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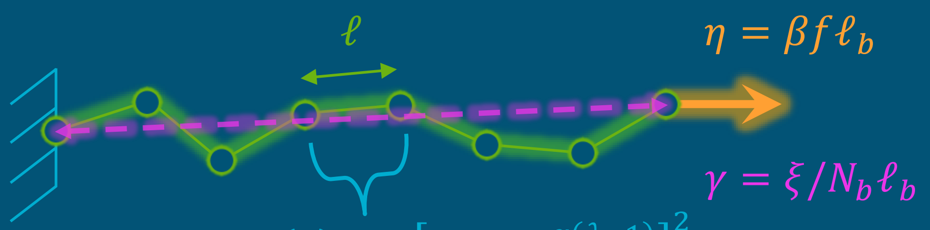
[4] Buche, Michael R. and Grutzik, Scott J. uFJC: the Python package for the uFJC single-chain model. Zenodo (2022).

# Freely jointed chain models with extensible links




$$\beta u(\lambda) = \varepsilon\left[1 - e^{-\alpha(\lambda-1)}\right]^2$$
$$\kappa = 2\alpha^2\varepsilon$$

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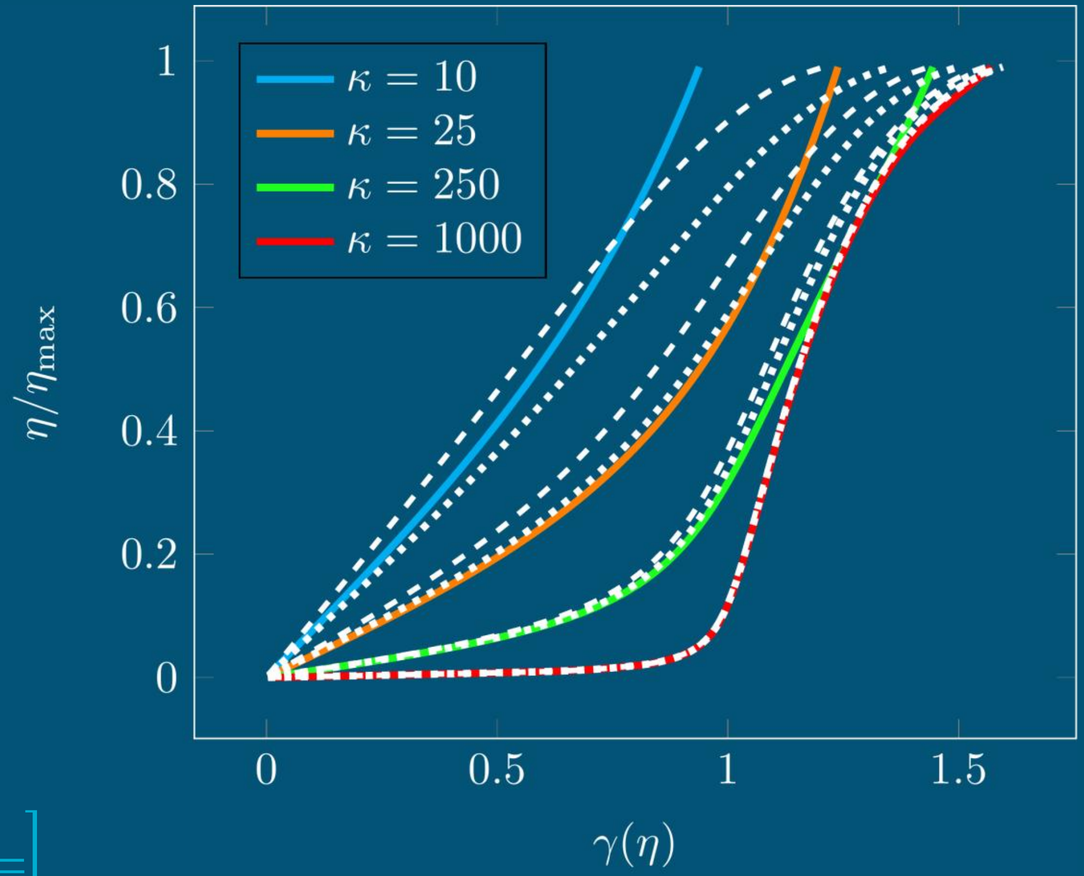



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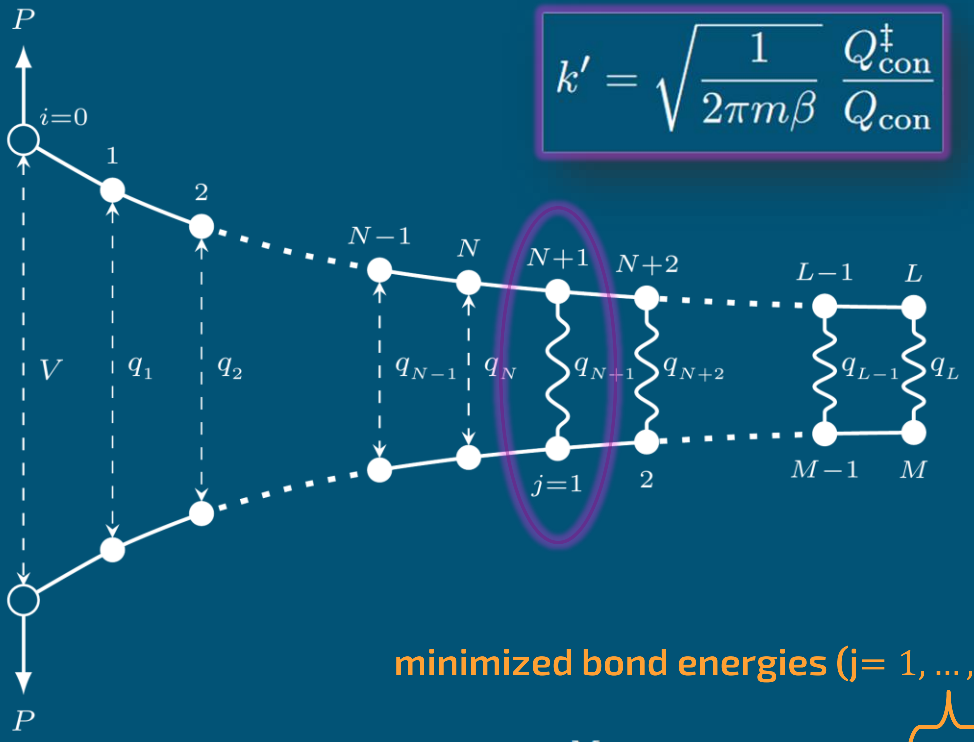
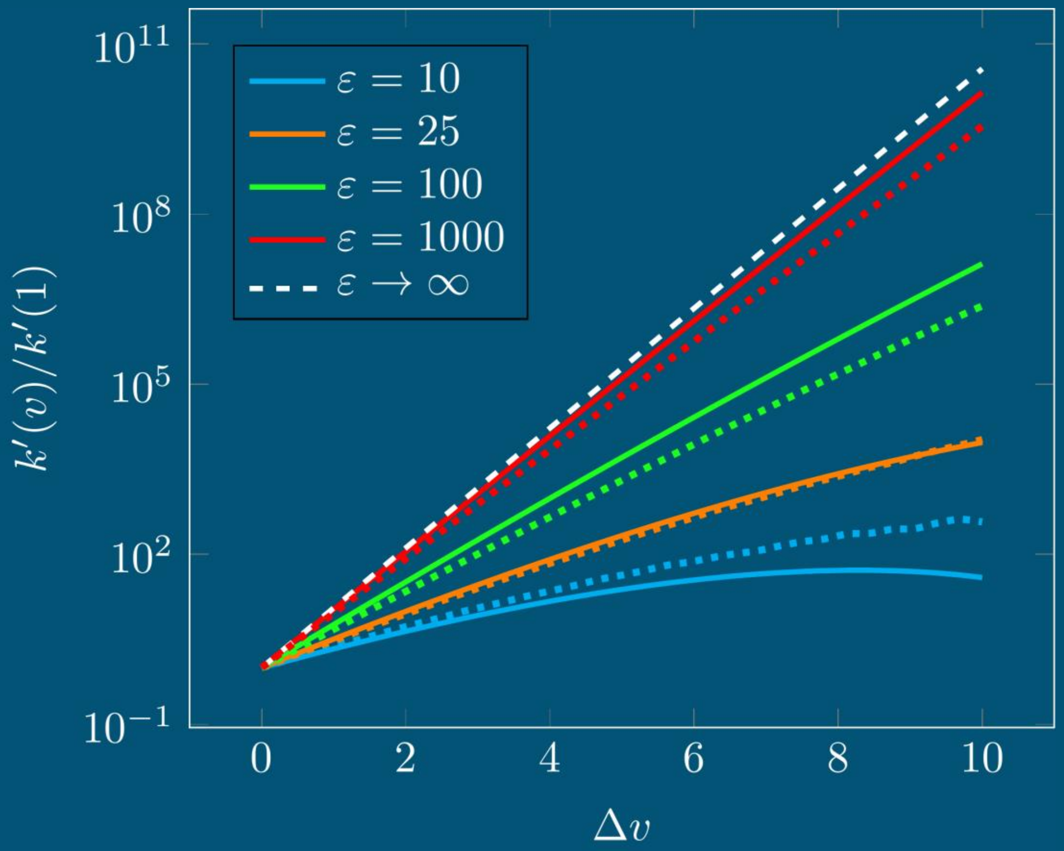
# Statistical mechanical model for crack growth




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

$$Q_{\mathrm{con}}(v) \sim \underbrace{Q_{0,\mathrm{con}}(v,\hat{\boldsymbol{\lambda}})}_{\text{bending crack faces } (i=1,\ldots,N)} \prod_{j=1}^{M} \sqrt{\frac{2\pi}{\beta u''(\hat{\lambda}_j)}}\, e^{-\beta \overbrace{u(\hat{\lambda}_j)}^{\text{minimized bond energies (j}=1,\ldots,M)}}$$





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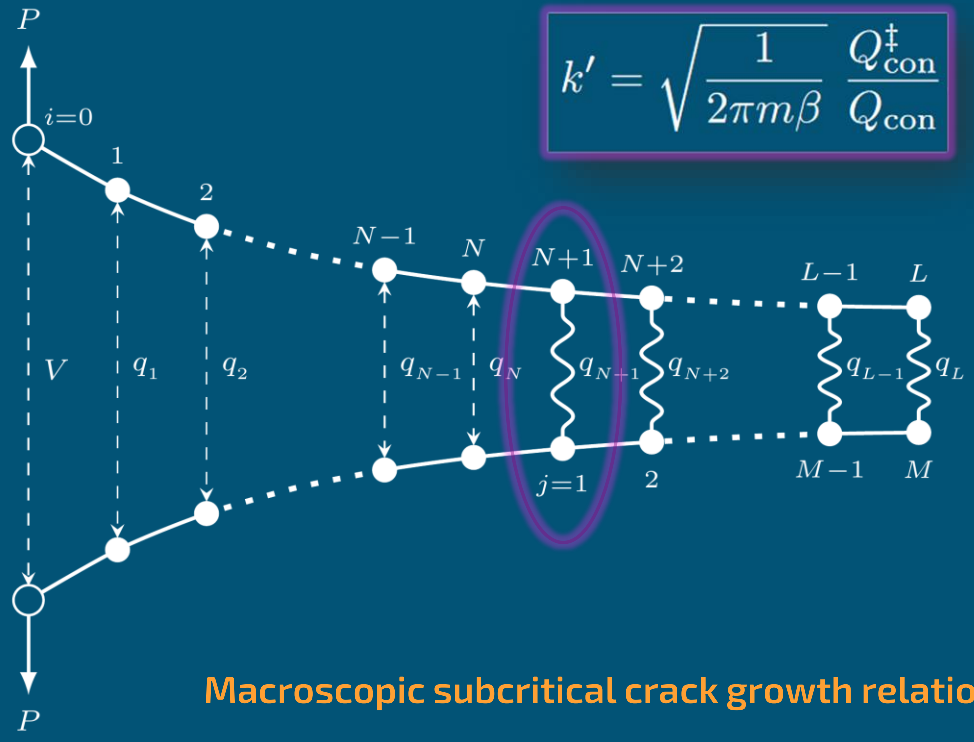
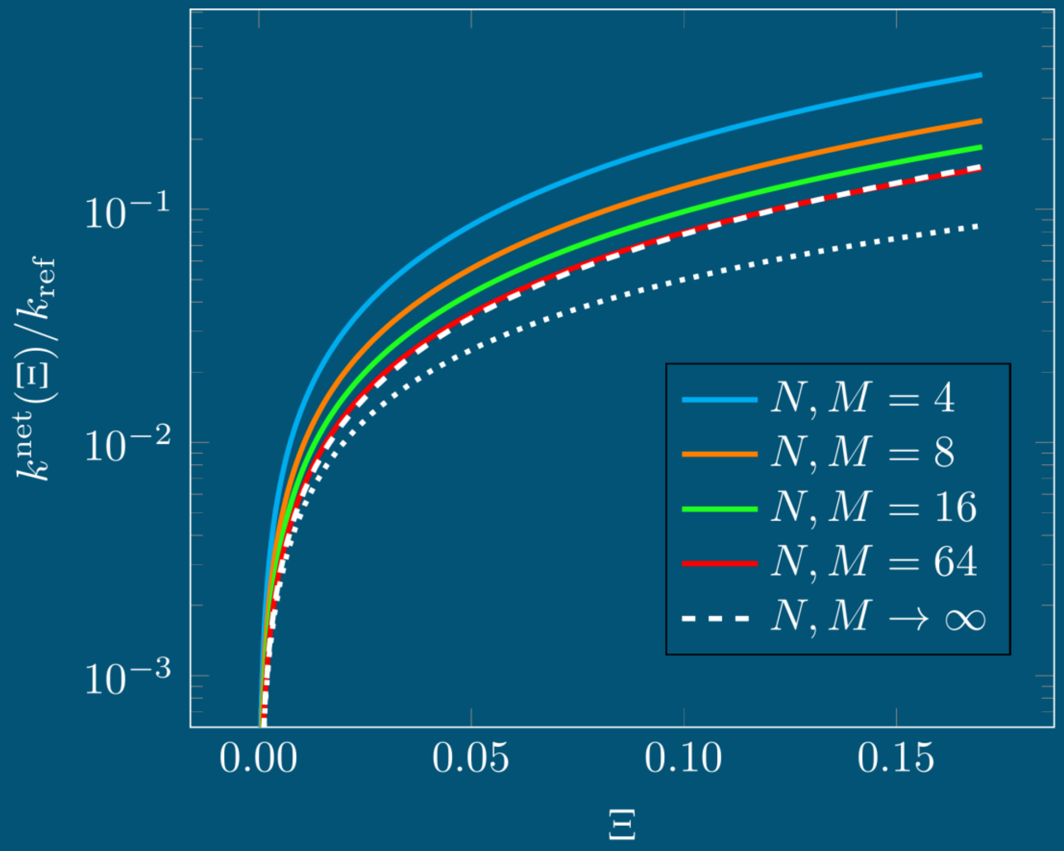



**Macroscopic subcritical crack growth relation**

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

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





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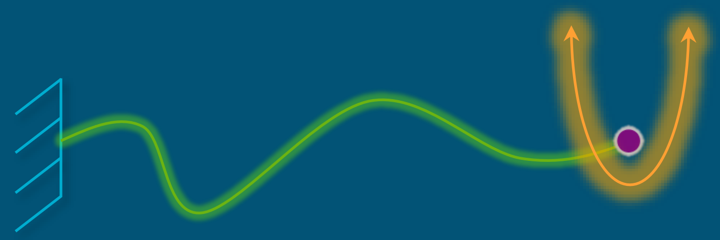
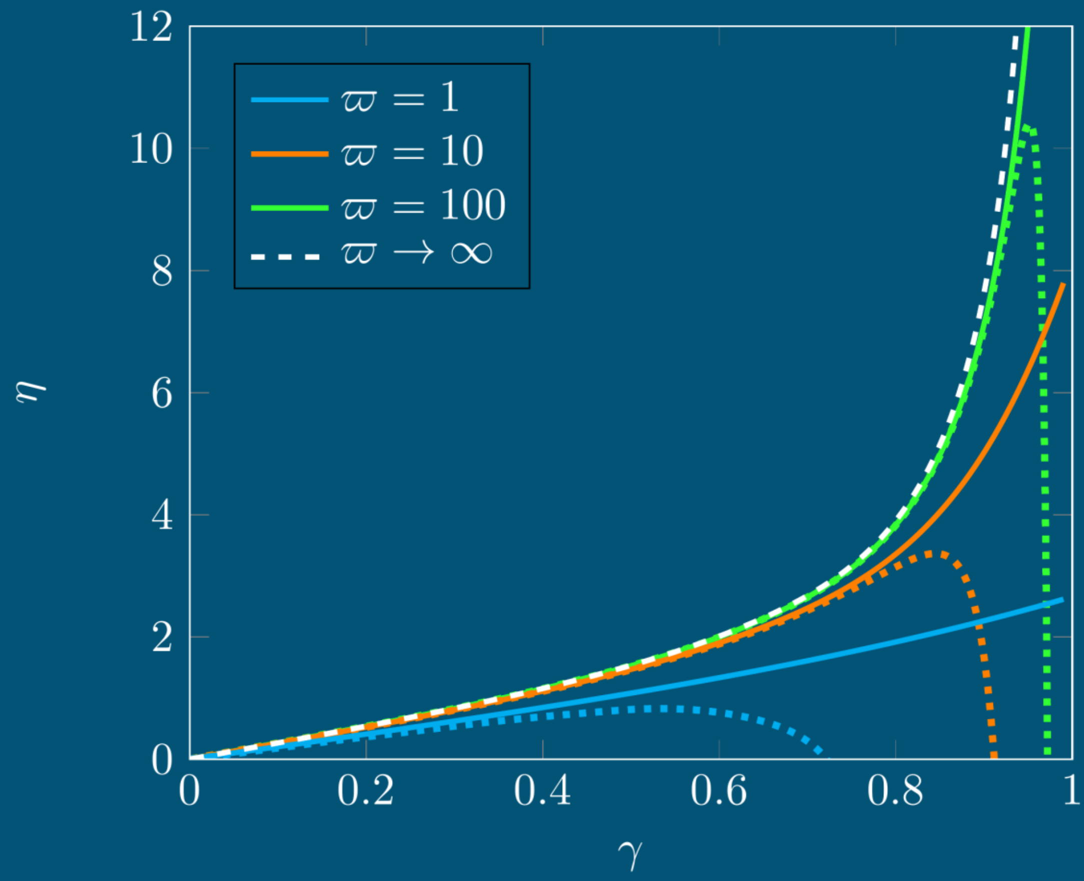
# Modeling single-molecule stretching experiments



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

FJC model under strong potential

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

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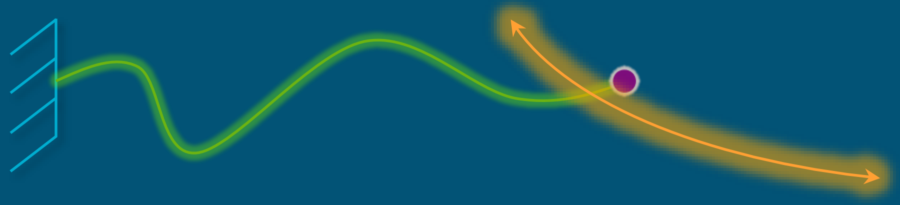
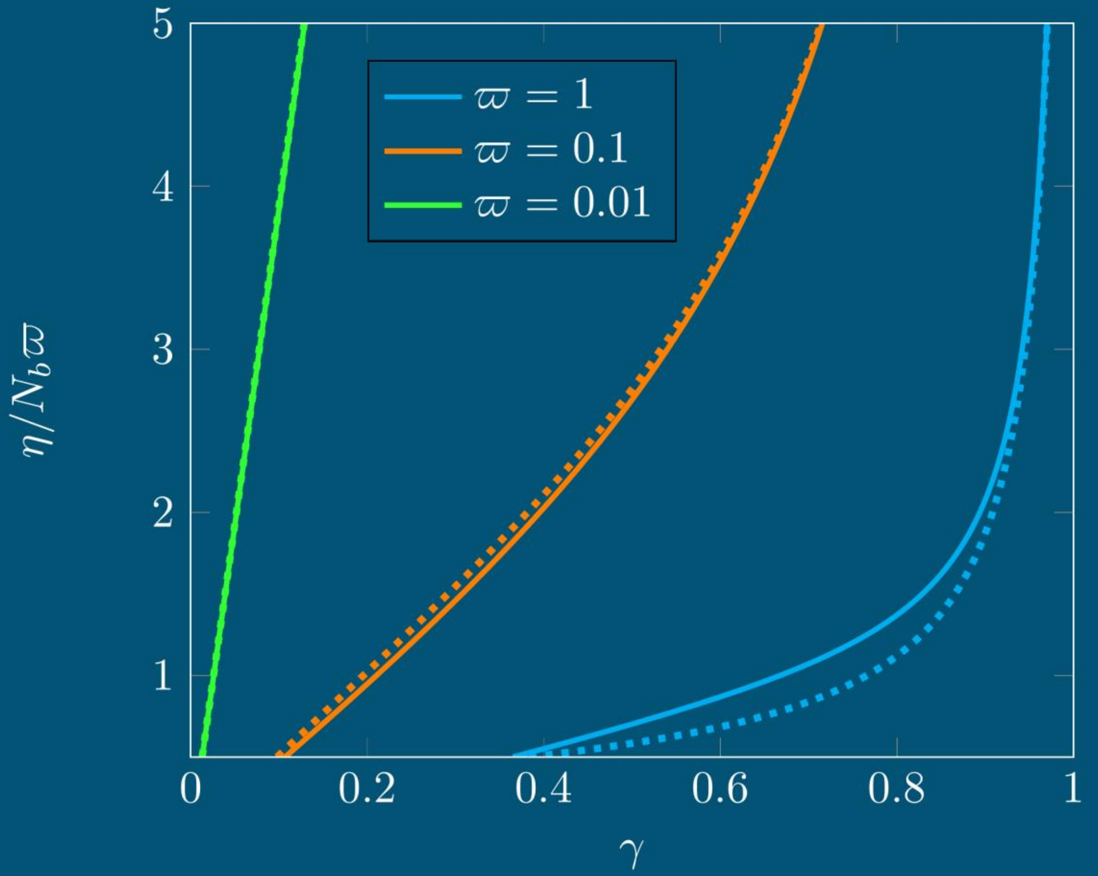


$$Q(\boldsymbol{\gamma}) = \iiint \underbrace{Q_0(\boldsymbol{\gamma}')}_{\text{isometric partition function}} e^{\overbrace{-\frac{\varpi}{2}N_b^2(\boldsymbol{\gamma}-\boldsymbol{\gamma}')^2}^{\text{applied potential}}} d^3\boldsymbol{\gamma}'$$

**FJC model under weak potential**

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

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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
  - Statistical mechanical model for crack growth
  - Modeling single-molecule stretching experiments
- Future work
  - Many more model systems
  - Quantum statistical thermodynamics

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