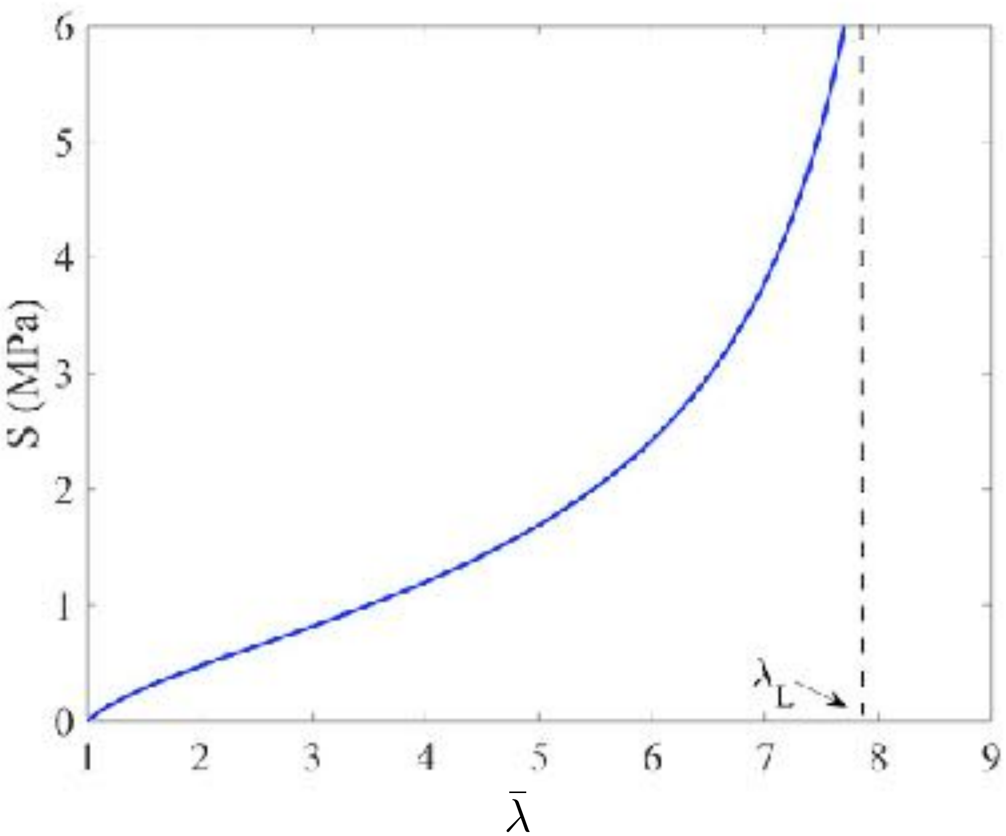
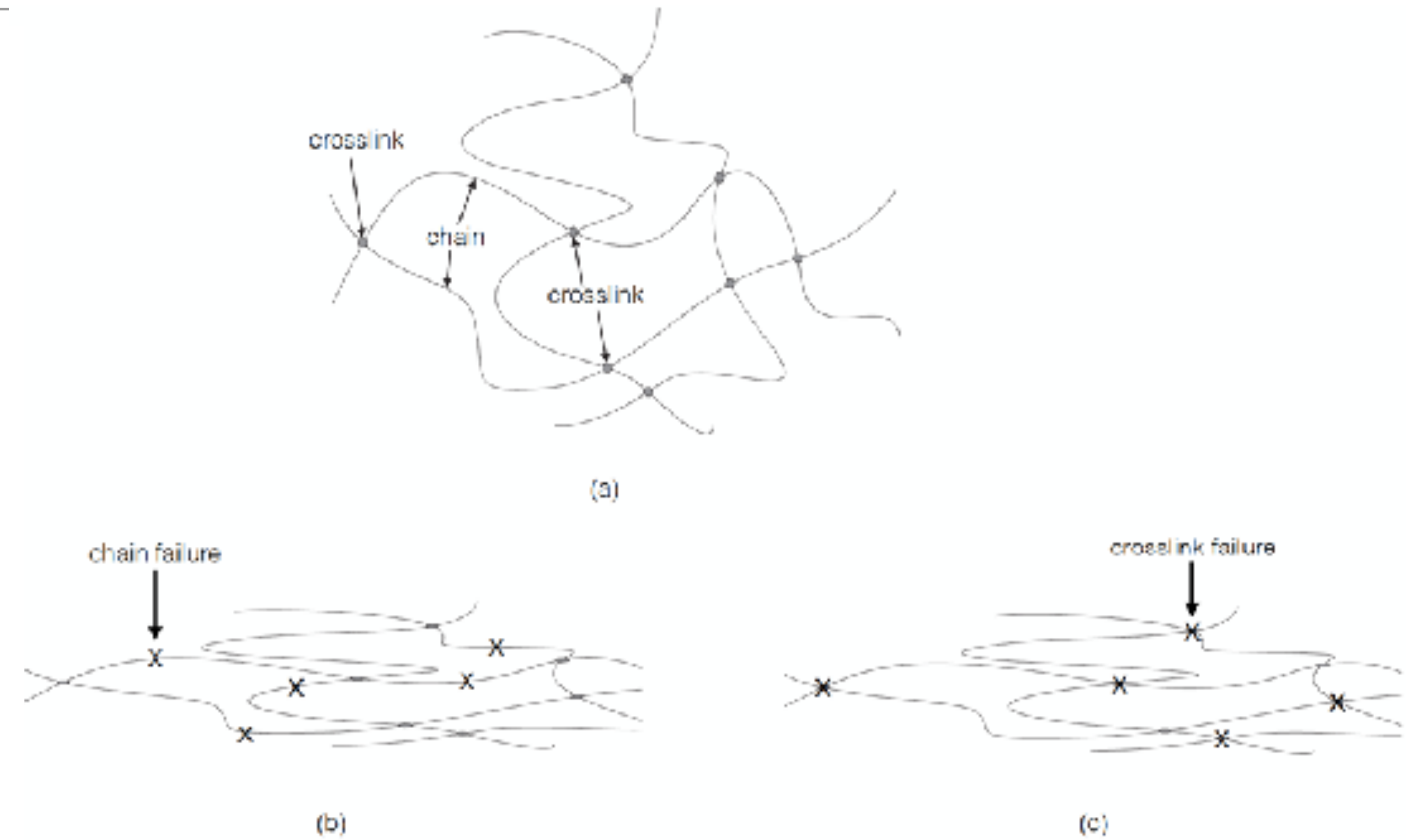
Possible failure mechanisms in an elastomer

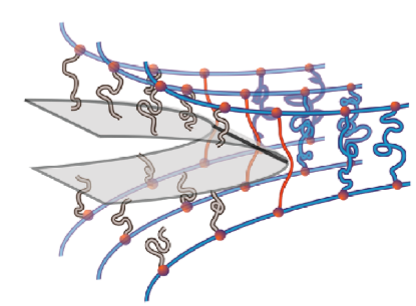




- The classical inverse Langevin-type free energy function based on a change in entropy, has a

$$\textbf{singularity} \quad \text{as} \quad \bar{\lambda} \to \lambda_L.$$

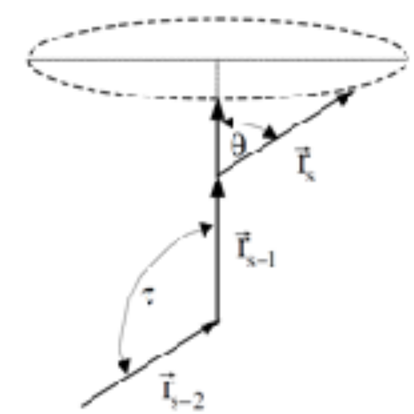
- Physically, as $\bar{\lambda} \to \lambda_L$, the polymer will fracture. There are two possible modes of fracture:
  - The monomers in the chains are stretched and ruptured
    — chain scission mode
    — Idea goes back to Lake and Thomas (1967).
  - The crosslinks in the polymer network are stretched and ruptured
    — crosslink failure mode.



Arruda-Boyce model is based on a classical freely-jointed model for a single chain

(Kuhn and Grün, 1942)

- A polymer molecule behaves like a chain of freely-jointed segments (Kuhn segments)
- The Kuhn segments are assumed to be rigid, but free to rotate about the joints
- n number of Kuhn segments in a chain
- L length of every Kuhn segment
- $r_0 = \sqrt{n}L$ rest length of chain
- r end-to-end distance of stretched chain
- $\lambda = \dfrac{r}{r_0}$ chain stretch

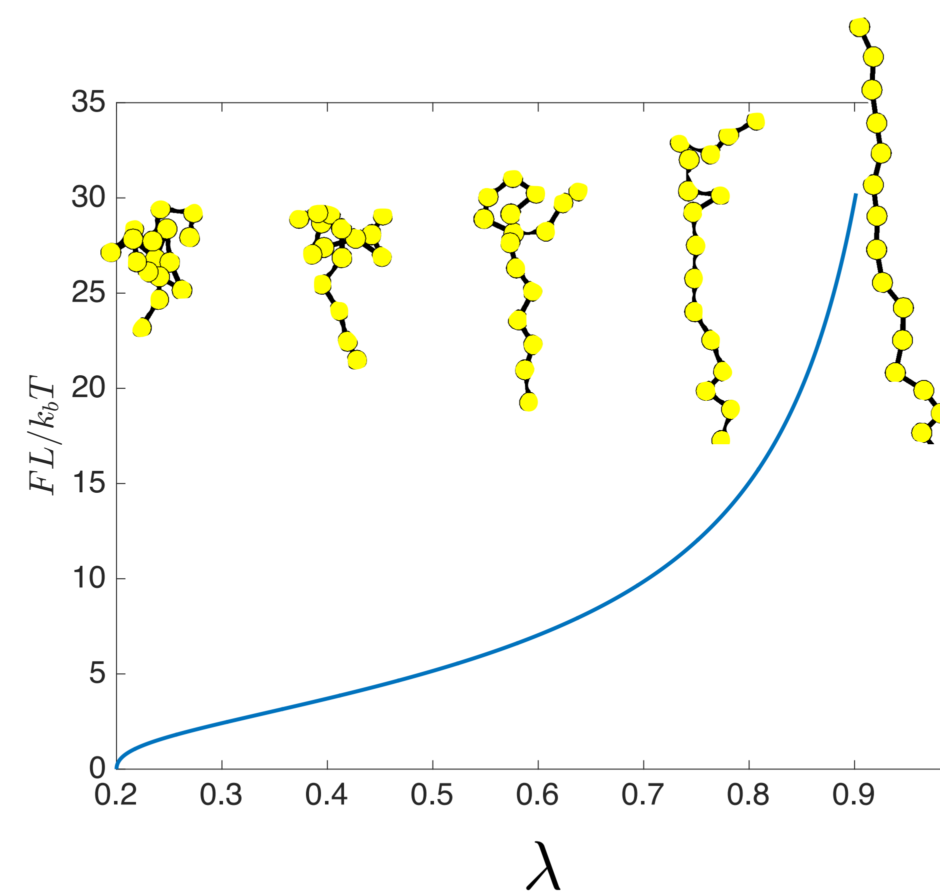


$$\psi(\lambda, \vartheta) = -\vartheta\eta(\lambda) = \vartheta\, n k_B \left[\frac{\lambda}{\sqrt{n}}\beta + \ln\left(\frac{\beta}{\sinh \beta} \right) \right]$$

$$\beta = \mathcal{L}^{-1}\left(\frac{\lambda}{\sqrt{n}} \right)$$

- Deformation response is adequately modeled

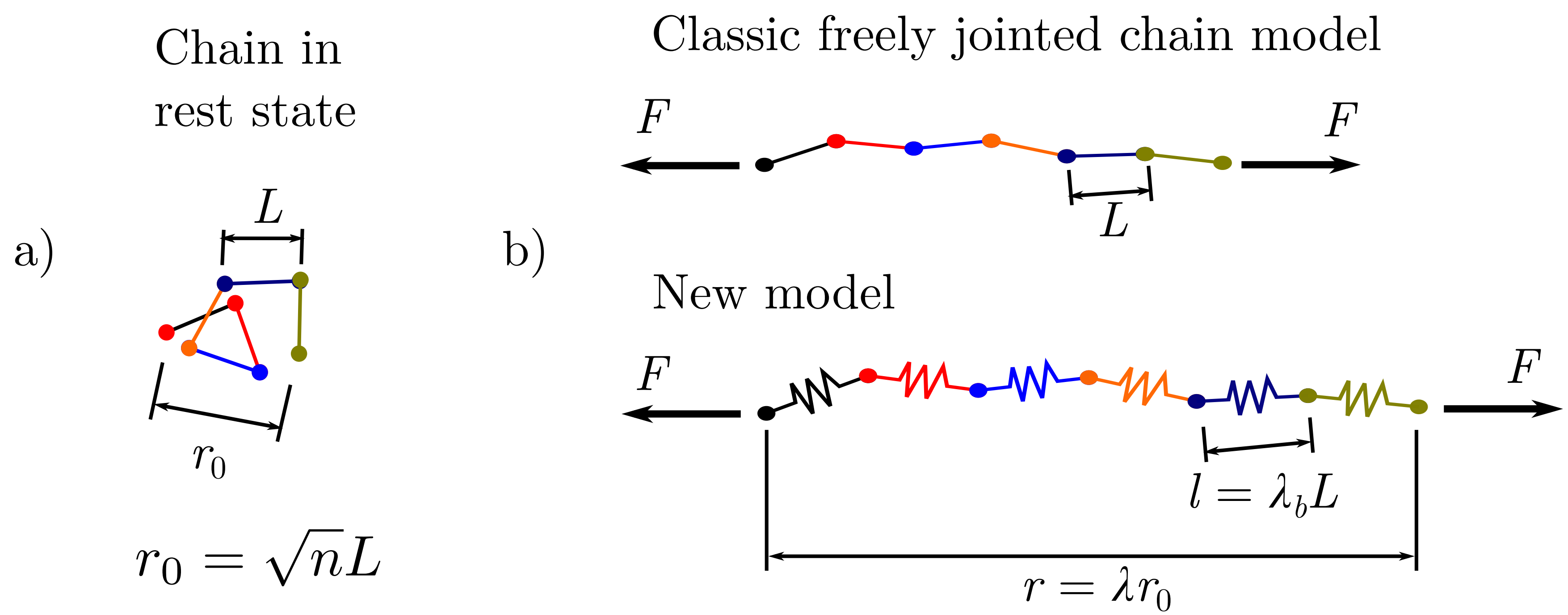
- However bond-stretching is not modeled
- The model does not say anything about chain-scission and fracture



Accounting for internal energy due to stretching of Kuhn segments

(Mao, Talamini, Anand, 2017 EML)

- A polymer molecule behaves like a chain of freely jointed segments (Kuhn segments)
- However each Kuhn segment is not rigid but **stretchable.**
- Every Kuhn segment has the same rest length L and deformed length l.



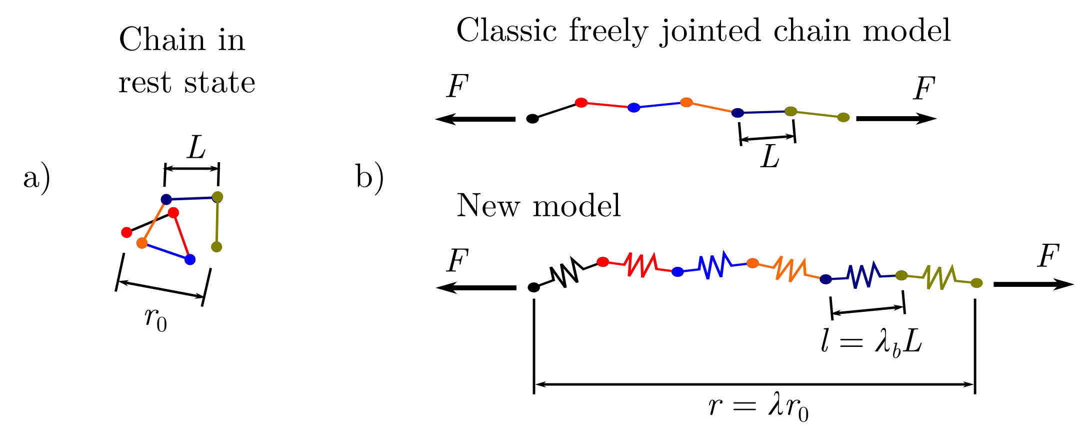
$$\lambda = \frac{r}{r_0} \quad \text{chain stretch}$$

$$\lambda_b = \frac{l}{L} \quad \text{bond stretch}$$

Accounting for internal energy due to bond-stretching of a single chain

$$\lambda = \frac{r}{r_0} \quad \text{chain stretch}$$

$$\lambda_b = \frac{l}{L} \quad \text{bond stretch}$$



- Configurational entropy of a chain:

$$\hat{\eta}(\lambda, \lambda_b) = -n k_B \left[\frac{\lambda \lambda_b^{-1}}{\sqrt{n}} \beta + \ln \left(\frac{\beta}{\sinh \beta} \right) \right] \qquad \beta = \mathcal{L}^{-1} \left(\frac{\lambda \lambda_b^{-1}}{\sqrt{n}} \right)$$

- Internal energy of a chain:

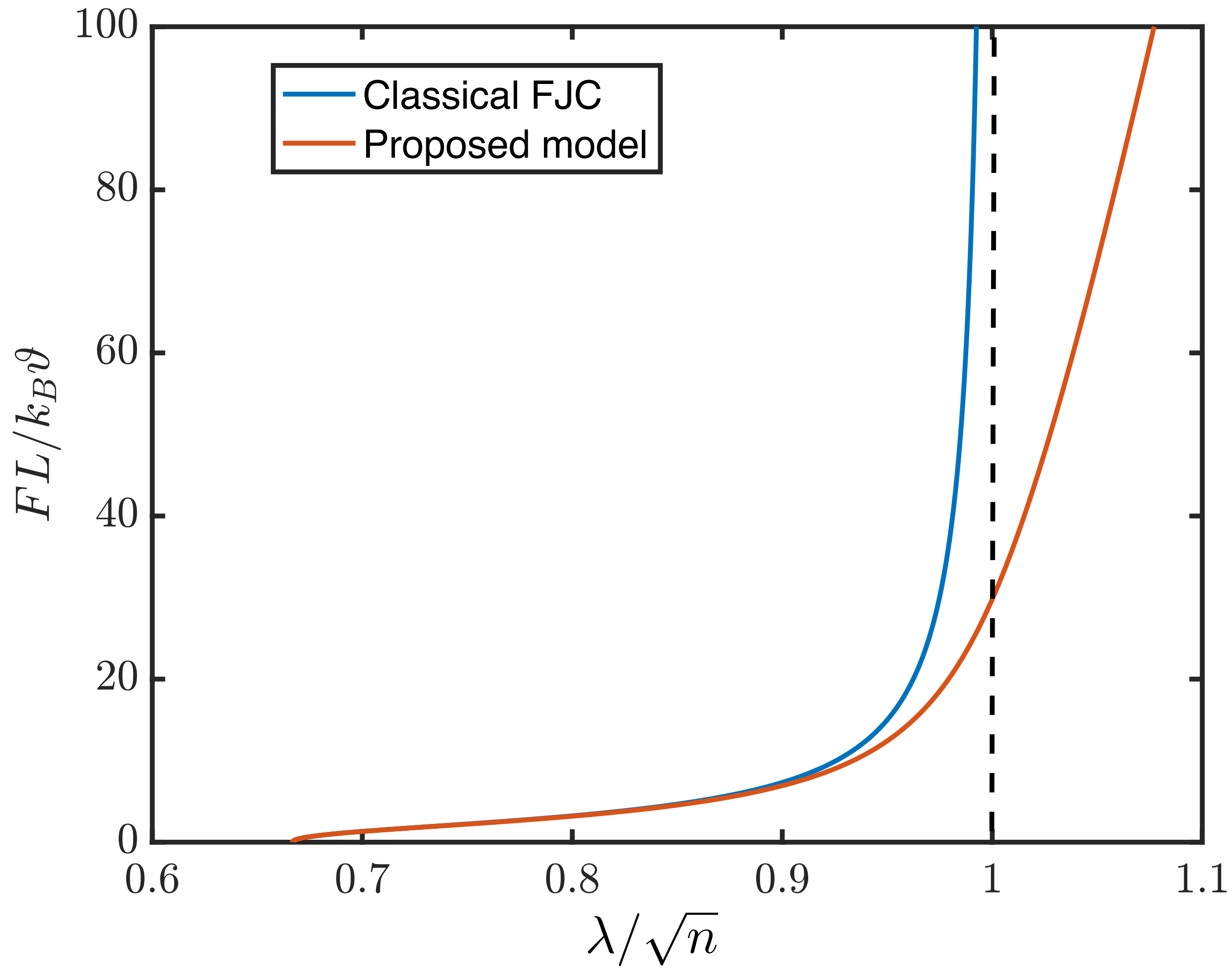
$$\hat{\varepsilon}(\lambda_b) = \frac{1}{2} n E_b (\lambda_b - 1)^2 \qquad E_b \quad \ldots \quad \text{bond stiffness}$$

- Helmholtz free energy: $\psi = \hat{\psi}(\lambda, \lambda_b) = \frac{1}{2} n E_b \left(\lambda_b - 1\right)^2 + n k_B \vartheta \left[\left(\frac{\lambda \lambda_b^{-1}}{\sqrt{n}} \right) \beta + \ln \left(\frac{\beta}{\sinh \beta} \right) \right]$

- Bond stretch is determined by free energy minimization: $\dfrac{\partial \hat{\psi}(\lambda, \lambda_b)}{\partial \lambda_b} = 0.$

Deformation response of a single chain

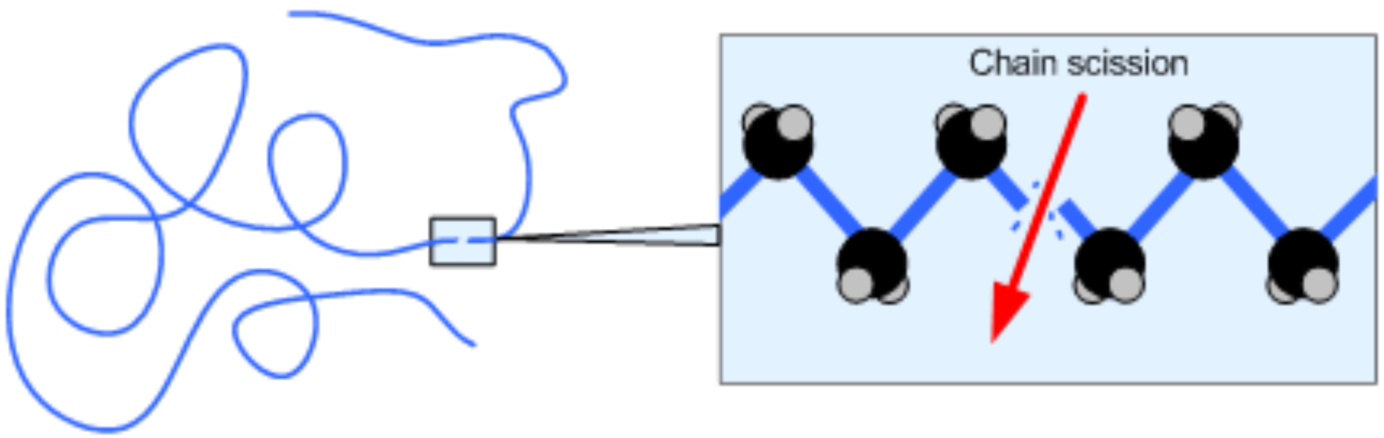
$$\psi = \hat{\psi}(\lambda, \lambda_b) = \frac{1}{2} n E_b \left(\lambda_b - 1\right)^2 + n k_B \vartheta \left[\left(\frac{\lambda \lambda_b^{-1}}{\sqrt{n}} \right) \beta + \ln \left(\frac{\beta}{\sinh \beta} \right) \right]$$



Singularity is suppressed

Scission of a single chain

Accounting for internal energy of bond deformation allows for modeling of chain scission:



- ε_b^f dissociation energy of a Kuhn segment
- $n\,\varepsilon_b^f$ dissociation energy of chain

Damage model for scission of a single chain

Introduce:

- $\mathsf{d} \in [0, 1]$, damage variable
- ϖ, microforce that expends power over $\dot{\mathsf{d}}$

Free energy: $\hat{\psi}(\lambda, \lambda_b, \mathsf{d}) = (1 - \mathsf{d})^2 \hat{\varepsilon}(\lambda_b) - \vartheta \hat{\eta}(\lambda, \lambda_b)$

$(1 - \mathsf{d})^2$ is a degradation function for the internal energy

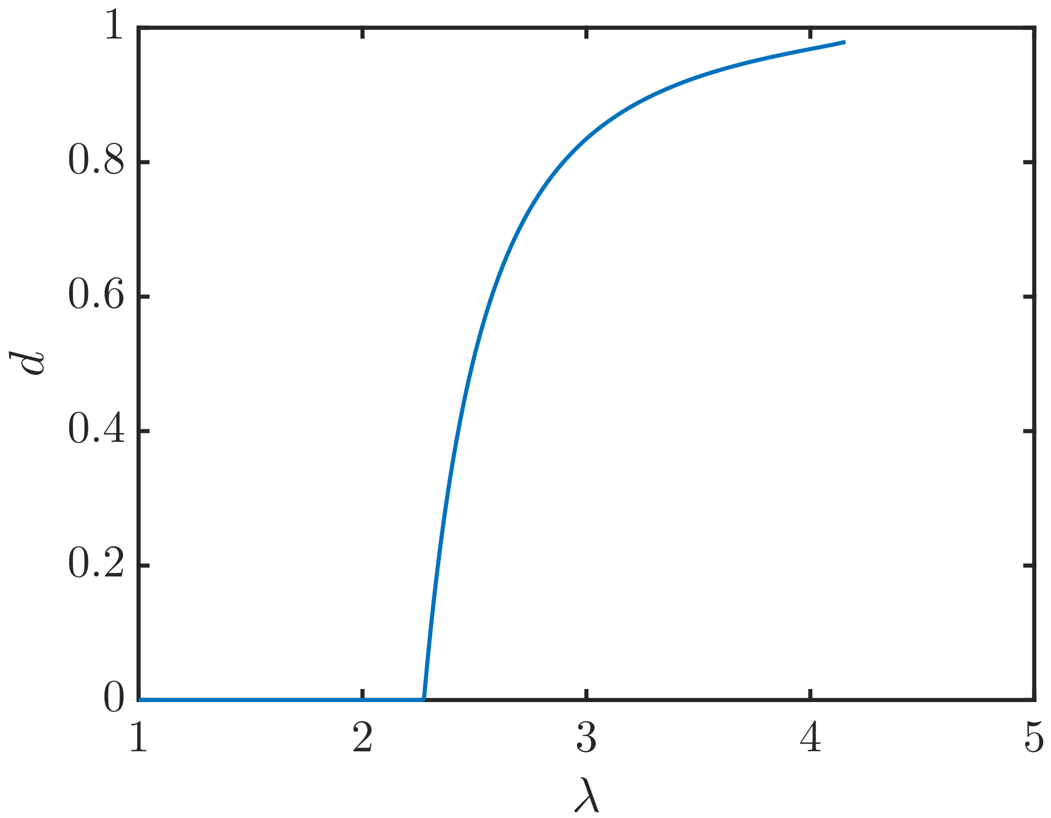
Microforce:

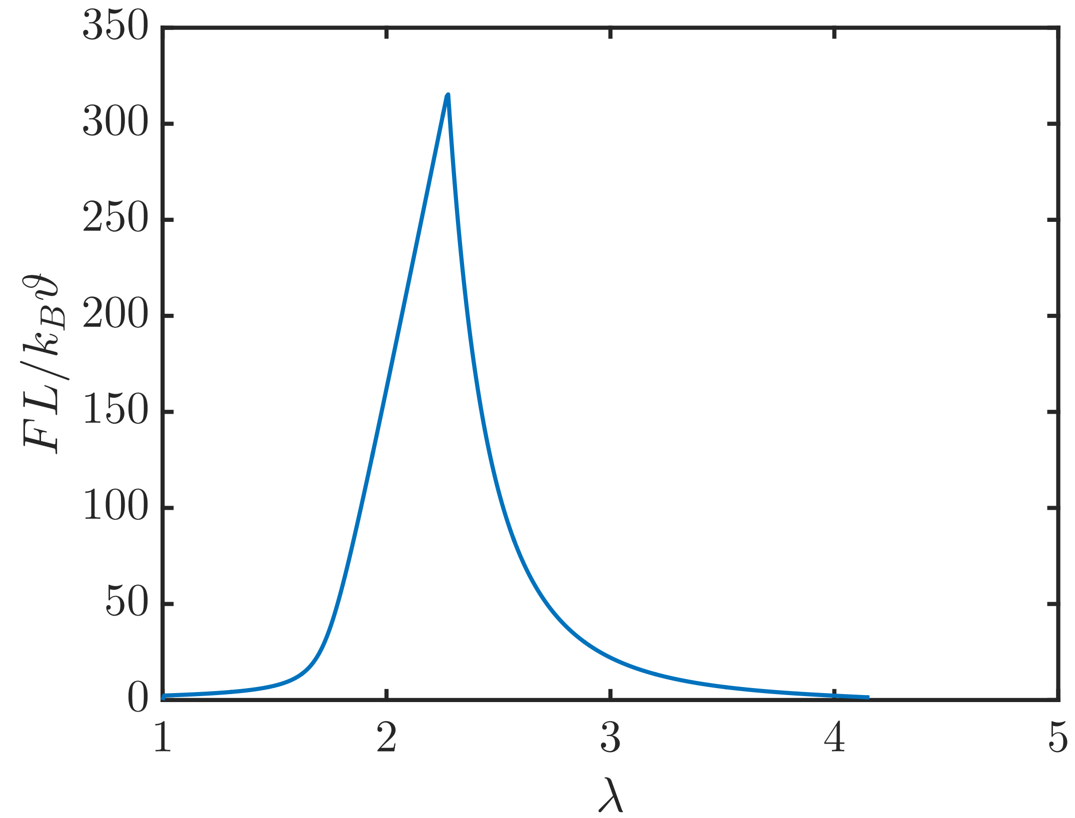
$$\varpi = \underbrace{\frac{\partial \hat{\psi}}{\partial \mathsf{d}}}_{\text{energetic}} + \underbrace{n \varepsilon_b^f + \zeta \dot{\mathsf{d}}}_{\text{dissipative}}$$

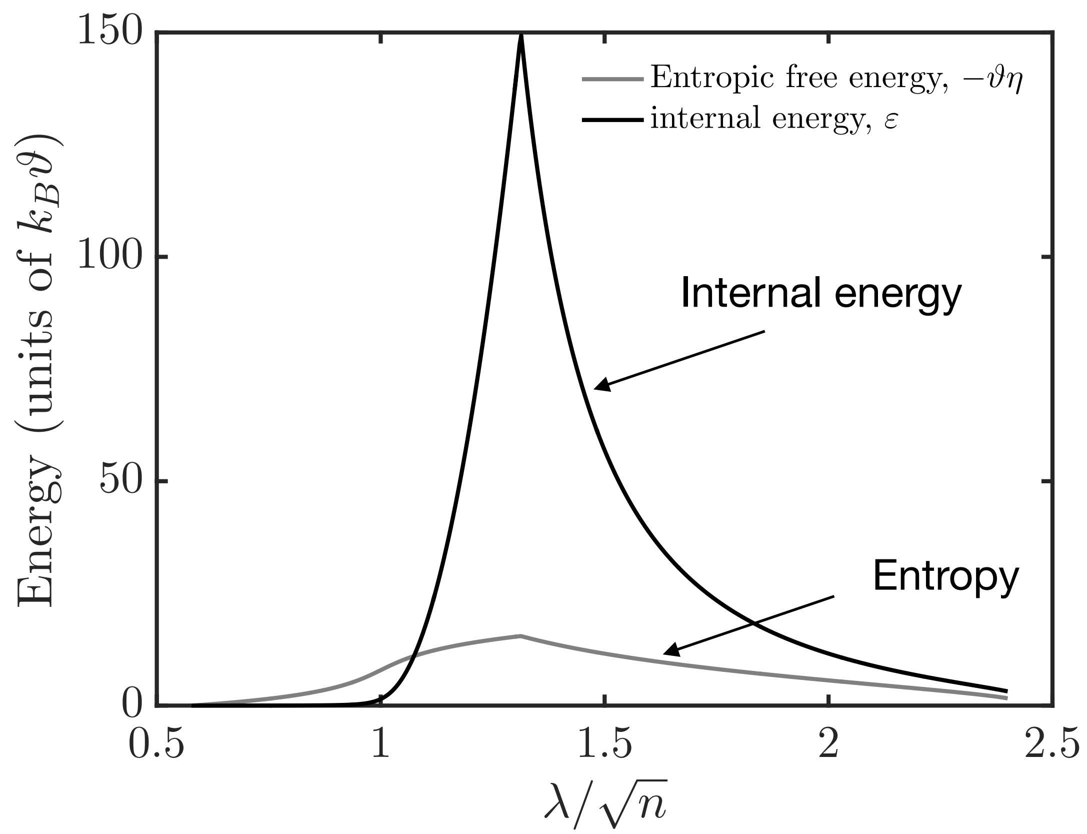
Microforce balance (from virtual power arguments) :

$$\zeta \dot{\mathsf{d}} = 2(1 - \mathsf{d}) \left\langle \hat{\varepsilon}(\lambda_b) - n \varepsilon_b^f / 2 \right\rangle + n \varepsilon_b^f \mathsf{d}$$

Damage model for scission of a single chain







Back to a continuum model

$\mathsf{x} = \boldsymbol{\chi}(\mathsf{X}, t)$,	motion;
$\mathsf{F} = \nabla\boldsymbol{\chi}, \quad J = \det \mathsf{F} > 0$,	deformation gradient;
$\bar{\mathsf{F}} = J^{-1/3}\,\mathsf{F}$,	disortional part of F;
$\mathsf{C} = \mathsf{F}^{\top}\mathsf{F}$,	right Cauchy-Green tensor;
$\bar{\mathsf{C}} = \bar{\mathsf{F}}^{\top}\bar{\mathsf{F}} = J^{-2/3}\mathsf{C}$,	distortional part of C;
$\mathsf{T}_{\mathsf{R}},\ \mathsf{T}_{\mathsf{R}}\mathsf{F}^{\top} = \mathsf{F}\mathsf{T}_{\mathsf{R}}^{\top}$	Piola stress;
$\mathsf{T}_{\mathsf{RR}} = \mathsf{F}^{-1}\mathsf{T}_{\mathsf{R}}$,	second Piola stress;
ε_{R},	internal energy density per unit reference volume;
η_{R},	entropy density per unit reference volume;
ψ_{R},	free energy density per unit reference volume;
$\lambda_b > 0$	effective bond stretch (an internal variable);
$\mathsf{d}(\mathsf{X}, t) \in [0, 1]$,	damage variable or phase-field variable;
ϖ	scalar microstress conjugate to $\dot{\mathsf{d}}$;
$\boldsymbol{\xi}$	vector microstress conjugate to $\nabla\dot{\mathsf{d}}$.

Constitutive equations

- **Free energy**

  This is given by

$$\psi_{\mathrm{R}} = \hat{\psi}_{\mathrm{R}}(\mathbf{\Lambda}),$$

  with $\mathbf{\Lambda}$ the list

$$\mathbf{\Lambda} = \{\mathsf{C}, \lambda_b, \mathsf{d}, \nabla \mathsf{d}\}.$$

- **Second Piola stress. Piola stress**

  The second Piola stress is given by

$$\mathsf{T}_{\mathrm{RR}} = 2\,\frac{\partial \hat{\psi}_{\mathrm{R}}(\mathbf{\Lambda})}{\partial \mathsf{C}},$$

  and the Piola stress by

$$\mathsf{T}_{\mathrm{R}} = \mathsf{F}\mathsf{T}_{\mathrm{RR}}.$$

- **Implicit equation for the effective bond stretch**

  The thermodynamic requirement

$$\frac{\partial \hat{\psi}_{\mathrm{R}}(\mathbf{\Lambda})}{\partial \lambda_b} = 0,$$

  reflects the fact that the actual value of the effective bond stretch λ_b adopted by the material is the one that ***minimizes*** the free energy. This equation serves as an implicit equation to determine λ_b in terms of the other constitutive variables.