# Deformation Model of Chains and Networks with Extendable Bonds

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## Abstract

The nonlinear stress-strain behavior of polymer networks, manifested in the monotonically increasing instantaneous modulus, is a product of the nonlinear deformation of individual network strands. This nonlinear network response to external deformations is described in the framework of a network model relating macroscopic stress-strain response to force-elongation behavior of individual network strands with finite bending rigidity and extendable bonds. The developed approach is used to correlate network shear modulus, bond deformation modulus and extensibility ratio with the strands' Kuhn length, bond elastic constant, and their dimensions in undeformed and fully extended states in both simulated and experimental networks.

## Chain Deformation Model

The Helmholtz free energy of a chain with end-to-end distance $R$, bond deformation ratio $\lambda_l$ and number of bonds $N$ is approximated by the sum of the conformational and bond stretching terms:

$$F_{chain}(R,\lambda_l) = F_{conf}(R,\lambda_l) + NU_{bond}(\lambda_l)$$

The bond deformation can be approximated by a harmonic potential with spring constant $K_b$ and equilibrium bond length $l_0$:

$$U_{bond}(\lambda_l) = 0.5K_b l_0^2(\lambda_l - 1)^2$$

The force needed to stretch the chain to end-to-end distance $R$ is defined as the derivative of the free energy with respect to $R$:

$$\frac{fl_0}{k_BT} = \frac{R}{\lambda_l^2 R_{\max}^0}\left(\frac{3l}{b_K} + 2\left[\sqrt{K^2 + \left(1 - \frac{R^2}{(\lambda_l R_{\max}^0)^2}\right)^{-2}} - \sqrt{K^2+1}\right]\right)$$

where $R_{\max}^0 = Nl_0$, $K$ is the chain bending constant, and Kuhn length

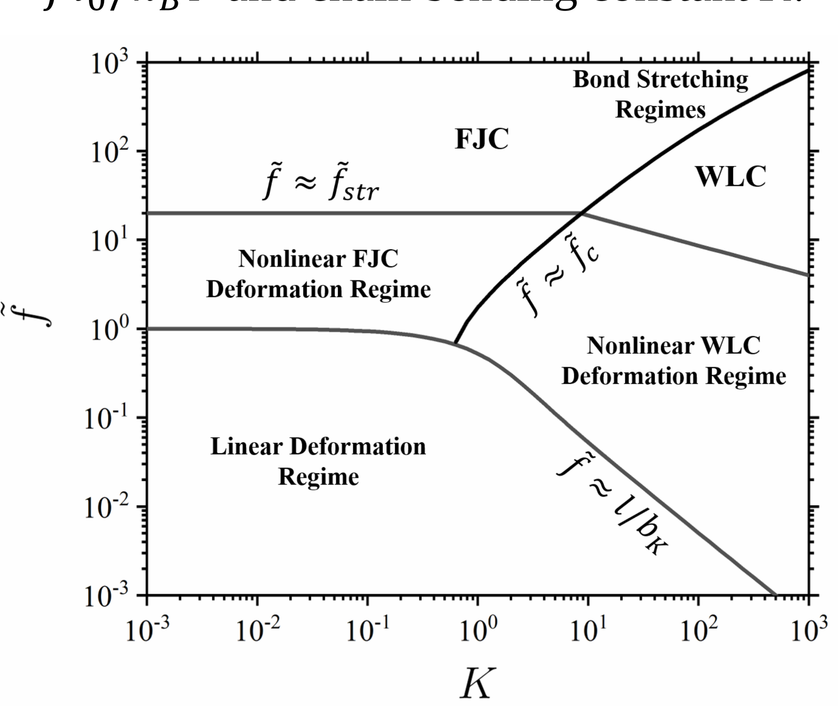
$$b_K = l\frac{1+\coth K - K^{-1}}{1-\coth K + K^{-1}} \approx \begin{cases} 2lK, & \text{for } K \gg 1 \\ l, & \text{for } K \ll 1 \end{cases}$$

The equilibrium bond deformation ratio $\lambda_l$ is obtained by minimizing the free energy with respect $\lambda_l$

$$fR = N\lambda_l\frac{dU_{bond}(\lambda_l)}{d\lambda_l} = NK_{sp}l_0^2\lambda_l(\lambda_l - 1)$$

These two equations are solved together to obtain force deformation curve accounting for bond deformations.

Diagram of chain deformation regimes in terms of reduced force $\tilde{f} = fl_0/k_BT$ and chain bending constant $K$:




Crossover force $\tilde{f}_c$ between the Freely Jointed Chain (FJC) and Worm-like Chain (WLC) regimes

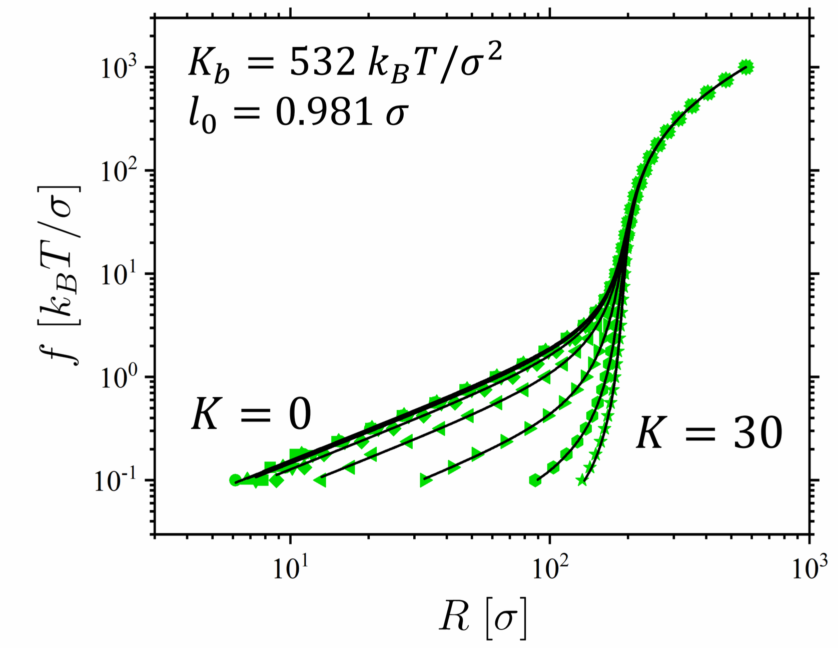
$$\begin{cases} \tilde{f}_c = 2.47\lambda_l^{-1}K(1-1/2K)^{1/2} \\ \lambda_l = 1 + f_c/K_b l_0 \end{cases}$$

Crossover force $\tilde{f}_{str}$ to bond stretching regimes:

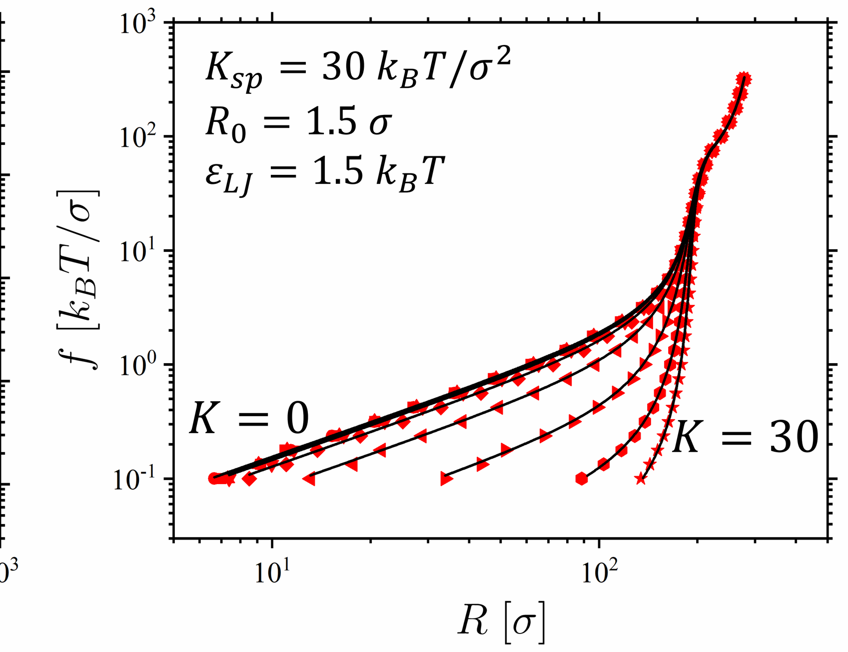
$$\tilde{f}_{str} = \frac{l_0}{k_BT}\begin{cases} \sqrt{k_BTK_b}, & \text{FJC} \\ K_b l_0(\lambda_l - 1), & \text{WLC} \end{cases}$$

## Chain Deformation Results

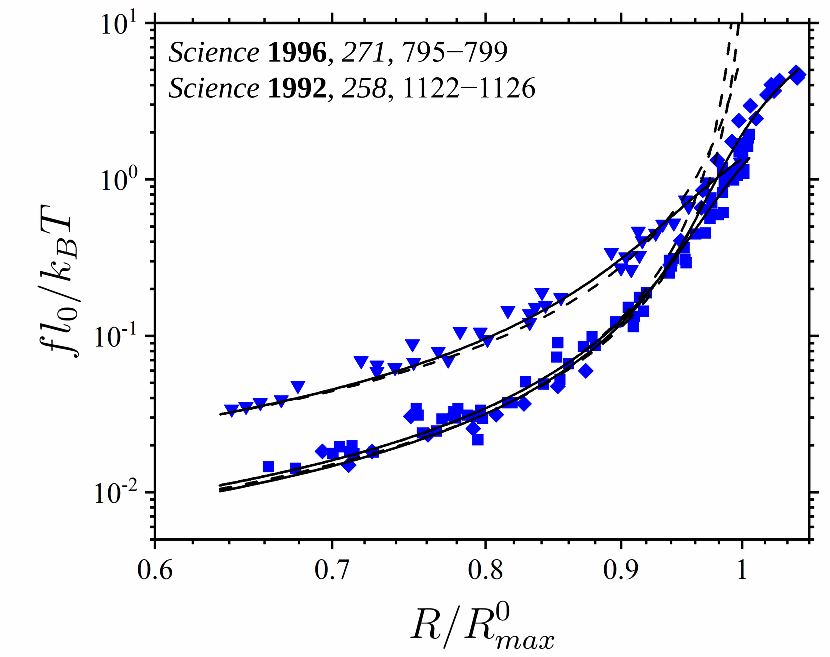
Harmonic Bonds



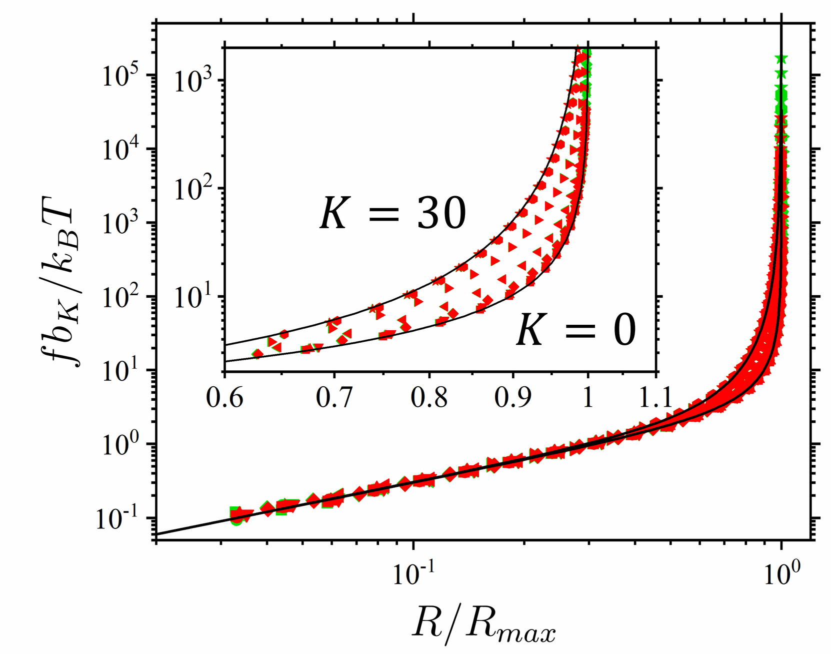

FENE Bonds




DNA Deformation

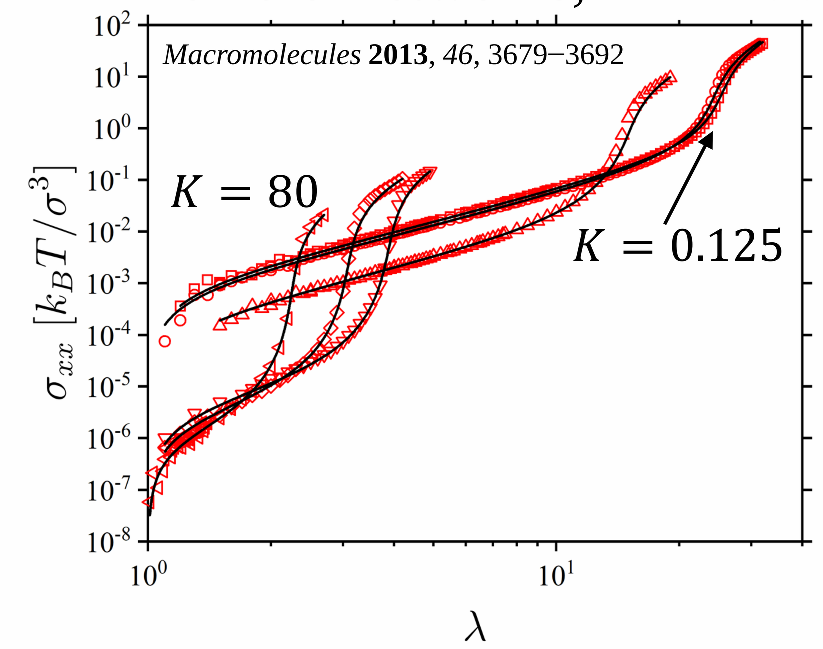



Universal Plot

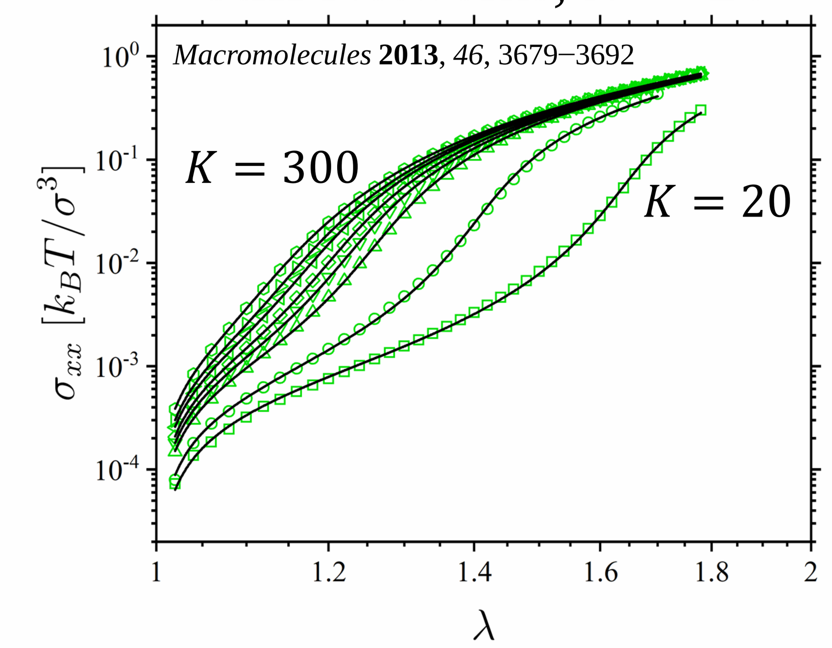



## Network Deformation Results

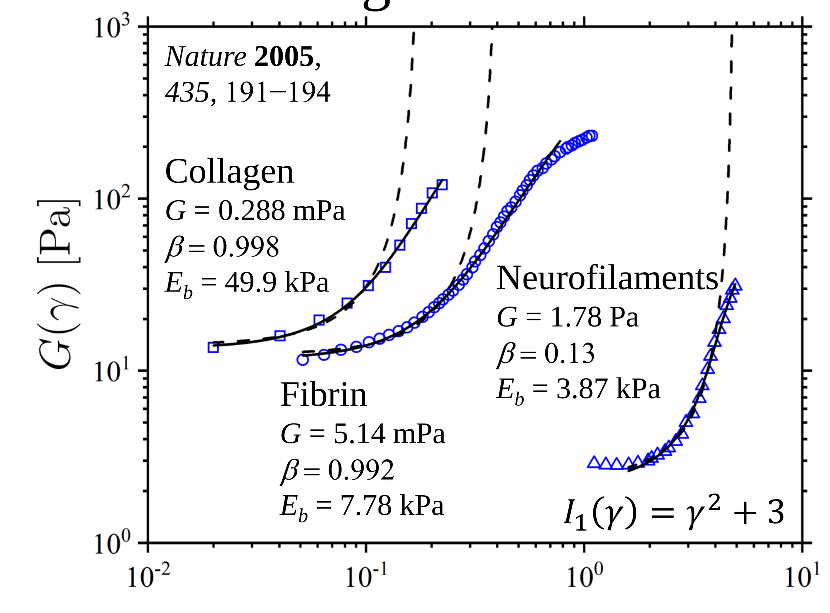
Flexible Networks, $N = 200$



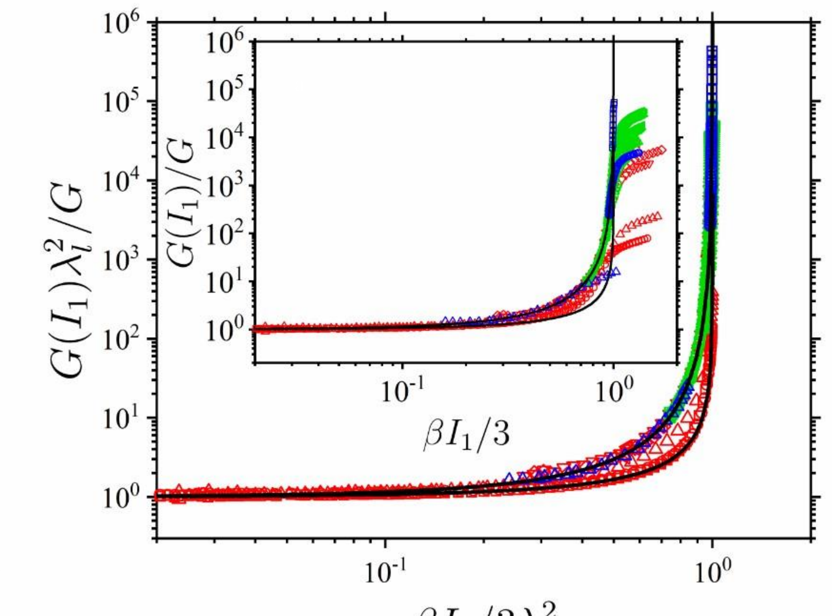

Stiff Networks, $N = 20$




Biological Networks




Universal Plot




## Network Deformation Model

The free energy of a network in the framework of the affine network model is given by the sum of individual chain contributions:

$$F_{net}(I_1,\lambda_l) = \sum_s F_{chain}(R_s,\lambda_l)$$

where the first deformation invariant $I_1 = \lambda_x^2 + \lambda_y^2 + \lambda_z^2$. For a network undergoing uniaxial deformation with deformation ratio $\lambda = L/L_0$ at constant volume $V$, $I_1 = \lambda^2 + 2\lambda^{-1}$ and the true stress in the network is

$$\sigma_{xx}(\lambda,\lambda_l) = \frac{\lambda}{V}\frac{\partial F_{net}(I_1(\lambda),\lambda_l)}{\partial\lambda}$$

$$= G\frac{(\lambda^2 - \lambda^{-1})}{\lambda_l^2}\left(1 + \frac{2b_K}{3l}\left[\sqrt{K^2 + \left(1 - \frac{\beta I_1(\lambda)}{3\lambda_l^2}\right)^{-2}} - \sqrt{K^2+1}\right]\right)$$

where $G$ is the structural network modulus, and $\beta$ is the extensibility ratio. Minimizing the network free energy with respect to $\lambda_l$, one obtains an expression for the equilibrium bond deformation ratio in terms of the network stress:

$$\sigma_{xx}(\lambda,\lambda_l)\frac{(\lambda^2 + 2\lambda^{-1})}{(\lambda^2 - \lambda^{-1})} = \lambda_l\rho C_E\frac{dU_{bond}(\lambda_l)}{d\lambda_l}$$

Parameter $C_E$ describes topology of the network with monomer density $\rho$.

## Simulation Details

- Coarse-grained bead-spring model
- Phantom chains
- NVT ensemble with Langevin thermostat
- Bending potential:
  $U_{bend}(\theta) = k_BTK(1 + \cos\theta)$
- Bond potentials:
  $U_{harmonic}(l) = \frac{1}{2}K_b(l - l_0)^2$
  $U_{FENE}(l) = -0.5K_{sp}R_0^2\ln\left(1 - \frac{l^2}{R_0^2}\right) + 4\varepsilon_{LJ}\left(\left(\frac{\sigma}{l}\right)^{12} - \left(\frac{\sigma}{l}\right)^6\right) + \varepsilon_{LJ}$

Single Chain Deformation

- Bead-spring chains with different bending constants, $K$, and deformable bonds.
- Force-deformation curves.

Diamond Network Deformation

- A diamond network of bead-spring chains with different bending constants $K$.
- Step-wise uniaxial deformation at constant volume.
- True stress as a function of deformation

## Summary

We have developed a generalized model of the deformation of polymer chains which accounts for bond extensibility. The model predictions are in excellent agreement with simulation data of chain deformations. It is used for analysis of experimental data for deformation of single-strand DNA. This model has been adapted to describe the mechanical response of polymer networks with deformable bonds. It was used for analysis of simulation results of diamond network deformation and experimental data for biological networks of collagen, fibrin, and neurofilaments.

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### References

*Macromolecules* **2020**, *53*, 10874−10881
*Macromolecules* **2013**, *46*, 3679−3692