Theory and Simulations of Hybrid Network Deformation

Michael Jacobs[1], Heyi Liang[2], Andrey Dobrynin[1]

[1]*Department of Chemistry, University of North Carolina, Chapel Hill, NC, 27599*

[2]*Pritzker School of Molecular Engineering, University of Chicago, Chicago, IL 60637, United States*

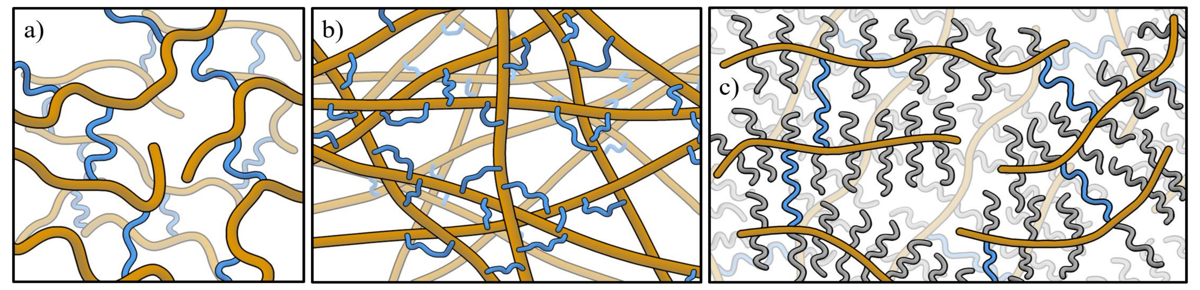
Dobrynin Research Group

THE UNIVERSITY of NORTH CAROLINA at CHAPEL HILL

ABSTRACT

Hybrid networks - networks consisting of different types of strands which could differ by their degree of polymerization (DP), chemical structure, or rigidity (Kuhn length). Here we report on a theoretical model and coarse-grained molecular dynamics simulations of hybrid networks made of two types of strands. The developed approach self-consistently accounts for entropic elasticity, bond deformation, and continuous redistribution of stress between different network strands as they undergo nonlinear deformations. The model predictions are tested by molecular dynamics simulations of hybrid network deformations, which confirm a breakdown of the simple mixture rule.

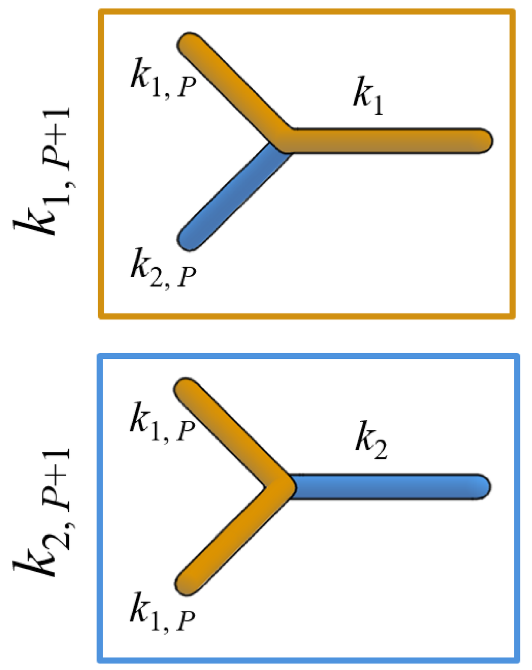
MOTIVATION



Polymer networks can be made of strands which differ by (a) degree of polymerization (DP), (b) rigidity, and (c) chemical structure. Such solvent-free elastomers have been shown to replicate the softness, strength, and toughness of biological tissues[1].

MODEL OF HYBRID NETWORKS

We represent the system as a phantom network of nonlinear springs with spring constants k_1 and k_2.



Recursive Relation

$$(k_1^\infty)^{-1} = k_1^{-1} + (k_1^\infty + k_2^\infty)^{-1}$$

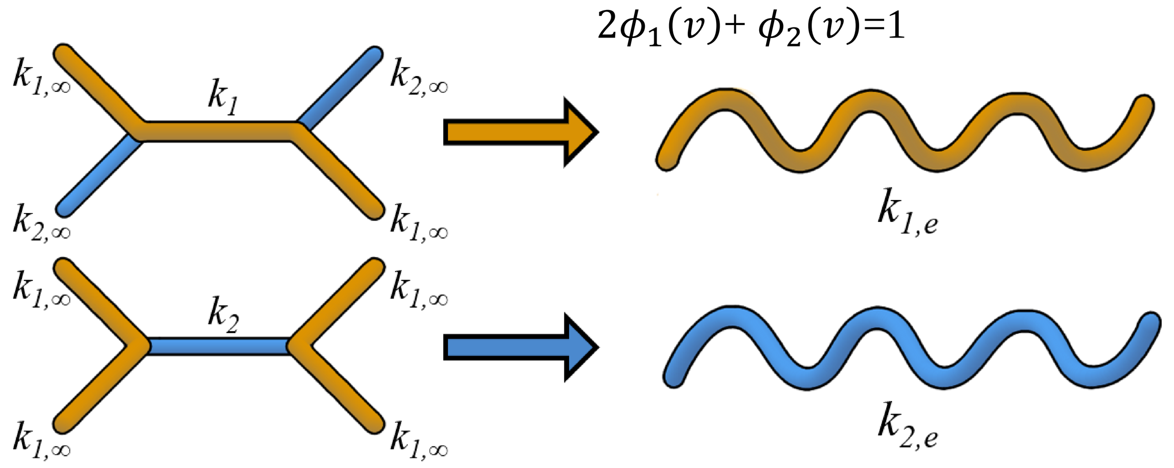
$$(k_2^\infty)^{-1} = k_2^{-1} + (2k_1^\infty)^{-1}$$

$$\frac{k_{1,e}}{k_1} \equiv \phi_1(v) = \frac{2}{1+\sqrt{9+16v}}$$

$$\frac{k_{2,e}}{k_2} \equiv \phi_2(v) = \frac{-3+\sqrt{9+16v}}{1+\sqrt{9+16v}}$$

where $v = k_1/k_2$.

$2\phi_1(v) + \phi_2(v) = 1$



NETWORK SHEAR MODULUS

General Consideration [1-3]

The total free energy of the s-th network strand of type i with the end-to-end vector $\boldsymbol{R}_{i,s}$, degree of polymerization N_i and bond deformation ratio $\lambda_{l,i}$ is a sum of the configurational and bond deformation contributions

$$F(\boldsymbol{R}_{i,s}, \lambda_{l,i}) = F_{conf}(\boldsymbol{R}_{i,s}, \lambda_{l,i}) + N_i U_{bond}(\lambda_{l,i})$$

Minimization of $F(\boldsymbol{R}_{i,s}, \lambda_{l,i})$ with respect to $\boldsymbol{R}_{i,s}$

$$\boldsymbol{f}_{i,s} = k_i \boldsymbol{R}_{i,s}$$

provides an expression for the nonlinear spring constant of the network strand

$$k_i = \frac{k_B T}{\lambda_{l,i}^2 b_i R_{max,i}} g\left(\langle R_i^2 \rangle / R_{max,i}^2 \lambda_{l,i}^2\right)$$

where $\langle R_i^2 \rangle$ is the mean-square average end-to-end distance of strands of type i and the function $g(x) = 1 + 2(1-x)^{-2}$.

Contour Length	Bond Deformation Ratio	Kuhn Length
$R_{max,i} = N_i l_0$	$\lambda_{l,i} = l/l_0$	$b_i = l_0 \frac{1+\coth K - K^{-1}}{1-\coth K + K^{-1}}$

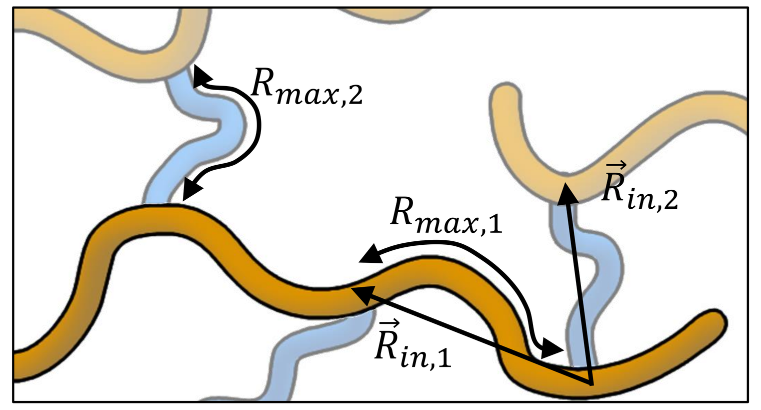
Minimization of $F(\boldsymbol{R}_{i,s}, \lambda_{l,i})$ with respect to $\lambda_{l,i}$ and averaging over all strands of type i in a network results in

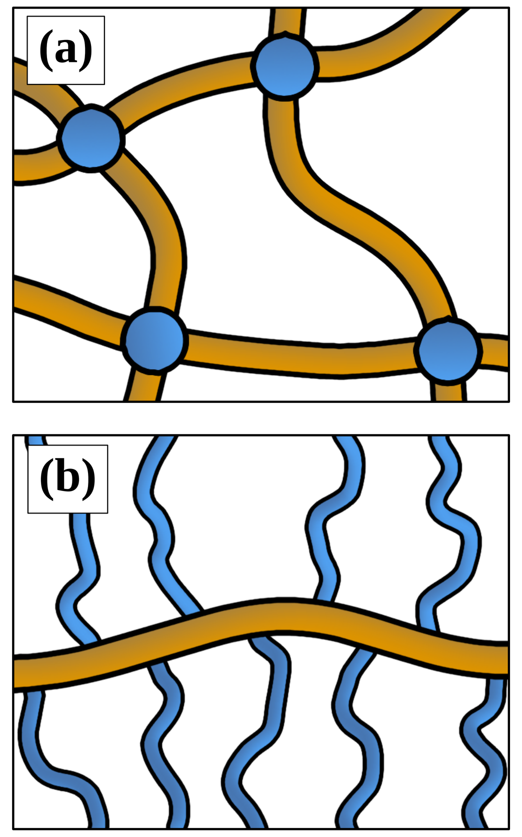
$$k_i \langle R_i^2 \rangle = N_i \lambda_{l,i} \frac{dU_{bond}(\lambda_{l,i})}{d\lambda_{l,i}}$$

In the framework of the phantom network model, each network strand is connected to a non-fluctuating background such that the mean-square end-to-end distance of strands of type i is

$$\langle R_i^2 \rangle = \frac{\langle R_{in,i}^2 \rangle I_1}{3} + \frac{3k_B T}{k_i}\left(1 - \phi_i(v)\right)$$

where $I_1 = \lambda^2 + 2\lambda^{-1}$ is the first deformation invariant for uniaxial network deformation.





(a) In a network of long chains and short crosslinkers $N_1 \gg N_2$, $G_0 \approx k_B T \frac{\rho}{2N_1}$, indicating that such networks behave as networks with tetra-functional crosslinks in the linear deformation regime. (b) In the opposite limiting case, $N_1 \ll N_2$, the network shear modulus is equal to ρ/N_2. Thus, in the linear deformation regime, the hybrid network shear modulus is controlled by the longest chains.

Linear Deformation Regime

$$k_i \approx 3k_B T / N_i l_0 b_i \qquad G_0 = \rho_{s,1}\frac{k_{1,e}\langle R_{in,1}^2\rangle}{3} + \rho_{s,2}\frac{k_{2,e}\langle R_{in,2}^2\rangle}{3}$$

$$= k_B T \rho_{s,1}\left(\phi_1(v) + \frac{1}{2}\phi_2(v)\right) = \frac{k_B T \rho}{2N_1 + N_2}$$

Nonlinear Deformation Regime [2,3]

$$G(I_1) = \frac{1}{3}\left[\lambda_{l,1}^{-2} G_1 \phi_1(v) g\left(\langle R_i^2\rangle / R_{max,i}^2 \lambda_{l,i}^2\right) + \lambda_{l,2}^{-2} G_2 \phi_2(v) g\left(\langle R_i^2\rangle / R_{max,i}^2 \lambda_{l,i}^2\right)\right]$$

Network Structural Modulus	Extensibility Ratio
$G_i = k_B T \rho_{s,i} \beta_i R_{max,i}/b_i$	$\beta_i = \langle R_{in,i}^2 \rangle / R_{max,i}^2$

Stress in Uniaxially Deformed Networks

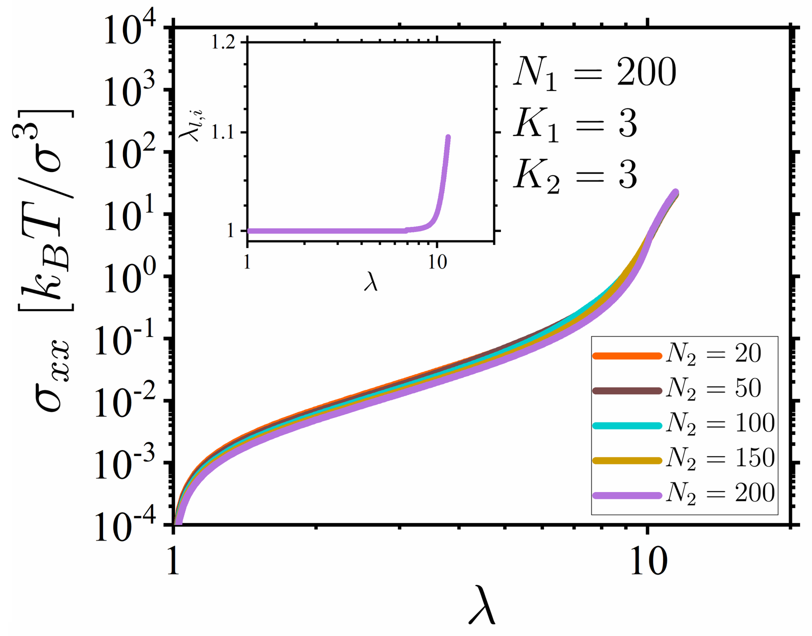
$$\sigma_{xx}(\lambda) = (\lambda^2 - \lambda^{-1}) G(I_1)$$

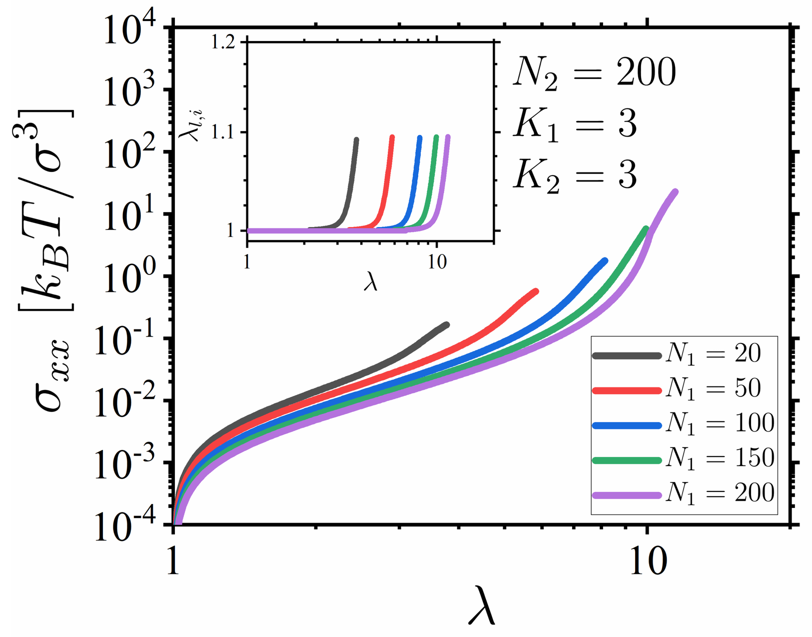
ANALYTICAL CALCULATIONS

The values of k_i, $\phi_i(v)$, $\langle R_i^2 \rangle$, and $\lambda_{l,i}$ are calculated as functions of the deformation ratio λ, using a harmonic bond potential

$$U_{bond}(\lambda_{l,i}) = 0.5 K_b l_0^2 (\lambda_{l,i} - 1)^2$$

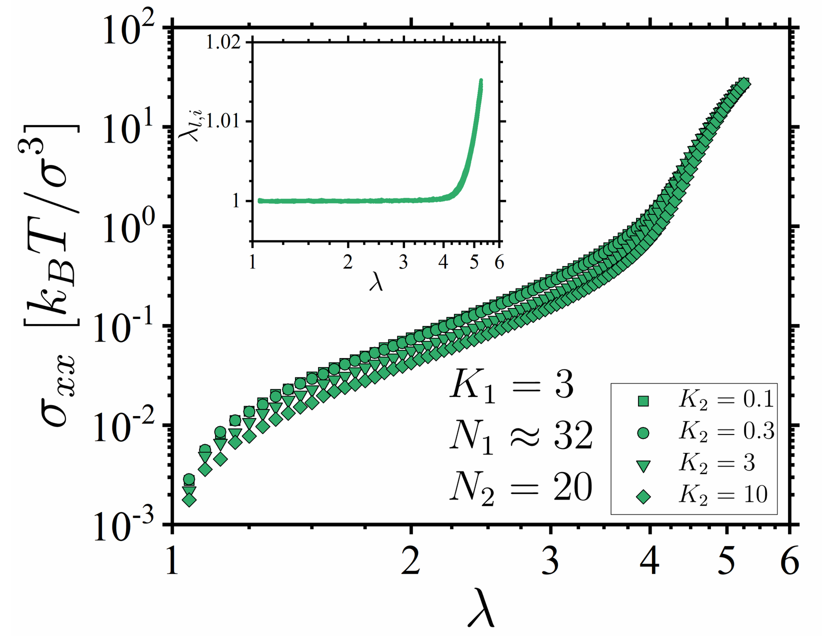
with spring constant $K_b = 532\ k_B T/\sigma^2$.

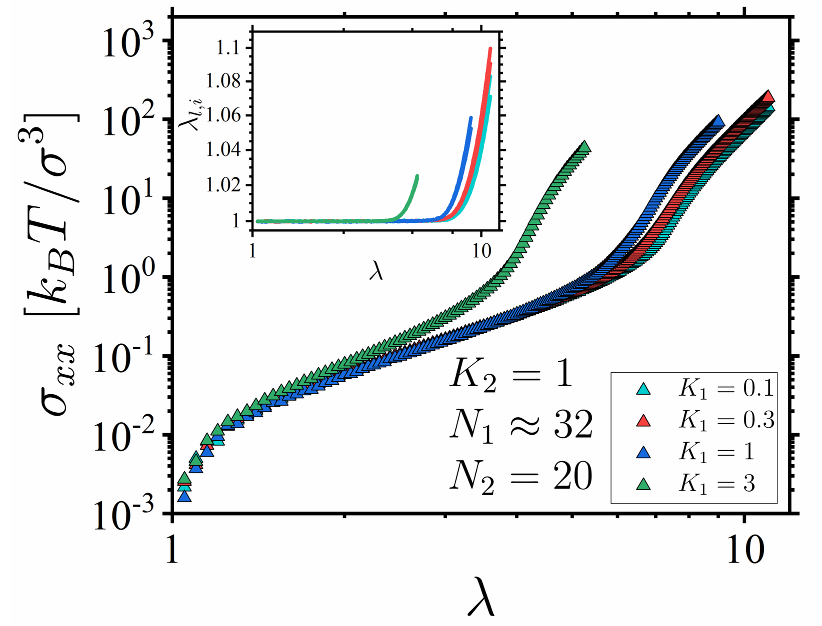




SIMULATION RESULTS

Networks are uniaxially deformed at constant volume. For constant values of K_1 at large network deformations, all stress-deformation curves collapse indicating the dominant contribution of bond deformation to the network stress.





SIMULATION DETAILS

Lennard-Jones Pairwise Interaction Potential

$$U_{LJ}(r) = \begin{cases} 4\varepsilon_{LJ}\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} - \left(\frac{\sigma}{r_{cut}}\right)^{12} + \left(\frac{\sigma}{r_{cut}}\right)^{6}\right], & r \le r_{cut} \\ 0, & r > r_{cut} \end{cases}$$

Bond Potential: FENE + LJ

$$U_{FENE}(r) = -\frac{1}{2} k_{spring} R_m^2 \ln\left(1 - \frac{r^2}{R_m^2}\right)$$

$\varepsilon_{LJ} = 1.5 k_B T$

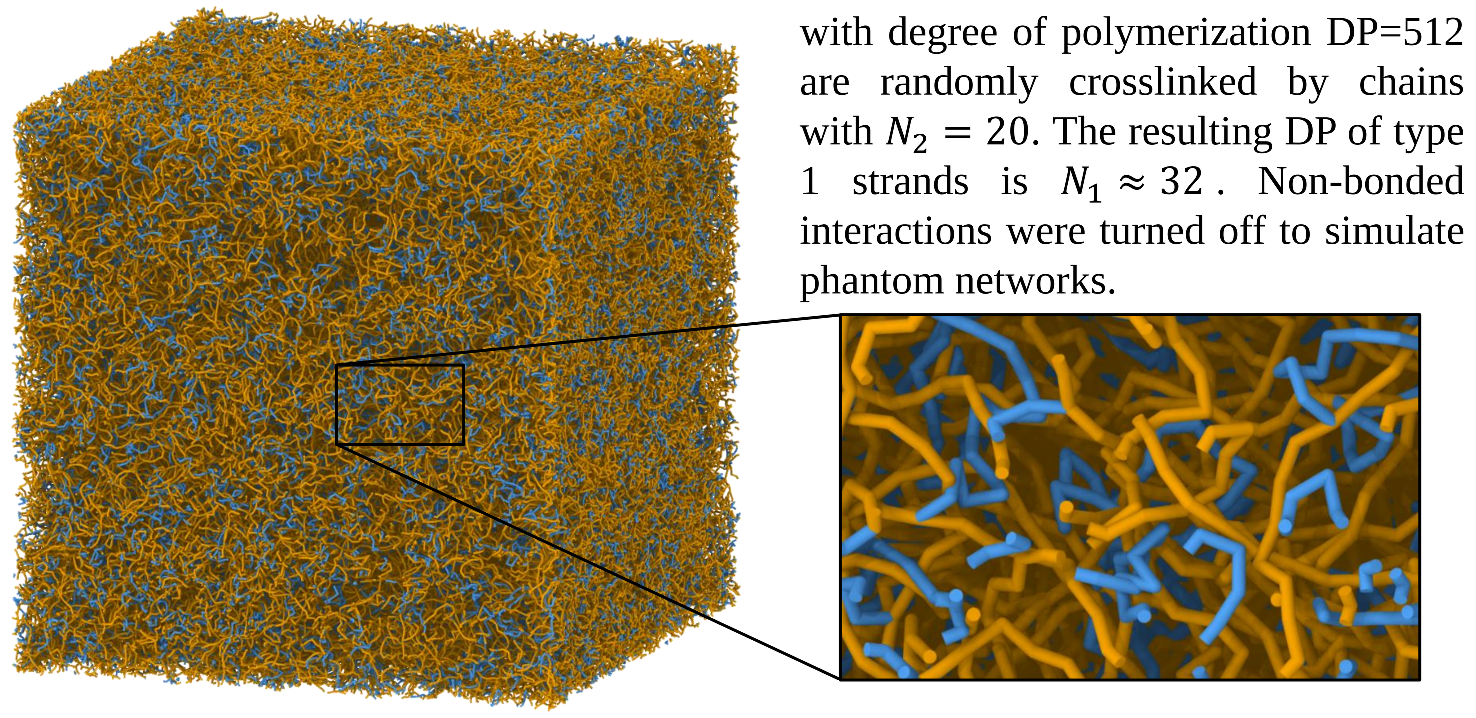
$r_{cut} = 2^{1/6}\sigma$

$k_{spring} = 100 k_B T/\sigma^2$

$R_m = 1.5\sigma$

Bending Potential

$$U_{bend}(\theta) = k_B T K(1 + \cos\theta)$$



Networks are made of bead-spring chains of beads with diameter σ. Chains with degree of polymerization DP=512 are randomly crosslinked by chains with $N_2 = 20$. The resulting DP of type 1 strands is $N_1 \approx 32$. Non-bonded interactions were turned off to simulate phantom networks.

SUMMARY

Using a combination of analytical calculations and coarse-grained molecular dynamics simulations, we developed a model which describes the elasticity of hybrid networks in the linear and nonlinear deformation regimes. The model predictions are in a good agreement with simulation results. In particular, we show that individual network strands deform in such a way to maintain a force balance at each junction point resulting in nonaffine deformation of the individual network strands.

REFERENCES

[1] *Macromolecules*, **2018**, 51, 638−645

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