Dobrynin Research Group

Effects of Chain Architecture on the Gel Modulus of Graft Polymer Networks

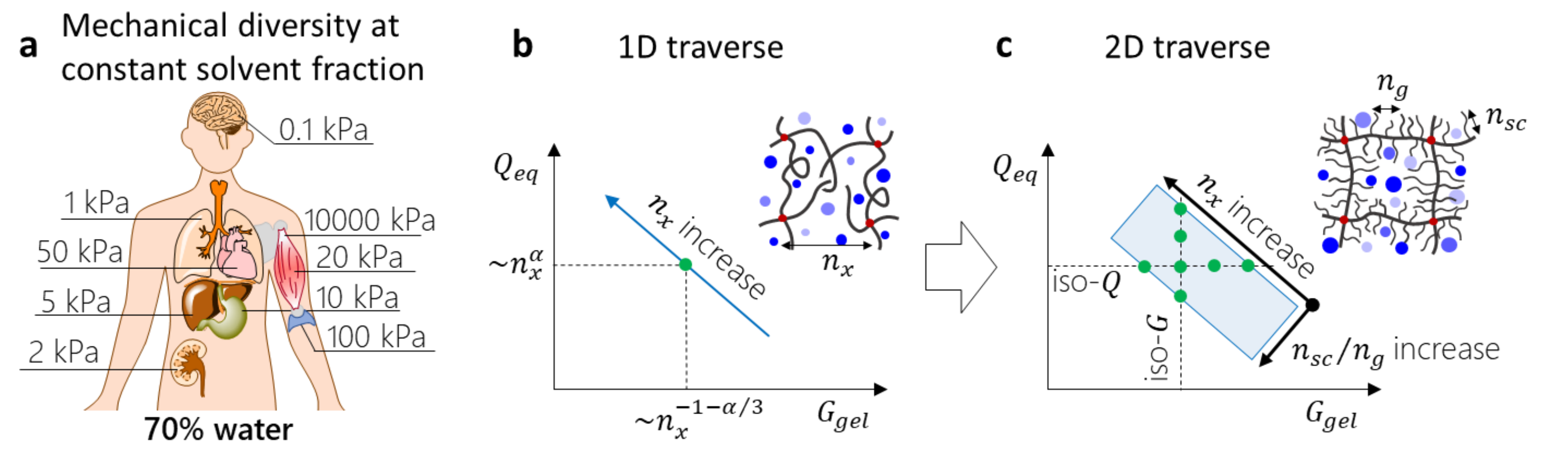
Michael Jacobs and Andrey V. Dobrynin
Department of Chemistry, University of North Carolina, Chapel Hill, NC 27599

UNC COLLEGE OF ARTS & SCIENCES

Abstract

Polymer networks whose strands are made of graft polymers have been shown to possess mechanical properties similar to biological tissues and been able to swell to larger volumes than their linear chain counterparts. We use a combination of theoretical analysis and molecular dynamics simulations to elucidate the effect of graft polymer architecture on the swelling ratio, Q, the modulus of the swollen gels, $G_{gel}(Q)$, and its relationship with the modulus of the dry networks, G_{dr}. Our analysis indicates that for networks made of comb-like strands with few grafted side chains the gel modulus scales as $G_{gel}(Q) = G_{dr}/Q^{\alpha}$, with exponent $\alpha \approx 0.56$ in a good solvent and 1/3 in a θ-solvent solution regimes. For networks with bottlebrush-like strands, however, we find that the additional chain thickness and rigidity introduced by swelling of the densely grafted side chains require a significant correction which is due to strong concentration dependence of the effective Kuhn length of the bottlebrush strands.

Architecture-Enabled Parameterization

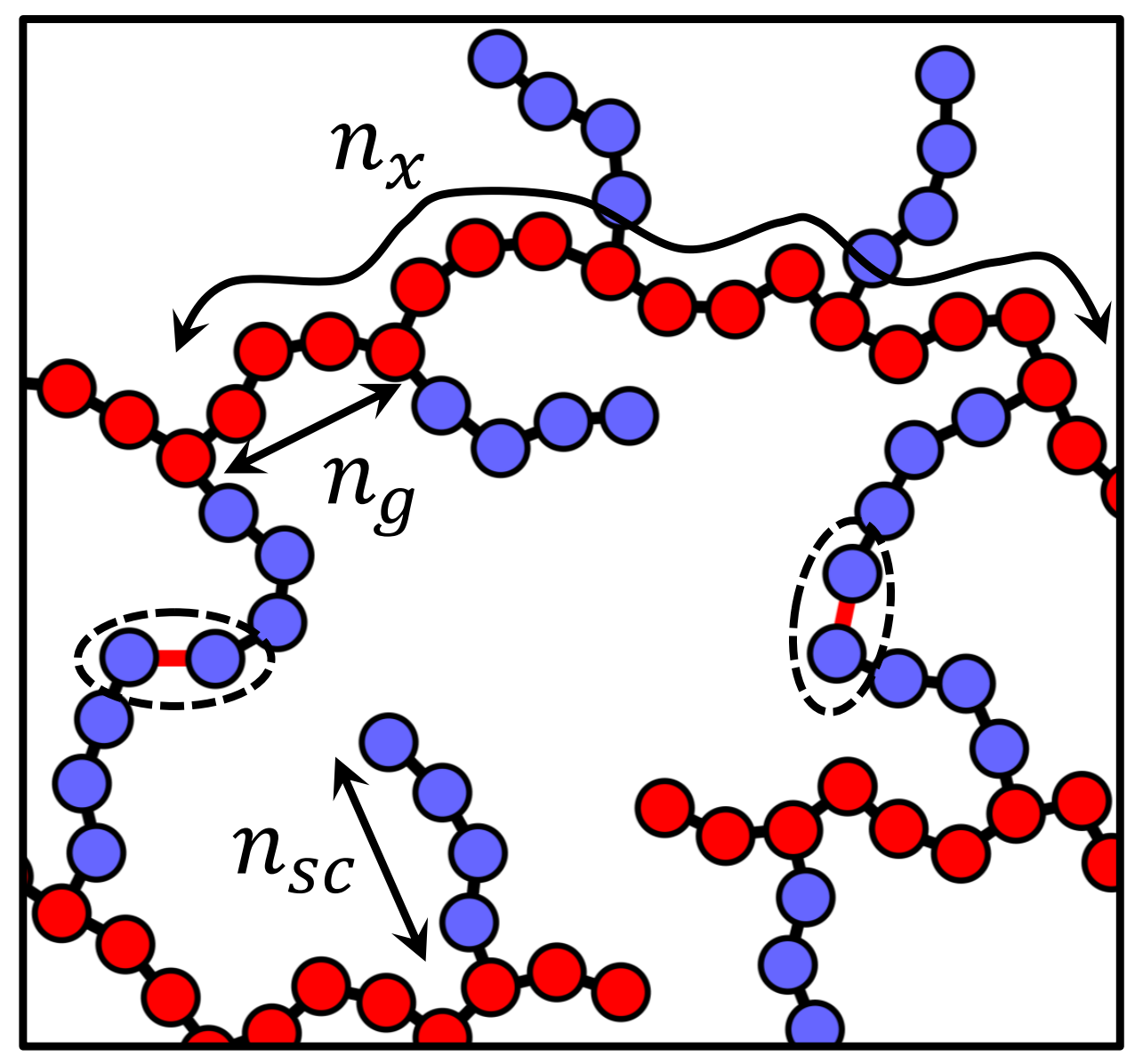


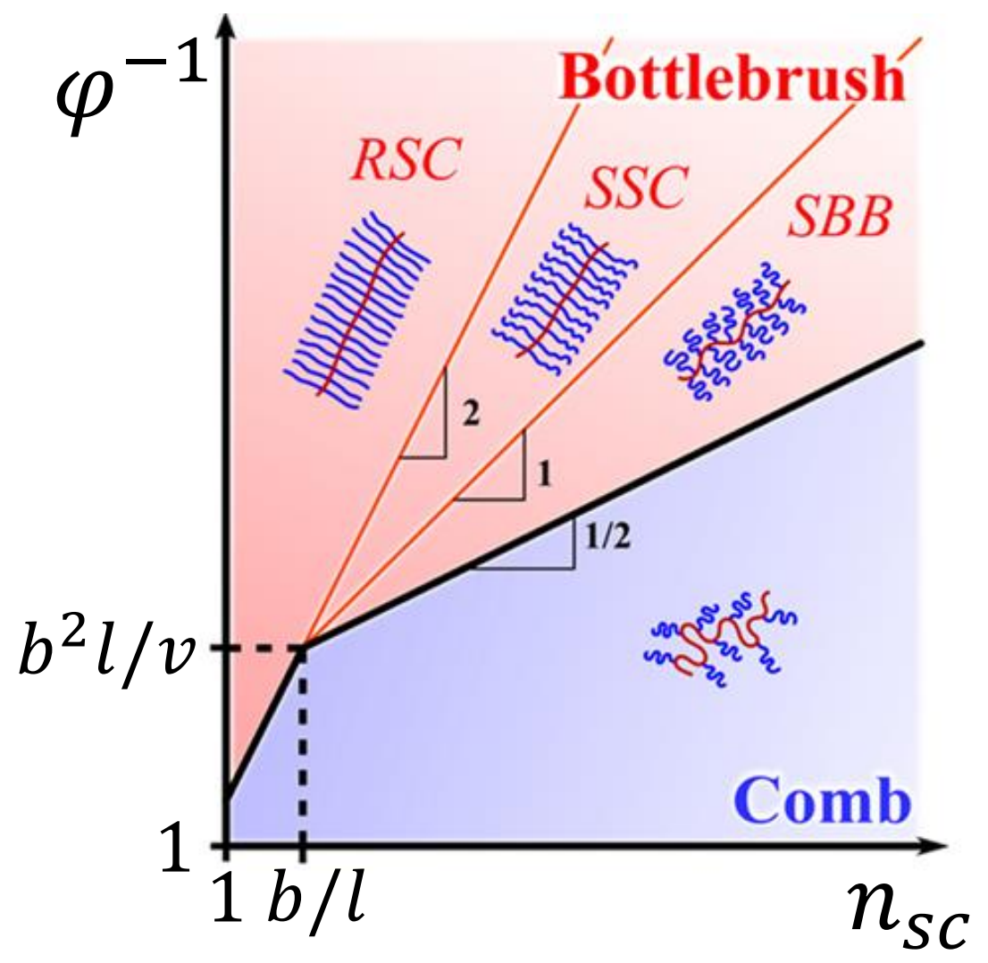
(a) Biological tissues possess a wide range of modulus at a constant solvent fraction of ~70%

(b) With linear chains, there is a direct tradeoff between swelling ratio Q and the gel modulus G_{gel}

(c) Network strands made of graft polymers allow for independent tuning of Q and G_{gel} by adjusting the chain architecture

Graft Polymer Chains



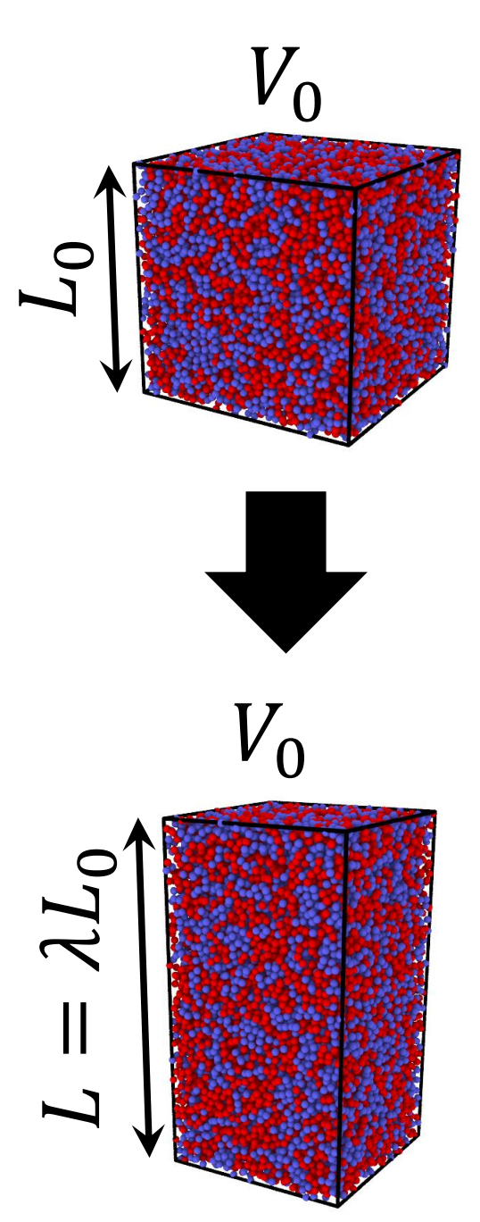


- n_g: number of bonds in backbone spacer
- n_{sc}: degree of polymerization (DP) of side chains
- n_x: DP of backbone between crosslinks

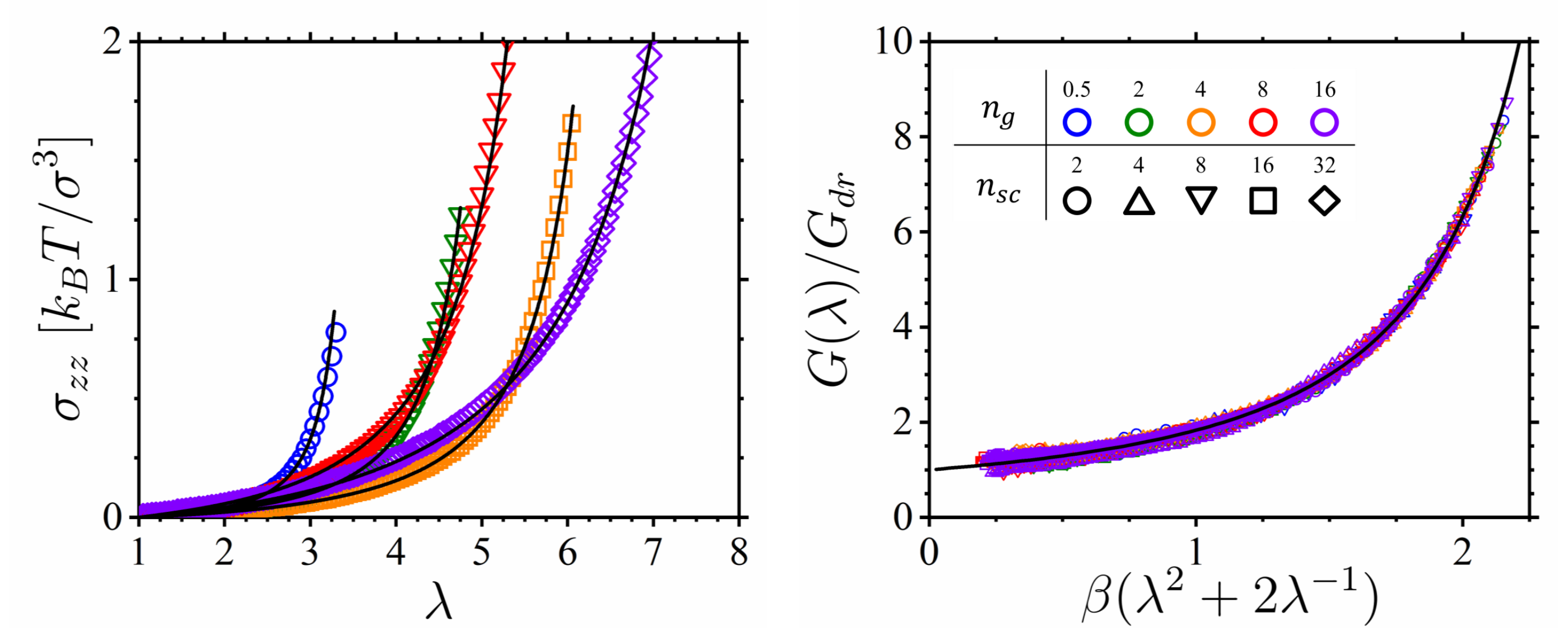
- Fraction of backbone monomers
  $\varphi = \frac{n_g}{n_g+n_{sc}}$
- Effective Kuhn length $b_K \geq b$, Kuhn length of bare backbone
- Monomer excluded volume v
- Monomer projection length l

Macromolecules **2017**, 50, 3430-3437

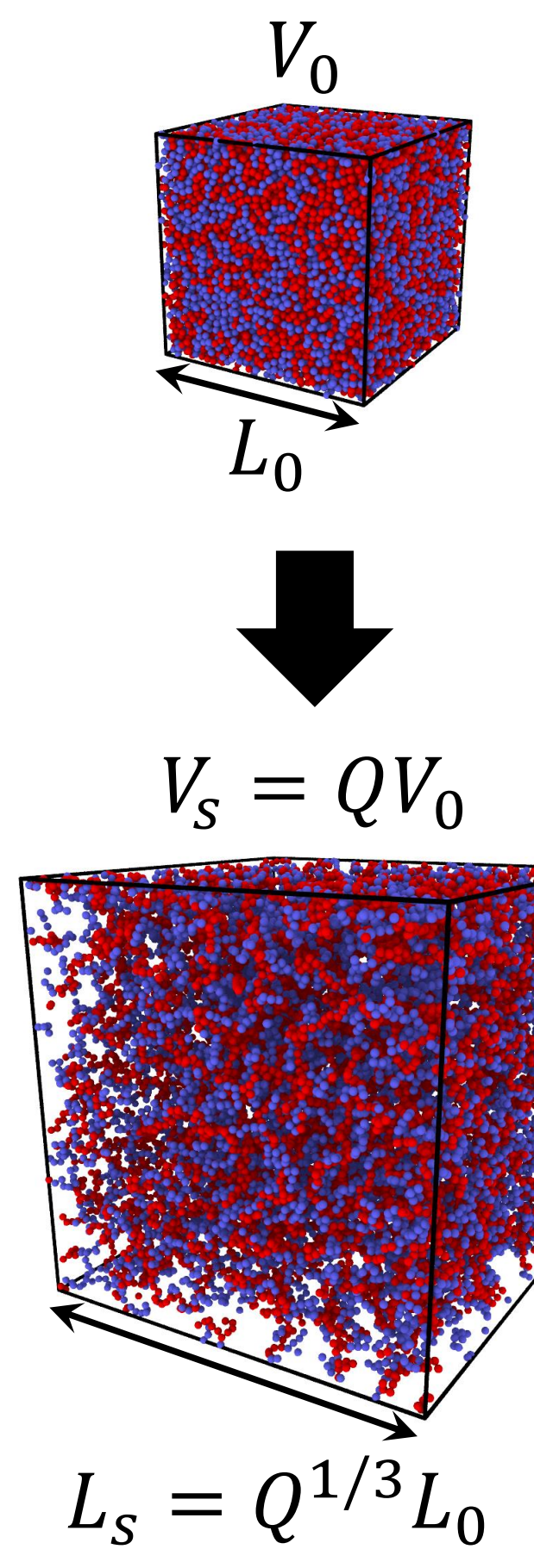
Dry Network Modulus



$$G(\lambda) = \frac{\sigma_{zz}}{\lambda^2 - \lambda^{-1}} = \frac{G_{dr}}{3}\left(1 + 2\left(1 - \frac{\beta}{3}(\lambda^2 + 2\lambda^{-1})\right)^{-2}\right)$$



Network Swelling



$$I_1 = \lambda_x^2 + \lambda_y^2 + \lambda_z^2$$

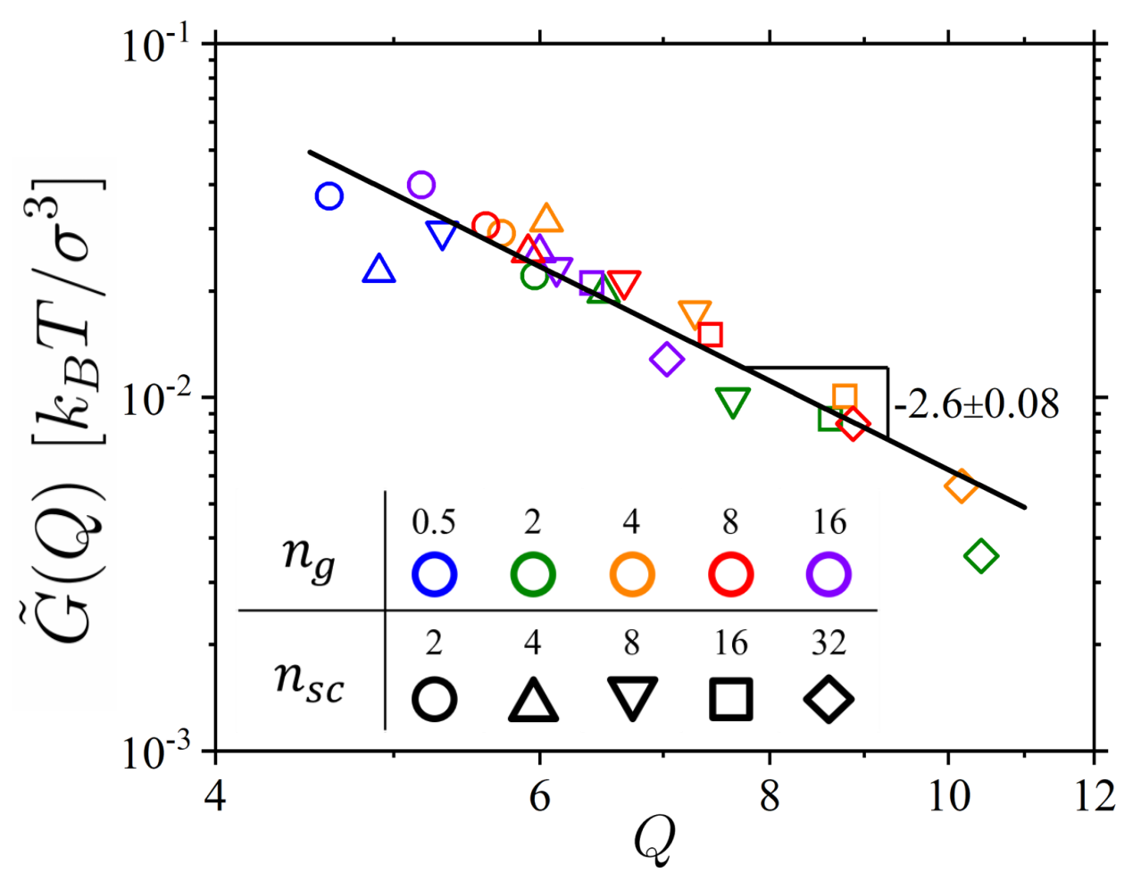
Stretching: $I_1 = \lambda^2 + 2\lambda^{-1}$

Swelling: $I_1 = 3Q^{2/3}$

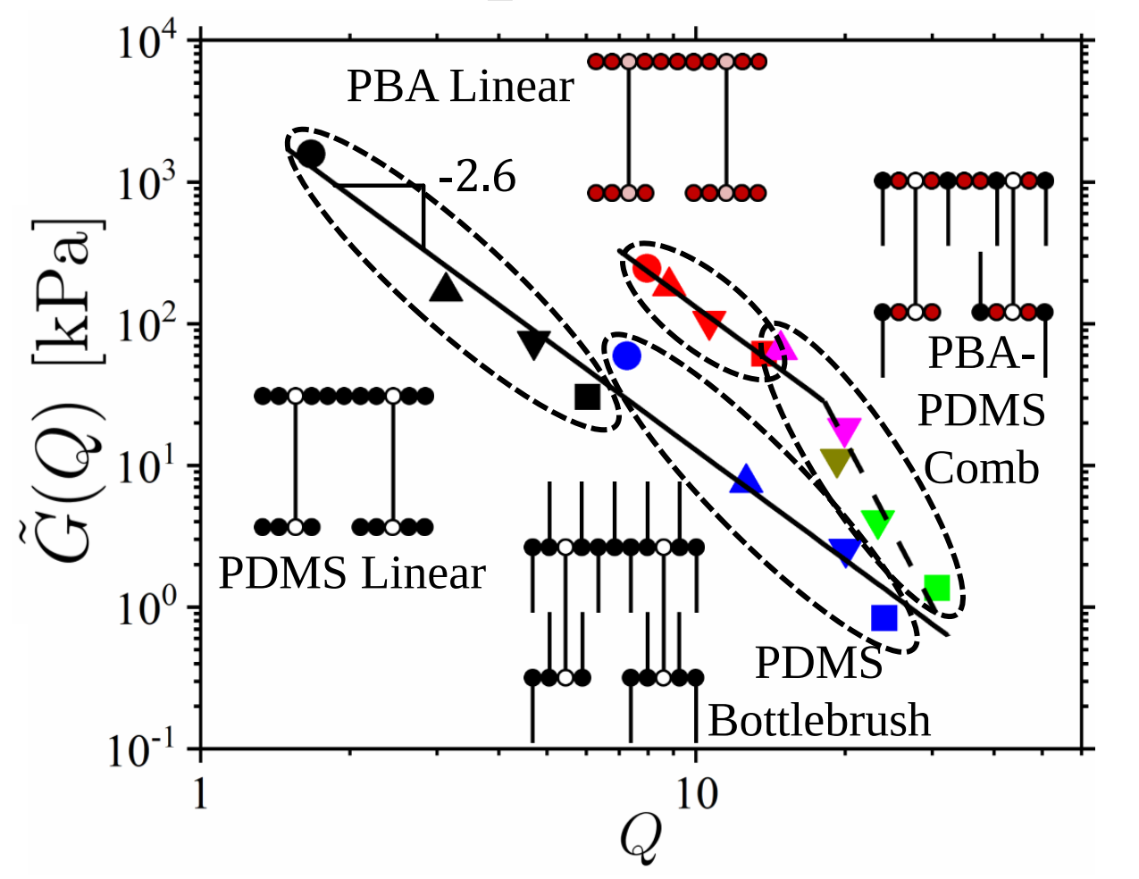
$$\tilde{G}(Q) = \frac{G_{dr}}{3}\left(1 + 2\left(1 - \beta Q^{2/3}\right)^{-2}\right)$$

$$\tilde{G}(Q) \approx \frac{k_BT}{v}\frac{Q^{-8/3}}{3} \approx Q^{1/3}\pi(Q)$$

Simulations



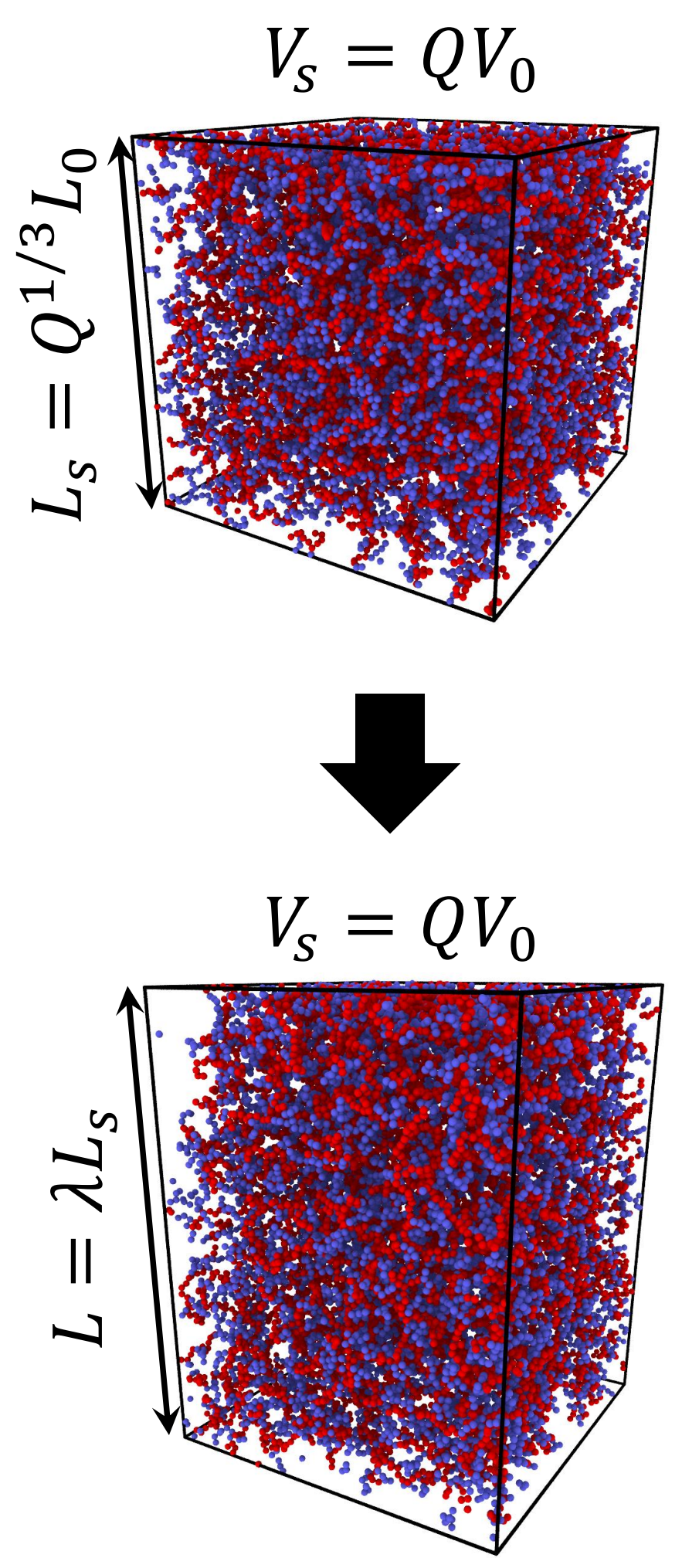
Experiments



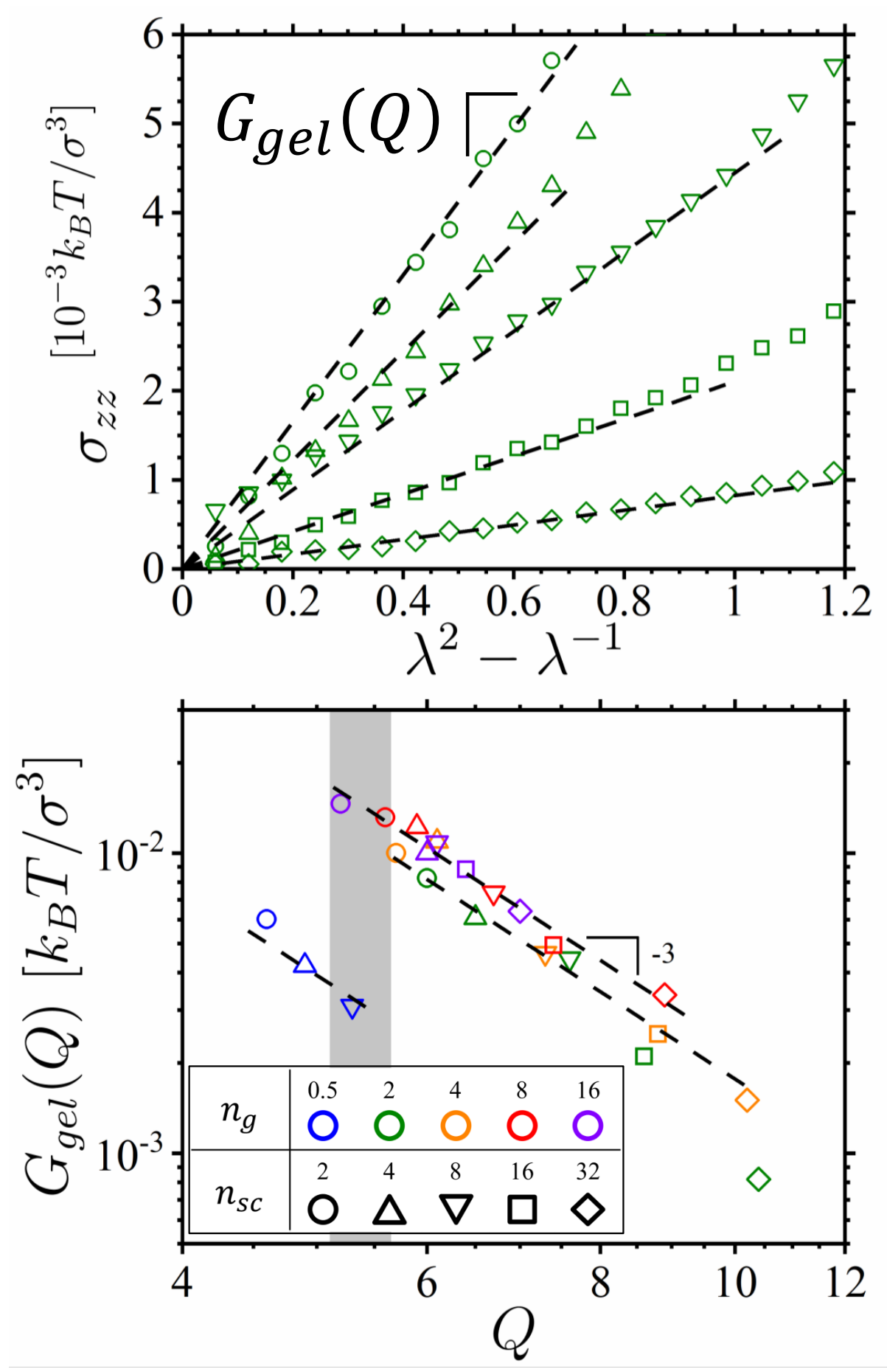
Macromolecules **2019**, 52, 5095-5101

Gel Modulus

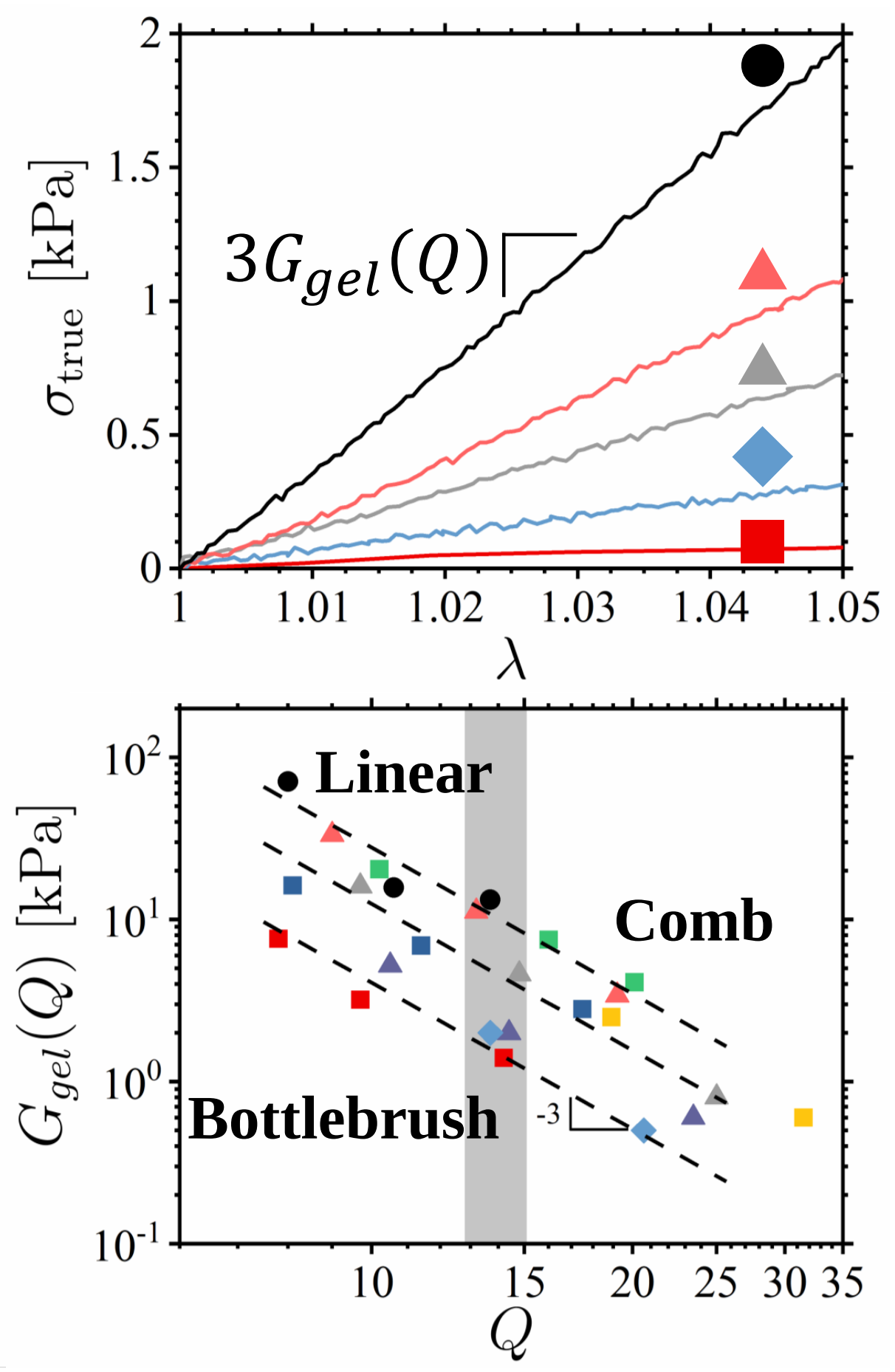
$G_{gel}(Q) \propto Q^{-3}$



Simulations



Experiments



Scaling Theory of Swollen Graft Polymers

In polymer solutions, correlation blobs with size

$$\xi = lg^{\nu}/B$$

contain g monomers; exponent $\nu = 0.5$ in θ solvents and 0.588 in good solvents, and scaling parameter

$$B = \left(\frac{l}{b_K}\right)^{1/2}\left(\frac{v}{(lb_K)^{3/2}}\right)^{1-2\nu}$$

Space-filling condition: backbone monomer number density

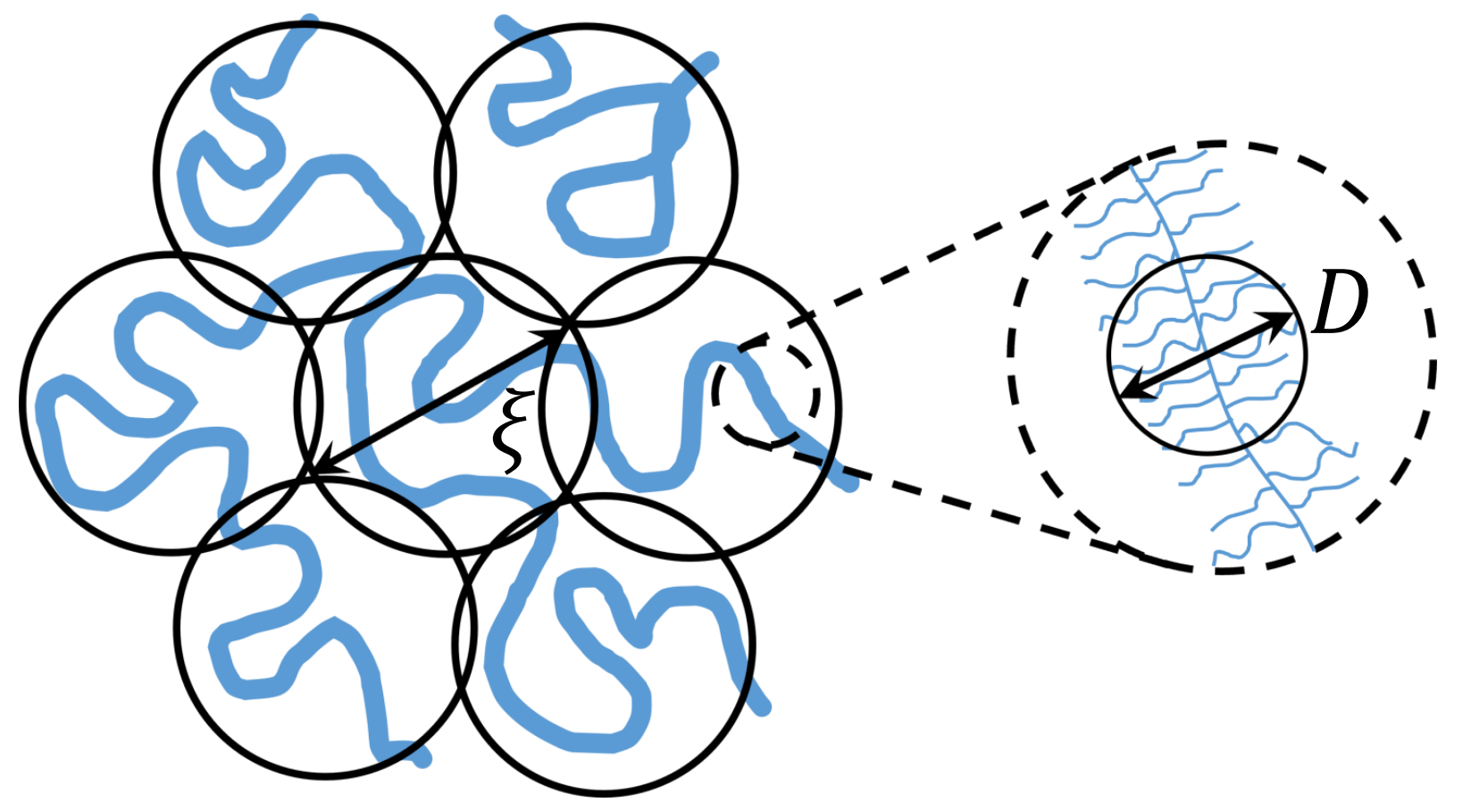
$$\rho \approx \frac{\varphi}{Qv} \approx \frac{g}{\xi^3}$$

Backbone network strand size

$$\langle R_{\xi}^2\rangle \approx \frac{\xi^2 n_x}{g} \approx l^2 n_x B^{\frac{1}{1-3\nu}}\left(\frac{Qv}{\varphi l^3}\right)^{\frac{2\nu-1}{3\nu-1}}$$

Combs

Effective Kuhn length $b_K \approx b$



Bottlebrushes

Act as a filament with diameter D; scaling parameter $B \approx (D/l)^{1-\nu}$

$$\frac{b_K}{b} \approx \begin{cases} v\varphi^{-1}/(l^3 b^3 n_{sc})^{1/2}, & \text{SBB regime} \\ (v\varphi^{-1}/lb^2)^{1/2}, & \text{SSC regime} \end{cases}$$

$$D \approx \begin{cases} (vb\varphi^{-1}n_{sc}^2)^{1/4} & \text{good solvent} \\ (v^2 b\varphi^{-1}n_{sc}^2/l)^{1/6} & \theta \text{ solvent} \end{cases}$$

Simulation Details

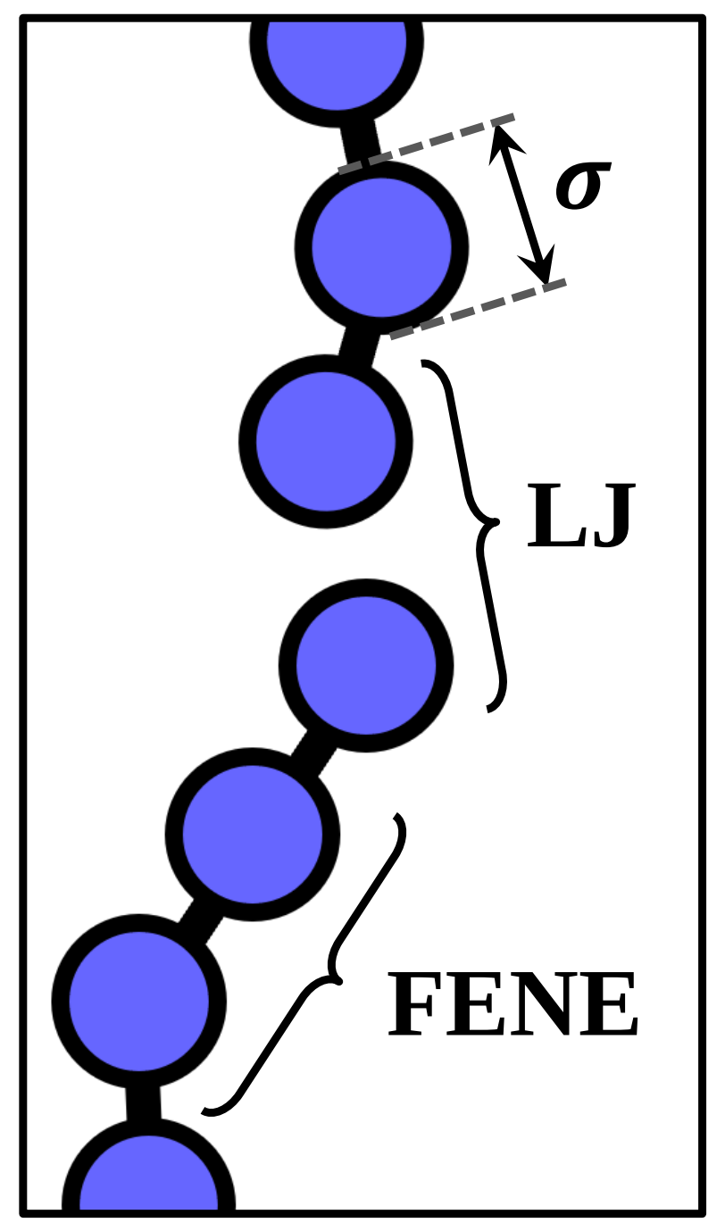
LAMMPS software package

Lennard-Jones (LJ) Pairwise Potential

Non-bonded interactions

$$U_{LJ}(r) = \begin{cases} 4\varepsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right) + \varepsilon, & 0 < r \leq 2^{1/6}\sigma \\ 0, & 2^{1/6}\sigma < r \end{cases}$$

$$\varepsilon = 1.5k_BT$$



Finite Extensible Nonlinear Elastic (FENE) Potential

Bonded interactions

$$U_{FENE}(r) = \frac{1}{2}K_b R_0^2 \ln\left(1 - \frac{r^2}{R_0^2}\right) + U_{LJ}(r)$$

$$K_b = 30k_BT/\sigma^2,\ R_0 = 1.5\sigma$$

Implicit Solvent Swelling

NPT with $P = 0k_BT/\sigma^3$, Nose-Hoover thermostat/barostat

Uniaxial Deformation

NVT with Langevin thermostat, incremental stepwise deformation, equilibrium stress $\sigma_{zz} = 0.5(P_{xx} + P_{yy}) - P_{zz}$

Conclusion

By adjusting the architecture of graft polymer networks, we can tune the Kuhn length and DP of the network strands to create a gel with a given swelling ratio and modulus. This independent control allows for the creation of materials with the ability to mimic the mechanics of a vast range of biological tissues.

Acknowledgments

National Science Foundation
DMREF-2049518

For more, visit our website by scanning the code!