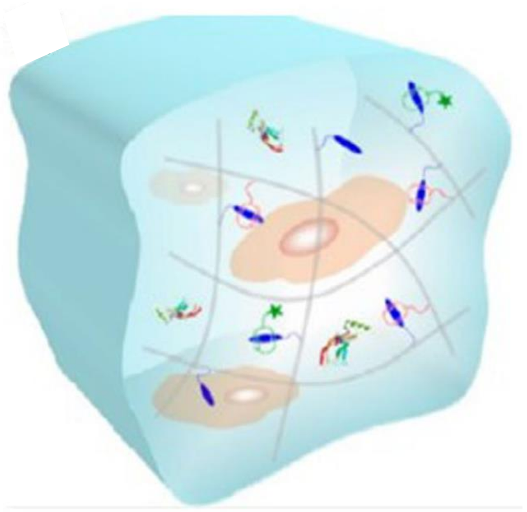
Swelling of Polyelectrolyte Networks with Brush-like Strands

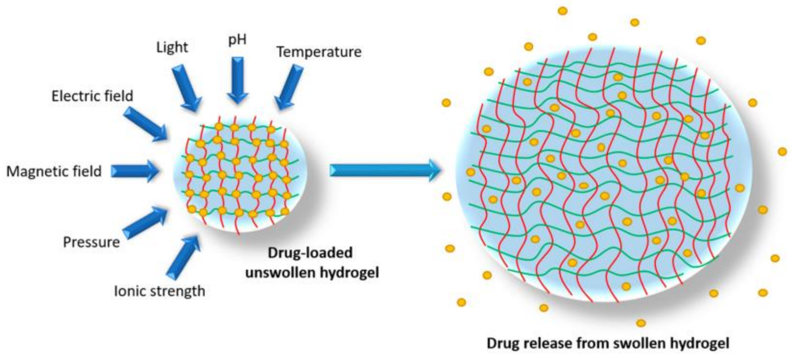
Michael Jacobs, Zilu Wang,
Andrey V. Dobrynin
Department of Polymer Science
The University of Akron

Charged Polymers and Biopolymers

Polyelectrolytes – polymers with positively or negatively charged groups



Eur. Cells and Mat. **2017**, 33, 59-75



Pharmaceutics **2018**, *10*(2), 71

Extracellular Matrix

Drug Delivery

Disposable Diapers

Balancing Network Elasticity and Interactions

$$F_{net} = F_{elastic} + F_{osmotic}$$

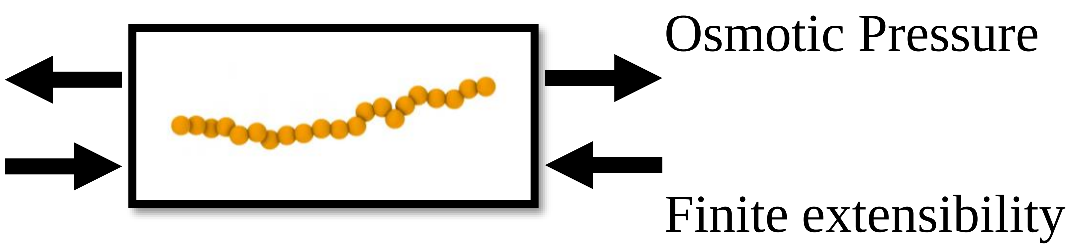
Equilibrium swelling volume is set by

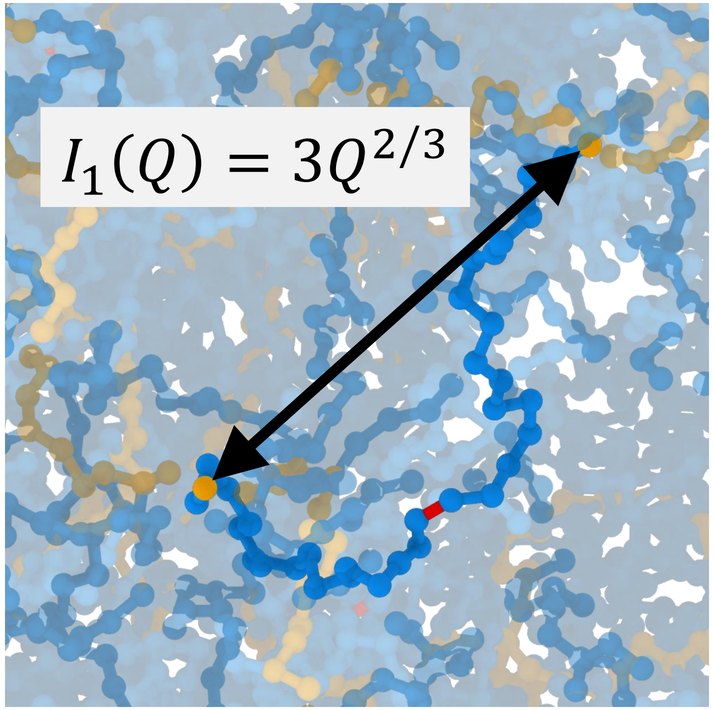
$$\frac{\partial F_{elastic}}{\partial V} + \frac{\partial F_{osmotic}}{\partial V} = 0$$

$$\frac{\partial F_{elastic}}{\partial V} = Q^{-1/3} G(Q) = Q^{-1/3} \frac{G_{dr}}{3} \left(1 + 2\left(1 - \frac{\beta I_1(Q)}{3}\right)^{-2}\right)$$

$$-\frac{\partial F_{osmotic}}{\partial V} = \pi(Q) = \begin{cases} \frac{k_B T}{v}\left(\tau \frac{Q^{-2}}{2} + \frac{Q^{-3}}{3}\right) & \text{neutral} \\ P_p - P_s & \text{charged} \end{cases}$$

$$\boxed{G(Q) = Q^{1/3} \pi(Q)}$$

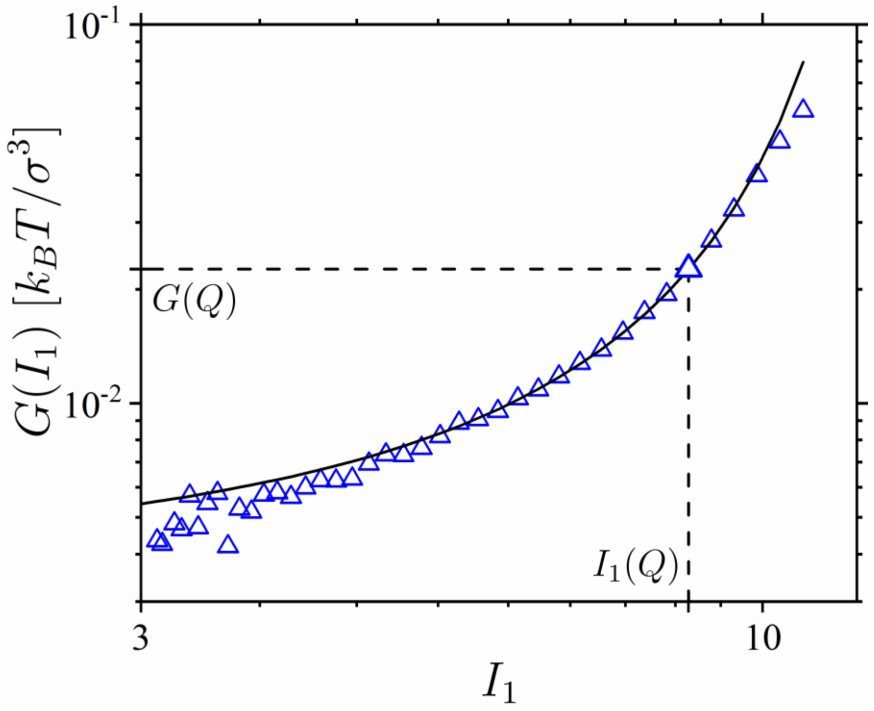




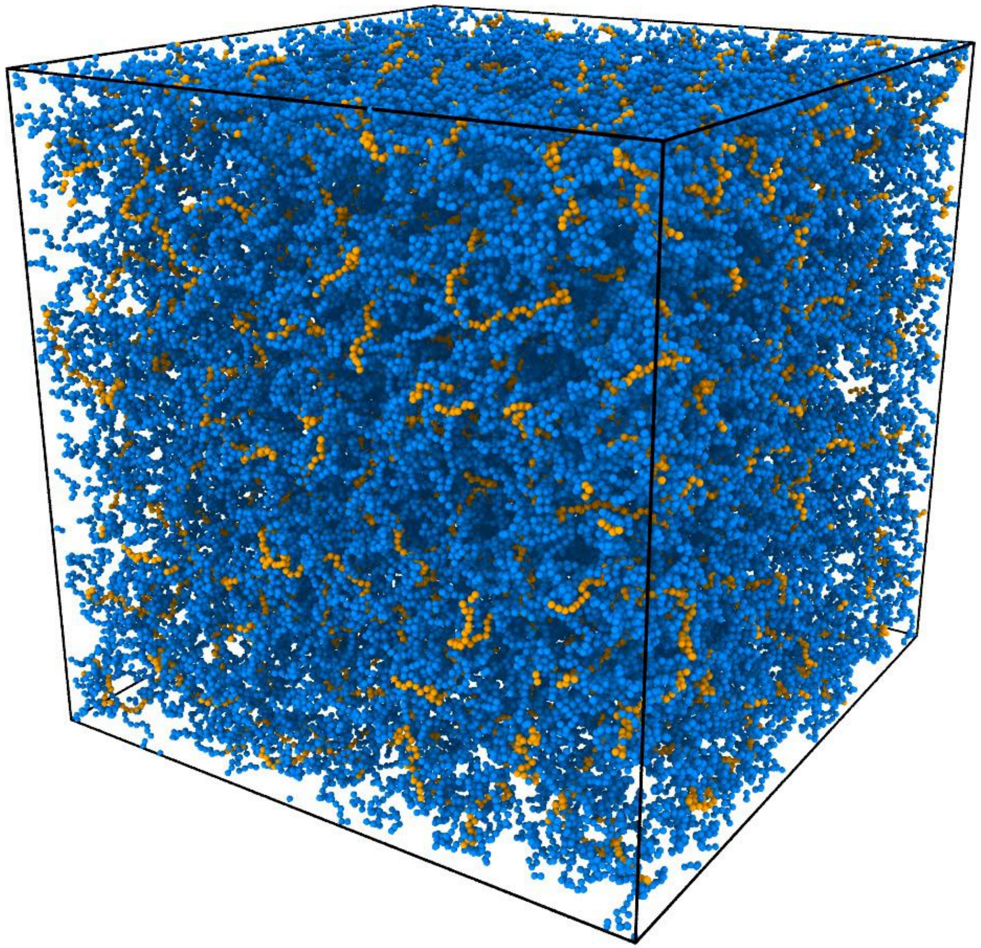
Nonlinear Shear Modulus

$$G(I_1) = \frac{G_{dr}}{3}\left(1 + 2\left(1 - \frac{\beta I_1}{3}\right)^{-2}\right)$$

- Stretch the sample to obtain the stress-strain curve. Translate this data to the nonlinear shear modulus using
$$G(I_1) = \frac{\sigma_{true}(\lambda)}{\lambda^2 - \lambda^{-1}} \text{ and } I_1 = \lambda^2 + 2\lambda^{-1}$$
- Swell the sample to obtain an equilibrium swelling ratio Q. Translate this to the first invariant using
$$I_1(Q) = 3Q^{2/3}$$
- Either fit the stress-strain data or interpolate the data to find $G(Q)$.



Neutral Bottlebrush Swelling



Crosslinked Brush-like Chains

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

$$U_{FENE}(r) = -\frac{K}{2}R_{max}^2 \ln\left[1 - \left(\frac{r^2}{R_{max}^2}\right)\right] + 4\varepsilon_{LJ}\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] + \varepsilon_{LJ}$$

$\sigma = 1.0$ $\quad$ $K = 30k_BT/\sigma^2$

$r_{cut} = 2^{1/6}$ $\quad$ $R_{max} = 1.5\sigma$

Effective bending potential due to side chain interaction

Isobaric-isothermal (NPT) ensemble: $P = 0.0k_BT/\sigma^3$

Polymer architecture range

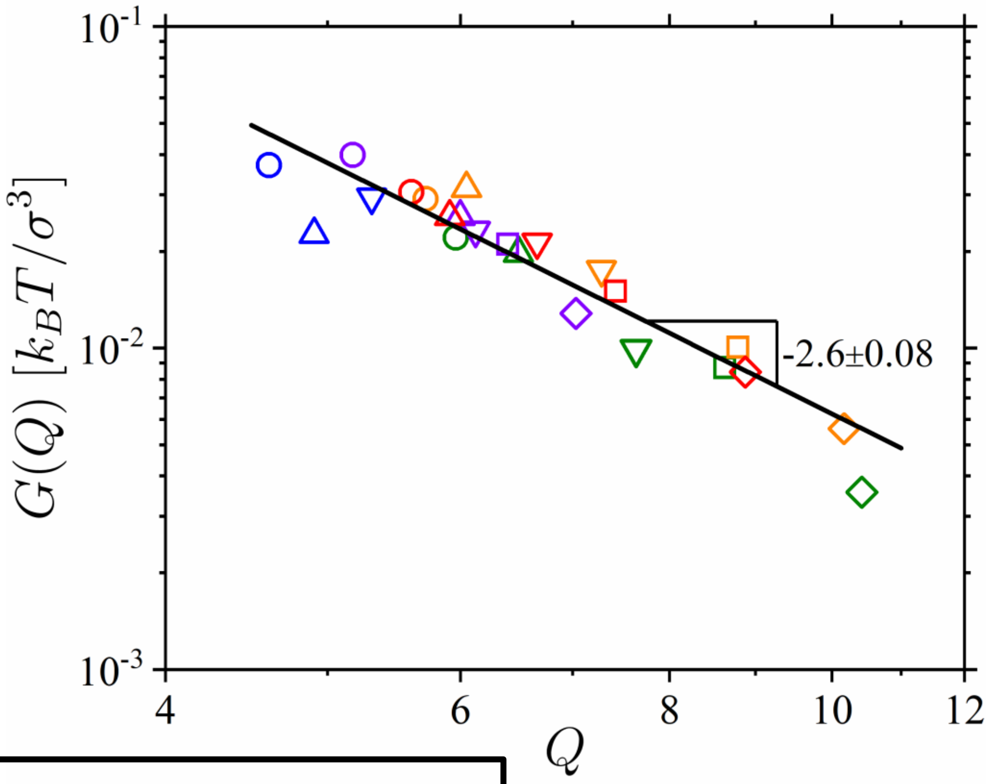
$$0.5 \le n_g \le 16 \qquad 2 \le n_{sc} \le 32$$

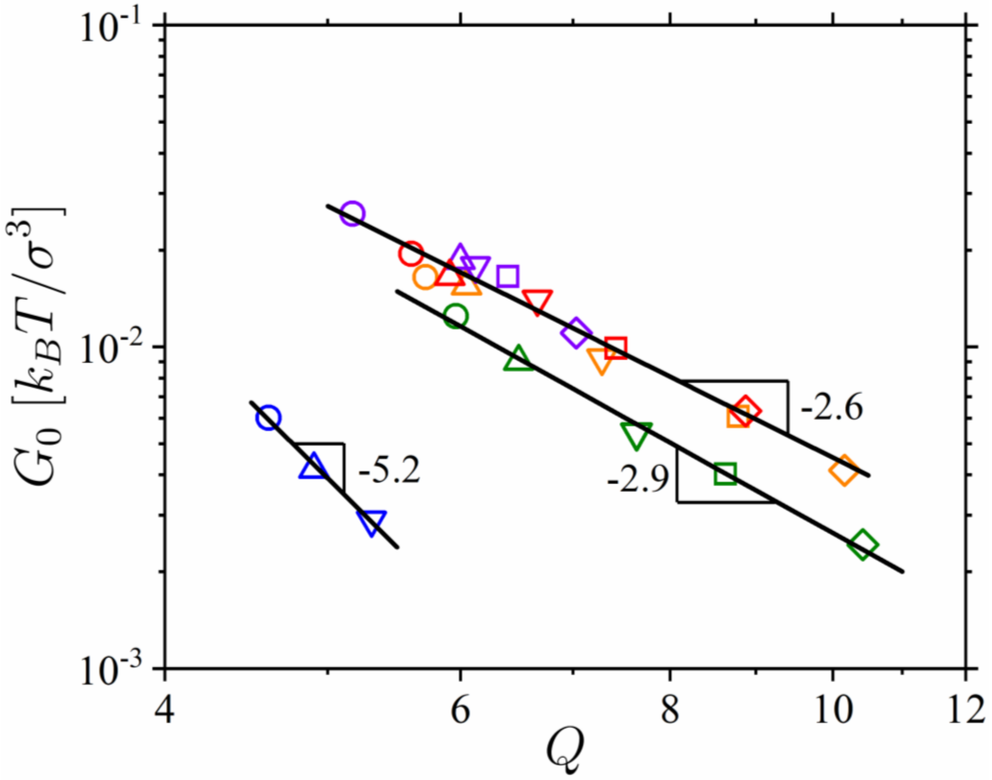
Simulations of Neutral Bottlebrush Swelling

$$\pi(Q) = \frac{k_B T}{v}\left(\tau \frac{Q^{-2}}{2} + \frac{Q^{-3}}{3}\right)$$

$$G(Q) = Q^{1/3}\pi(Q) \rightarrow G(Q) \propto Q^{-8/3}$$

$$G_0 = G(Q = 1) = \frac{G_{dr}}{3}\left(1 + 2(1-\beta)^{-2}\right)$$





Poster Session III #123

Charged Systems

Coulombic potential

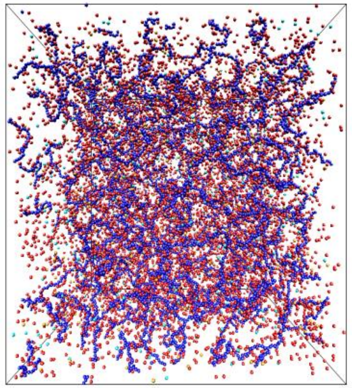
$$U_{Coul}(r_{ij}) = k_B T \frac{l_B q_i q_j}{r_{ij}}$$

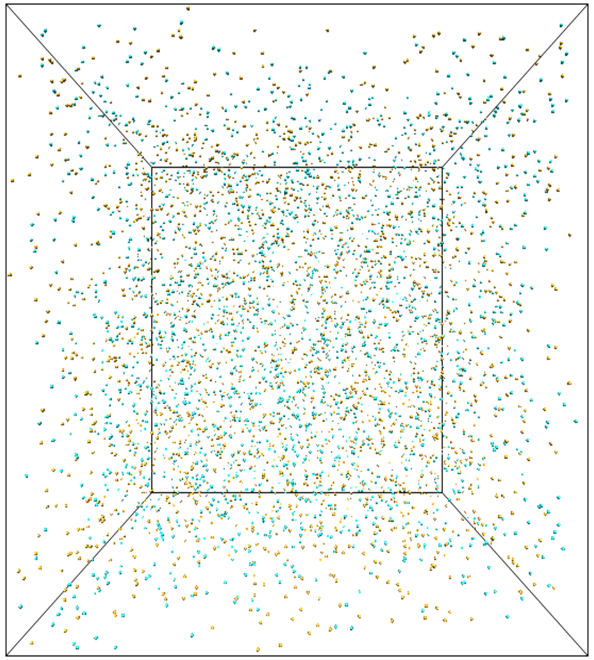
- Bjerrum length $l_B = \frac{e^2}{\varepsilon k_B T} = \sigma$

Linear Salt Solutions

LJ potential + FENE bonds

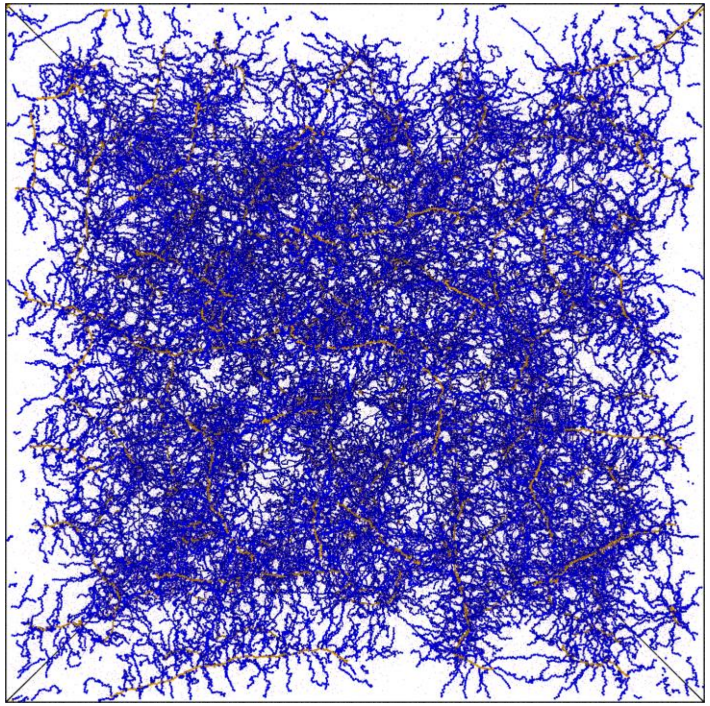
Fraction of charged monomers $f = 1$



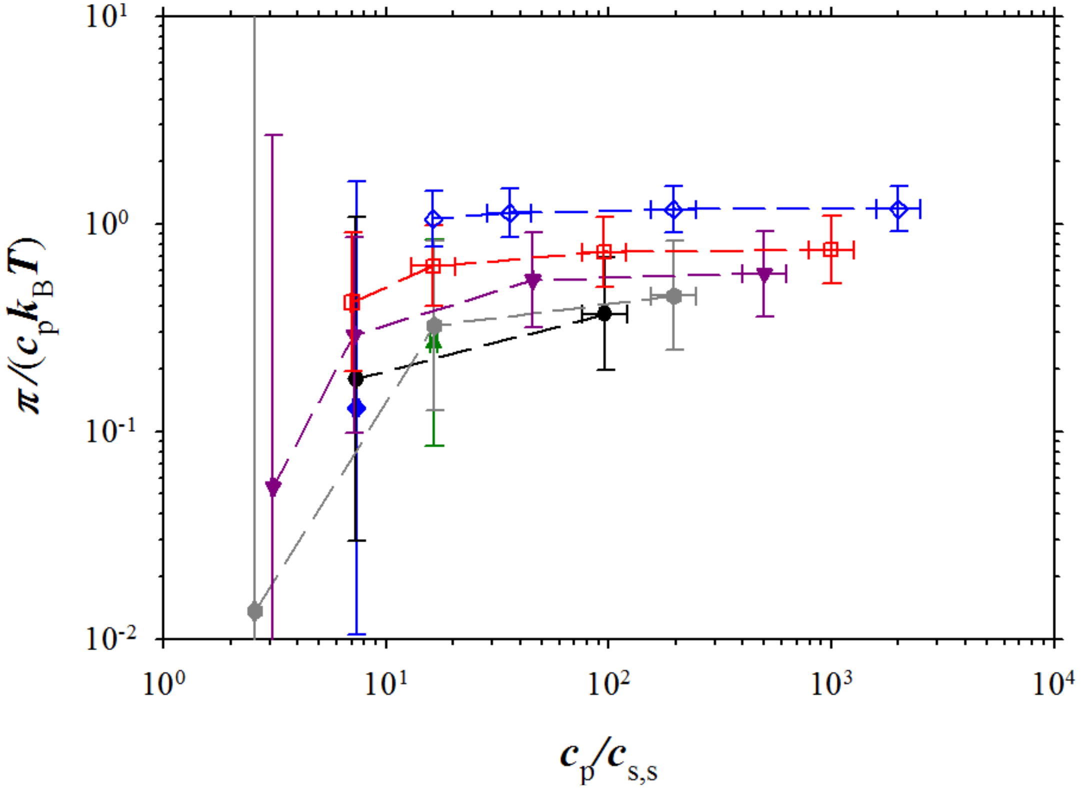


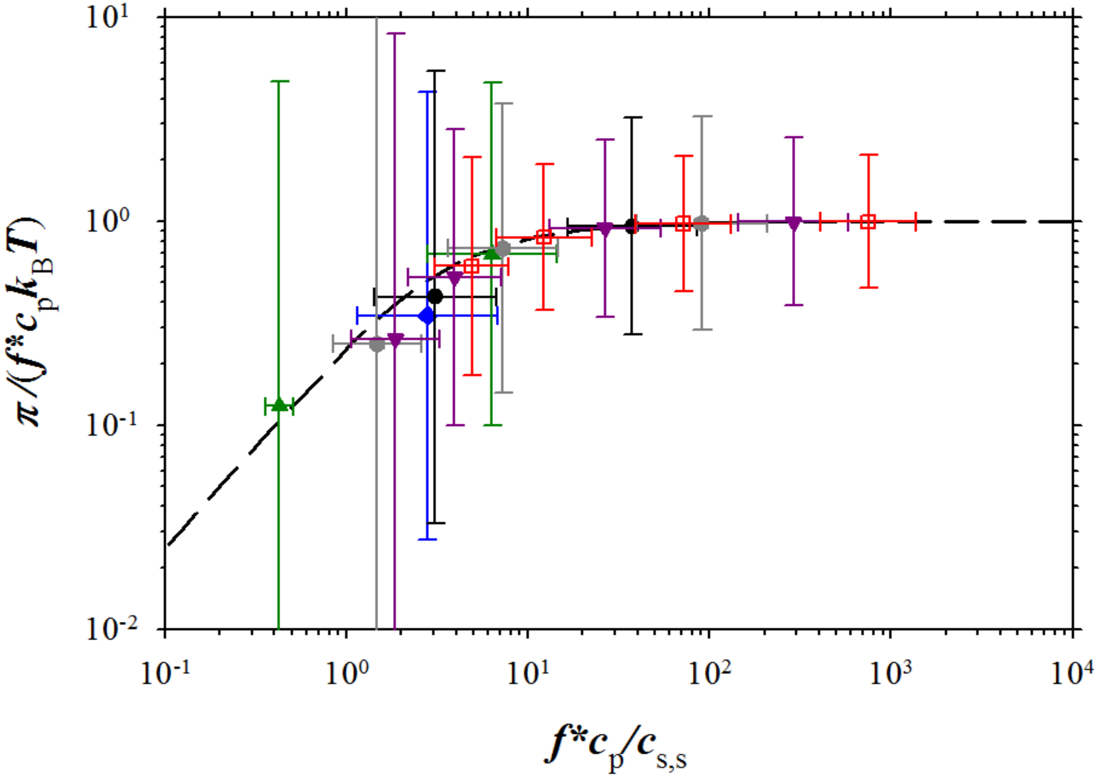
Bottlebrush Networks

The same systems as the neutral networks, with positive charges added every 1, 2, or 4 side chain monomers, and counterions added for system neutrality



Osmotic Pressure





$$\frac{\pi}{k_B T} \approx c_{s,p}^{+} + c_{s,p}^{-} - 2c_{s,s} = \sqrt{\left(f^* c_p\right)^2 + 4c_{s,s}^2} - 2c_{s,s}$$

→

$$\frac{\pi}{k_B T f^* c_p} \approx \sqrt{1 + 4\left(\frac{c_{s,s}}{f^* c_p}\right)^2} - 2\frac{c_{s,s}}{f^* c_p}$$

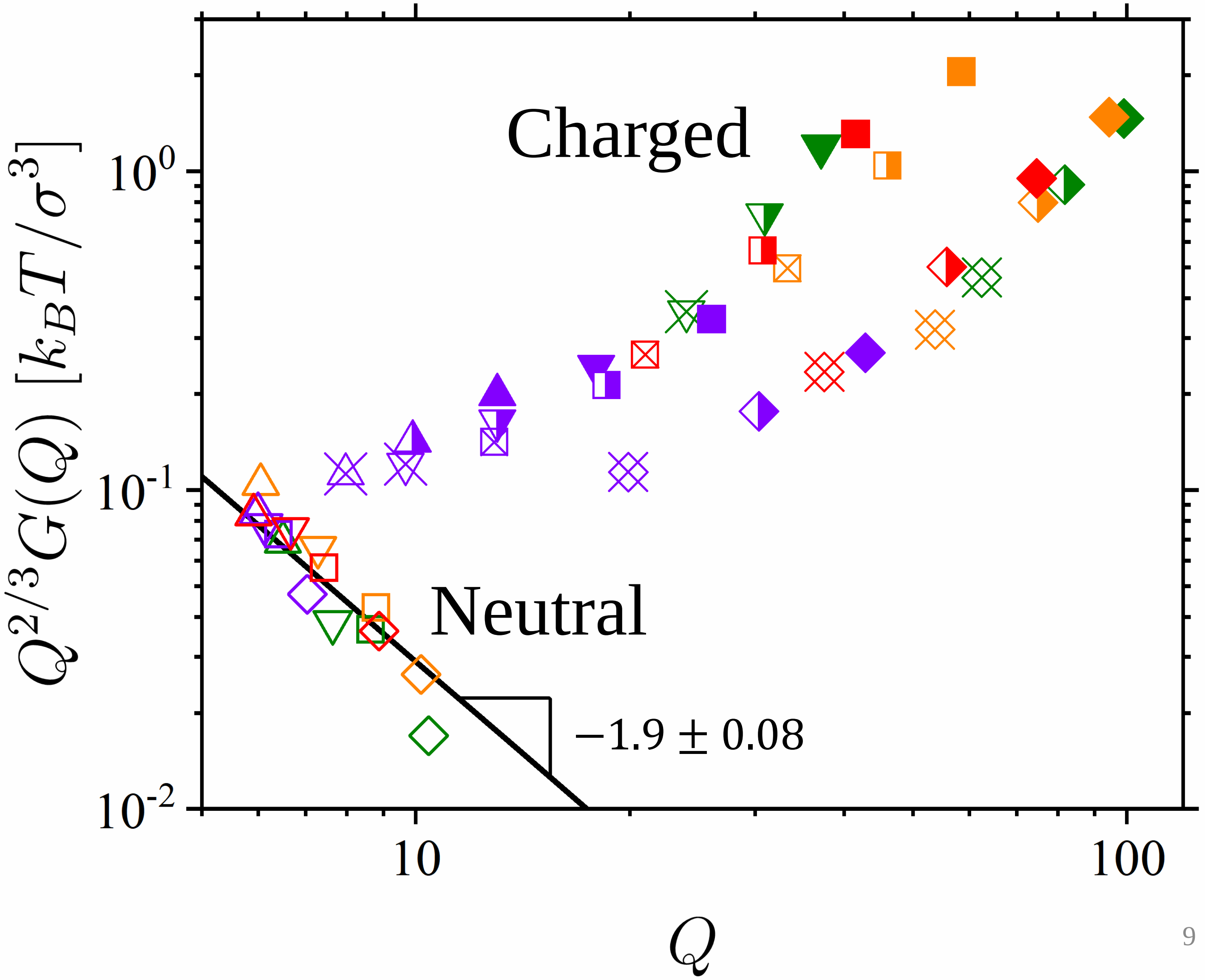
Polymers **2014**, 6, 1897-1913

Comparison of Charged and Neutral Networks

$$\pi(Q) = Q^{-1/3} G(Q)$$

$$\frac{G(Q)}{\rho k_B T} = f Q^{-2/3} + B Q^{-8/3}$$

$$Q^{2/3} \frac{G(Q)}{\rho k_B T} = f + B Q^{-2}$$

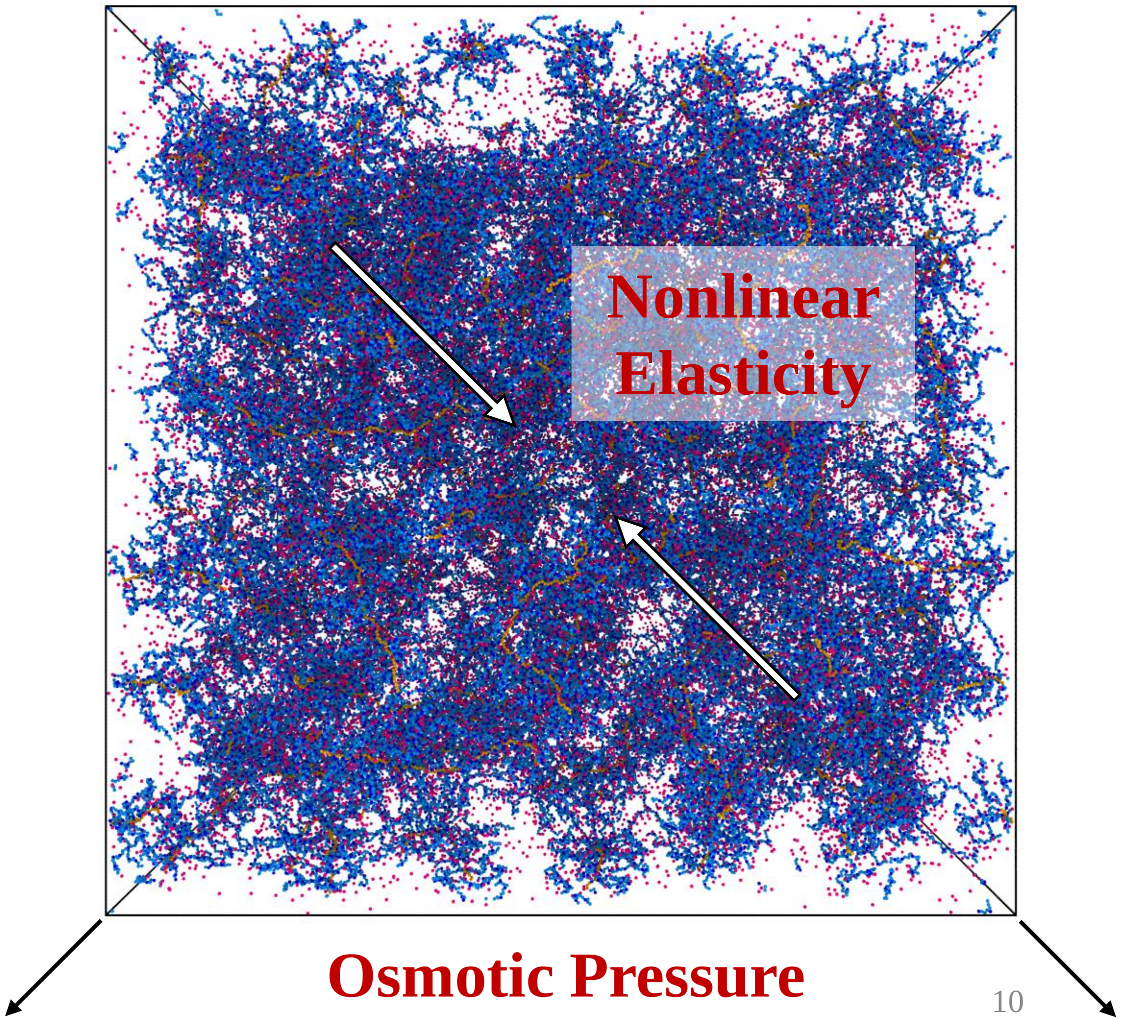


Conclusions

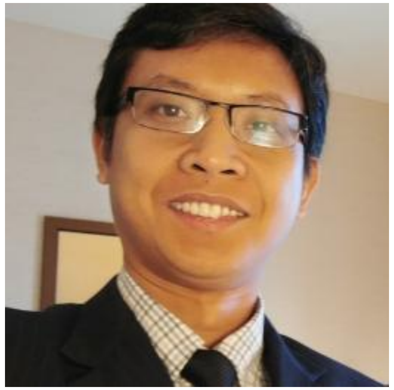
- Network swelling is the result of an interplay between osmotic pressure and nonlinear elasticity.

- In neutral systems, osmotic pressure is driven by particle-solvent interaction, while in charged systems it is dominated by osmotic pressure of counterions.

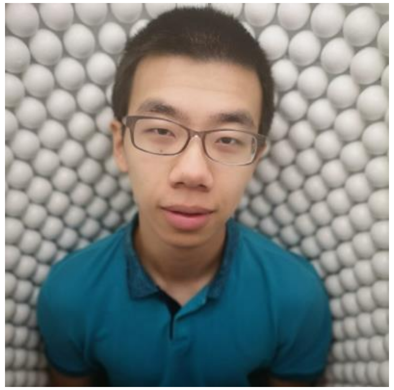
- Our analysis has shown that it is necessary to use melt-state stress-strain data to properly analyze network swelling properties for both charged and neutral systems.



Acknowledgements



Dr. Jan-Michael Carrillo (ORNL)



Dr. Heyi Liang (Univ. of Chicago)

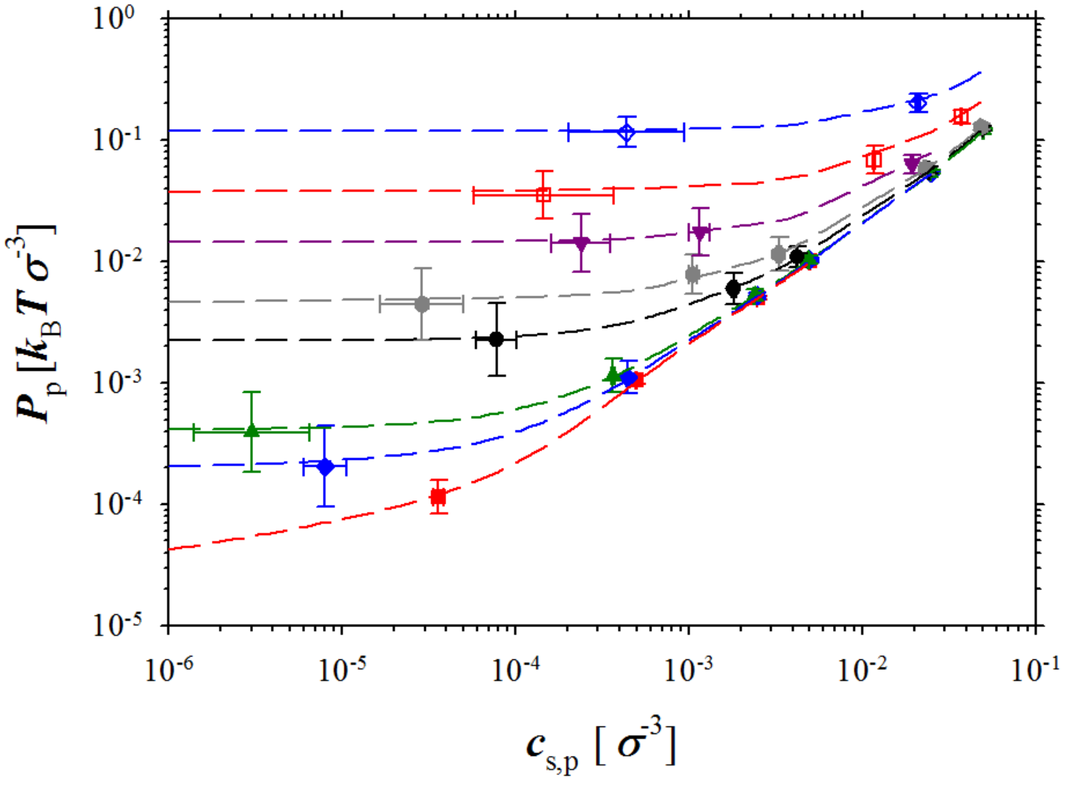
Dr. Zilu Wang

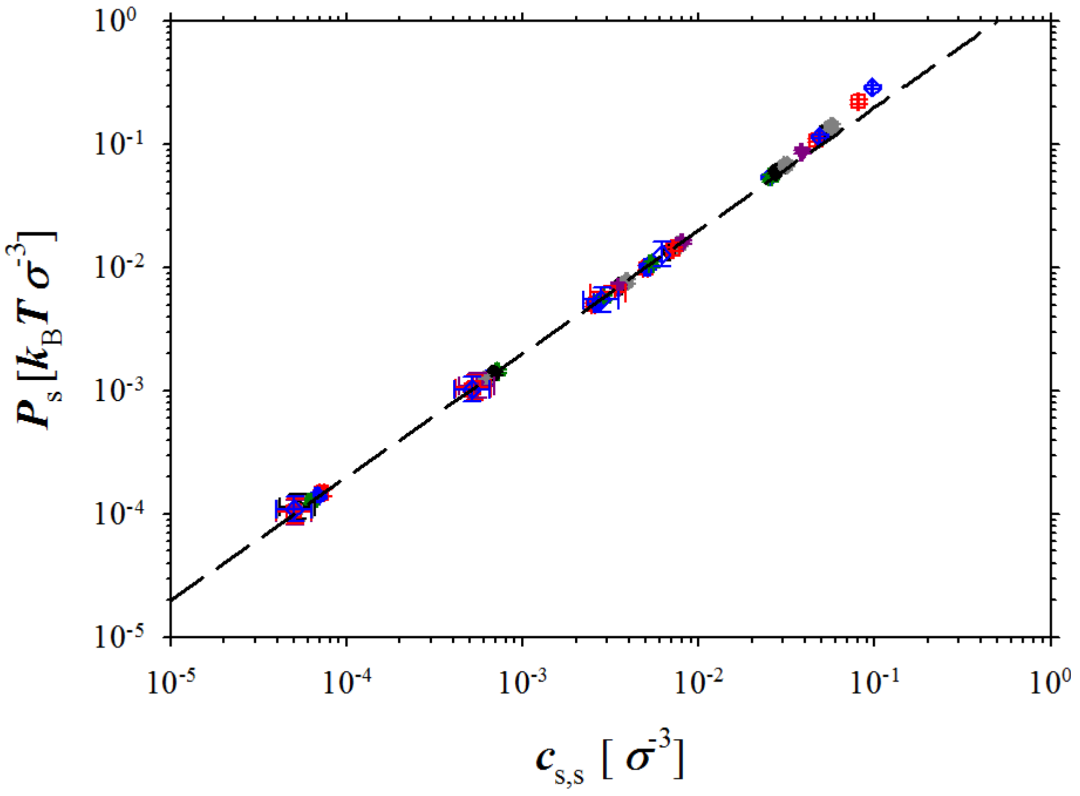
Prof. Andrey V. Dobrynin

National Science Foundation
(DMR 1921923)

Dobrynin Research Group

Pressure Dependence





Polymers **2014**, 6, 1897-1913