Dobrynin Research Group

THE UNIVERSITY of NORTH CAROLINA at CHAPEL HILL

Quantifying the Effect of Multivalent Ions in Polyelectrolyte Solutions

Presented by Michael Jacobs

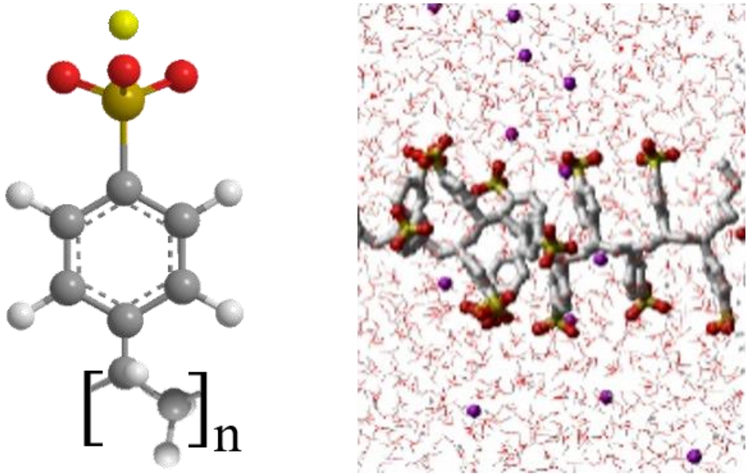
Michael Jacobs

Carlos G. Lopez
RWTH Aachen University

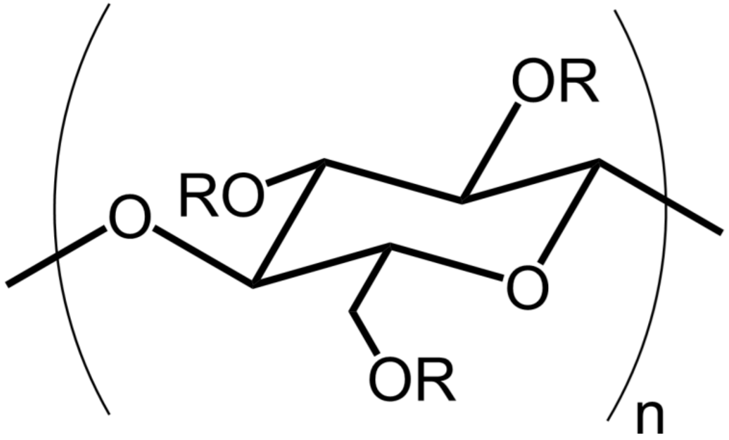
Andrey V. Dobrynin

Polyelectrolytes

Sodium Poly(styrene sulfonate)
(NaPSS)



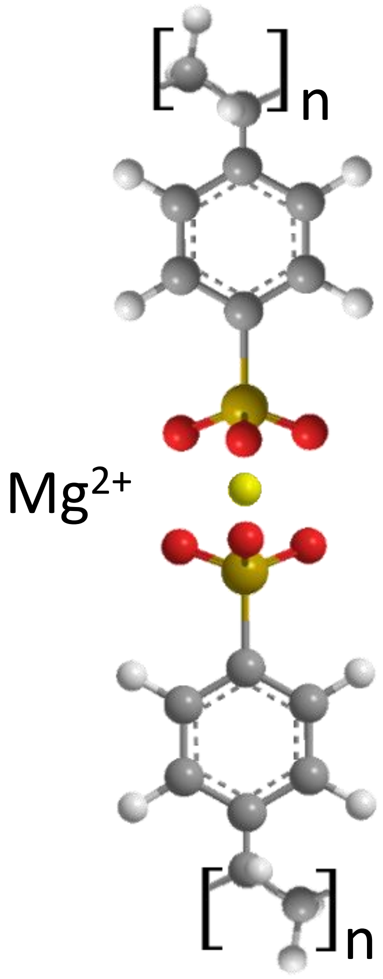
Sodium Carboxymethyl Cellulose
(NaCMC)



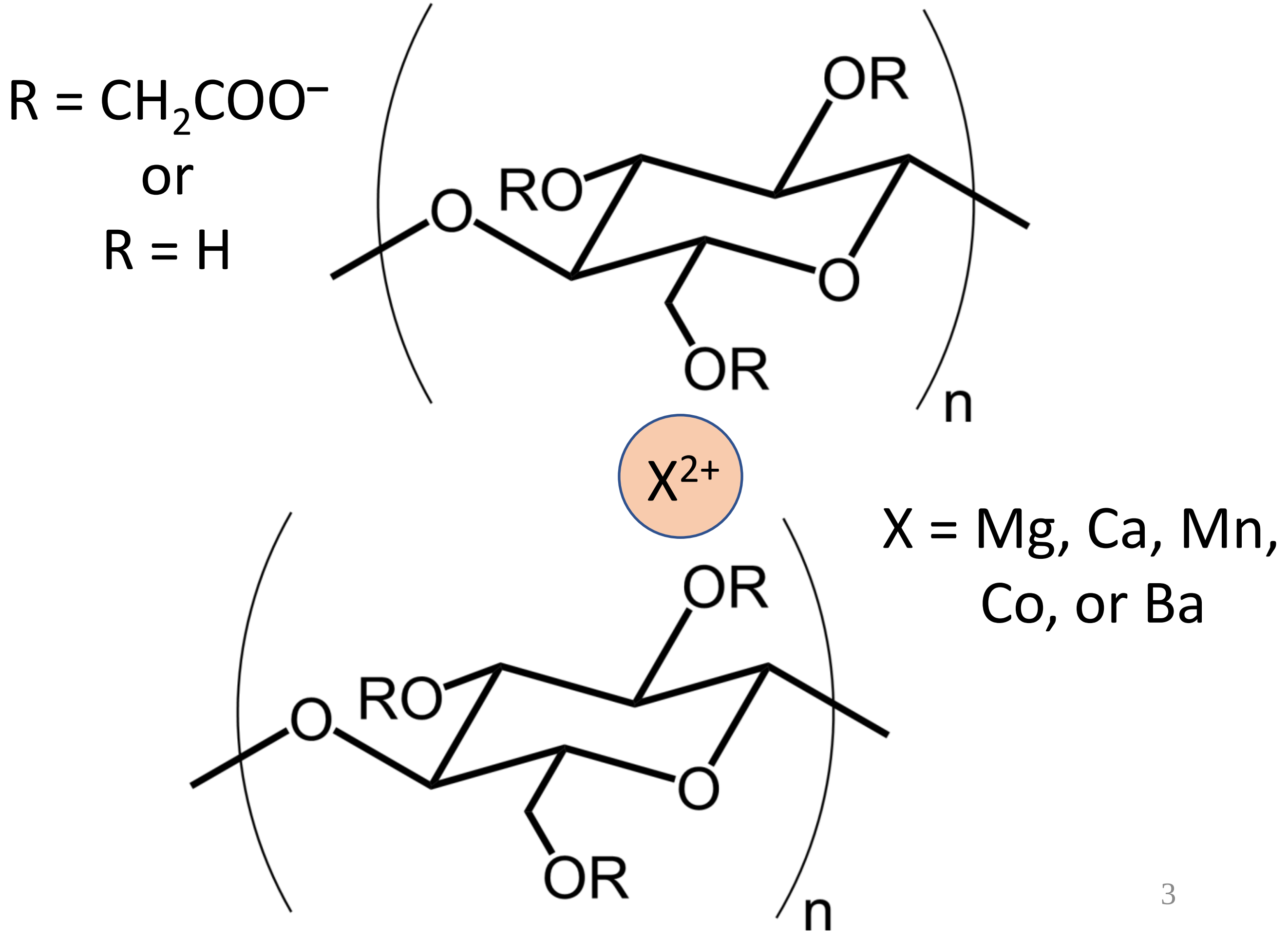
$R = CH_2COONa$
or
$R = H$

Polyelectrolytes with Divalent Counterions

Magnesium Poly(styrene sulfonate)
(MgPSS)

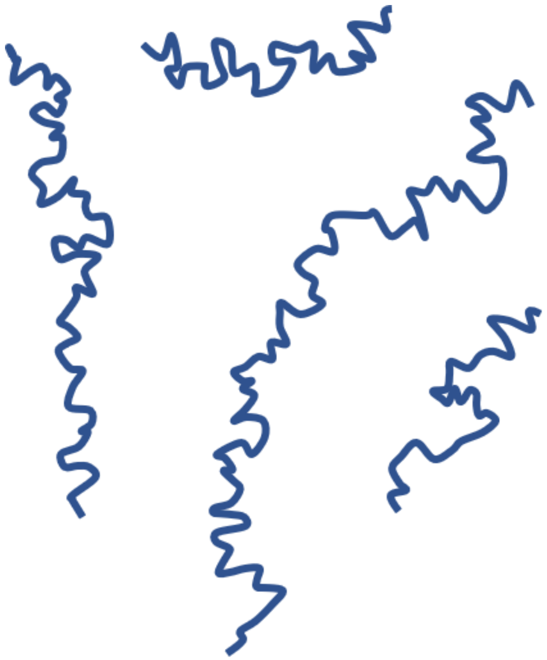


X^{2+} Carboxymethyl Cellulose
(X^{2+}CMC)



Church of the Holy Blob

Chains in Semidilute Solutions



Chain Size

$$R = \xi (N_w / g)^{0.5}$$

Correlation Length (Blob)

$$\xi = D_e \, g / g_e = l \, g / B_{pe}$$

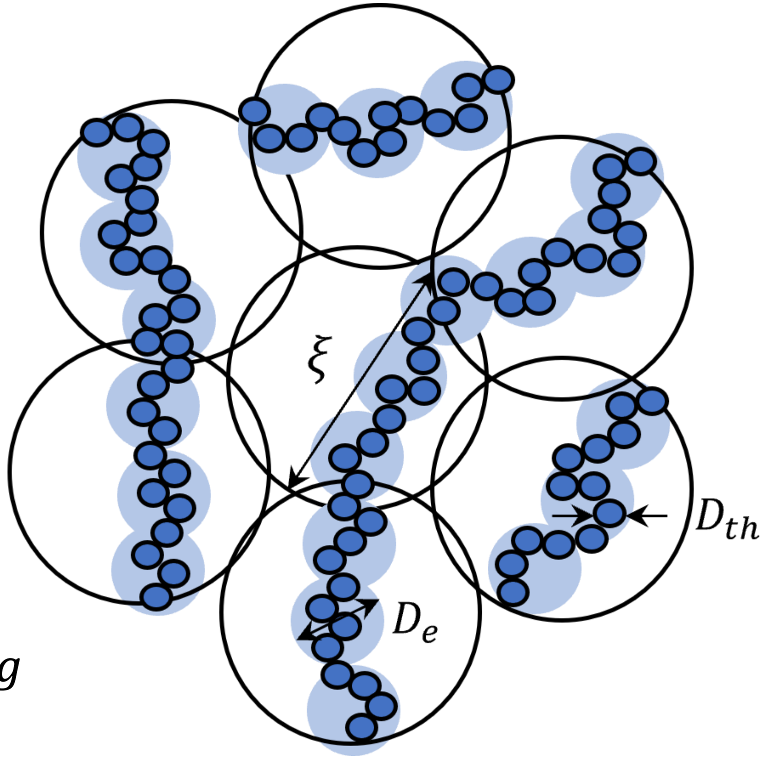
Electrostatic Blob

$$D_e = D_{th} (g_e / g_{th})^{0.588} = l \, g_e^{0.588} / B_g$$

Thermal Blob

$$D_{th} = (l b g_{th})^{0.5} = l \, g_{th}^{0.5} / B_{th}$$

Chains of Blobs



N_w – weight-average degree of polymerization
l – monomer projection length
b – Kuhn length

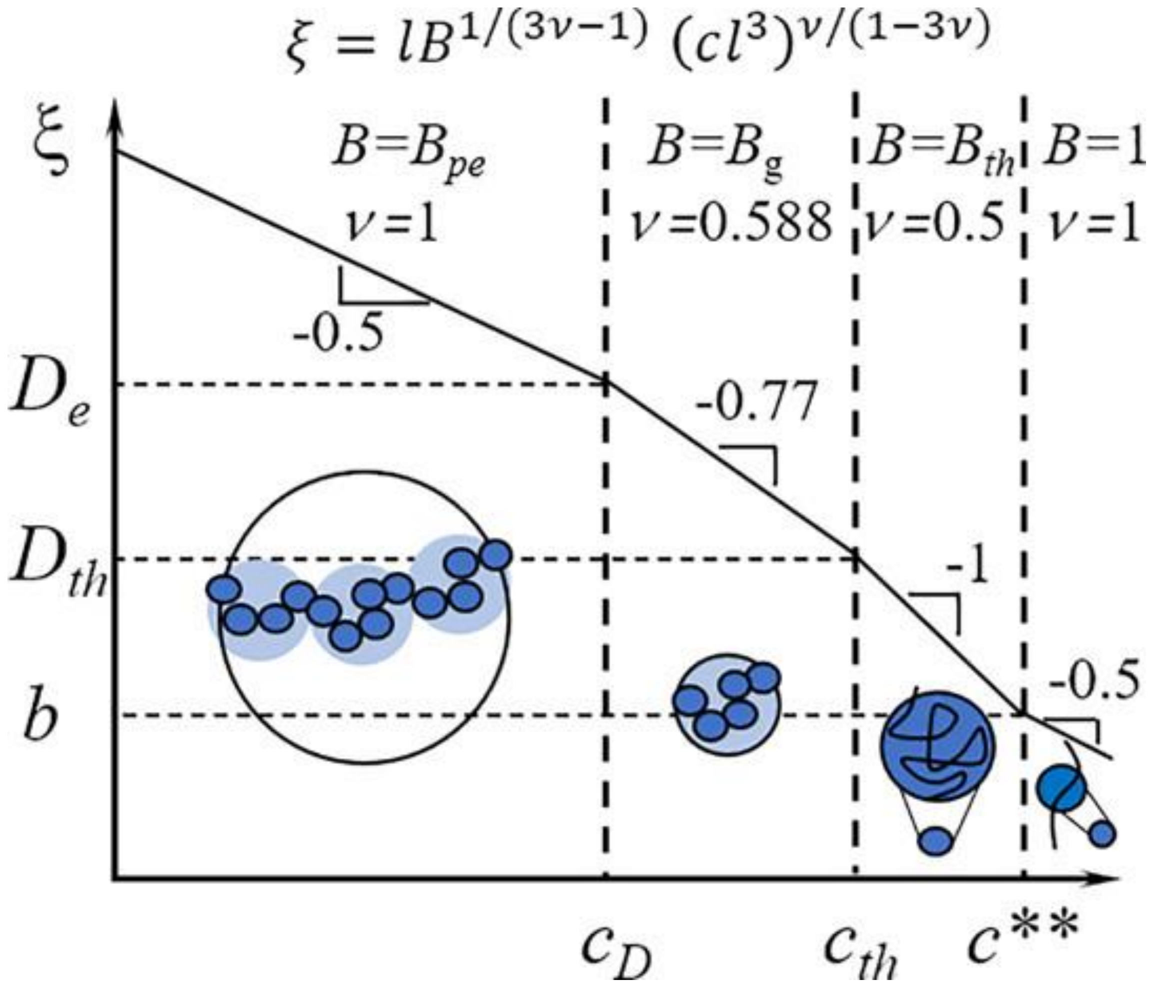
Correlation Length

Space-filling condition

$$\xi = l g^{\nu}/B \qquad g = c\xi^3$$

$$\xi = l B^{1/(3\nu-1)}(cl^3)^{\nu/(1-3\nu)}$$

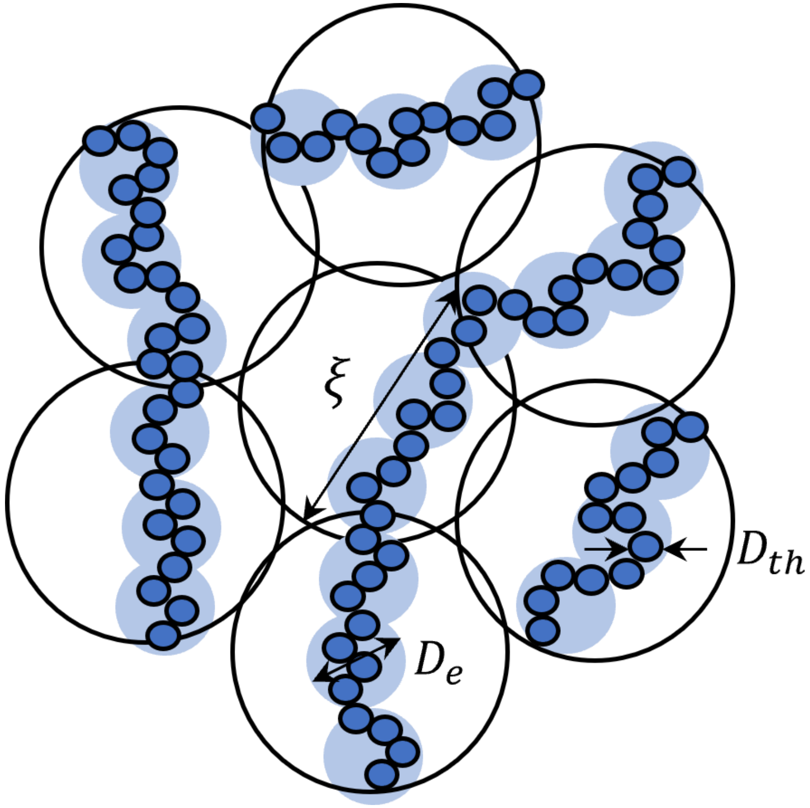
$$g = B^{3/(3\nu-1)}(cl^3)^{1/(1-3\nu)}$$



Macromolecules **2021**, 54, 1859

Unentangled (Rouse) Dynamics

Chains of Blobs



Blob Relaxation Time

$$\tau_\xi = \frac{\eta_s}{k_B T}\xi^3$$

Terminal Shear Modulus

$$G = k_B T c / N_w$$

Longest Chain Relaxation Time

$$\tau_R = \tau_\xi \frac{N_w^2}{g^2} = \frac{\eta_s}{k_B T}\frac{N_w^2}{gc}$$

Solution Viscosity

$$\eta - \eta_s = G\tau_R = \eta_s N_w / g$$

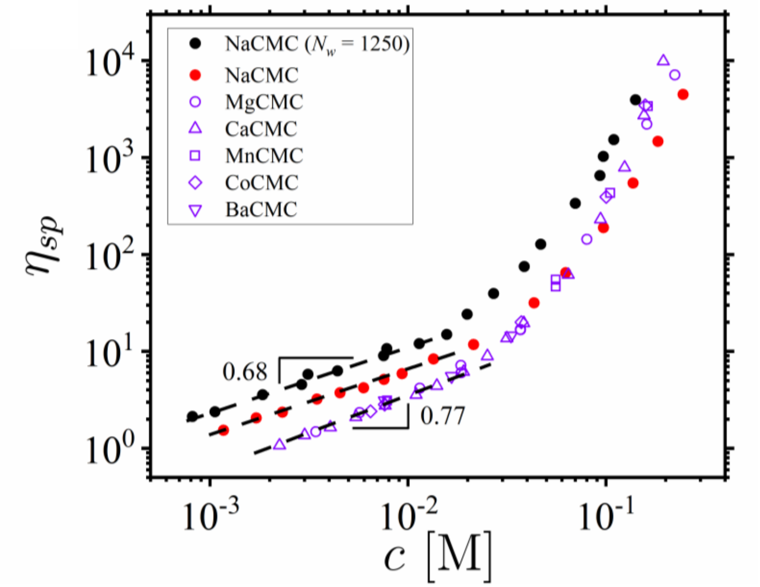
Specific Viscosity

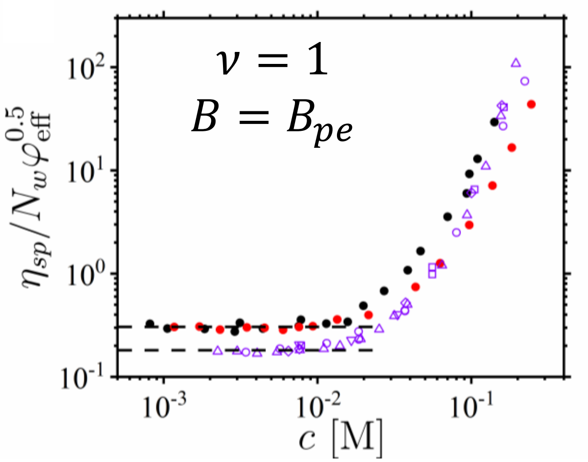
$$\eta_{sp,R} = \frac{N_w}{g}$$

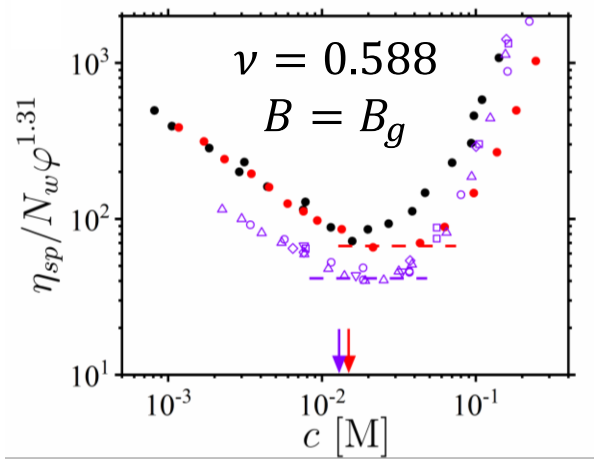
Viscosity Data Analysis

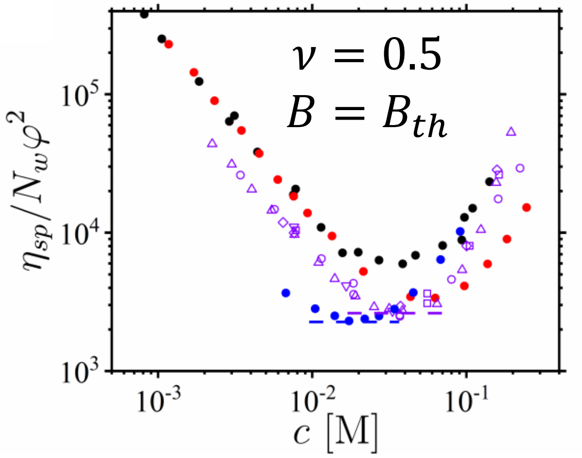
Aqueous solutions of NaCMC and X^{2+}CMC with N_w = 720 and 1250 and l = 0.515nm.

$$\eta_{sp,R} = N_w/g = N_w B^{3/(1-3\nu)}(cl^3)^{1/(3\nu-1)}$$









$$\varphi_{\mathrm{eff}}^{0.5} = \varphi^{0.5}(1 + 2c_s/zf^*c)^{-0.75}$$

Low salt correction
(*Macromolecules* **1995**, 28, 1859)

$$g = l\, B_{pe}^{1.5}(cl^3)^{-0.5}\left(1 + \frac{2c_s}{zf^*c}\right)^{0.75}$$

Residual salt concentration

$c_s/f^* = 3.3\times10^{-4}$M ($Na^+$)

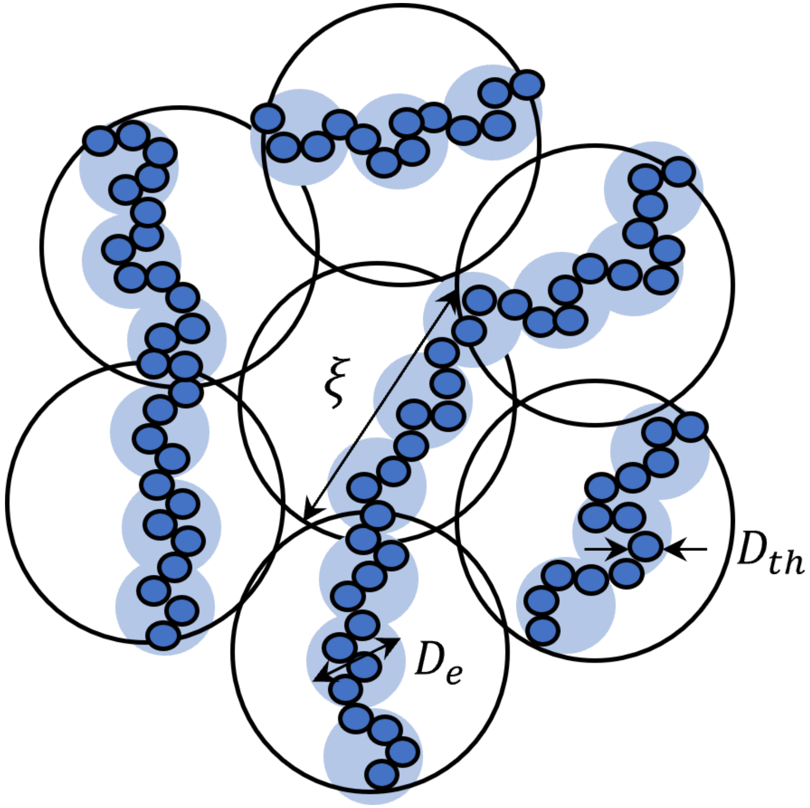
$c_s/f^* = 2.0\times10^{-4}$M ($X^{2+}$)

$$B = C_p^{1/3-\nu}$$

$$\varphi = cl^3$$

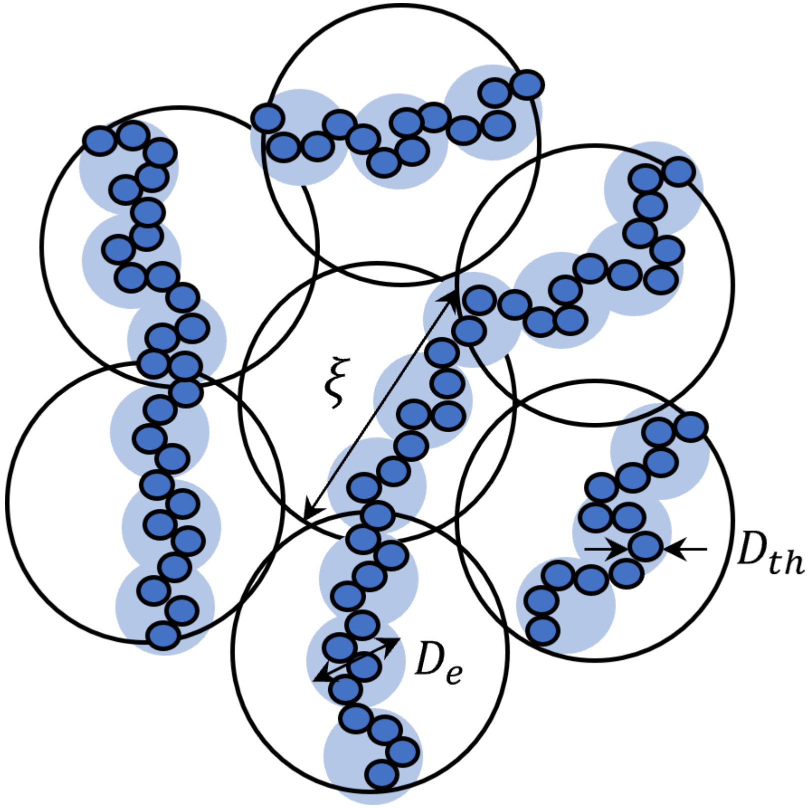
Viscosity data from: Lopez & Richtering, *Cellulose* **2019**, 26, 1517 and Lopez, et al., *Macromolecules* **2017**, 50, 332

Extracting Molecular Parameters



Kuhn length	Excluded volume
$b = l\, B_{th}^{-2}$	$v = (lb)^{1.5} \left(\frac{B_g}{B_{th}}\right)^{\frac{1}{1-2\nu}}$
2.2nm (NaPSS)	0.11nm^3 (NaPSS)
⬇	⬇
2.0nm (MgPSS)	0.052nm^3 (MgPSS)
6.8nm (NaCMC)	1.77nm^3 (NaCMC)
⬇	⬇
7.1nm (X^{2+}CMC)	0.89nm^3 (X^{2+}CMC)

Free Counterions



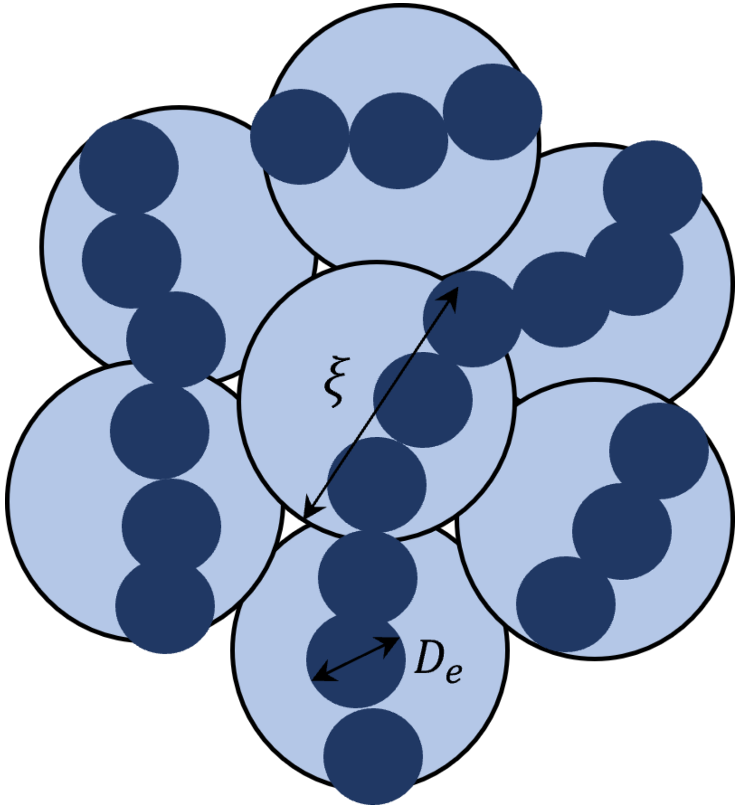
Fraction f^* of free counterions:

$$\frac{l_B (f^* g_e)^2}{D_e} k_B T \approx 4 k_B T \Rightarrow f^* \approx \frac{2}{g_e} \left(\frac{D_e}{l_B} \right)^{0.5}$$

Bjerrum length in water $l_B = 0.7\text{nm}$

7.1% (NaPSS)	11.8% (NaCMC)
⬇	⬇
2.0% (MgPSS)	6.8% (X^{2+}CMC)

Free Counterions



Counterions are largely condensed inside the electrostatic blobs

Fraction f^* of free counterions:

$$\frac{l_B (f^* g_e)^2}{D_e} k_B T \approx 4 k_B T \Rightarrow f^* \approx \frac{2}{g_e}\left(\frac{D_e}{l_B}\right)^{0.5}$$

Bjerrum length in water $l_B = 0.7\text{nm}$

7.1% (NaPSS)	11.8% (NaCMC)
⬇	⬇
2.0% (MgPSS)	6.8% (X^{2+}CMC)

Conclusions

Multivalent counterions

- do not significantly affect the Kuhn length (~10%)
- reduce the excluded volume by a factor of two
- reduce the fraction of free counterions

Acknowledgements

Collaborators

Ryan Sayko
Quantifying Properties of Polysaccharide Solutions
9:12

Andrey V. Dobrynin

Carlos G. Lopez
RWTH Aachen University

Solution Rheology of Polyelectrolytes with Monovalent and Divalent Counterions
10:00

Financial Support

The National Science Foundation
DMREF-2049518