Time-dependence of Conformational changes in Polyelectrolyte systems

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14 February 2019

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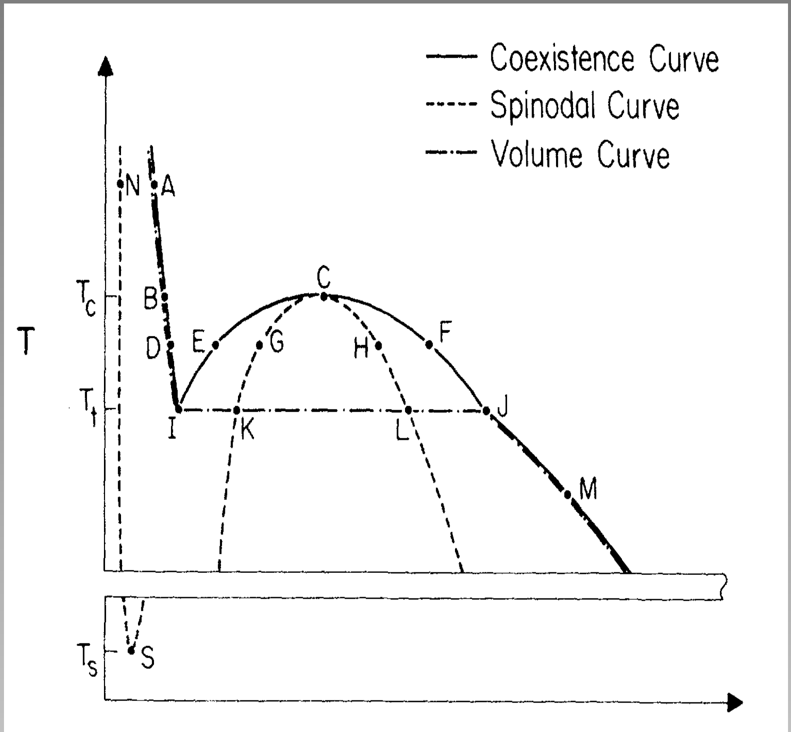
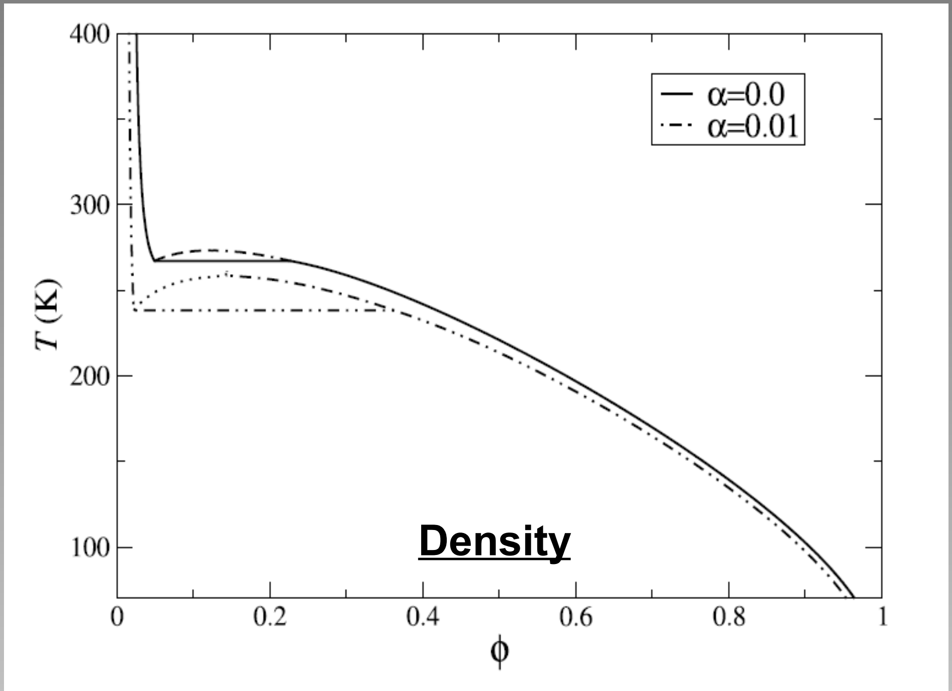
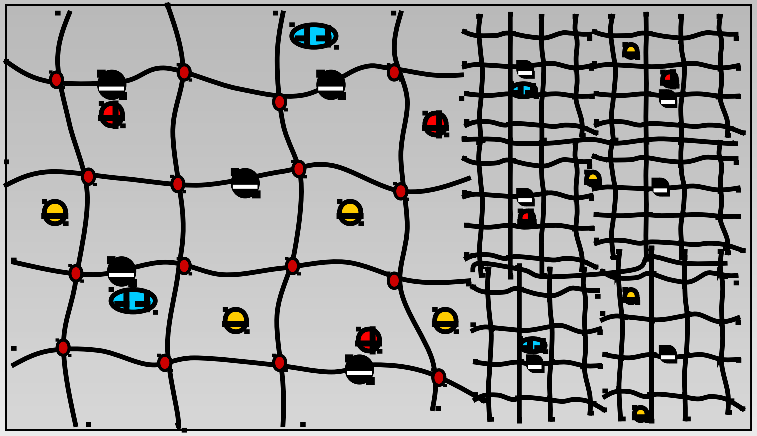
Phase behaviour – charged gels - theory:





Swati Sen and A. Kundagrami, JCP, 143, 224904 (2015)



Electrostatic interactions

Hydrophobic interactions

Elasticity

1. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press
2. Jing Hua, Mithun K. Mitra, and M. Muthukumar JCP, 136, 134901 (2012).

Polyelectrolyte gel - free energy:

$$f_s = \frac{\phi}{N}\log\phi + \phi_c \log\phi_c + \phi_s \log\phi_s$$

$$\phi = nN\ell^3/\Omega$$

$$\phi_c = \alpha nN\ell^3/\Omega$$

$$f_{sa} = [\alpha\log\alpha + (1-\alpha)\log(1-\alpha)]\phi$$

$$\phi + \phi_c + \phi_s = 1$$

$$f_\chi = \chi\phi\phi_s$$

FLORY

SALT FREE

$$\tilde{\kappa}^2 = 4\pi\tilde{\ell}_B\alpha\phi$$

$$f_{el} = 2\pi\alpha^2\ell_B\phi^2 \frac{N^{2/3}}{\left[\frac{3^{4/3}\pi^{7/6}}{2^{5/3}}\phi^{2/3} + \tilde{\kappa}^2 N^{2/3}\right]}$$

Lever rule

$$\phi = x\phi^a + (1-x)\phi^b$$

Minimize the TOTAL free energy (the sum of both coexisting phases), w.r.t. 4 variables – 2 densities, 2 charges of two phases.

$$f_{fl,i} = -\frac{1}{4\pi}\left[\log(1+\tilde{\kappa}) - \tilde{\kappa} + \frac{1}{2}\tilde{\kappa}^2\right]$$

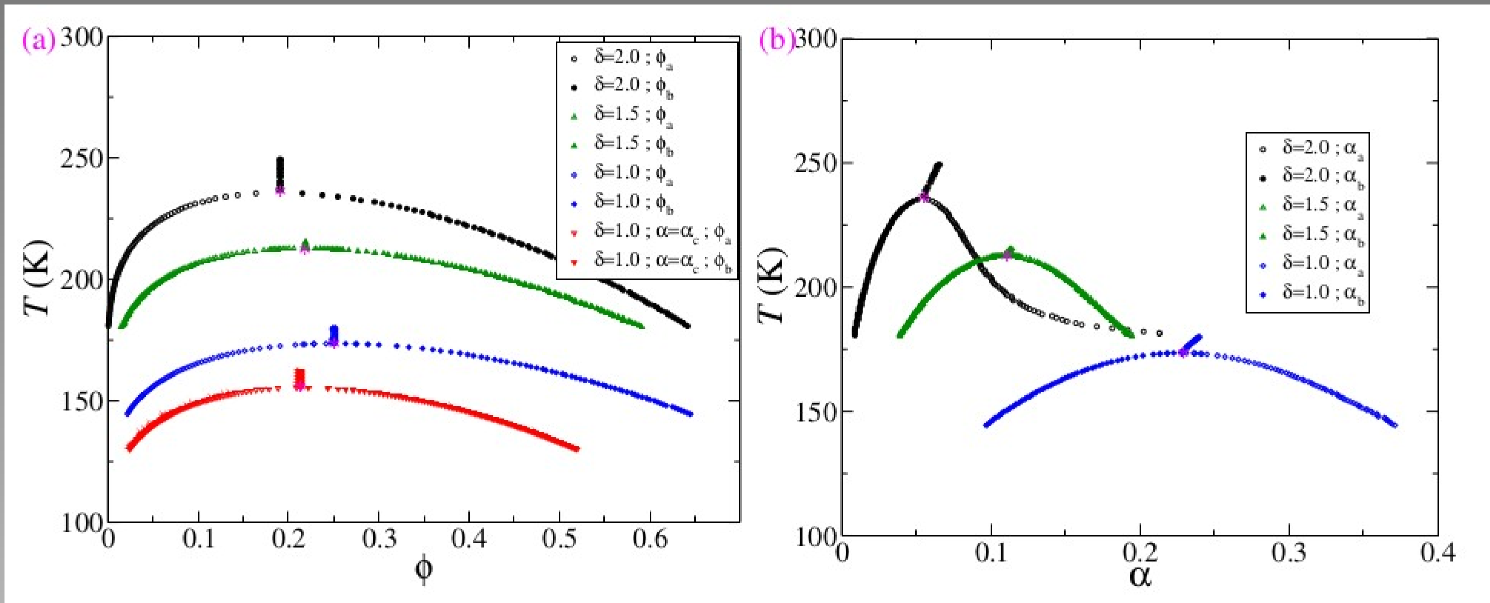
$$f_{ad} = -(1-\alpha)\phi\tilde{\ell}_B\delta$$

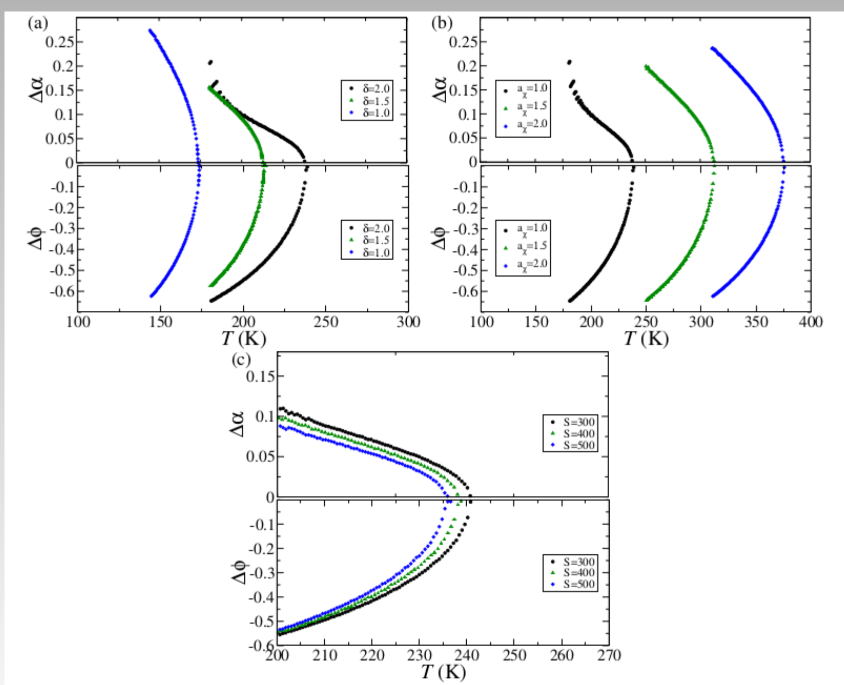
$$f = f_s + f_{sa} + f_\chi + f_{el} + f_{ad} + f_{fl,i}$$

$$f_{elast} = \frac{3}{2}S\phi_0^3\left[\left(\frac{\phi}{\phi_0}\right)^{1/3} - \frac{\phi}{\phi_0} + \frac{1}{3}\frac{\phi}{\phi_0}\ln\frac{\phi}{\phi_0}\right]$$

M. Muthukumar, J. Hua, and A. Kundagrami JCP, 132, 084901 (2010).
2. Jing Hua, Mithun K. Mitra, and M. Muthukumar JCP, 136, 134901 (2012)

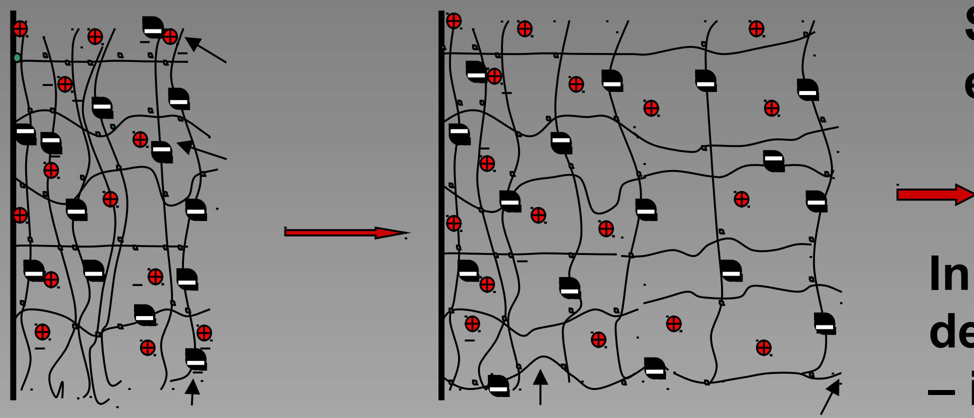
Polyelectrolyte gels – coexistence in equilibrium :





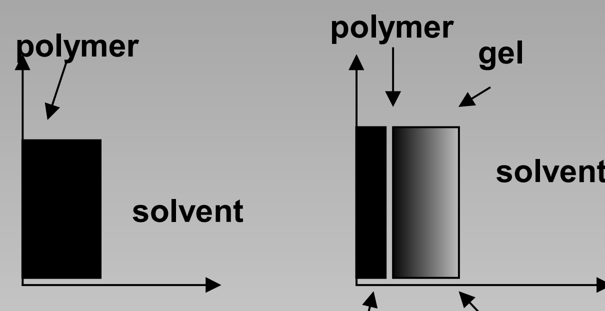
Unpublished: PhD student: Swati Sen

Swelling kinetics of a charged gel – Aim of study:

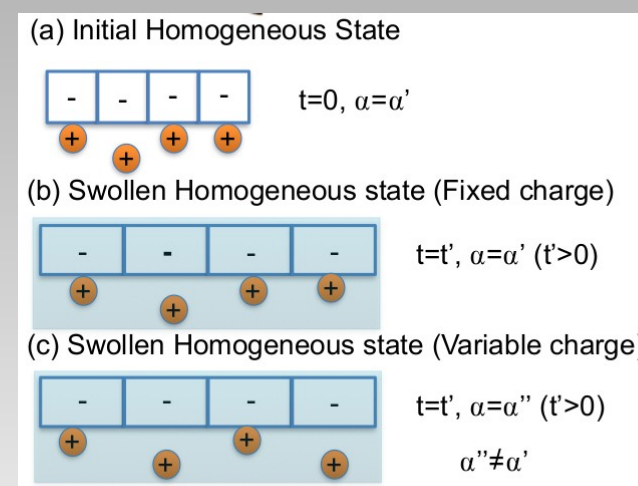


Swelling starts with a homogenous gel, ends with a homogeneous gel

In between,
density, charge, osmotic pressure/stress,
– inhomogenous and evolves with time



t=0



We want to find:

Spatial and temporal profiles of
density, charge, osmotic pressure/stress

as functions of

a) charge content / dielectric constant
b) hydrophobicity
c) cross-link density

Displacement (strain)

$$\langle \mathbf{u}(\mathbf{r}, t \to \infty) \rangle = 0$$

Effective Bulk Modulus of a Polyelectrolyte (PE) Gel:

$$\rho \frac{\partial^2 \mathbf{u}}{\partial t^2} = \nabla \cdot \tilde{\sigma} - f \frac{\partial \mathbf{u}}{\partial t}$$

Bulk Modulus Method

$$u_{ik} = \frac{1}{2}\left(\frac{\partial u_k}{\partial x_i} + \frac{\partial u_i}{\partial x_k}\right)$$

$$\sigma_{ik} = K \nabla \cdot \mathbf{u} \delta_{ik} + 2\mu \left(u_{ik} - \frac{1}{3} \nabla \cdot \mathbf{u} \delta_{ik}\right)$$

$$\frac{\partial \mathbf{u}}{\partial t} = \left(K + \frac{4\mu}{3}\right) \nabla (\nabla . \mathbf{u}) + \frac{\mu}{f} \nabla^2 \mathbf{u}$$

$$\frac{\partial \mathbf{u}}{\partial t} = \frac{K}{f} \frac{\partial^2 u}{\partial x^2}$$

$$\sigma_x = K \frac{\partial u}{\partial x}$$

Stress Relaxation Method

$$\frac{\partial \mathbf{u}}{\partial t} = \frac{1}{f} \frac{\partial}{\partial x} \sigma_{xx} (\phi, \alpha, \delta, \chi, S)$$

$$\Pi(\phi, \alpha, \chi, S, T) = \frac{K_B T}{\nu_c} \left[\phi \left(\frac{\partial f_{en}}{\partial \phi}\right)_T - f_{en}\right]$$

$$\phi(x,t) = \frac{\phi_f}{1 - \frac{\partial u}{\partial x}}$$

$$F \sim f_{en} \Omega \qquad F(\phi, \alpha, \chi, S, T)$$

$$K \frac{\partial u}{\partial x} \longrightarrow \sigma_{xx} (\phi, \alpha, \delta, \chi, S)$$

Aim: To find an effective bulk modulus for the Polyelectrolyte gel from the kinetics of relaxation of osmotic stress

Swati Sen and A. Kundagrami, JCP, 143, 224904 (2015).

Acknowledgment: T. Tanaka and D. J. Fillmore, JCP, 70, 1214 (1979), E. S. Matsuo and T. Tanaka, JCP, 89, 1695 (1988)

Osmotic pressure from free energy of a PE gel:

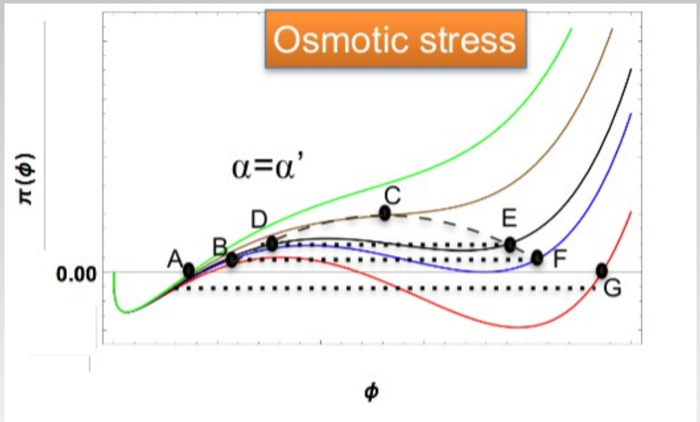
$$\Pi(\phi, \alpha, \chi, S, T)$$

Polyelectrolyte gel

$$\sigma_{xx} = \frac{K_B T}{\nu_c}\Big[-\phi - ln(1-(1+\alpha)\phi) - \chi\phi^2(1+\alpha) + S\phi_0^3\left(\frac{\phi}{2\phi_0} - \left(\frac{\phi}{\phi_0}\right)^{\frac{1}{3}}\right) + \frac{1}{4\pi}\left\{ ln(1+\tilde{\kappa}) - \frac{\tilde{\kappa}}{2(1+\tilde{\kappa})} - \frac{\tilde{\kappa}}{2}\right\} + \frac{2\pi b\alpha^2 N^{\frac{2}{3}}\tilde{l}_B}{3}\frac{\phi^{8/3}}{\left(b\phi^{2/3} + N^{\frac{2}{3}}\tilde{\kappa}^2\right)^2}\Big];$$

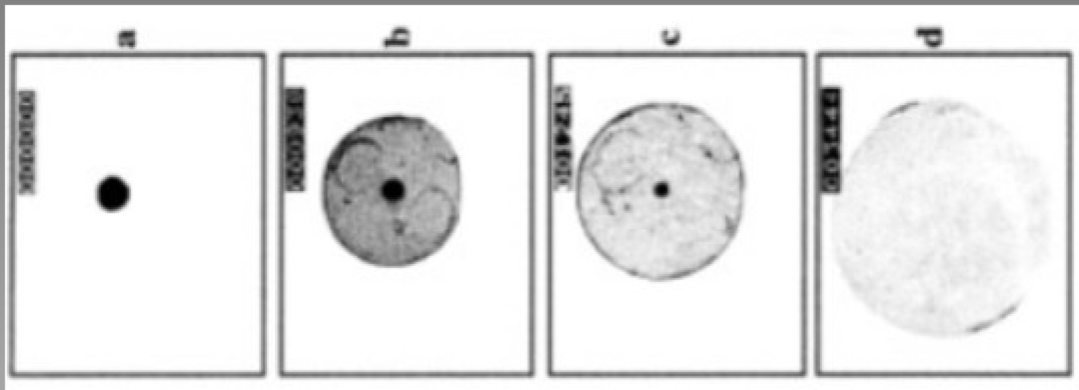
Polymer (uncharged) gel

$$\sigma_{xx} = \pi_{os} = \frac{K_B T}{\nu_c}\Big[-\phi - \ln(1-\phi) - \chi\phi^2 + S\phi_0^3\left\{\frac{\phi}{2\phi_0} - \left(\frac{\phi}{\phi_0}\right)^{\frac{1}{3}}\right\}\Big].$$

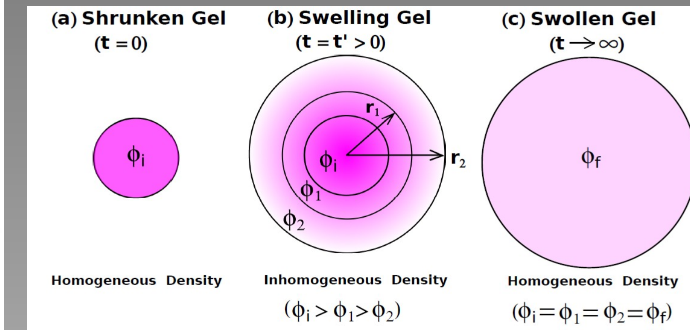


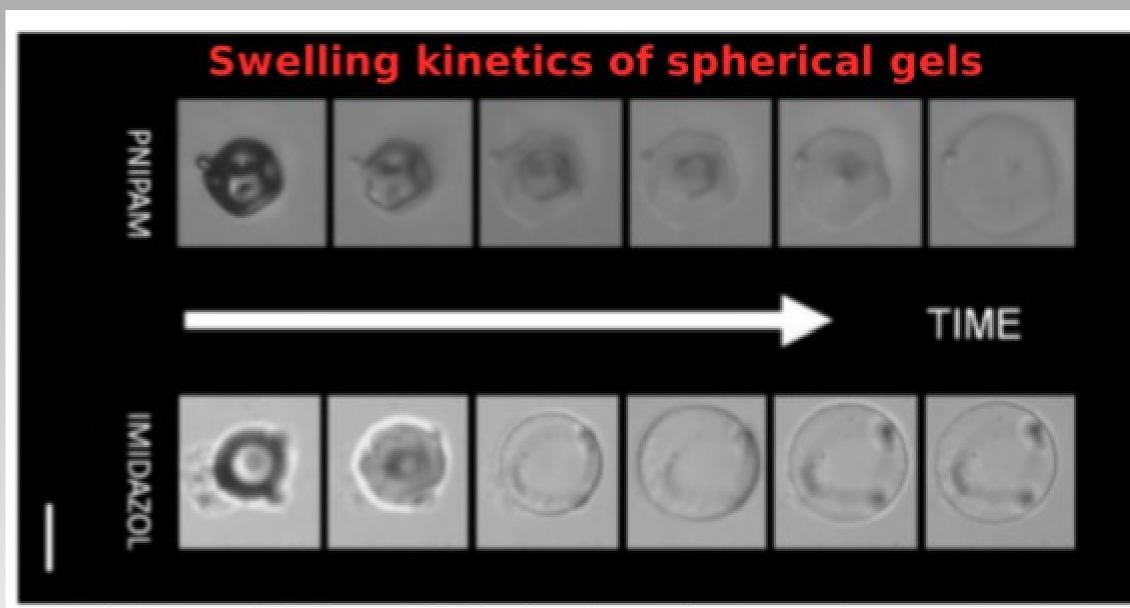
Swati Sen and A. Kundagrami, JCP, 143, 224904 (2015).

Swelling of PE gels – real, spherical gels:



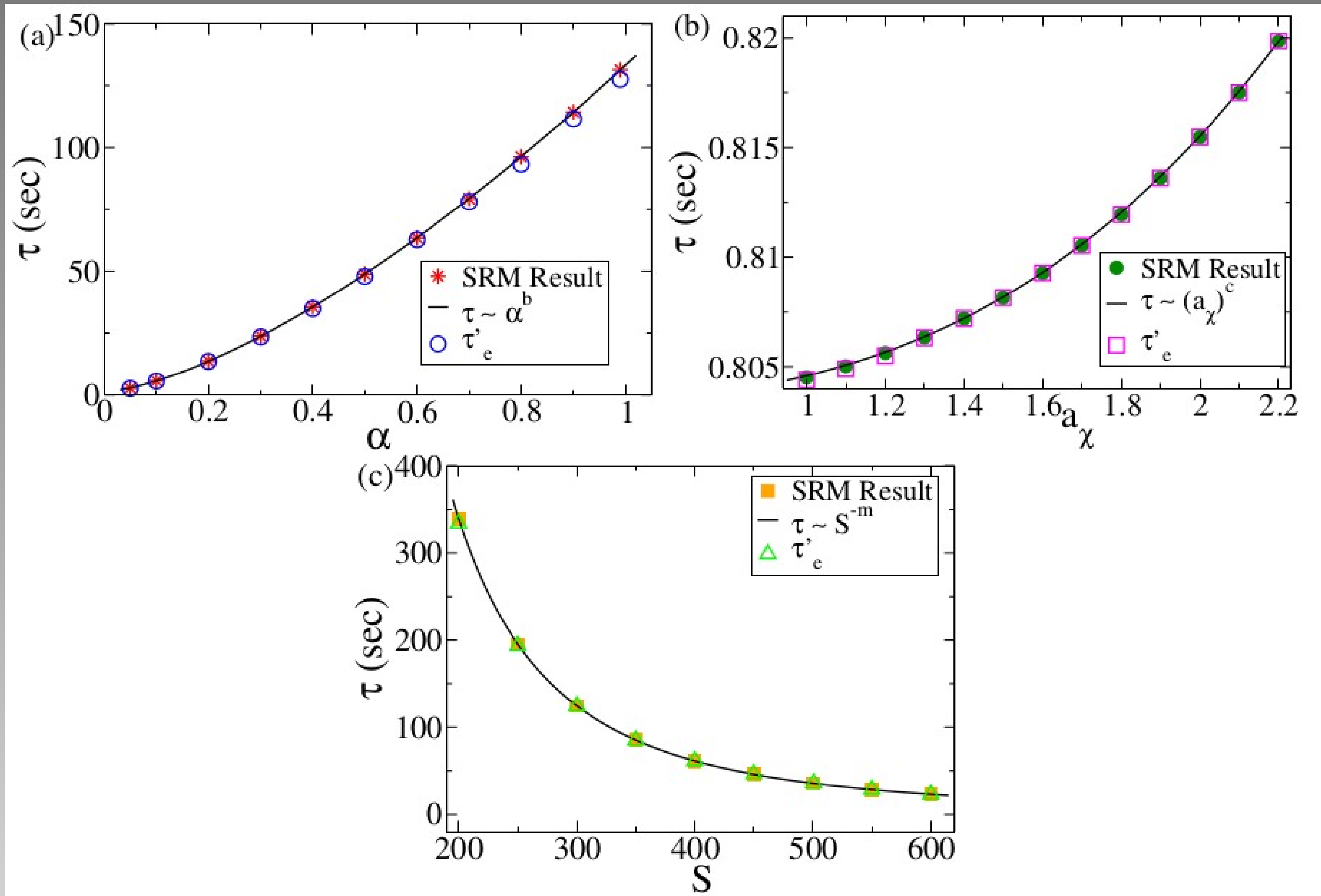
Macromolecules **31**, 25, 1995





Colloids and Surfaces A: Physicochem. Eng. Aspects 343 (2009) 30–33

Swelling time-scales – linear and non-linear theory:

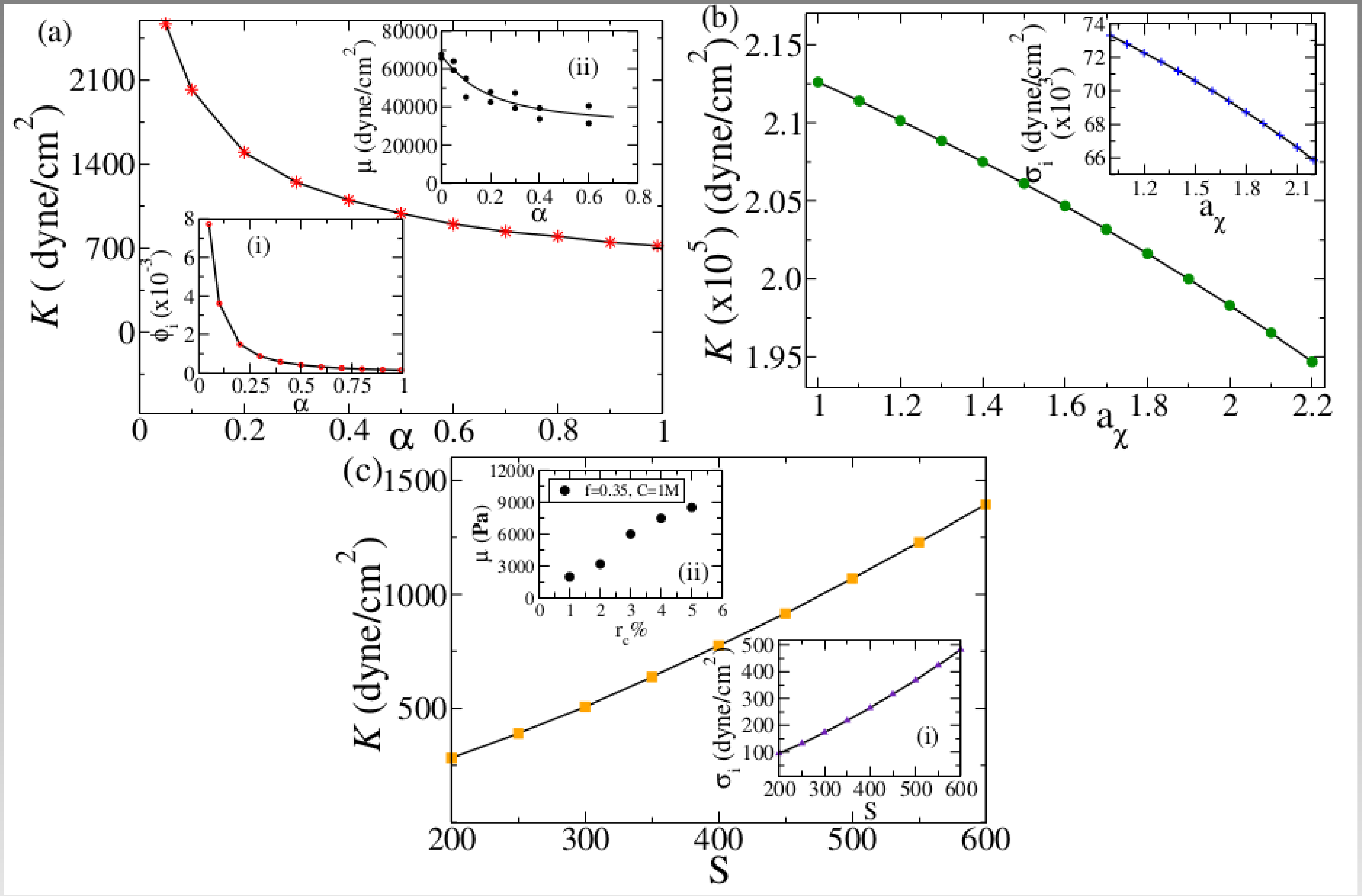


$$u(r,t) = -\sum_{n=1}^{\infty} \frac{6\Delta a_0(-1)^n}{k_n a}\left(\frac{\cos(k_n r)}{k_n r} - \frac{\sin(k_n r)}{(k_n r)^2}\right)\exp^{-k_n^2 Dt}$$

$$\tau_e \equiv a_f^2 / D_0$$

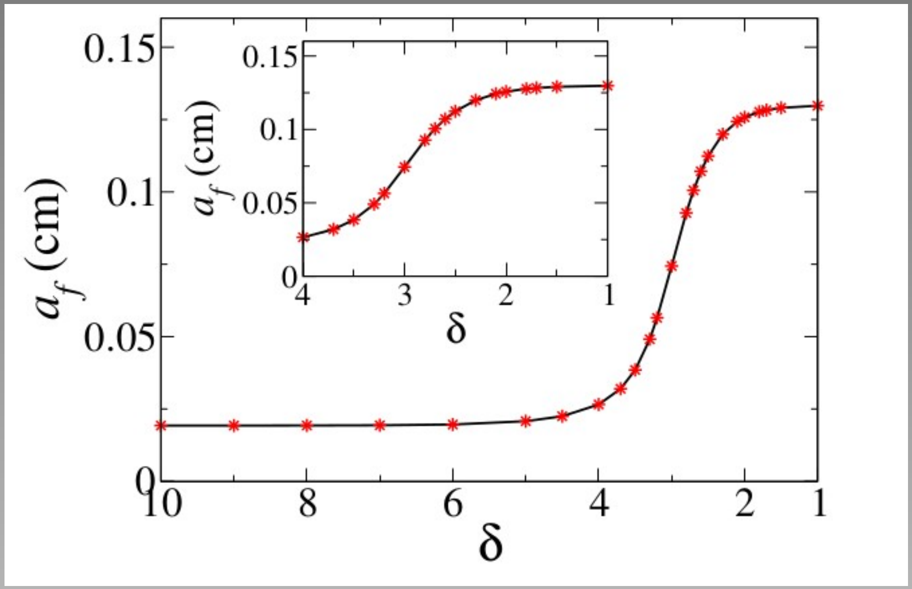
Swati Sen, Ananya Krishnan and A. Kundagrami, *Unpublished*

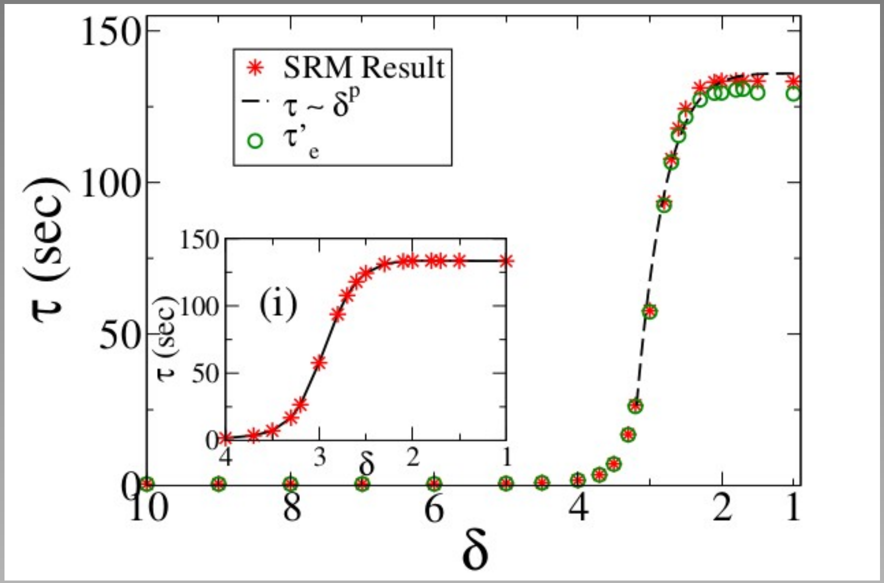
Effective elastic modulus – linear and non-linear theory:

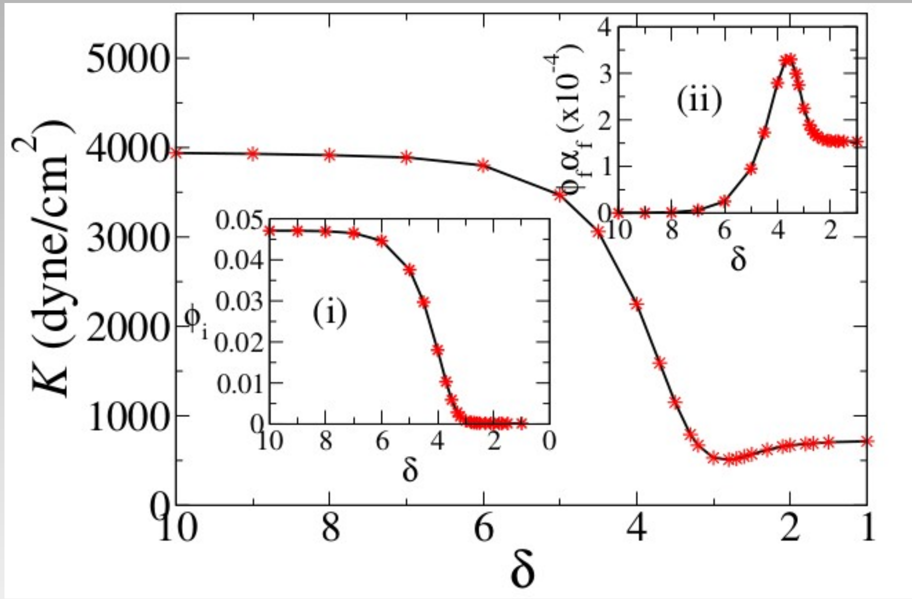


Swati Sen, Ananya Krishnan and A. Kundagrami, *Unpublished*

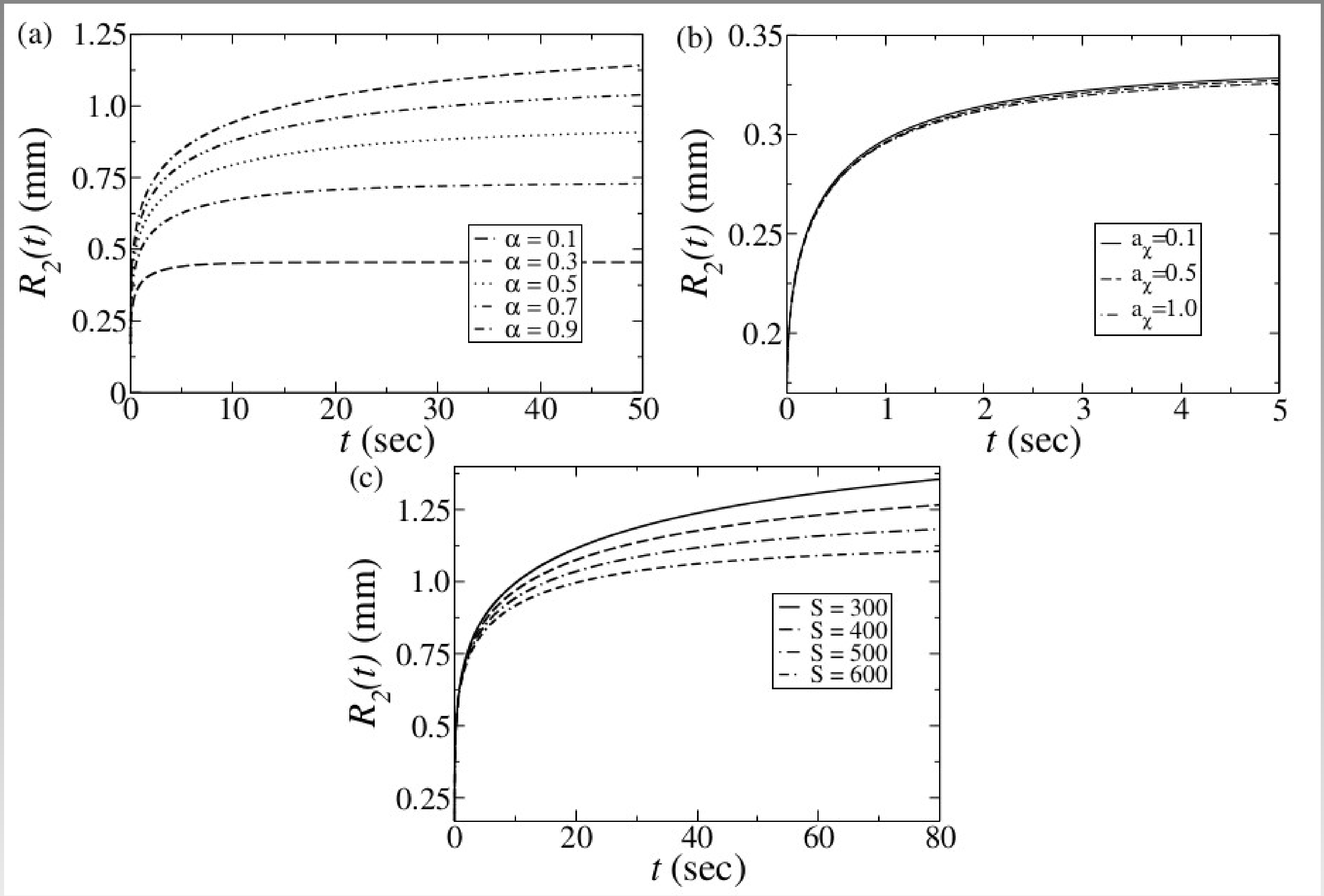
Swelling time-scales and modulus – variable charge:





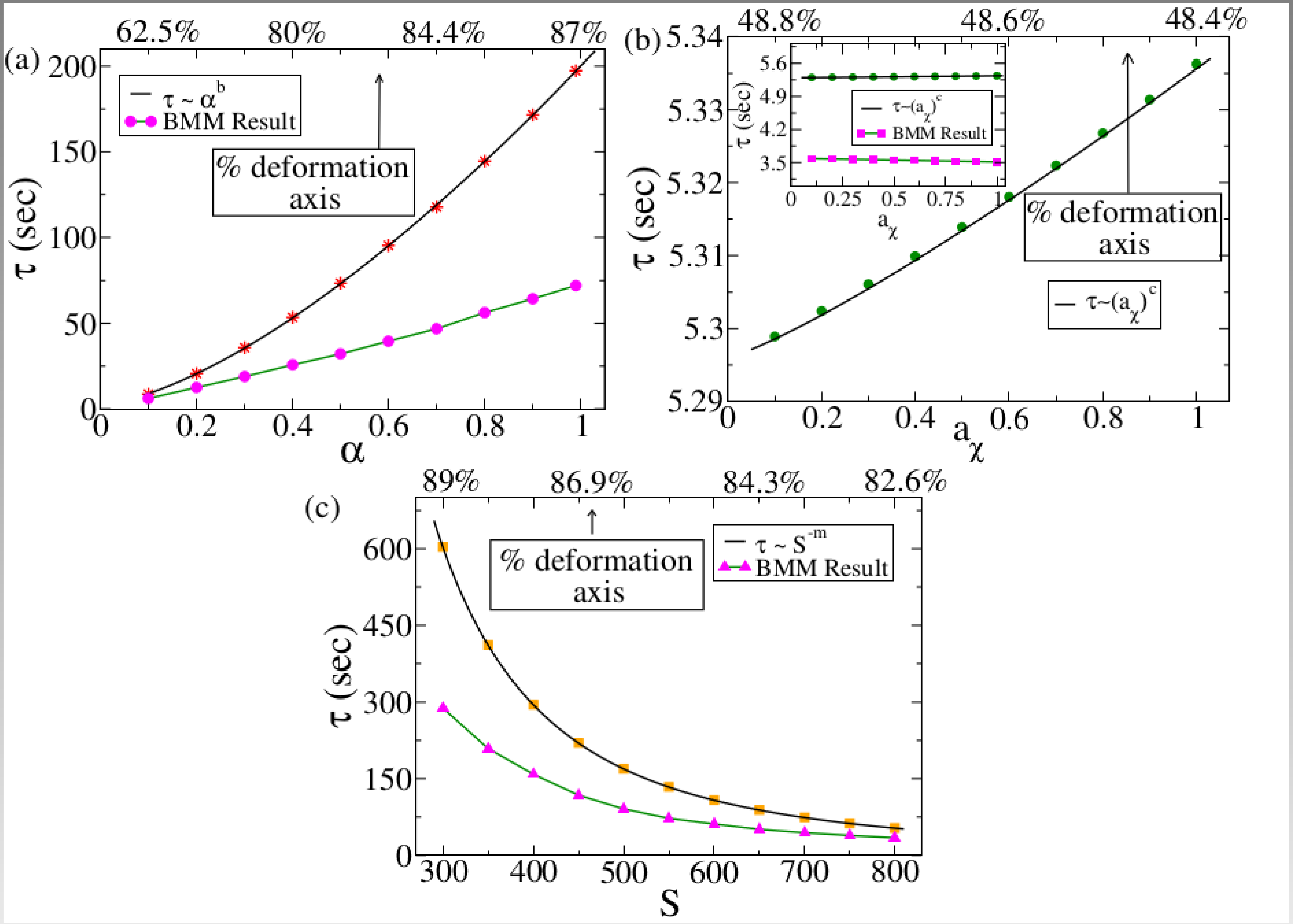


Large deformation of polyelectrolyte gesl:



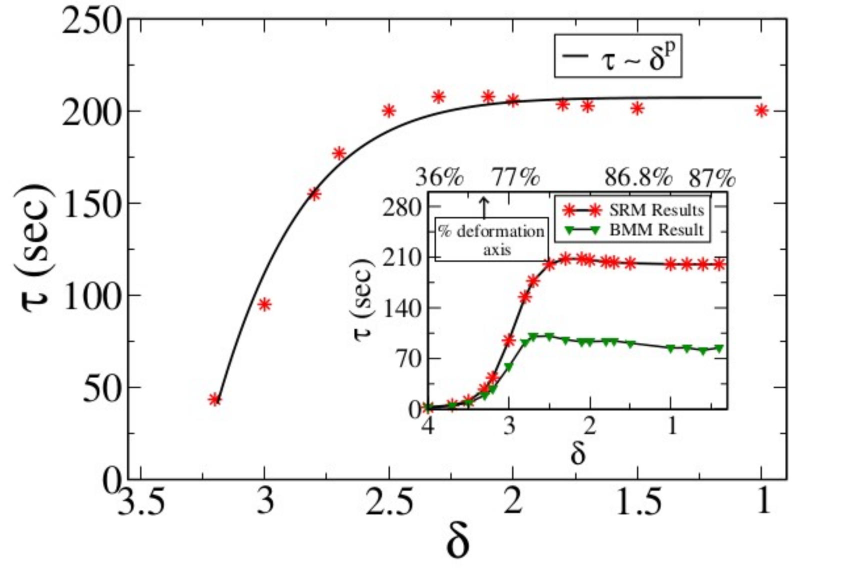
Swati Sen, Ananya Krishnan and A. Kundagrami, *Unpublished*

Deviation from linear theory for large deformations:



Swati Sen, Ananya Krishnan and A. Kundagrami, *Unpublished*

Large deformations – variable charge - exponents:

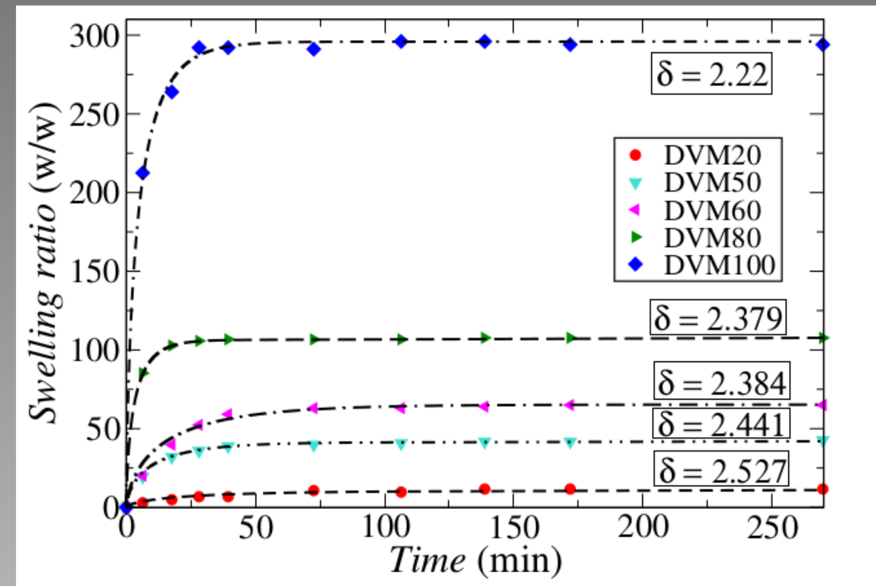


Fixed charge	α	a_χ	S
Small deformation	1.469	3.151	2.484
Large deformation	1.481	1.187	2.493

Variable charge	δ	a_χ	S
Small deformation	7.900	5.214	2.496
Large deformation	9.091	2.183	2.460

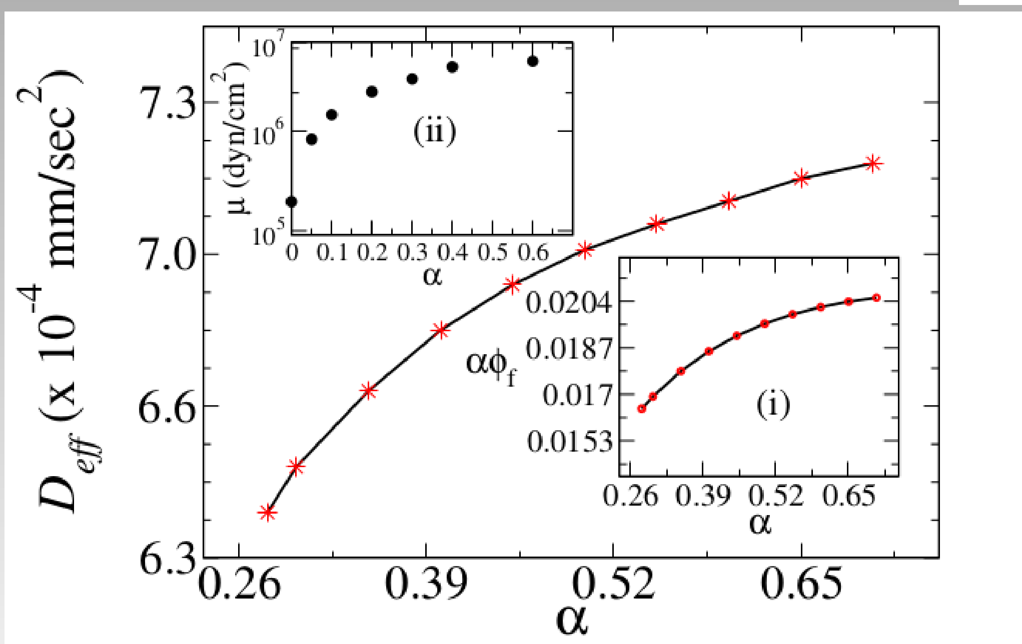
Swati Sen, Ananya Krishnan and A. Kundagrami, *Unpublished*

Comparison with experiments – size vs. time and modulus:



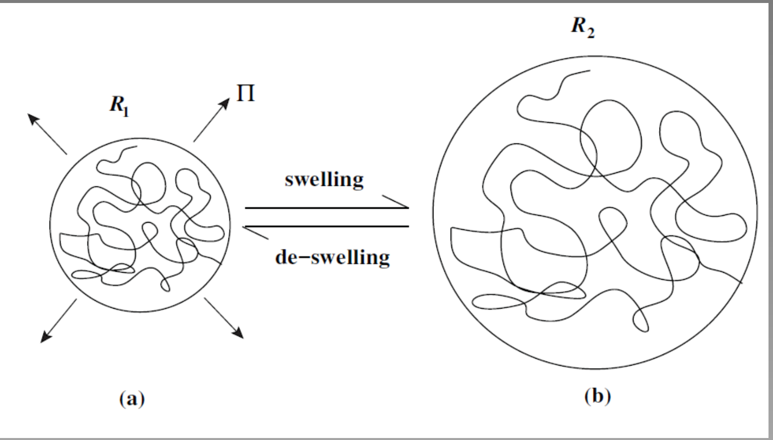
Matching of gel-front w/ Experiments: SRM

S. Ghosh Roy, U. Halder, and P. De, ACS Appl. Materials & Interfaces 6, 4233 (2014)



Swati Sen, Ananya Krishnan and A. Kundagrami, *Unpublished*

Equation of motion – osmotic and viscous forces:



Swelling and collapse of:

Single, isolated, flexible polyelectrolyte (PE) chain

Uniform spherical expansion model

EOM for surface element – osmotic stress and viscous force

$$\sigma_s \Delta S \frac{d^2 R}{dt^2} = -\zeta \Delta S \frac{dR}{dt} + \Pi \Delta S$$

Osmotic stress obtained through the free energy

$$\Pi = -\left(\frac{\partial F}{\partial V}\right)_{N,T} = -\frac{1}{4\pi R^2}\frac{\partial F}{\partial R}\bigg|_{N,T}$$

Free energy

$$F(\tilde{l}_1, f, N, T)$$

Equation of Motion:

$$\zeta \frac{d\tilde{l}_1}{dt} + \frac{1}{\pi}\left(\frac{6}{Nl^2}\right)^2 \frac{\partial F}{\partial \tilde{l}_1} = 0$$

$$\tilde{l}_1 = \left(\frac{6}{Nl^2}\right) R_g^2$$

Soumik Mitra and A. Kundagrami, Macromolecules, 50, 2504 (2017)

A free-energy to derive the osmotic pressure:

$$F(\tilde{l}_1, f, N, T)$$

$$F_1 = f \log f + (1-f)\log(1-f)$$

$$F_2 = (f\tilde{\rho} + \tilde{c}_s)\log(f\tilde{\rho} + \tilde{c}_s) + \tilde{c}_s \log \tilde{c}_s - (f\tilde{\rho} + 2\tilde{c}_s)$$

$$F_3 = -\frac{1}{3}\sqrt{4\pi}\tilde{l}_B^{3/2}(f\tilde{\rho} + 2\tilde{c}_s)^{3/2}$$

$$F_4 = -(1-f)\delta(l_B/l)$$

$$F_5 = \frac{3}{2N}[\tilde{l}_1 - 1 - \log \tilde{l}_1] + \frac{4}{3}\left(\frac{3}{2\pi}\right)^{3/2}\frac{w}{\sqrt{N}}\frac{1}{\tilde{l}_1^{3/2}} + \frac{w_3}{N\tilde{l}_1^3} + 2\sqrt{\frac{6}{\pi}}f^2\tilde{l}_B\frac{N^{1/2}}{\tilde{l}_1^{1/2}}\Theta_0(a)$$

$$\Theta_0(a) = \frac{\sqrt{\pi}}{2}\left(\frac{2}{a^{5/2}} - \frac{1}{a^{3/2}}\right)\exp(a)\,\mathrm{erfc}(\sqrt{a}) + \frac{1}{3a} + \frac{2}{a^2} - \frac{\sqrt{\pi}}{a^{5/2}} - \frac{\sqrt{\pi}}{2a^{3/2}}$$

$$a = \tilde{\kappa}^2 N\tilde{l}_1/6 \qquad \tilde{\kappa}^2 = 4\pi\tilde{l}_B(f\tilde{\rho} + 2\tilde{c}_s) \qquad \tilde{l}_B = e^2/4\pi\epsilon\epsilon_0 l k_B T$$

M. Muthukumar, JCP, 120, 9343 (2004)

A. Kundagrami and M. Muthukumar, Macromolecules, 43, 2574 (2010)

Low- and high-salt limits – equations of motion:

Low-salt limit:

$$\zeta' \frac{d\tilde{l}_1}{dt} + \frac{T}{N}\left\{ \frac{3}{2N}\left[1 - \frac{1}{\tilde{l}_1}\right] - 2\left(\frac{3}{2\pi}\right)^{3/2} \frac{w}{\sqrt{N}} \frac{1}{\tilde{l}_1^{5/2}} - \frac{3}{N}\frac{w_3}{\tilde{l}_1^4} - \frac{2}{15}\sqrt{\frac{6}{\pi}} f^2 \tilde{l}_B \frac{N^{1/2}}{\tilde{l}_1^{3/2}} \right\} = 0$$

High-salt limit:

$$\zeta' \frac{d\tilde{l}_1}{dt} + \frac{T}{N}\left\{ \frac{3}{2N}\left[1 - \frac{1}{\tilde{l}_1}\right] - 2\left(\frac{3}{2\pi}\right)^{3/2} \frac{w}{\sqrt{N}} \frac{1}{\tilde{l}_1^{5/2}} - \frac{3}{N}\frac{w_3}{\tilde{l}_1^4} - \frac{3}{2}\left(\frac{6}{N}\right)^{1/2} \frac{1}{\pi^{3/2}} \frac{f^2}{(f\tilde{\rho} + 2\tilde{c}_s)} \frac{1}{\tilde{l}_1^{5/2}} \right\} = 0$$

$$w' = w + \frac{f^2}{(f\tilde{\rho} + 2\tilde{c}_s)}$$

1. **Simpler differential equations – analytical expressions for derivatives of free energy**
2. **In high-salt limit, electrostatic interaction is screened and becomes Short-ranged. Hence, just the two-body interaction parameter is re-scaled**

Soumik Mitra and A. Kundagrami, Macromolecules, 50, 2504 (2017)

Analytical Expressions – Size vs. Time:

Size vs. Time

Swelling:

$$\tilde{l}_1^{5/2} - \tilde{l}_{10}^{5/2} = \frac{5}{2}\frac{T}{N\zeta'}\frac{2}{15}\sqrt{\frac{6}{\pi}}f^2\tilde{l}_B N^{1/2} t$$

Low-salt

$$\tilde{l}_1^{7/2} - \tilde{l}_{10}^{7/2} = \frac{7}{8\zeta'}\left(\frac{6}{N\pi}\right)^{3/2}\frac{Tf^2}{f\tilde{\rho} + 2\tilde{c}_s}t$$

High-salt

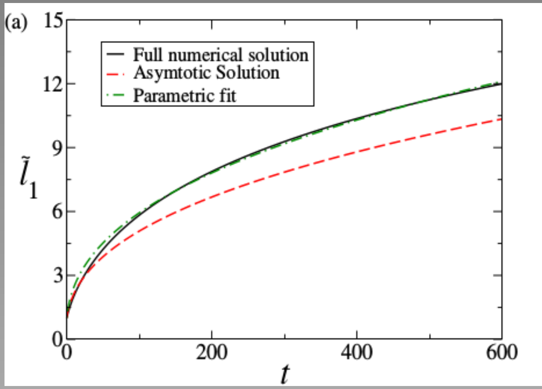
$$w' = w + \frac{f^2}{(f\tilde{\rho} + 2\tilde{c}_s)}$$

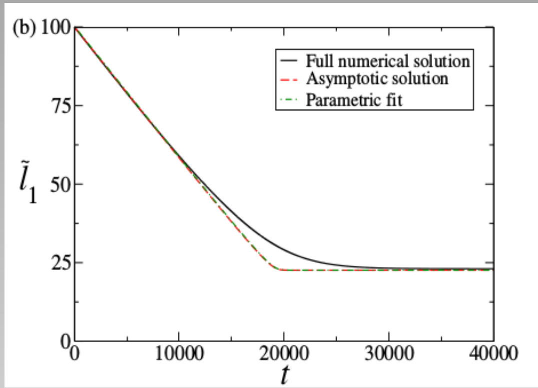
De-swelling:

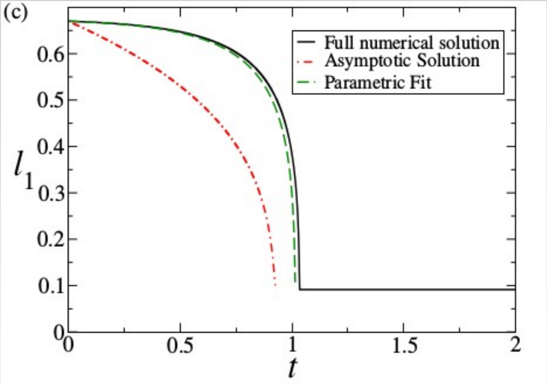
$$(\tilde{l}_1 - \tilde{l}_{1f})\exp(\tilde{l}_1) = \exp(\tilde{l}_{10})(\tilde{l}_{10} - \tilde{l}_{1f})\exp\left(-\frac{3T}{2N^2\zeta'}t\right)$$

Collapse:

$$\tilde{l}_1^{7/2} - \tilde{l}_{10}^{7/2} = \frac{7}{2}\frac{2T}{N\zeta'}\left(\frac{3}{2\pi}\right)^{3/2}\frac{wt}{\sqrt{N}}$$







Soumik Mitra and A. Kundagrami, Macromolecules, 50, 2504 (2017)

Conclusions:

1. Swelling of polyelectrolyte systems – both gels and isolated chains – can be treated in the same footing – motion of polymer through the solvent – osmotic stress vs. viscous damping

2. Motion of small-ion charge species much faster than polymer:
- charge is regularized (self-adjusted) all along the kinetics

2. Swelling of a polymer gel: for small deformation – is diffusive
- single chain: sub-diffusive

3. Effective bulk-modulus of polyelectrolyte gels decreases with charge
- small deformation

4. Single polyelectrolyte chain:
   a) like-charge repulsion → swelling, entropy → de-swelling, hydrophobicity → collapse
   b) chain swells faster and farther for higher temperature
   c) de-swells faster and deeper for higher salt
   d) kinetics is slower for higher molecular weight
   e) self-consistent dependency between size and charge strong in the vicinity of the Gaussian size