Equilbrium and Kinetics of Polyelectrolytes

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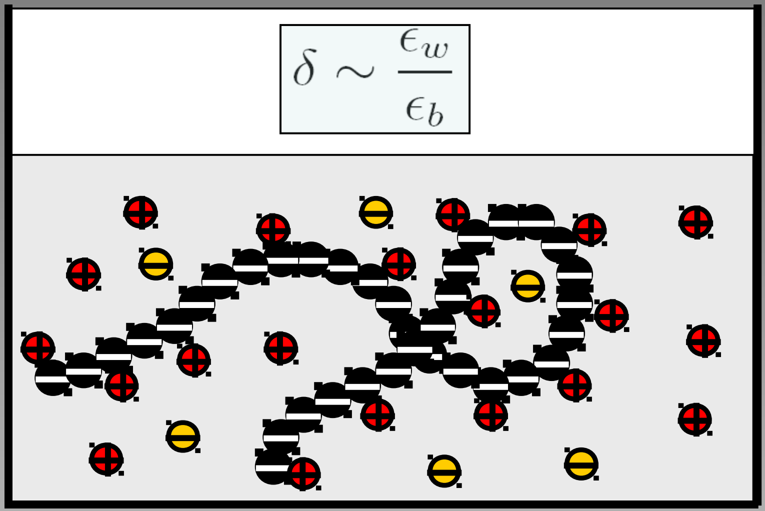
ISPCM 2018, ICTS, Bangalore
16-18 February 2018

16 February 2018

Funding: **Indian Institute of Science Education Research (IISER) Kolkata (MHRD)**

Charged polymers – energy and entropy:

Do all Na+ ions dissolve? NO!



$$\delta \sim \frac{\epsilon_w}{\epsilon_b}$$

Counterion condensation. WHY?

Effective ϵ low close to backbone

Condense → gain in Coulomb energy

$$-\frac{e^2}{4\pi\epsilon_0\epsilon d}$$

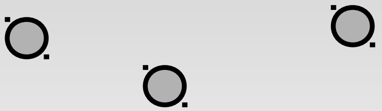
Let's predict qualitatively:

Remember: ***E* - *TS***

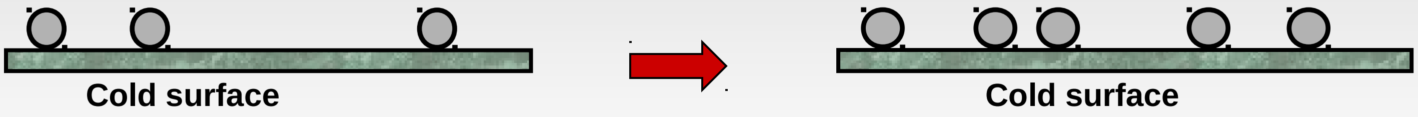
E = Coulomb energy, ***S*** = free ion entropy → $k_B T$

1. ***T*** ↓ → ***S*** fixed, ***E***/ion-pair fixed → more ion-pairs → less charge
2. ϵ ↓ → ***S*** fixed, ***T*** fixed, ***E***/ion-pair increases → more ion-pairs
3. ***V*** ↑ → ***S*** increases, ***T*** fixed, ***E***/ion-pair fixed → less ion-pairs

Similar to DEW formation: at low ***T*****,** air can't hold vapor → condensation

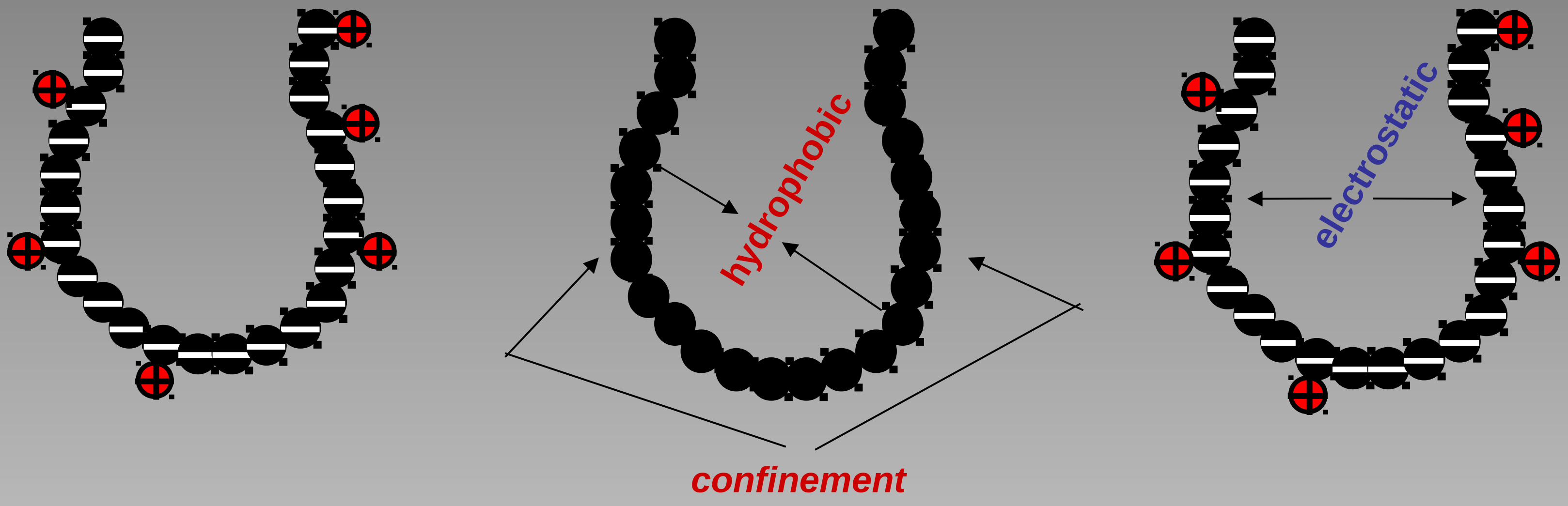


SALT ⟷ WET WEATHER



Interactions (energy) in a charged polymer chain:

E – TS, but is it so simple? What are the contributions**?**



Chain entropy: maximized if Gaussian coil

Excluded volume: chemical affinity **(hydrophilicity)**, or mismatch **(hydrophobicity)**

Coulomb repulsion: between bare charges ⟶ chain expansion

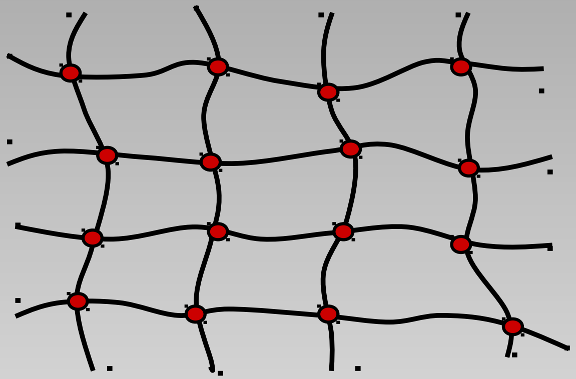
EXAMPLE – Mutual Dependency:

poor solvent ⟶ Collapsed chain ⟶ Ion condensation

SCHEME: ***E – TS*** must be **MINIMIZED.** But, **SIZE** and **CHARGE** coupled.

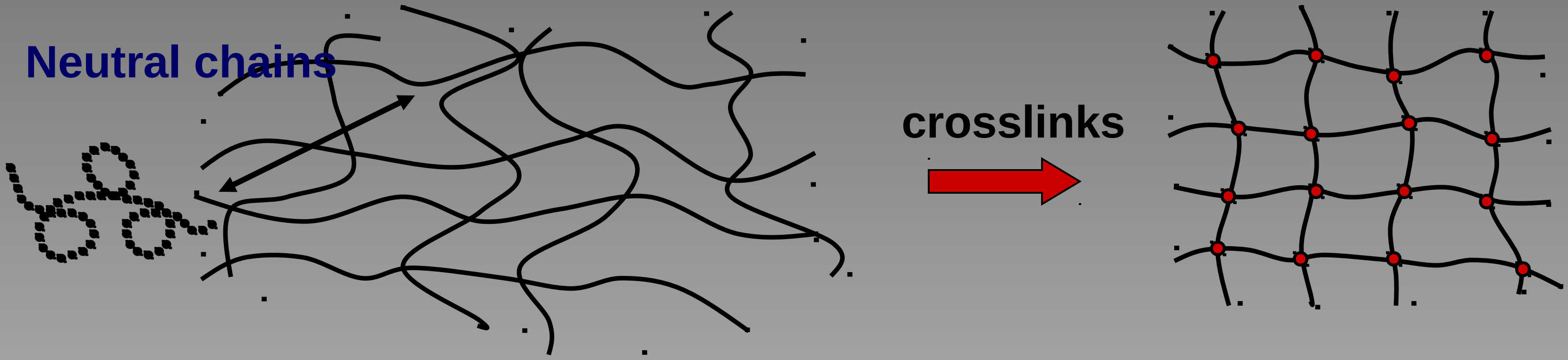
DOUBLE MINIMIZATION : SELF-CONSISTENCY

Kinetics of swelling of polymer gels



Graduate Student: Swati Sen (Poster)

Polymer gels - uncharged:

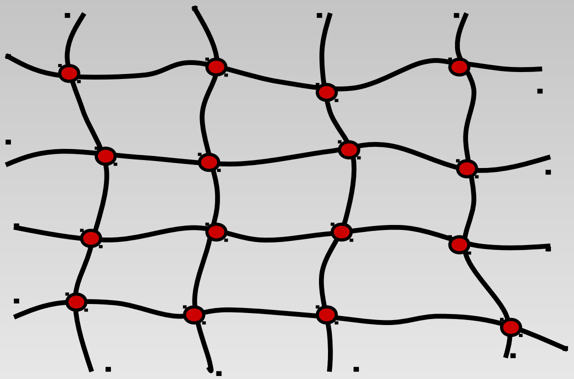


Gel: large single molecule – different kind

Many chains connected at different points

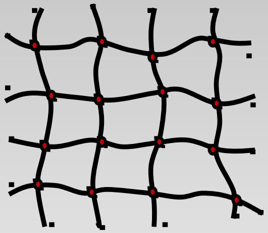
Strand between two crosslinks → similar to single chain

Follows all properties of a single chain → one-to-one correspondence



Good solvent

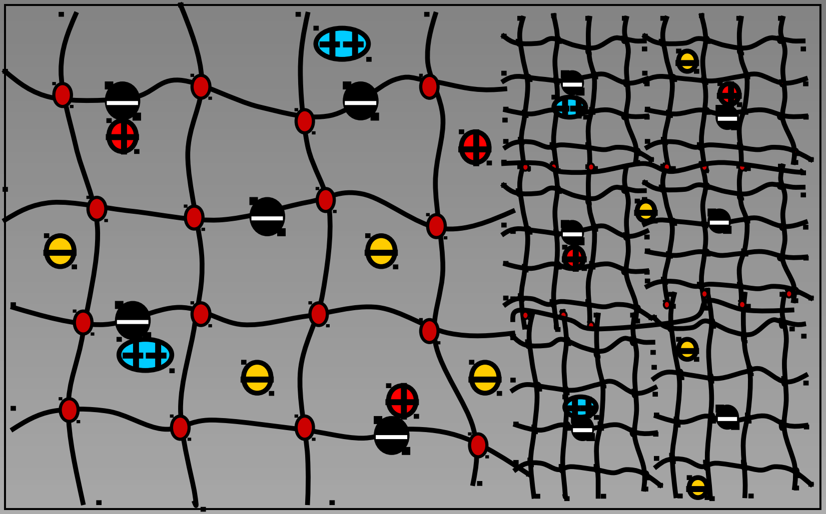
Poor solvent

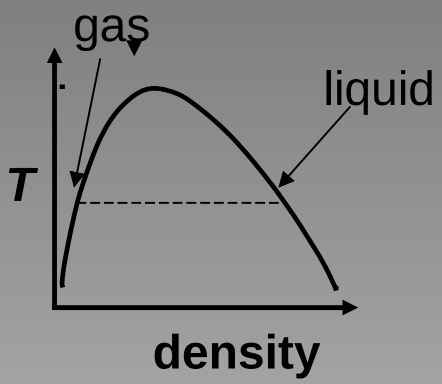


Contribution to **free energy (*E – TS*)**?

Energy: mixing (hydrophobicity) **Entropy:** chain entropy → elasticity

Phase transition – charged gels - schematic:

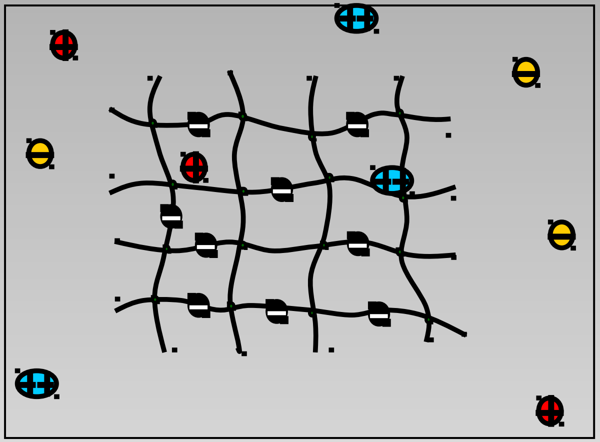




Issues:

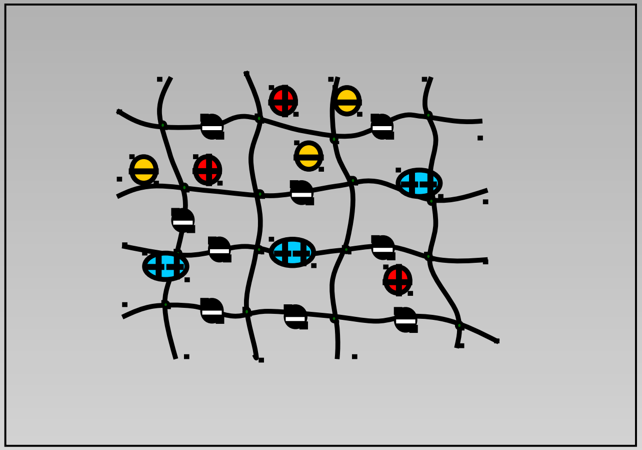
A. Coexistence in charged polymer gels,

B. Interplay of hydrophobic and electrostatic interactions



Repulsion - monomers

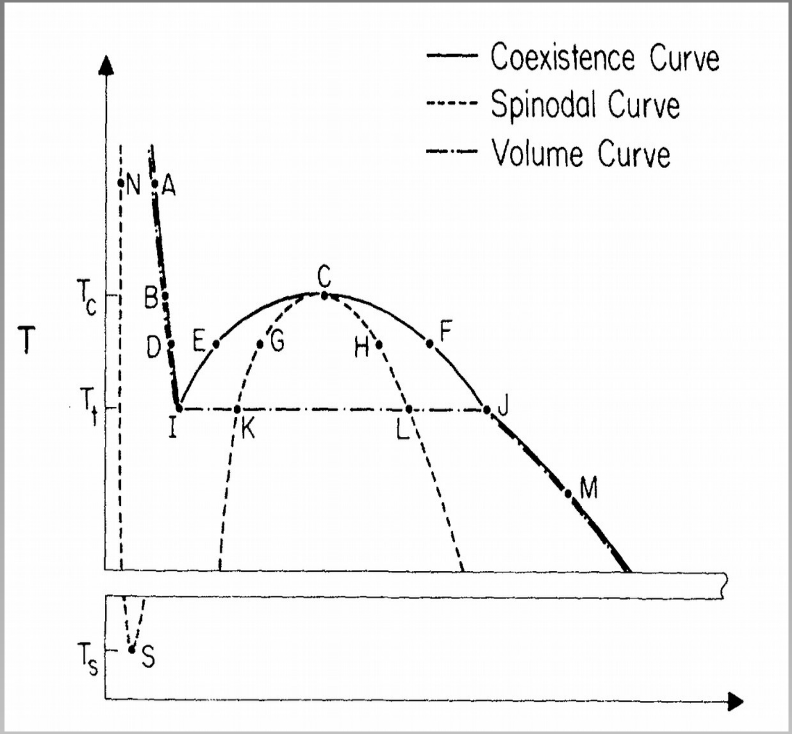
What does swell the gel? Electrostatics or free ion entropy?

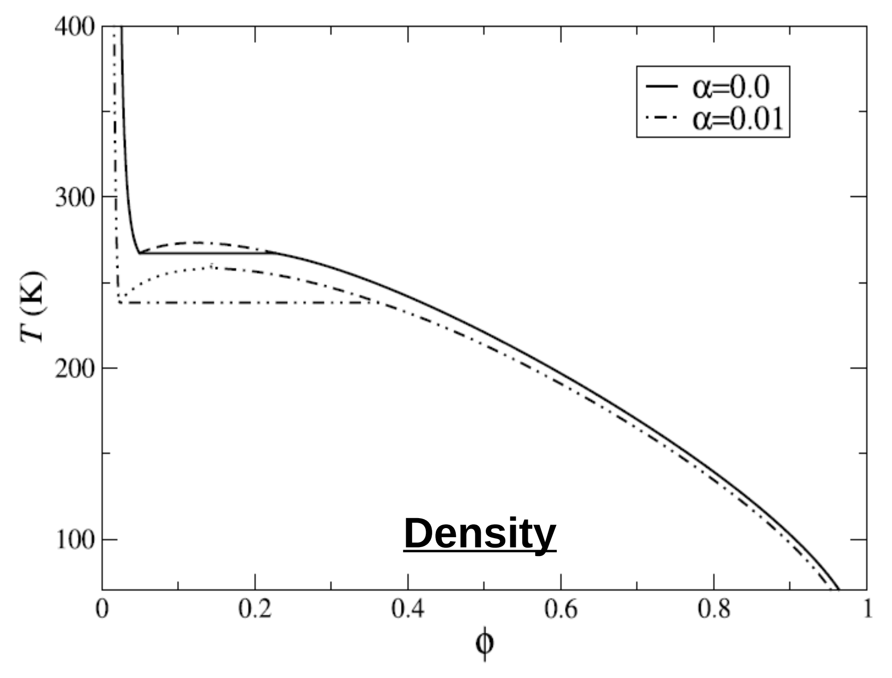


Entropy - counterions

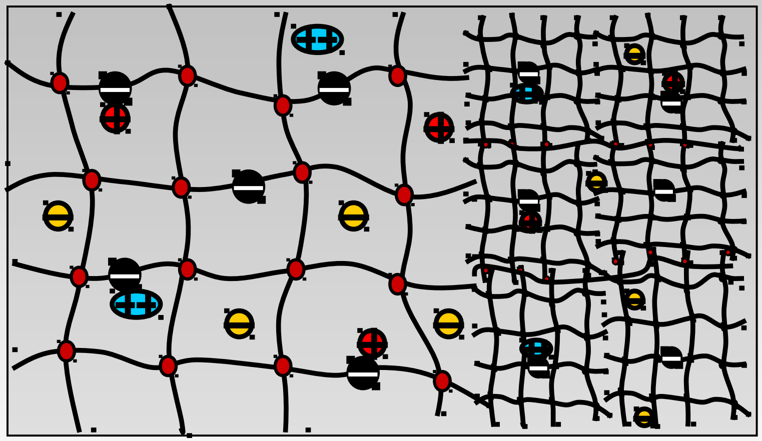
1. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press
2. Jing Hua, Mithun K. Mitra, and M. Muthukumar JCP, 136, 134901 (2012).

Phase behaviour – charged gels - theory:

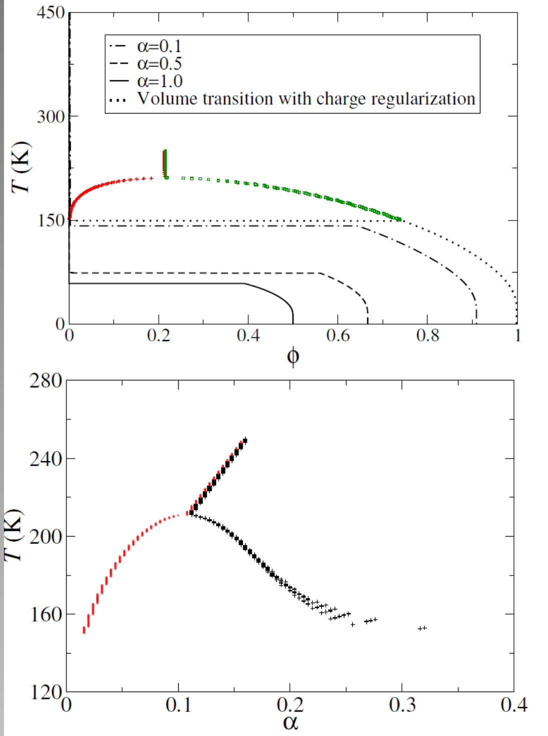




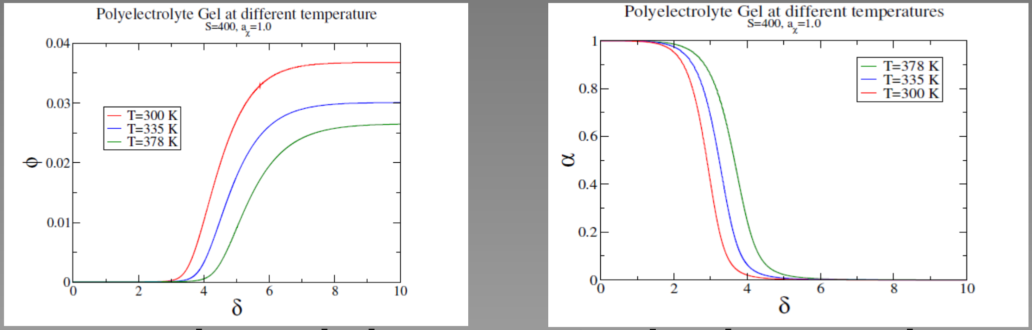
Swati Sen and A. Kundagrami,
JCP, 143, 224904 (2015)



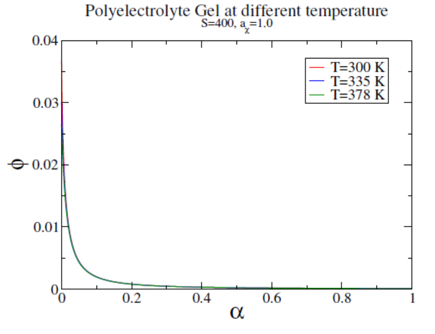
Polyelectrolyte gels: equilibrium properties:



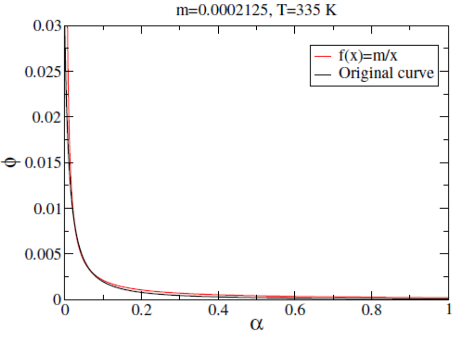
Coexistence curves:
Density and charge



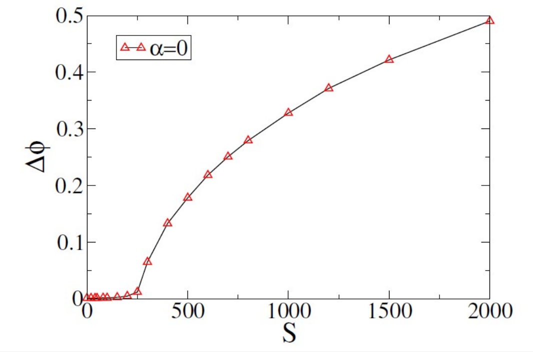
Density and charge vs. Coulomb strength



Density vs. charge:
invariant with Coulomb strength;



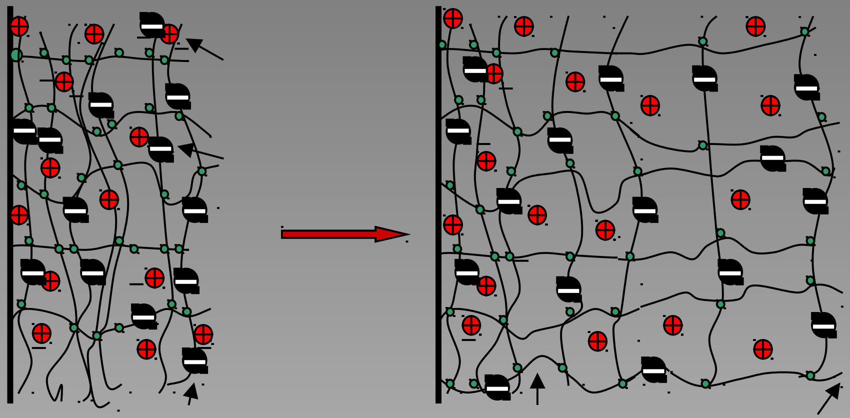
Density vs. charge:
product is constant



Collapse volume change with crosslink density:
Critical exponent?

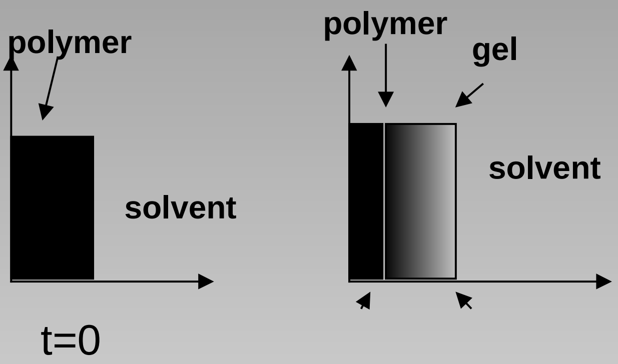
Unpublished: PhD student: Swati Sen

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



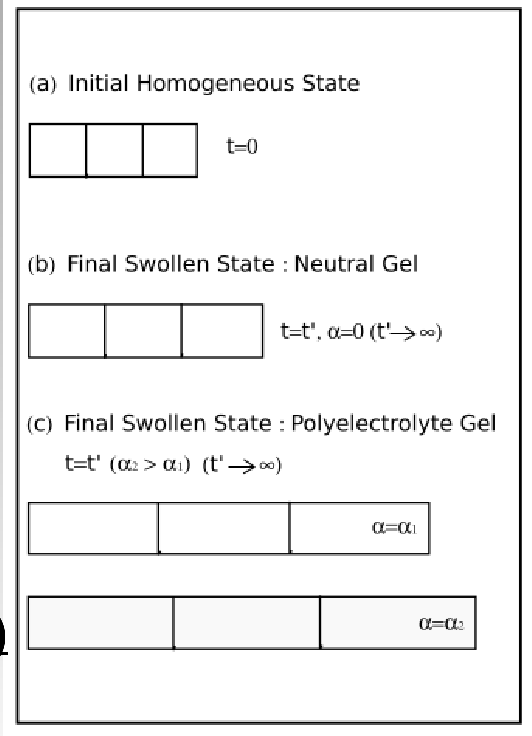
We want to find:

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)

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



Effective Bulk Modulus of a Polyelectrolyte (PE) Gel:

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

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

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

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

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

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

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

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)

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

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

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

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).

Osmotic pressure from free energy of a PE gel:

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

Polyelectrolyte gel

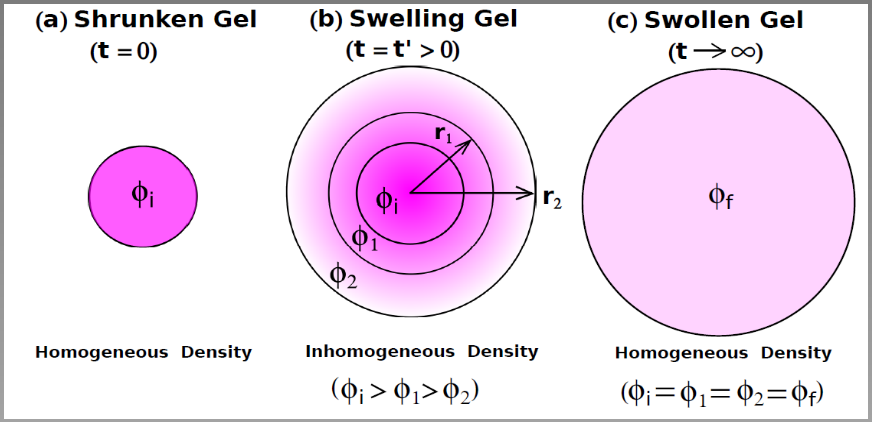
$$\sigma_{xx} = \frac{K_B T}{\nu_c}\Big[-\phi - ln(1-(1+\alpha)\phi) - \chi\phi^2(1+\alpha) + S\phi_0^3\left(\frac{\phi}{2\phi_0} - \left(\frac{\phi}{\phi_0}\right)^{\frac{1}{3}}\right) + \frac{1}{4\pi}\left\{ ln(1+\tilde{\kappa}) - \frac{\tilde{\kappa}}{2(1+\tilde{\kappa})} - \frac{\tilde{\kappa}}{2}\right\}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

Polymer (uncharged) gel

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

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

Swelling of PE gels – variable degree of ionization:



Schematic of swelling

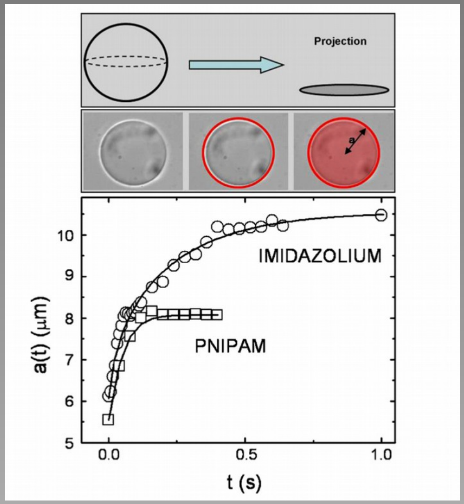
BMM

$$\frac{\partial u}{\partial t} = \frac{K}{f}\frac{\partial}{\partial r}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 u_r\right)\right)$$

SRM w/ charge-regularization

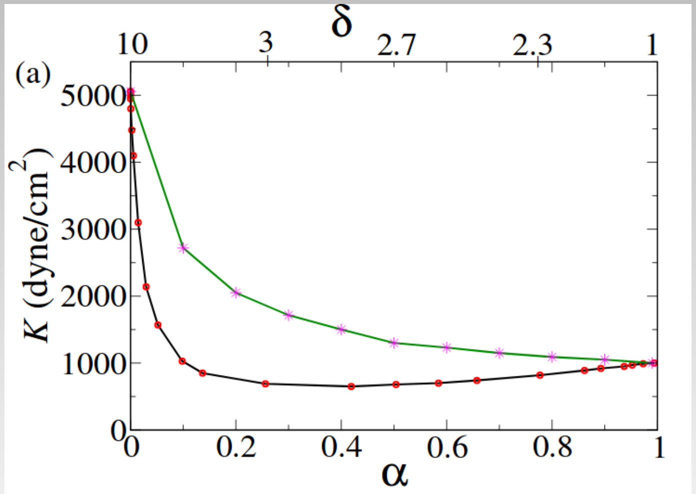
$$\frac{\partial u}{\partial t} = \frac{1}{f}\frac{\partial}{\partial r}\Pi_{rr}$$

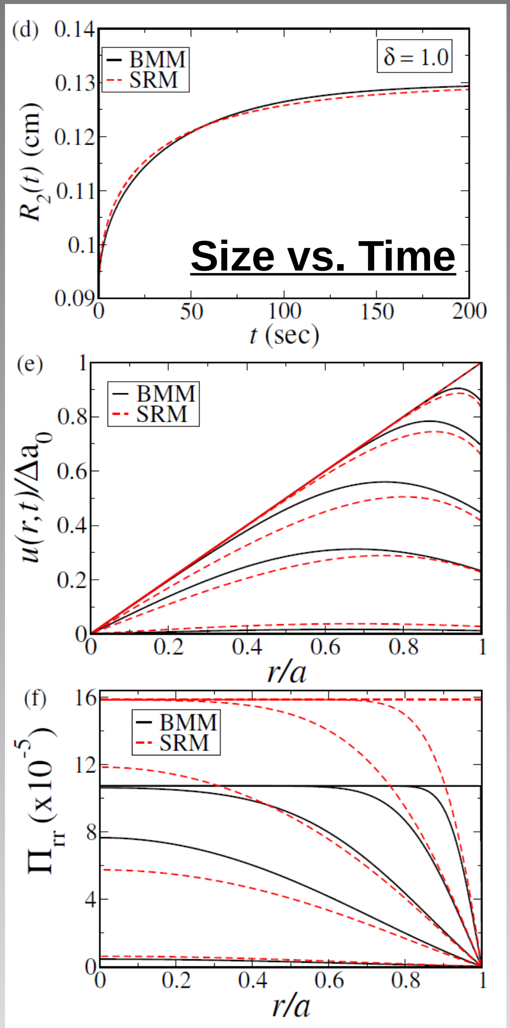
$$\partial f_{\mathrm{en}}/\partial\alpha|_{\phi} = 0$$



Matching of gel-front w/ Experiments: BMM

I. J. Suarez et al.
Colloids and Surfaces A: Phys. Eng. Asp. 343, 33 (2009)





Matching between BMM & SRM: Size & Osmotic Pressure

Swati Sen and A. Kundagrami, JCP, 147, 174901 (2017)

Analytical expression for the bulk modulus:

$$\Pi = \Pi_0 + K\left(\frac{\partial u}{\partial r} + 2\frac{u}{r}\right) \longrightarrow K(\phi, \alpha, \chi, S)$$

Expand Π_{rr} in powers of $\partial u/\partial r$

$b\phi^{2/3} << N^{2/3}\tilde{\kappa}^2$ for $\phi << 1$

Replace the polymer density by: $\phi(r,t) = \phi_f/\{(1-\partial u/\partial r)(1-u/r)^2\}$

Taylor series expansion of: $(1-\partial u/\partial r)^{-1}(1-u/r)^{-2}$

Collect the coefficient of: $(\partial u/\partial r + 2u/r)$

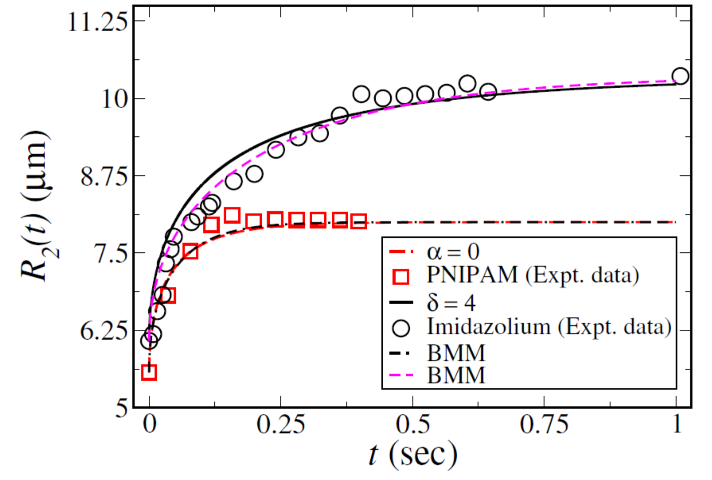
$$\begin{aligned}K(\phi,\alpha,\chi,S) = \frac{K_BT}{\nu_c}\Bigg[&-\phi + \frac{\phi(1+\alpha)}{1-\phi(1+\alpha)} - 2\chi(1+\alpha)\phi^2\\
&+S\phi_0^3\left\{\frac{\phi}{2\phi_0} - \frac{1}{3}\left(\frac{\phi}{\phi_0}\right)^{\frac{1}{3}}\right\} + \frac{1}{4\pi}\left\{\frac{\tilde{\kappa}}{4(1+\tilde{\kappa})}\right.\\
&\left.+\frac{\tilde{\kappa}^2}{4(1+\tilde{\kappa})^2} - \frac{\tilde{\kappa}}{4}\right\} + \frac{\frac{\pi^{7/6}3^{4/3}}{2^{5/3}}\phi^{2/3}}{36\pi N^{\frac{2}{3}}\tilde{l}_B}\Bigg]. \qquad (4.2)\end{aligned}$$

$$\begin{aligned}K_{\alpha=0}(\phi,\chi,S) = \frac{K_BT}{\nu_c}\Bigg[&-\phi + \frac{\phi}{1-\phi} - 2\chi\phi^2\\
&+S\phi_0^3\left\{\frac{\phi}{2\phi_0} - \frac{1}{3}\left(\frac{\phi}{\phi_0}\right)^{\frac{1}{3}}\right\}\Bigg],\end{aligned}$$

Swati Sen and A. Kundagrami, JCP, 147, 174901 (2017)

Matching with experiments – variable degree of ionization:

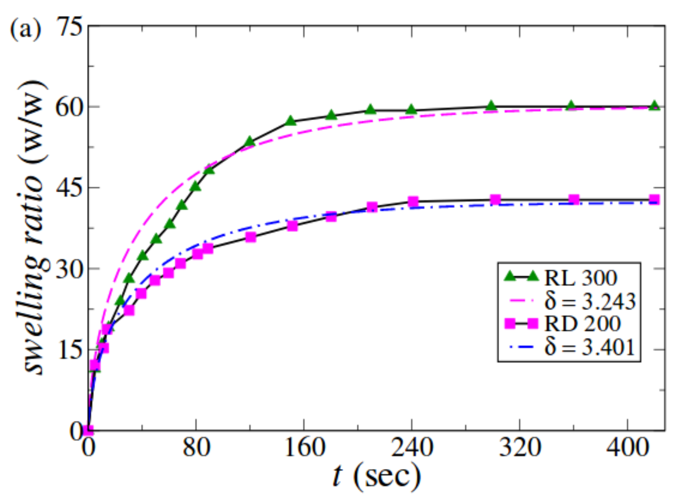
Size vs. Time



Matching of gel-front w/ Experiments: BMM

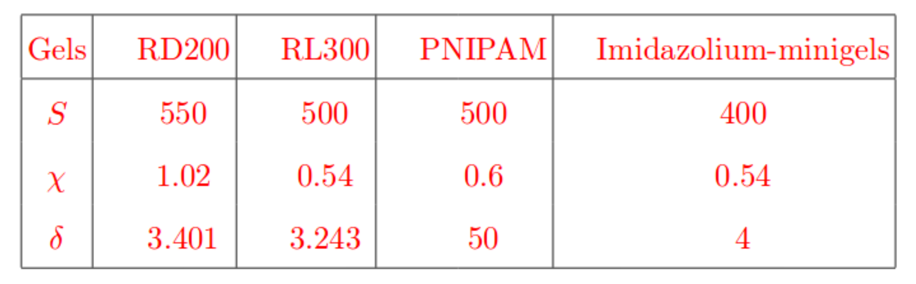
I. J. Suarez et al.
Colloids and Surfaces A:
Phys. Eng. Asp. 343, 33 (2009)

Size vs. Time



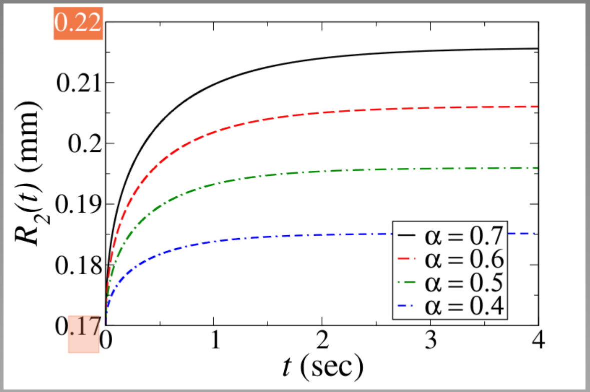
Matching of gel-front w/ Experiments: SRM

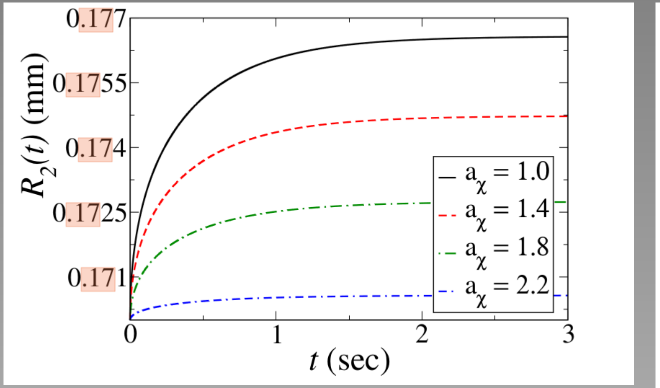
S. Ghosh Roy, U. Halder, and P. De,
ACS Appl. Materials & Interfaces 6, 4233 (2014)

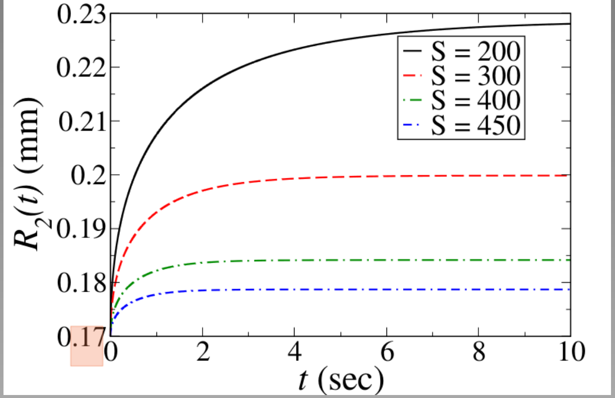


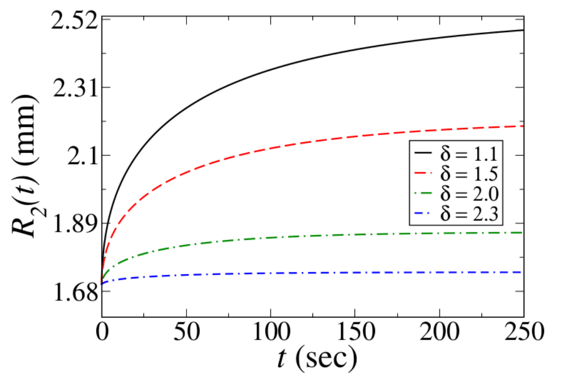
Gels	RD200	RL300	PNIPAM	Imidazolium-minigels
S	550	500	500	400
χ	1.02	0.54	0.6	0.54
δ	3.401	3.243	50	4

Elasticity, Chemical mismatch, diffusion – Size vs Time:









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

Elasticity, Chemical mismatch, diffusion – Timescale and Diffusivity:

$$\tau_e \equiv a^2/D$$

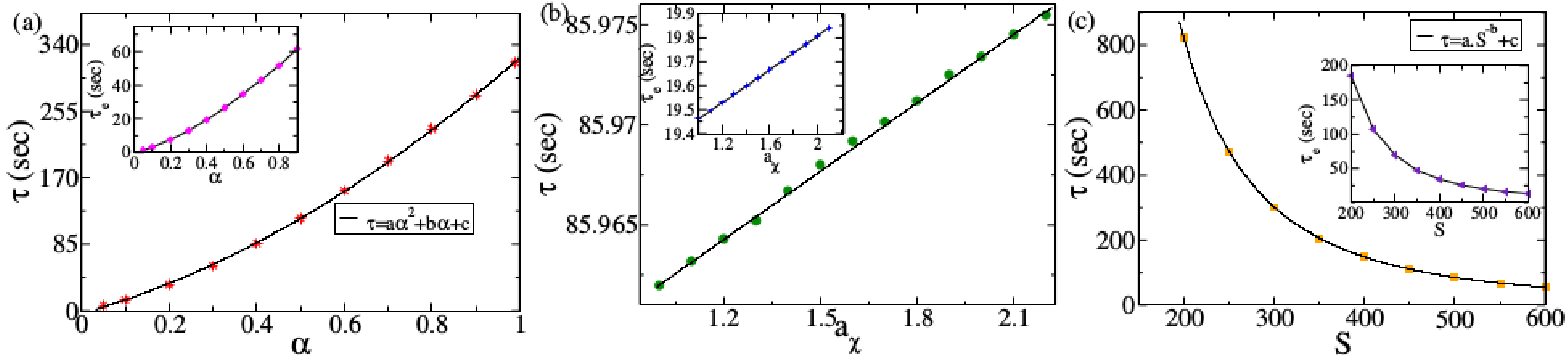


Fig. 1 Fixed degree of deformation (10%), fixed charge case : This plot shows the variation of τ with α, a_χ and S.

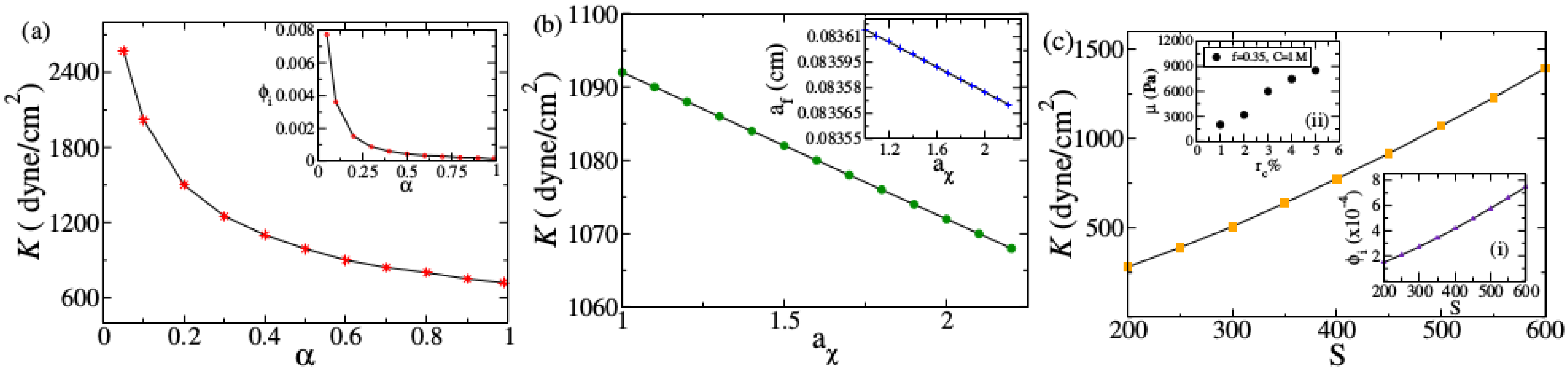
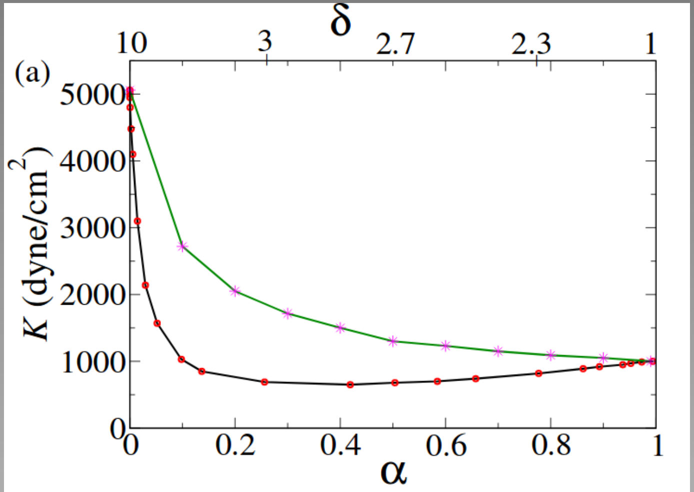
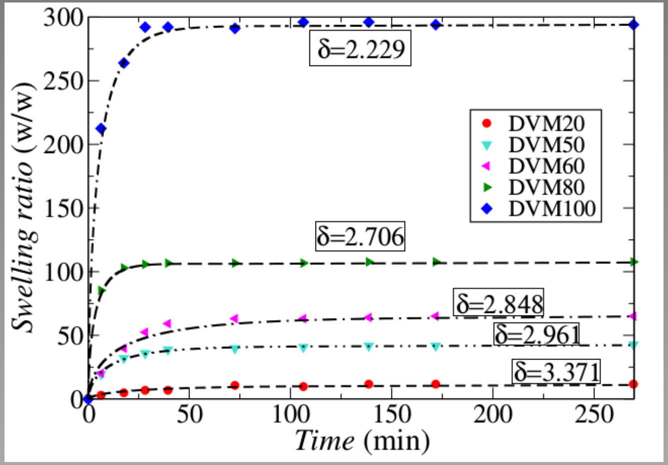


Fig. 2 Fixed degree of deformation (10%), fixed charge case : This plot shows the variation of K with α, a_χ and S.

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

Elasticity, Chemical mismatch, diffusion - Miscellaneous:





Matching of gel-front w/ Experiments: SRM

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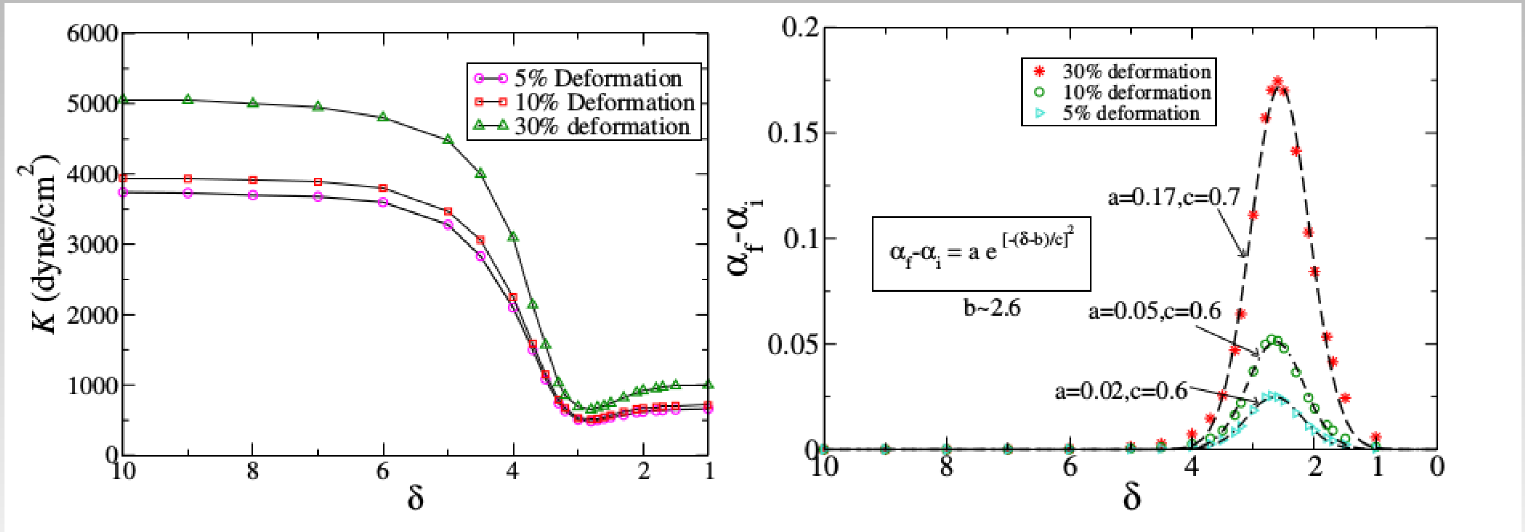


Swati Sen, Ananya Krishnan and A. Kundagrami, *Unpublished*

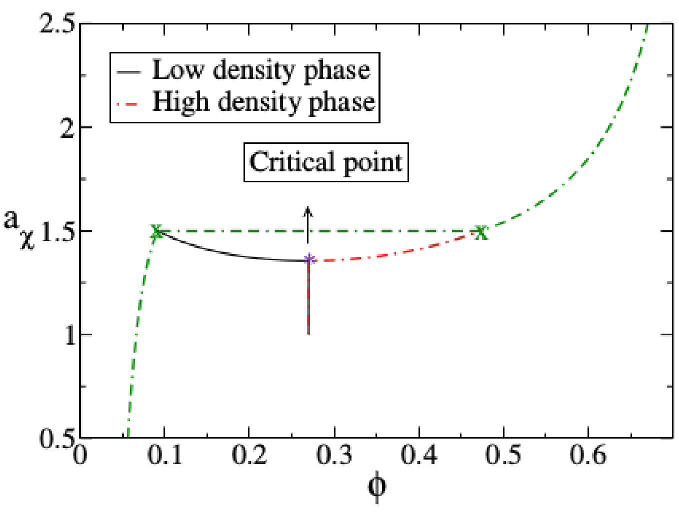
Charge of a gel – analytical expression:

PE gel

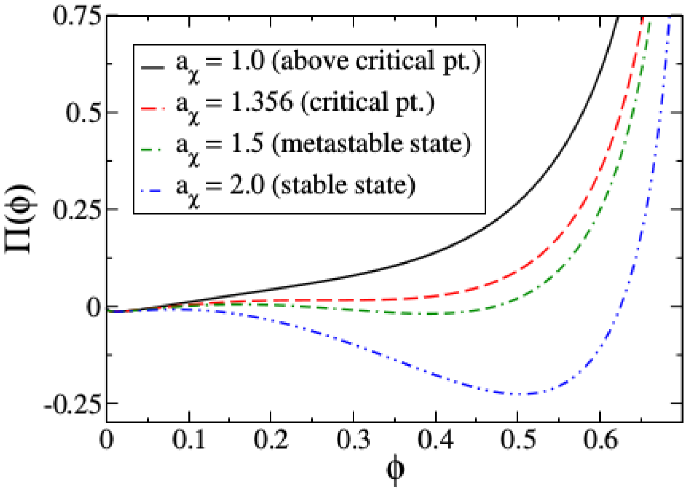
$$\alpha(\delta, \tilde{l}_B, \chi, \phi) = \frac{1}{2\phi(1 - e^{1+2(\delta\tilde{l}_B - \chi\phi)})}[1 + e^{1/2+(\delta\tilde{l}_B - \chi\phi)} - \sqrt{(1 + e^{1/2+(\delta\tilde{l}_B - \chi\phi)})(e^{1/2+(\delta\tilde{l}_B - \chi\phi]} + (1-2\phi)^2 + 4\phi(1-\phi)e^{1+2(\delta\tilde{l}_B - \chi\phi)})}]$$

$$f = \frac{-(\tilde{c}_s + e^{-\delta\tilde{l}_B}) + \sqrt{(\tilde{c}_s + e^{-\delta\tilde{l}_B})^2 + 4\tilde{\rho}e^{-\delta\tilde{l}_B}}}{2\tilde{\rho}}$$

Single PE chain

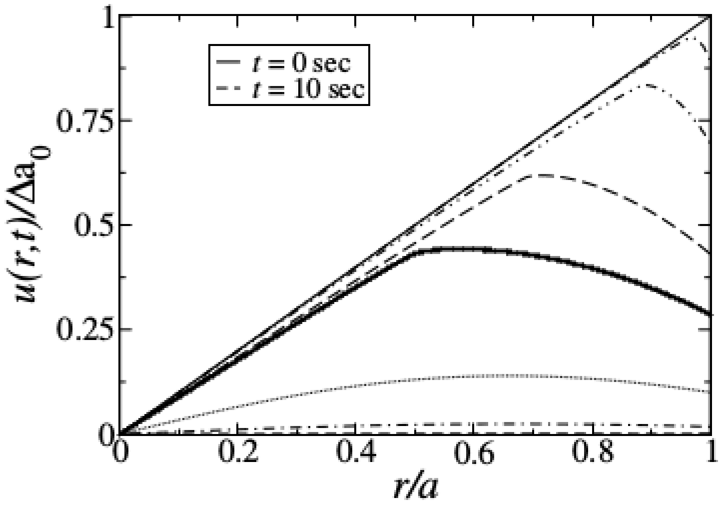


(f) Phase diagram for fixed charge case

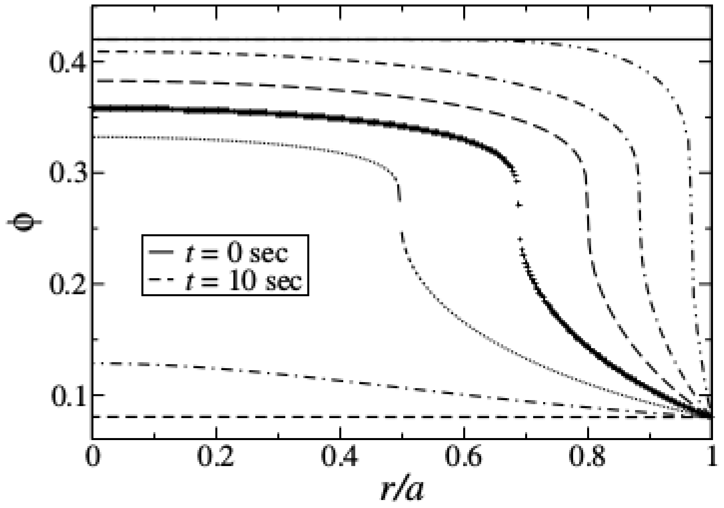


(g) Osmotic pressure-density diagram

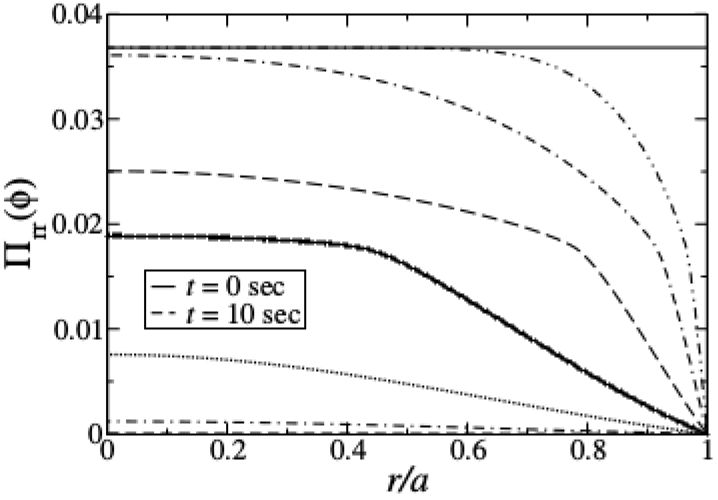
Swelling close to the critical point – slowing down:



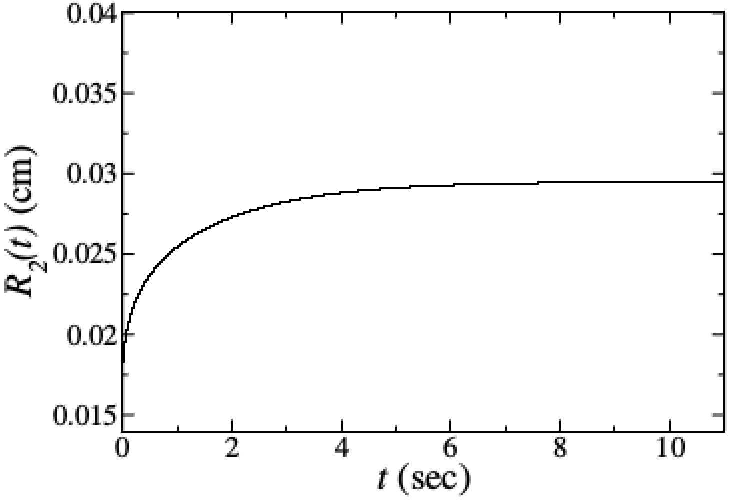
(h) Displacement



(i) Density

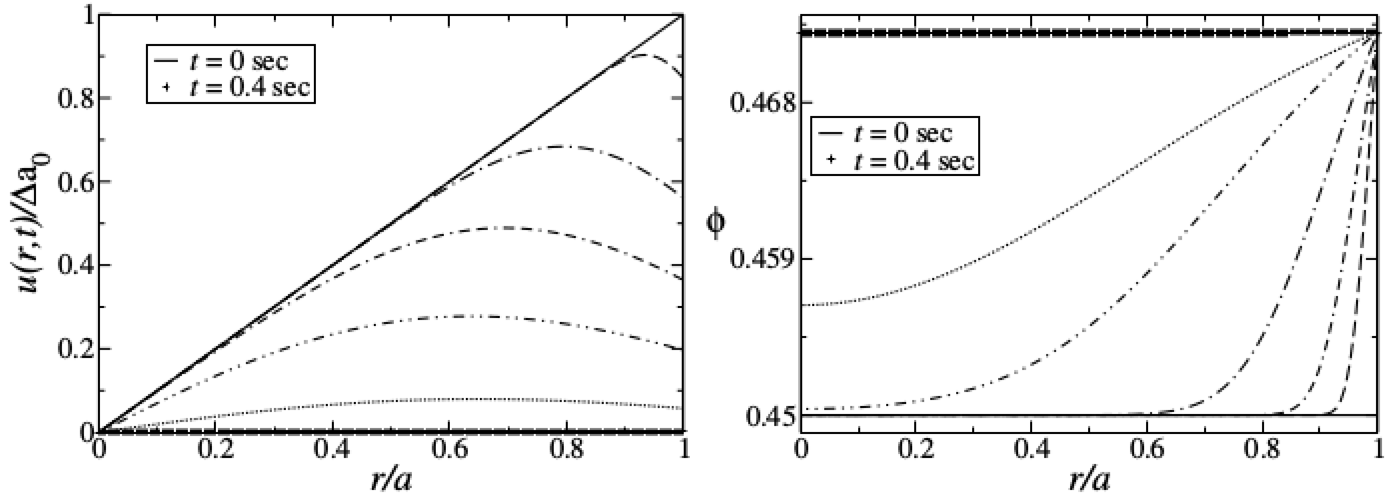


(j) Stress



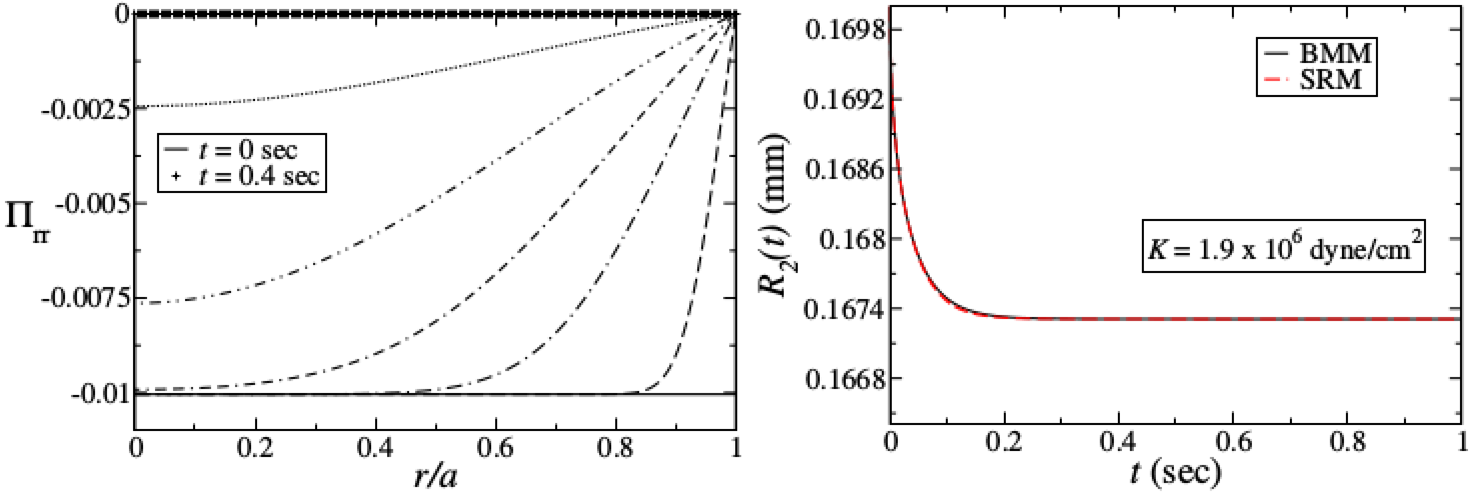
(k) gel-front location

Deswelling:



(m) Displacement

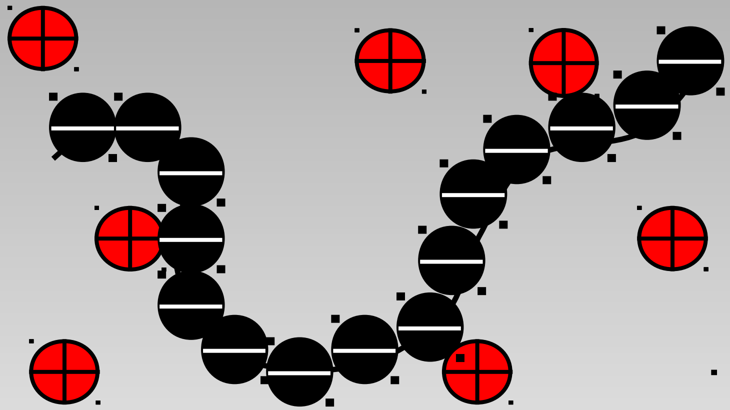
(n) Density



(o) Stress

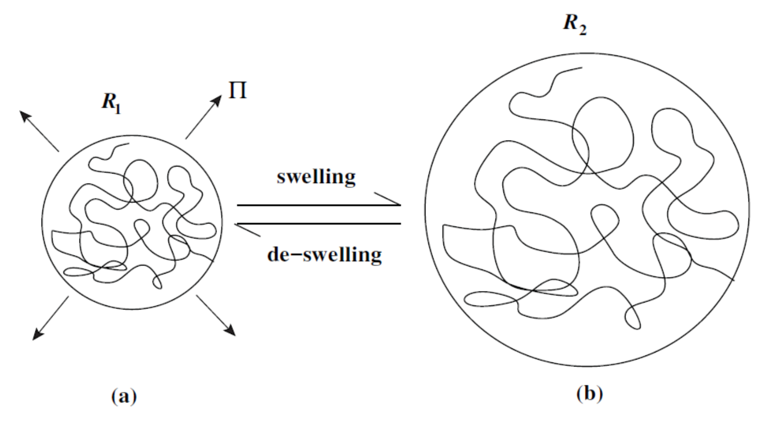
(p) SRM-BMM gel-front matching

Kinetics of swelling and collapse of a single polymer chain



Graduate Student: Soumik Mitra (Poster)

Equation of motion – osmotic and viscous forces:



Uniform spherical expansion model

Swelling and collapse of:

Single, isolated, flexible polyelectrolyte (PE) chain

EOM for surface element – osmotic stress and viscous force

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

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)

Analytical Expressions – 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

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

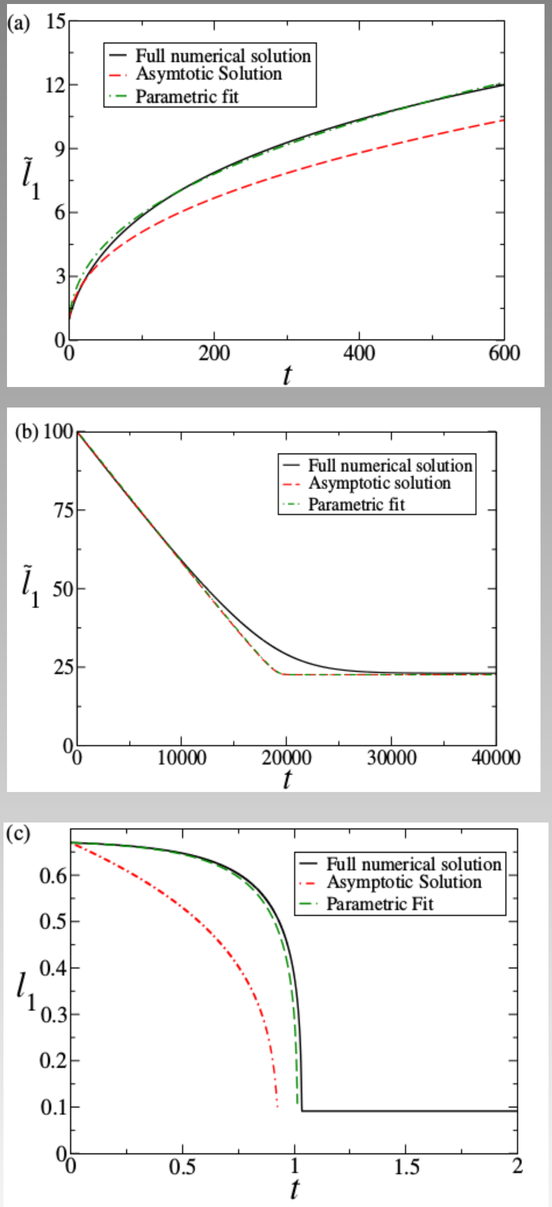
De-swelling:

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

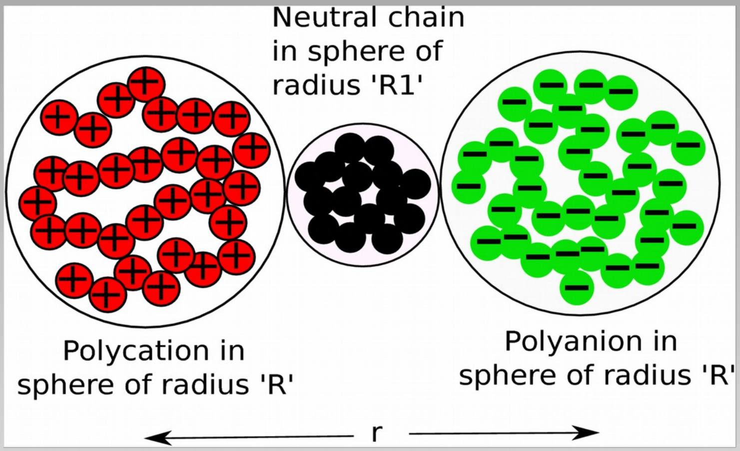
Collapse:

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

Size vs. Time



Complexation of oppositely charged polyelectrolytes



Graduate Student: Soumik Mitra

Complexation – oppositely charged polyelectrolytes:

Model

- Two oppositely charged PE chains driven towards mutual overlap due to **Coulomb attraction** and **free-ion entropy**
- Complex formation by **monomer-monomer adsorption** in the overlap process

Energetics:

(i)entropy of condensed counterions

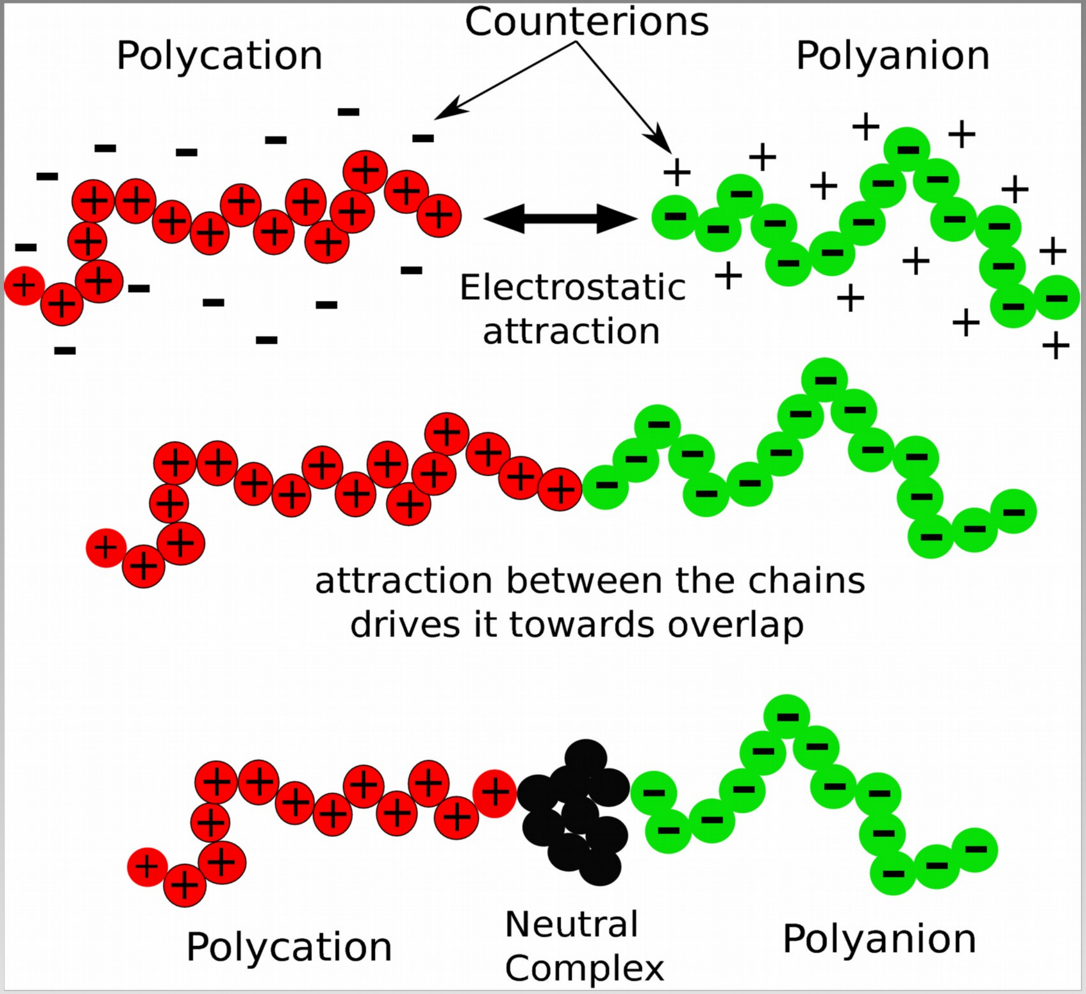
(ii)entropy of mobile counterions

(iii)fluctuations of mobile ions

(iv)adsorption energy of ion-pairs

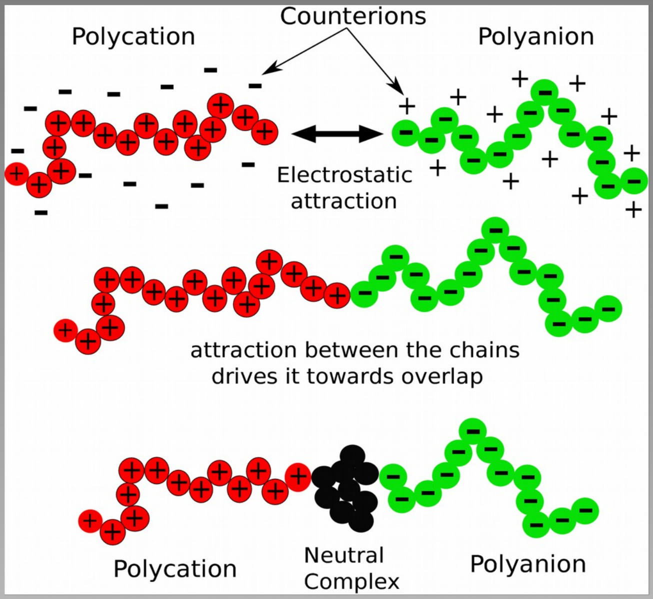
(v)configurational free energy of the polycation, polyanion, and complex

(vi) electrostatic binding energy of complex



Schematic of the electrostatic attraction driven complexation of the polcation and polyanion

Free energy of complexed polyelectrolytes:



$$\frac{F_1}{(N-n)k_BT} = 2\left[f\log f + (1-f)\log(1-f)\right]$$

$$\frac{F_2}{(N-n)k_BT} = 2\left(f + \frac{\tilde{c}_s}{\tilde{\rho}}\right)\log(f\tilde{\rho}+\tilde{c}_s) - \left(2f + \frac{\tilde{c}_s}{\tilde{\rho}}\right)$$

$$\frac{F_3}{(N-n)k_BT} = -\frac{1}{3}\sqrt{4\pi}\tilde{l}_B^{3/2}\frac{\left[2(f\tilde{\rho}+\tilde{c}_s)\right]^{3/2}}{\tilde{\rho}}$$

$$\frac{F_4}{(N-n)k_BT} = -\left[(1-f)\delta_1 + (1-f)\delta_2\right]\tilde{l}_B$$

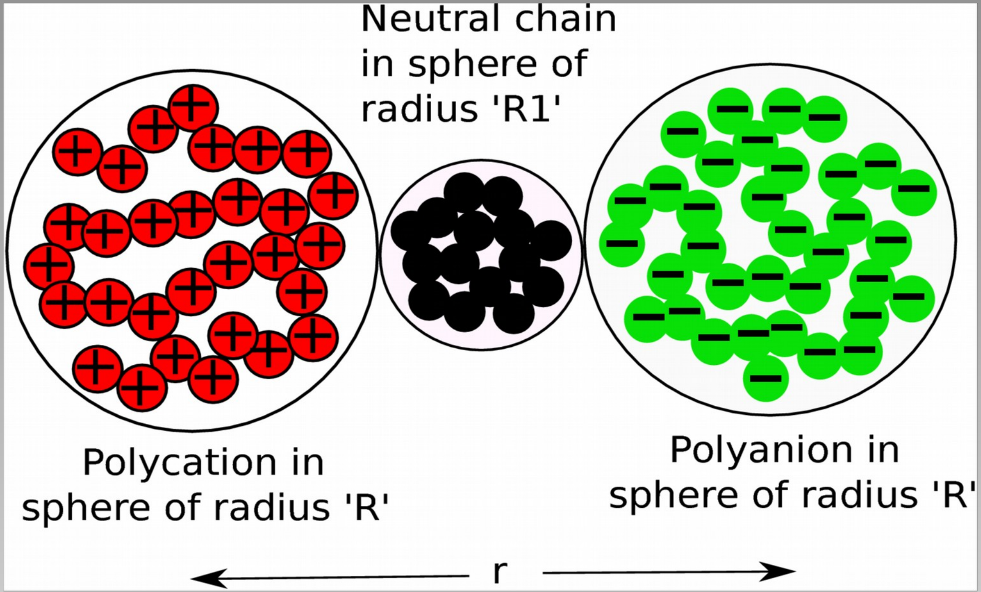
$$\frac{F_{5,chain}}{(N-n)k_BT} = \frac{3}{2(N-n)}\left[\tilde{l}_1 - 1 - \log\tilde{l}_1\right] + \frac{4}{3}\left(\frac{3}{2\pi}\right)^{3/2}\frac{w}{(N-n)^{1/2}}\frac{1}{\tilde{l}_1^{3/2}} + \frac{w_3}{(N-n)\tilde{l}_1^3} + 2\sqrt{\frac{6}{\pi}}f^2\tilde{l}_B\frac{(N-n)^{1/2}}{\tilde{l}_1^{1/2}}\Theta_0(a)$$

$$\frac{F_{5,complex}}{(N-n)k_BT} = \frac{3}{2(N-n)}\left[\tilde{l}_2 - 1 - \log\tilde{l}_2\right] + \frac{4}{3}\left(\frac{3}{2\pi}\right)^{3/2}\frac{n^{1/2}}{(N-n)}\frac{w}{\tilde{l}_2^{3/2}} + \frac{w_3}{(N-n)\tilde{l}_2^3}$$

$$F_5 = 2F_{5,chain} + F_{5,complex}$$

The uniform sphecrical model for complexation:

- the two oppositely charged chain interacts via the Yukawa potential
- PE chains are considered to be interacting spheres, within the DLVO theory



$$\frac{F_6}{(N-n)k_BT} = (N-n) f^2 \tilde{l}_B \left(\frac{\exp[\tilde{\kappa}\tilde{R}]}{1+\tilde{\kappa}\tilde{R}}\right)^2 \left\{\frac{\exp[-\tilde{\kappa}\tilde{r}]}{\tilde{r}}\right\}$$

- R -radius of the spheres encapsulating the PE chains
- r -centre-to-centre distance between the two PE chains

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**

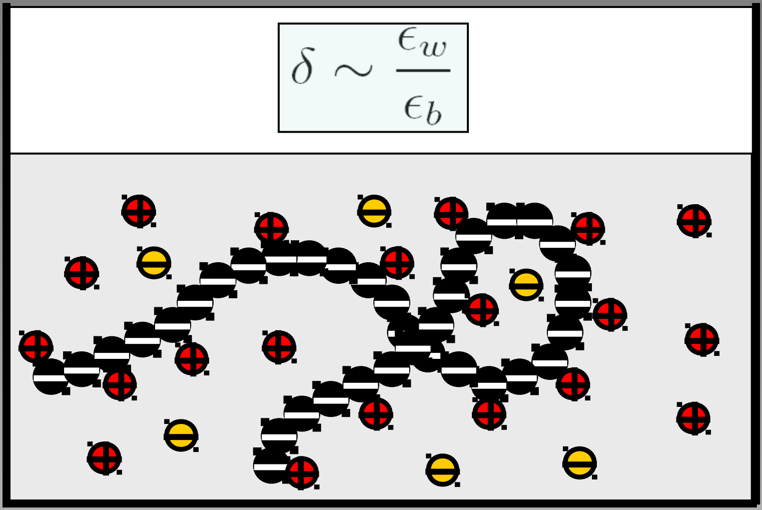
Charged polymers – energy and entropy:

Do all Na+ ions dissolve? **NO!**

Counterion condensation. WHY?

Effective ϵ low close to backbone

Condense → gain in Coulomb energy



$$\delta \sim \frac{\epsilon_w}{\epsilon_b}$$

Let's predict qualitatively:

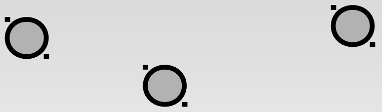
$$-\frac{e^2}{4\pi\epsilon_0\epsilon d}$$

Remember: *E - TS*

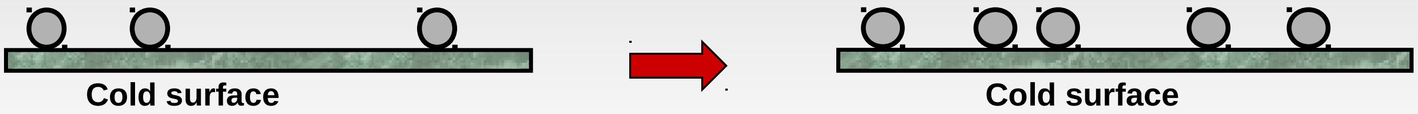
E = Coulomb energy, ***S*** = free ion entropy → $k_B T$

1. ***T*** ↓ → ***S*** fixed, ***E***/ion-pair fixed → more ion-pairs → less charge
2. ϵ ↓ → ***S*** fixed, ***T*** fixed, ***E***/ion-pair increases → more ion-pairs
3. ***V*** ↑ → ***S*** increases, ***T*** fixed, ***E***/ion-pair fixed → less ion-pairs

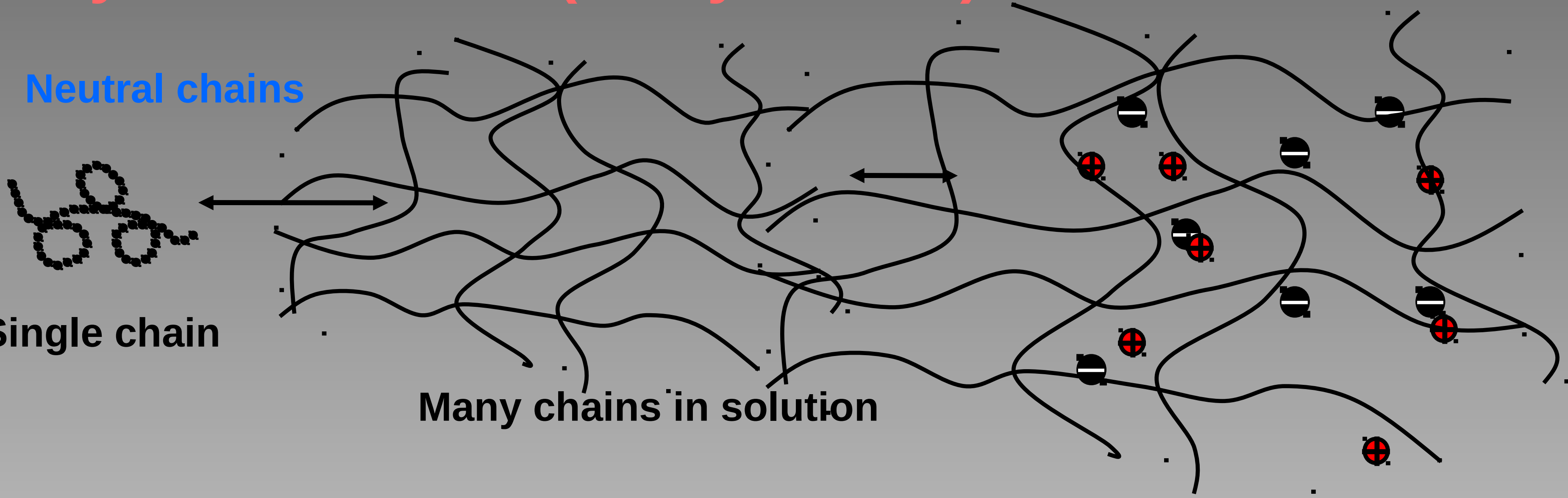
Similar to **DEW** formation: at low ***T*****,** air can't hold vapor → condensation



SALT ⟷ WET WEATHER



Polymer solutions (many chains) - schematic:



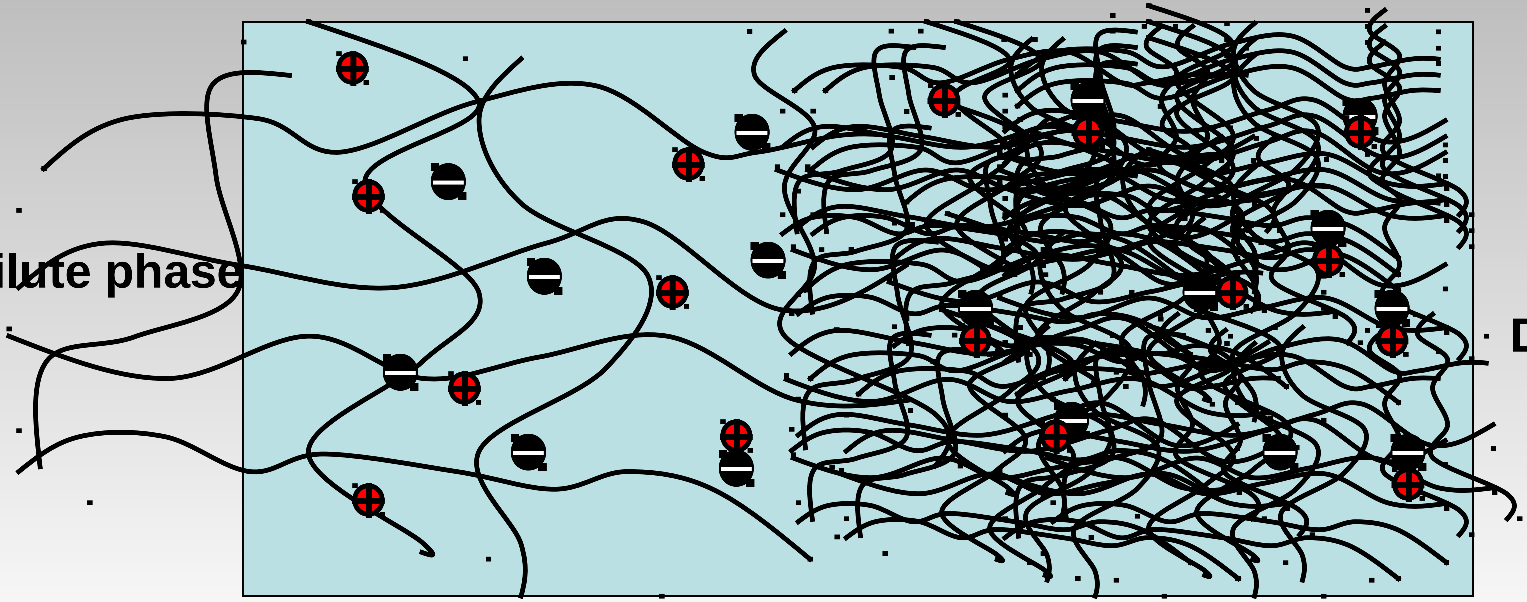
Neutral chains

Single chain

Many chains in solution

Charged polymer solution

Coexistence in phase separation



Dilute phase

Dense phase

Polymer solutions (many chains) - free energy:

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

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

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

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

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

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

SALT FREE

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

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

Lever rule

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

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

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

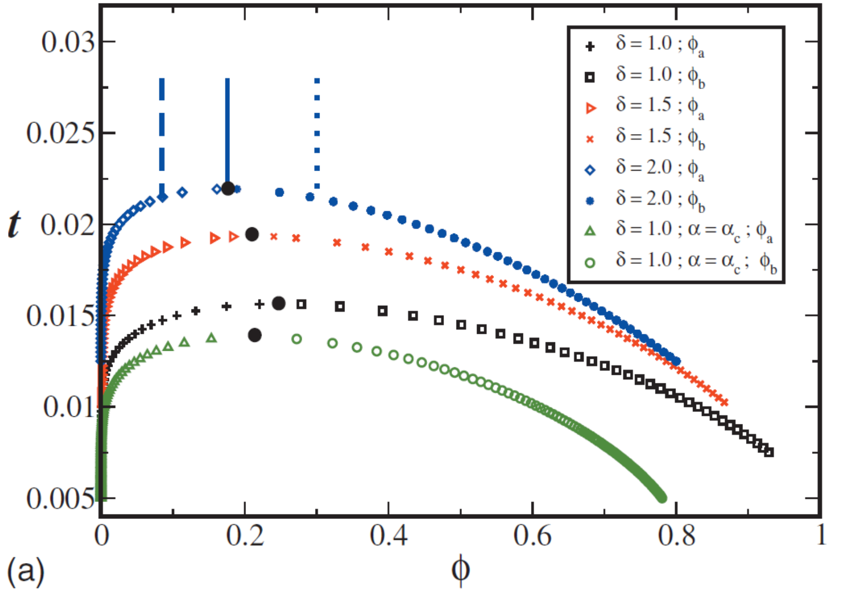
$$f_{ad} = -(1-\alpha)\phi\tilde{\ell}_B\delta$$

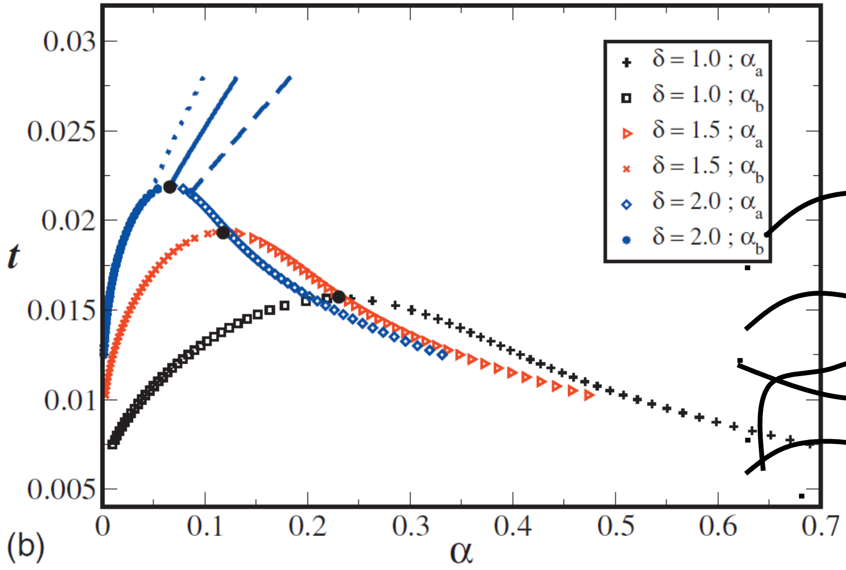
FLORY

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

M. Muthukumar, J. Hua, and A. Kundagrami JCP, 132, 084901 (2010).

Polymer solutions – phase diagrams - theoretical :



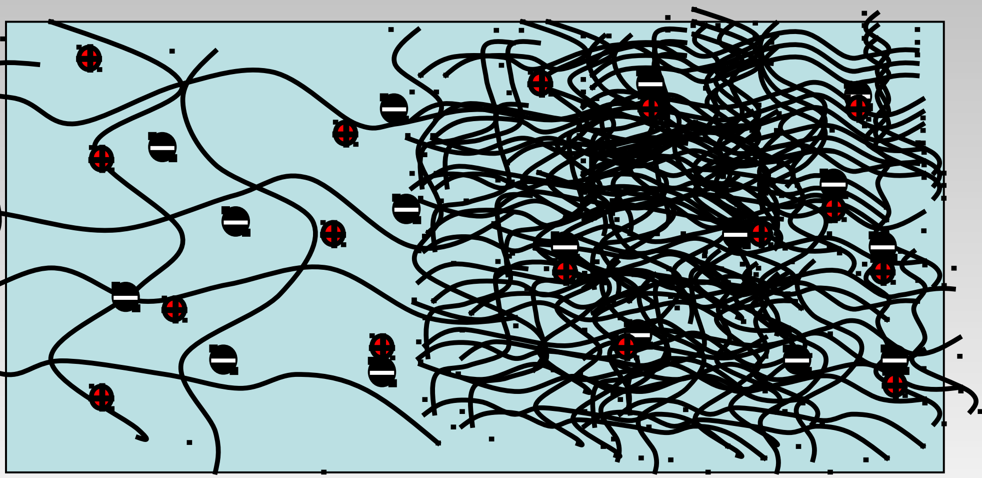


Coexisting daughter phases have different degrees of ionization – denser phase has lower charge.

Charge in dilute phase increases w/ decreasing T although lower T favours more condensation - entropy in dilute Solution wins);

Charge in condensed phase decreases w/ T due to synergistic effects from T and dense-ness.

$$\delta \sim \frac{\epsilon_w}{\epsilon_b}$$



M. Muthukumar, J. Hua, and A. Kundagrami JCP, 132, 084901 (2010).

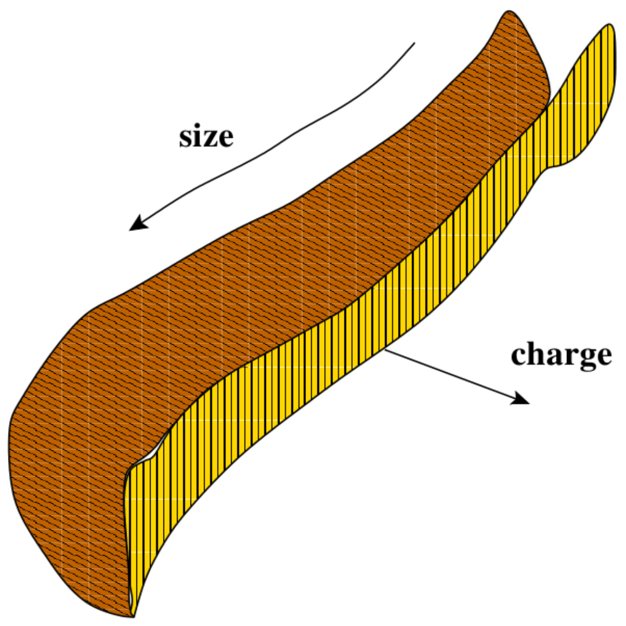
Charge regularization:

Assumption: Motion of counterions much faster than that of monomers

1. Counterions re-adjust themselves with virtually frozen configuration of polymer

2. Gel is stable with respect to counterion density variation – chemical equilibrium

Kinetics:
Downhill in free energy with size
But, minimum in charge



General expression:

$$\left.\frac{\partial F}{\partial \tilde{l}_1}\right|_{N,T} = \left.\frac{\partial F}{\partial \tilde{l}_1}\right|_{f,N,T} + \left.\frac{\partial F}{\partial f}\right|_{\tilde{l}_1,N,T} \left(\frac{\partial f}{\partial \tilde{l}_1}\right)$$

Special condition applicable to this system:

$$\left.\frac{\partial F}{\partial f}\right|_{\tilde{l}_1,N,T} = 0$$

Expression of derivative of free energy for fixed charge applies!

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**

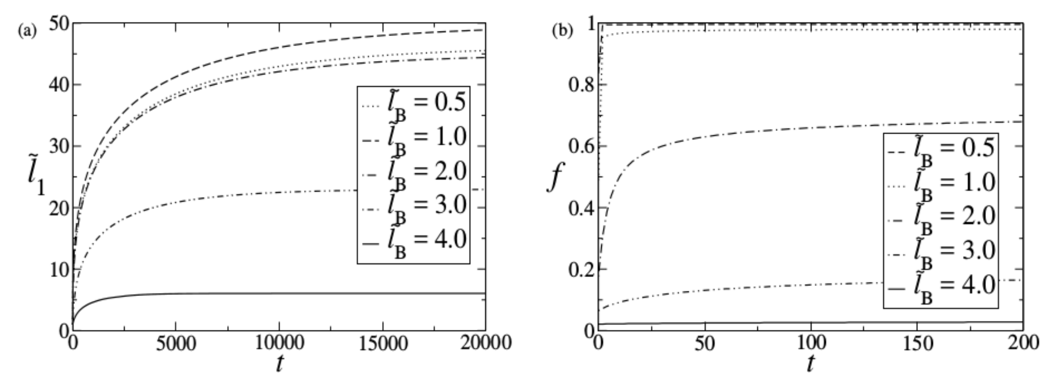
Swelling profiles:

$$f = \frac{-(\tilde{c}_s + e^{-\delta \tilde{l}_B}) + \sqrt{(\tilde{c}_s + e^{-\delta \tilde{l}_B})^2 + 4\tilde{\rho} e^{-\delta \tilde{l}_B}}}{2\tilde{\rho}}$$

Expression of charge – expanded state

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

Size vs. Time   Charge vs. Time



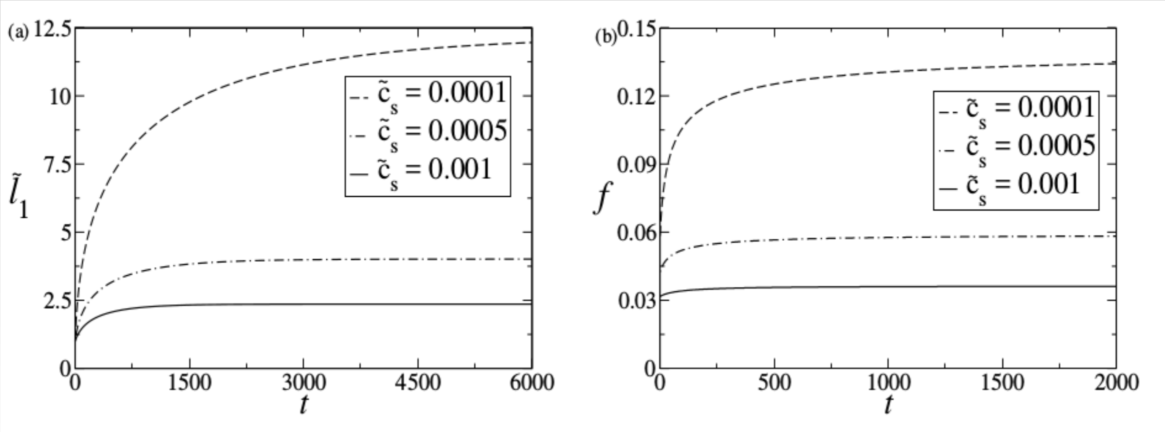
Swelling at different temperatures:

1. Swells faster and farther for higher *T.*
2. Lower temperature – condensation reduces final size
3. Extended chain – charge is not dependent on size

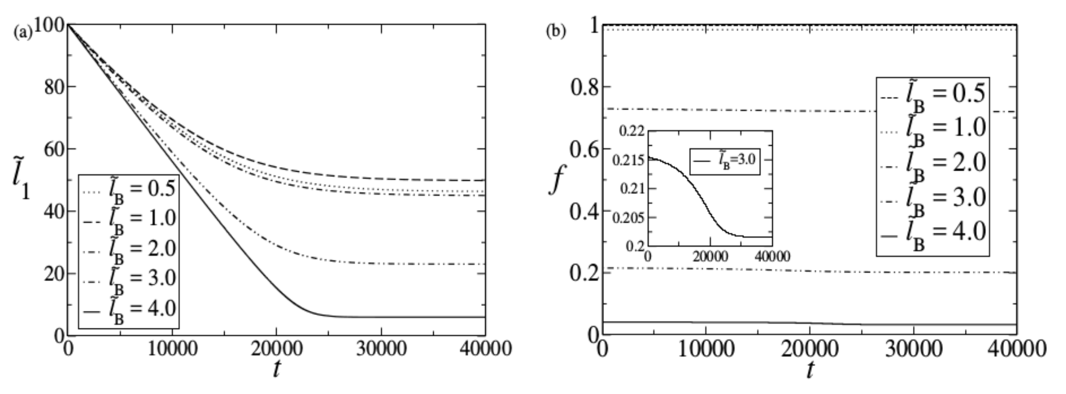
Size vs. Time   Charge vs. Time

Swelling at different salt:

1. Swells faster and farther for lower monovalent salt.
2. Extended chain – charge is not dependent on size



De-swelling profiles:

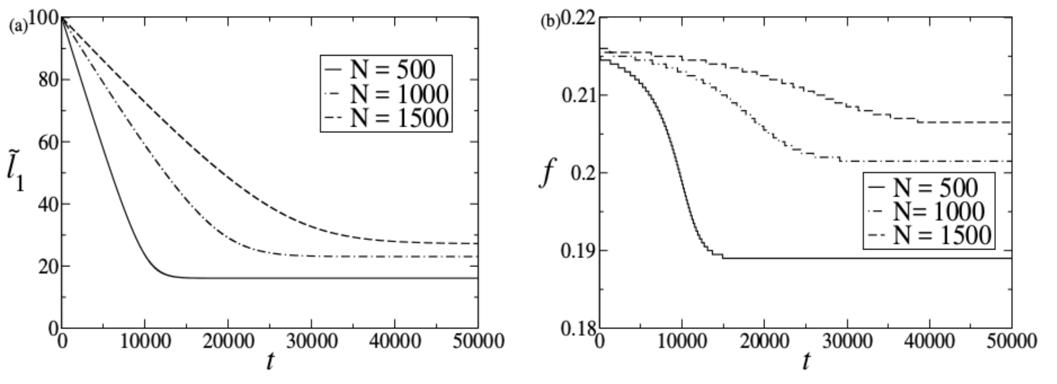


Size vs. Time

Charge vs. Time

De-swelling at different temperatures:

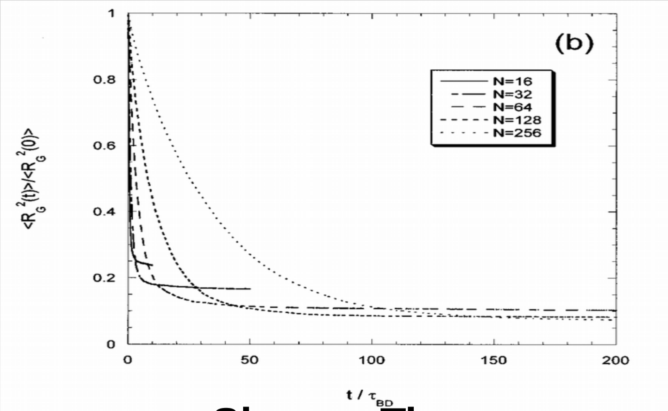
1. **De-swells faster and deeper for lower *T***
2. **Lower temperature – condensation reduces final size**
3. **Extended chain – charge is not dependent on size**



De-swelling for different molecular weights:

1. **De-swells slower for higher molecular weight**
2. **Matches qualitatively with experimental results with PMMA gels**

Simulations:
Chang and Yethiraj,
JCP, 114, 7688 (2001)

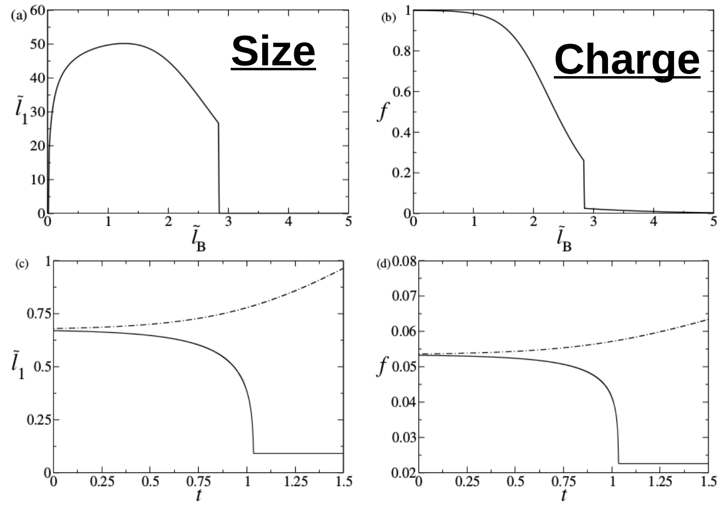


Size vs. Time

Collapse profiles:

1. Poor solvent – hydrophobic – negative two-body parameter
2. Size goes below Gaussian - \tilde{l}_1 <1

Equilibrium



Size

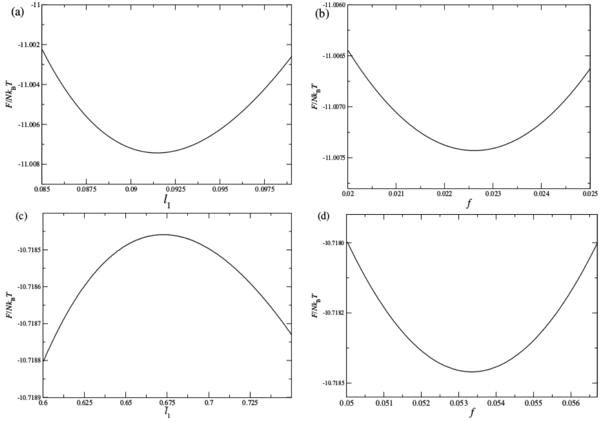
Charge

Kinetics

Equilibrium result – first order transition – both in size and charge

Local maximum prohibits direct collapse to the global minimum

Free energy



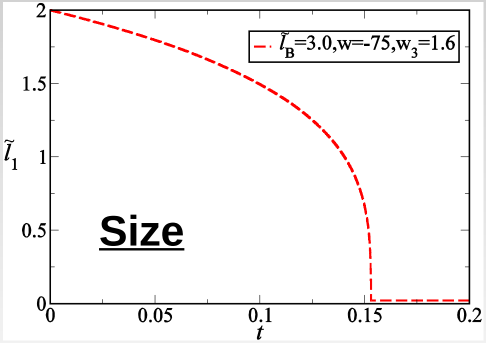
Size

Charge

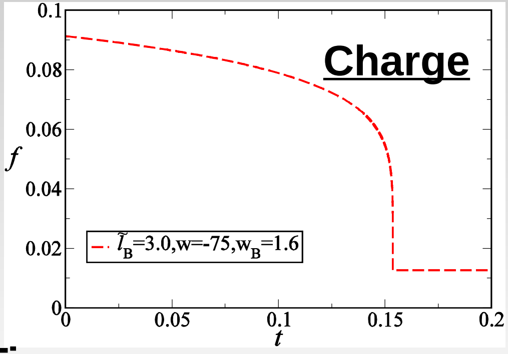
Local maximum

Global minimum

Direct collapse: extended to globule



Size



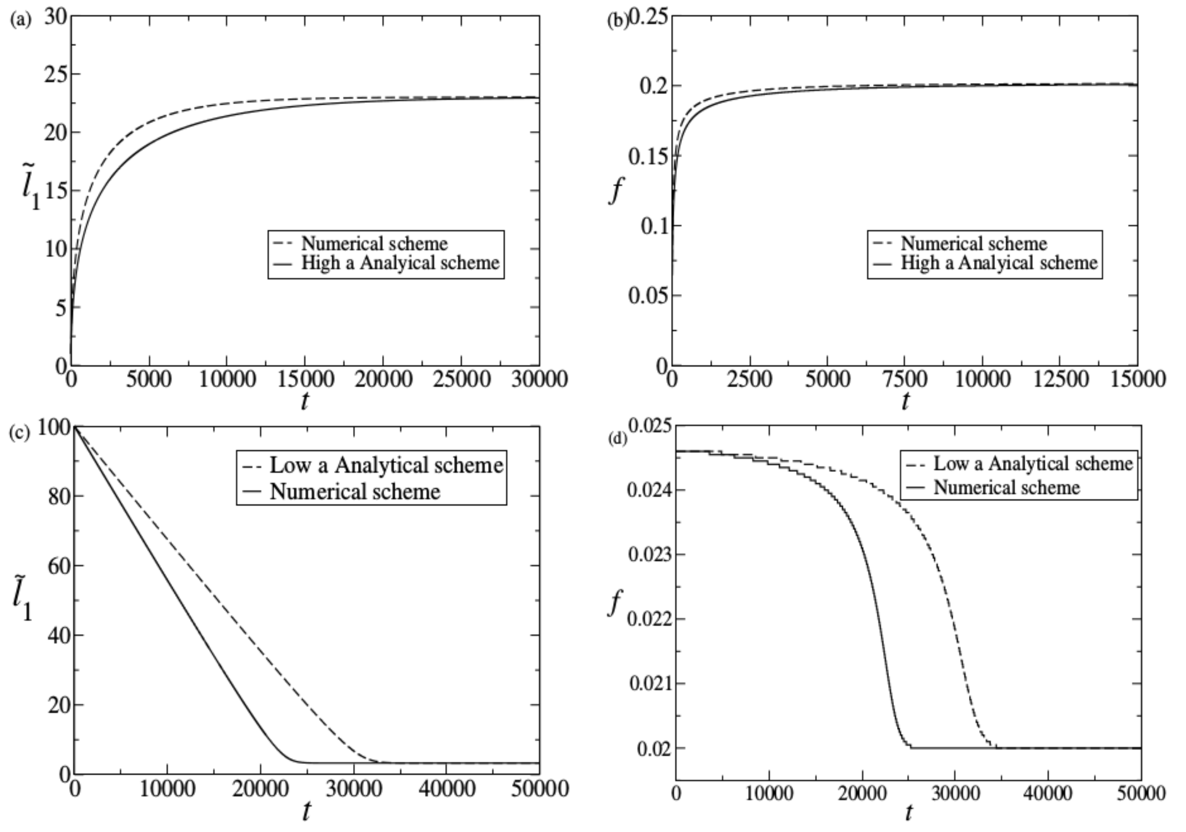
Charge

Time

Limiting results – comparison to full numerical results:

High-salt

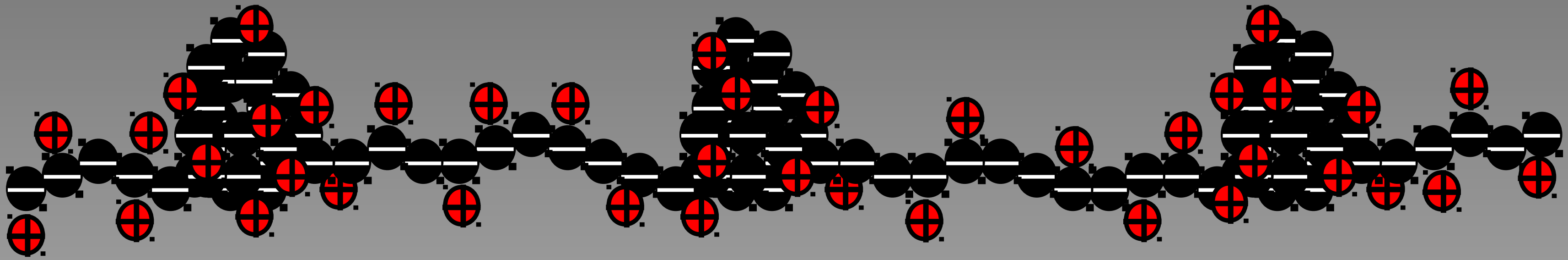
Low-salt



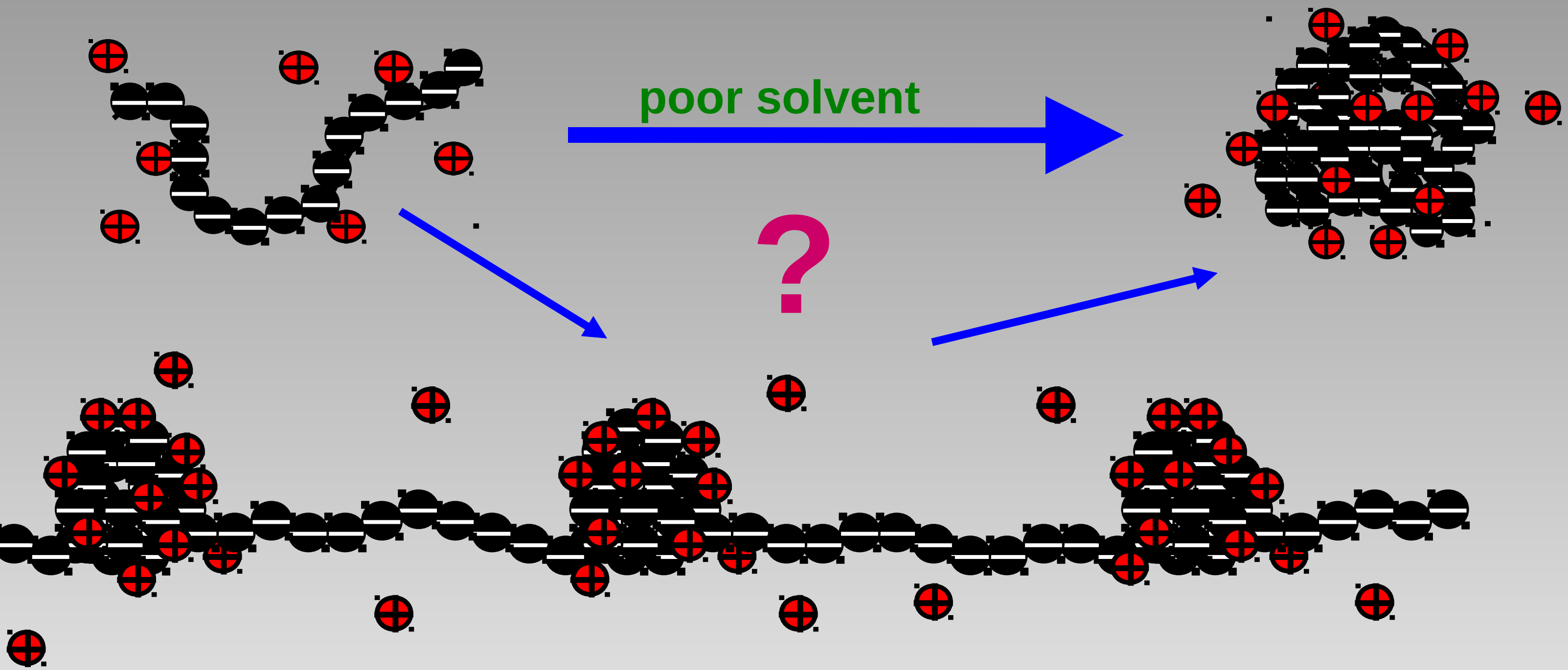
Size vs. Time

Charge vs. Time

Charged chain in poor solvent – a pearl-necklace phase?:



Issues:

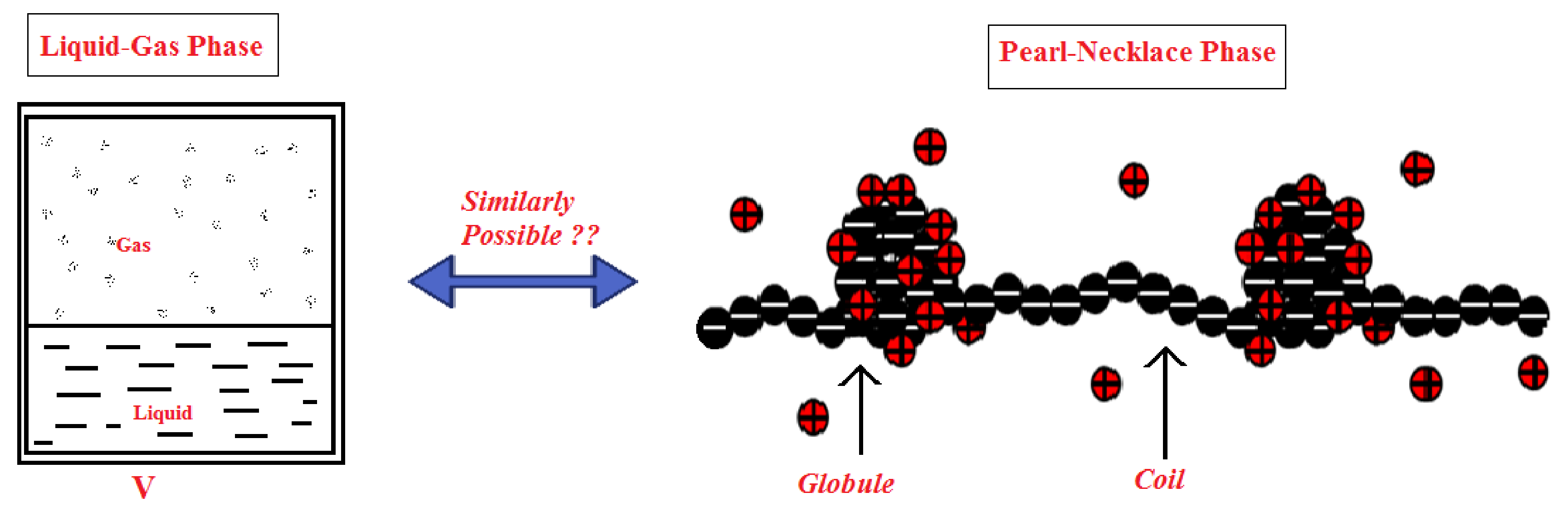


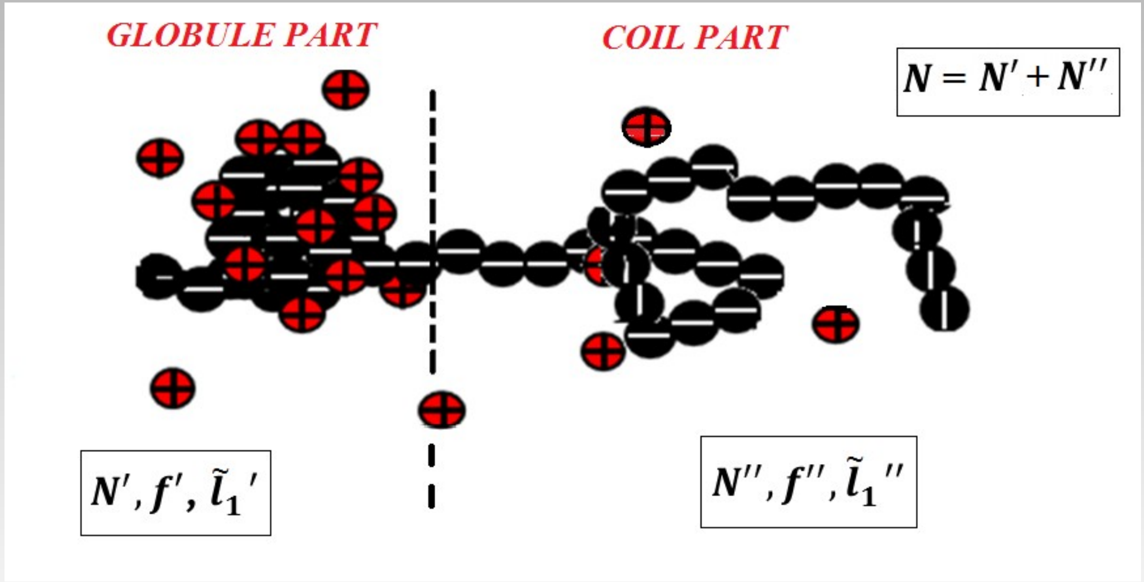
Simulations do not consider oily backbone → Low dielectric constant

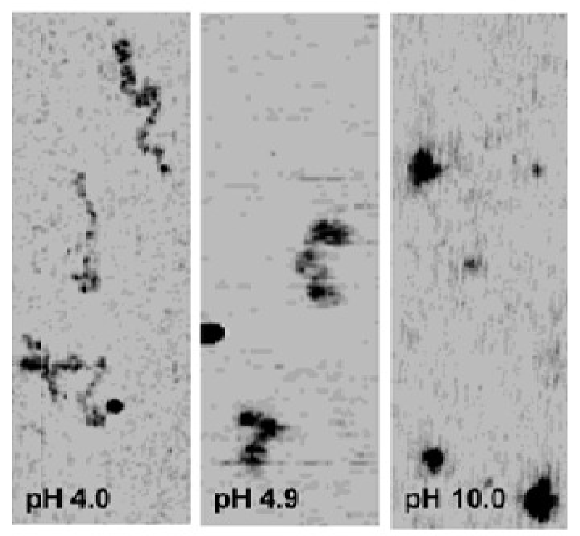
Can free ion entropy win over electrostatic energy gain of bound pairs?

IPhD student: Sourav Sadhukhan (joined August 2014)

Coexistence of coil and globule in a single chain – stability? :

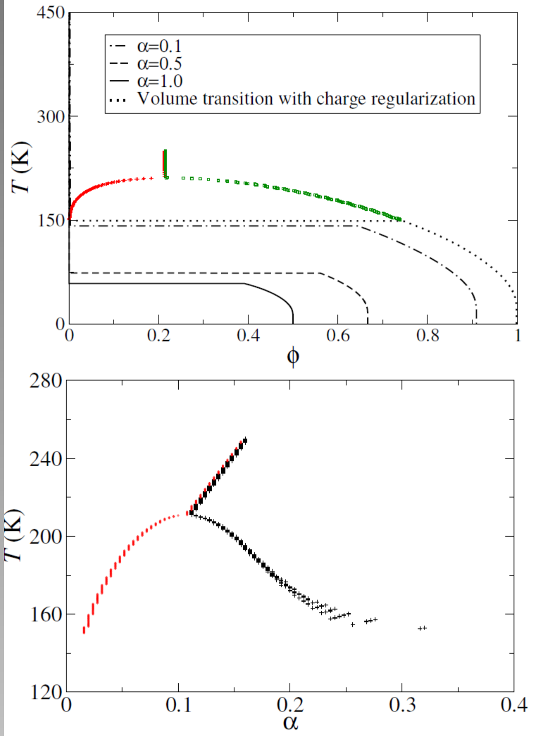




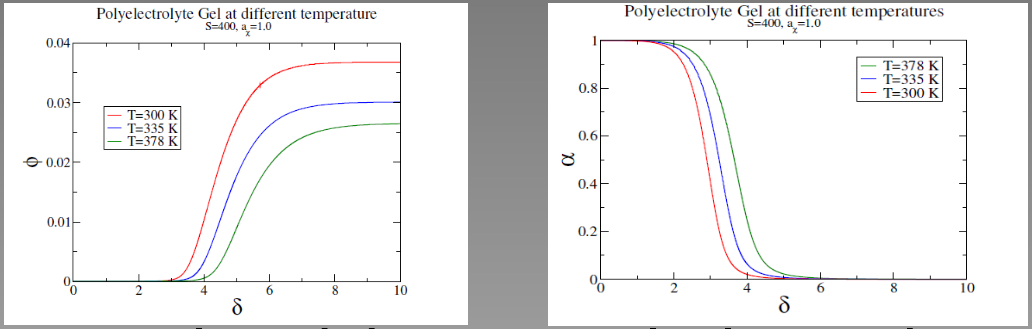


L. J. Kirwan, G. Papastavrou,
M. Borkovec, Nano Lett., 4, 149 (2004)

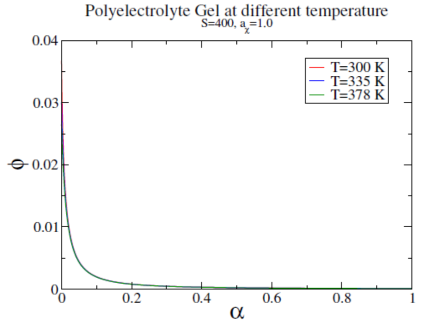
Polyelectrolyte gels: equilibrium results:



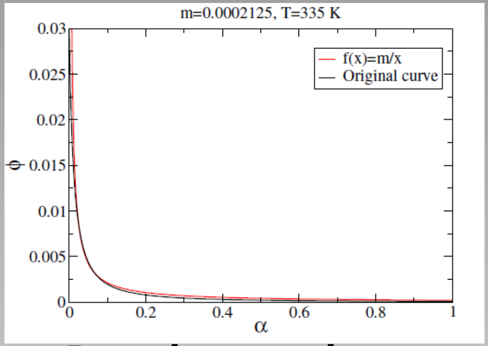
Coexistence curves:
Density and charge



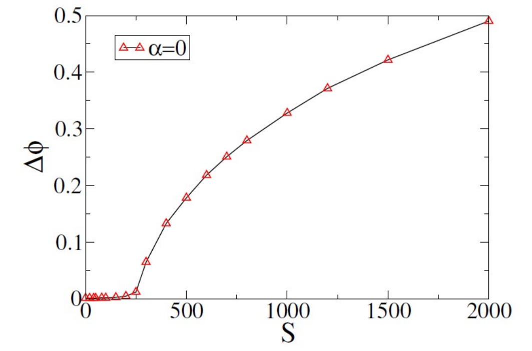
Density and charge vs. Coulomb strength



Density vs. charge:
invariant with Coulomb strength;



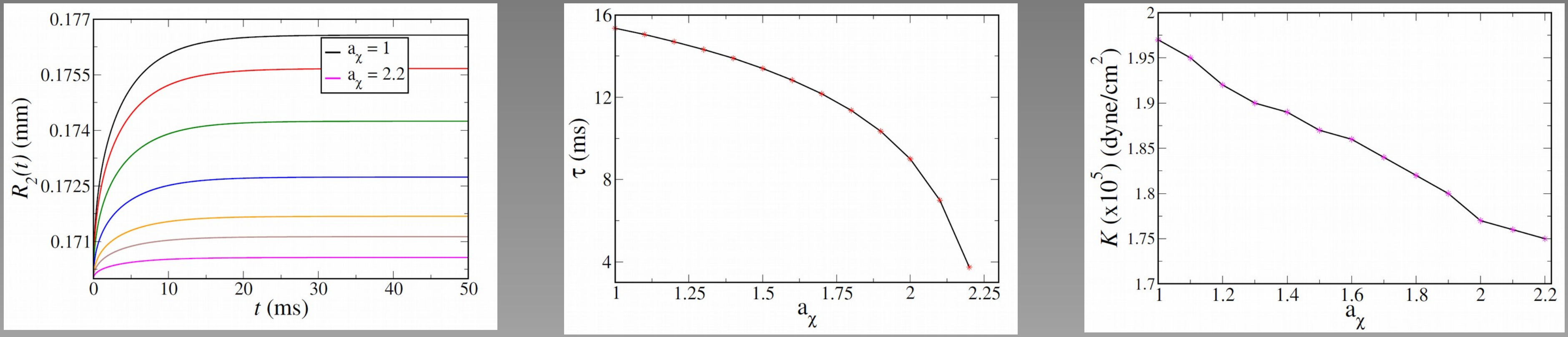
Density vs. charge:
product is constant



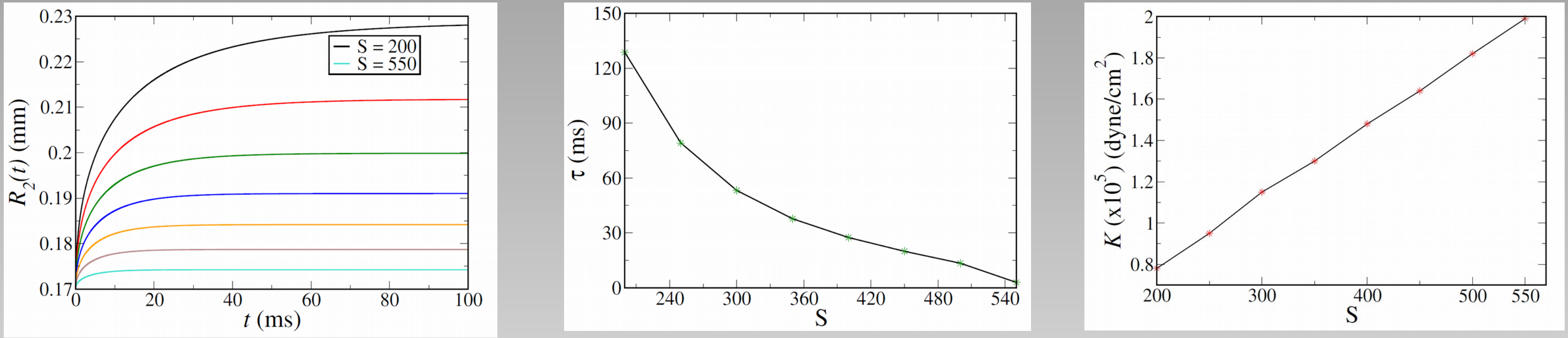
Collapse volume change with crosslink density:
Critical exponent?

PhD student: Swati Sen (SRF)

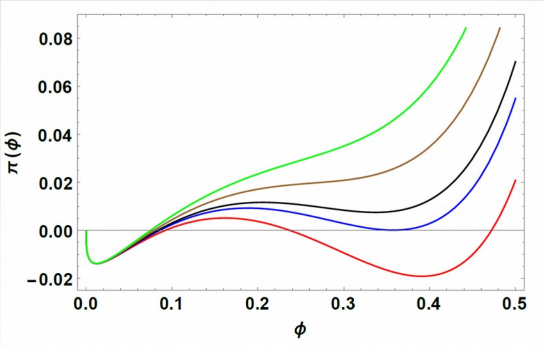
Swelling: solvent quality, crosslink density, critical dynamics:



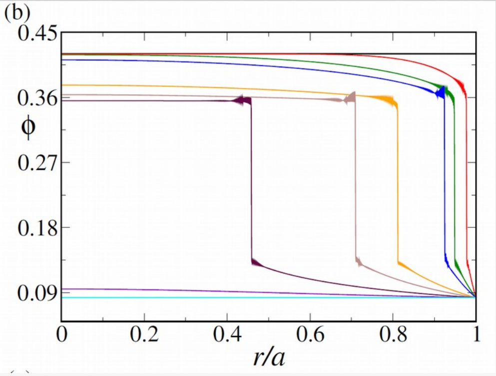
Swelling characteristics: solvent quality



Swelling characteristics: crosslink density



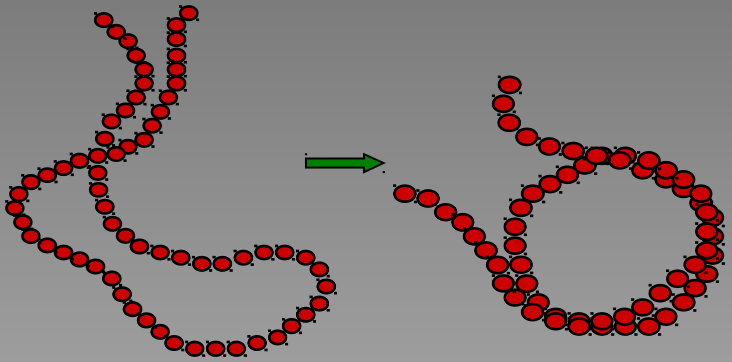
Critical dynamics



PhD student: Swati Sen (SRF)

Future Directions

Collapse of a semi-flexible chain - toroids:

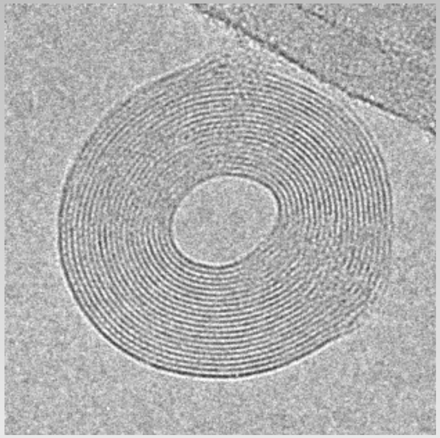


Issues: stiff chain $\xrightarrow{\text{condensing agent}}$ no globules

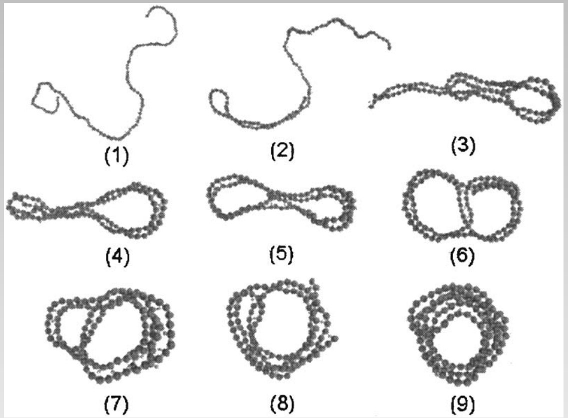
toroids

Kinetics of nucleation and growth of toroids

All PE issues: free energy, phase diagrams – important for dsDNA

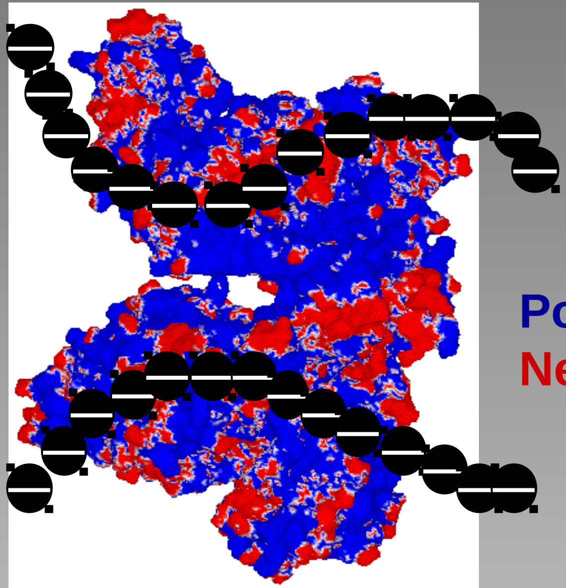


Experiments: Nick Hud, Georgia Tech.



Simulations: Ou, Muthukumar, UMass

Complexation of protein and flexible charged chain:



Human Serum Albumin

Positive
Negative

Issues:

Protein - both positive and negative charged zones

Role of chain entropy: benefactor or prohibitor?

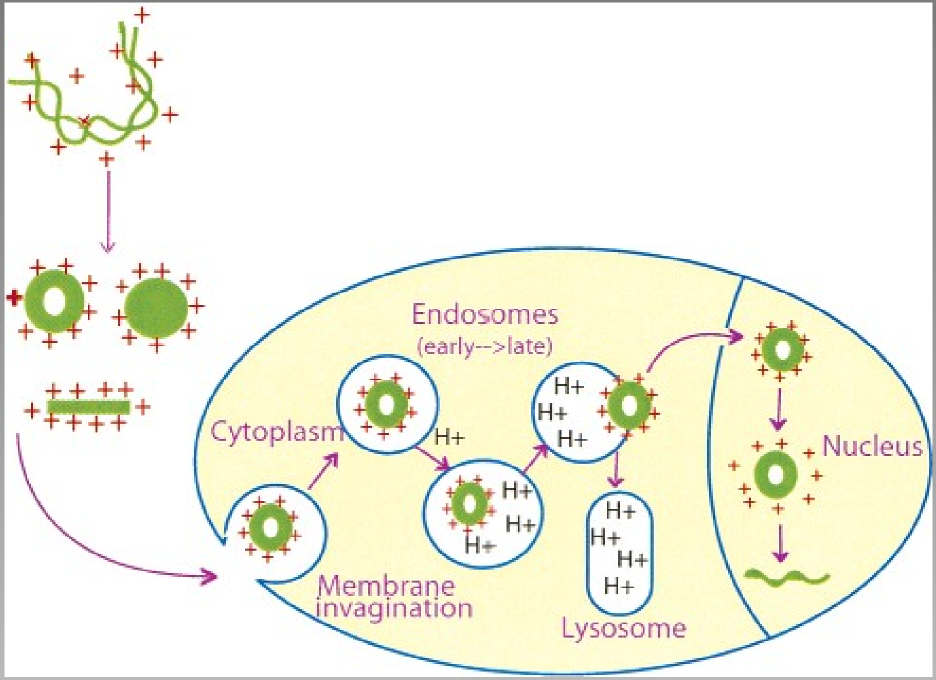
Simple theories of overcharging inapplicabl

Possible aggregation and detachment depending on salt

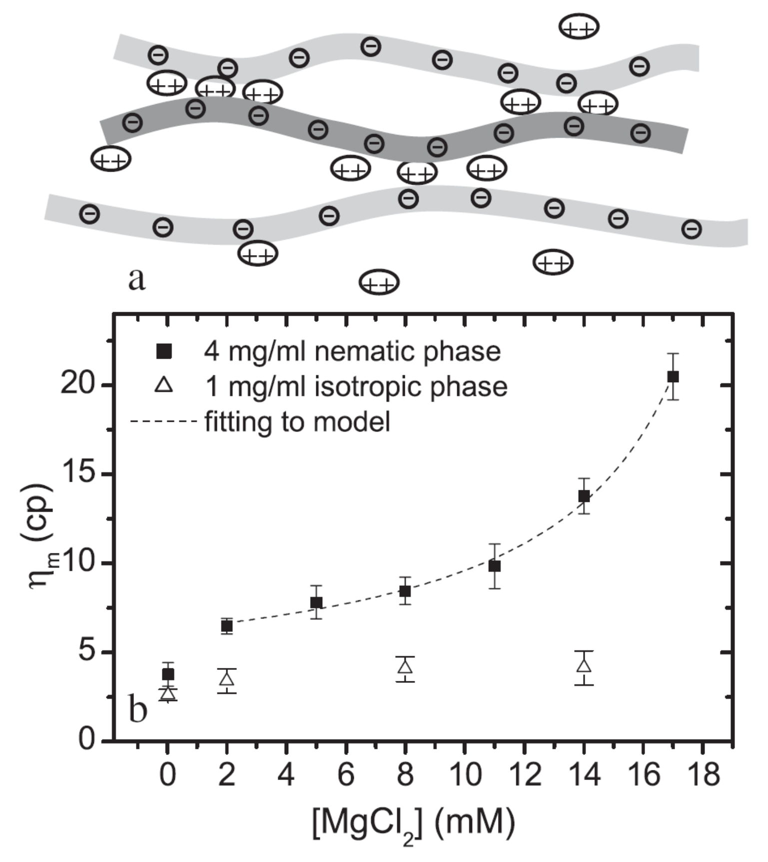
Examples: aggregation of flexible anionic polyion (sodium polyacrylate) and DOTAP lipids

Extensions: anionic dendrimers-cationic polymers, colloid-anionic polymer

Charge inversion and ion-bridging – applications, effects:



V. Vijayanathan *et al***., Biochemistry, 41,** 14085 (2002)



J. He *et al.* **PRL 99,** 068103 (2007)

1. **DNA uptake for gene therapy: condensing DNAs to nanoparticles**

2. **Reduced diffusivity of F-actin filaments near isotropic-nematic transition**