Kinetics of Swelling and Collapse in Polyelectrolyte Systems

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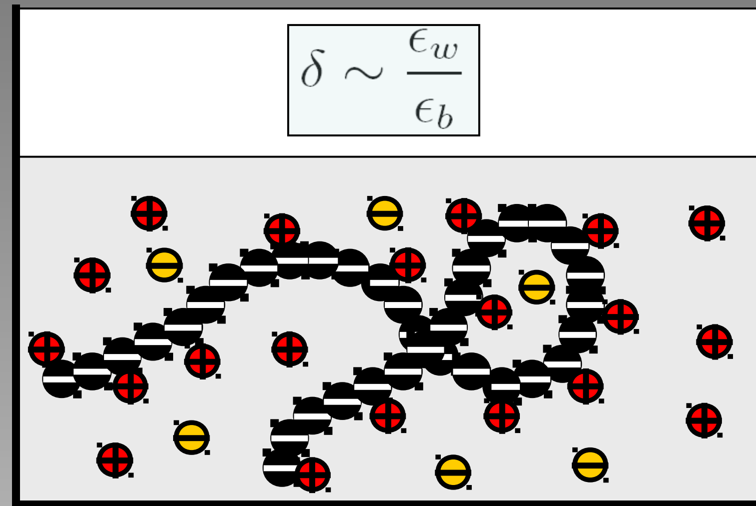
Charged polymers – energy and entropy:

Do all Na+ ions dissolve? NO!

Counterion condensation. WHY?

Effective ϵ low close to backbone



Condense ⟶ gain in Coulomb energy

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

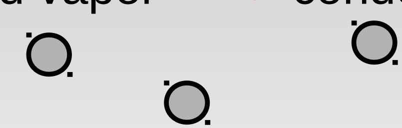
Let's predict qualitatively:

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

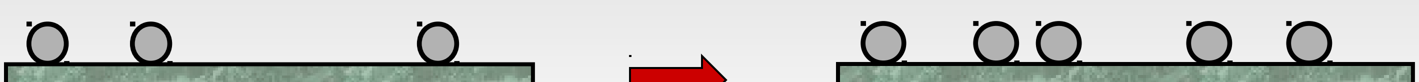
E = Coulomb energy, ***S*** = free ion entropy ⟶ $k_B T$

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



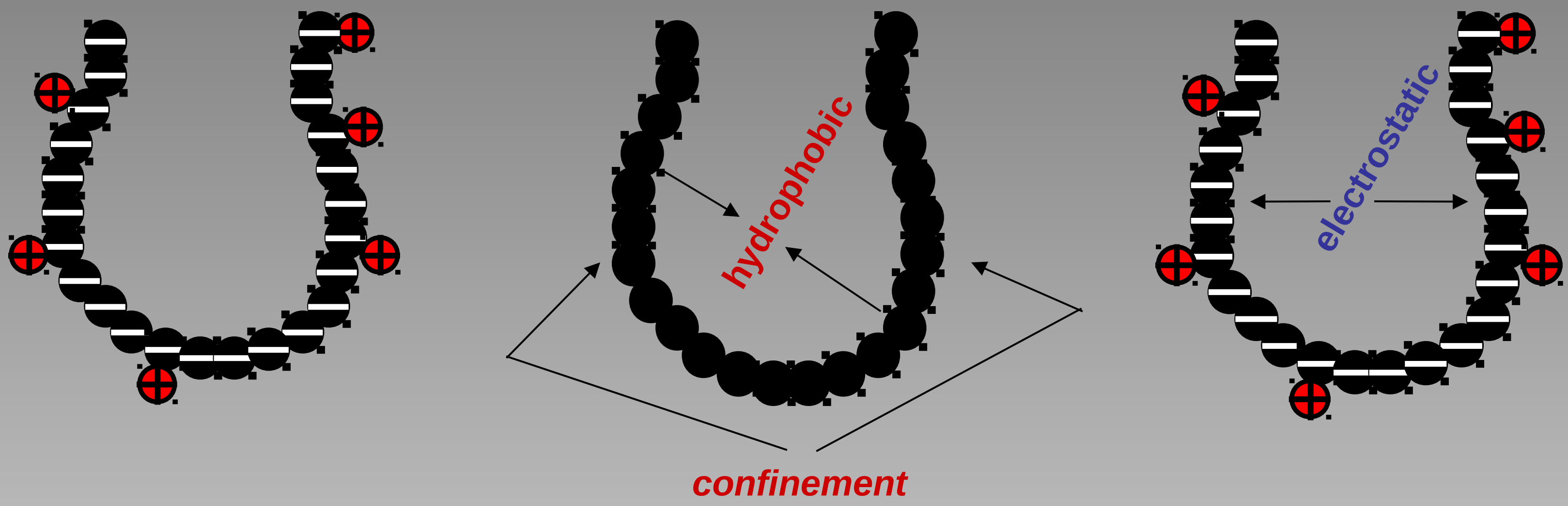
SALT ⟷ WET WEATHER



Cold surface **Cold surface**

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

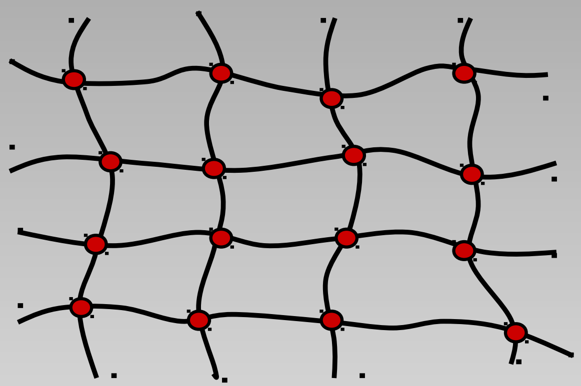
EXAMPLE – Mutual Dependency:

poor solvent → Collapsed chain → Ion condensation

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

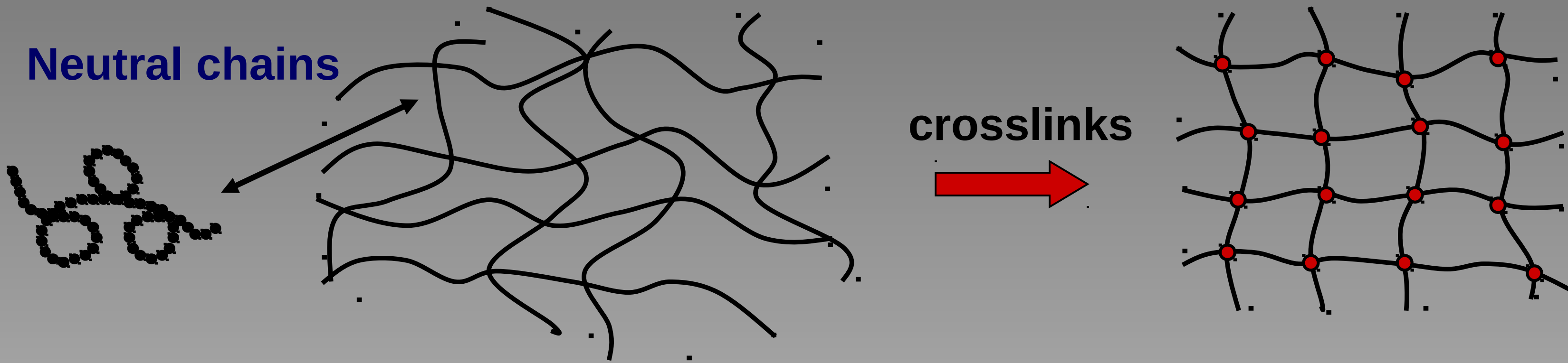
DOUBLE MINIMIZATION : SELF-CONSISTENCY

Kinetics of swelling of polymer gels



More details: Poster by Swati Sen

Polymer gels - uncharged:

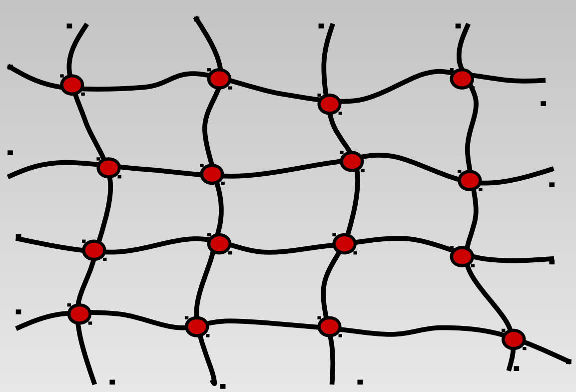


Gel: large single molecule – different kind

Many chains connected at different points

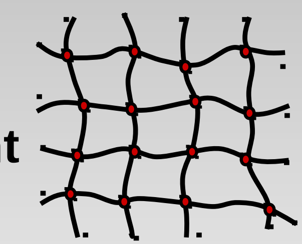
Strand between two crosslinks → similar to single chain

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



Good solvent

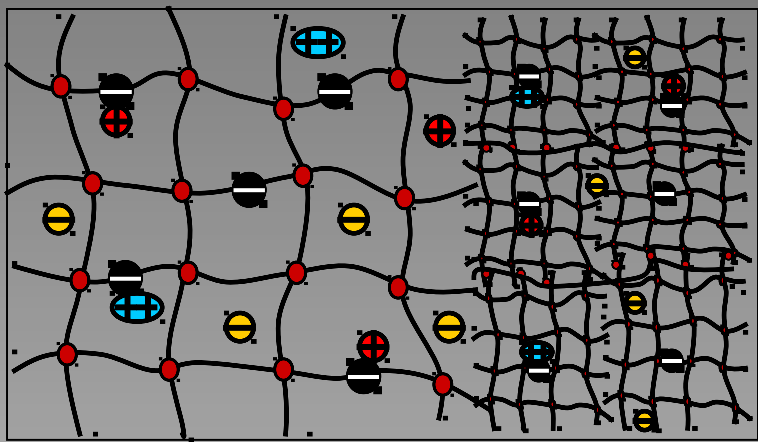
Poor solvent

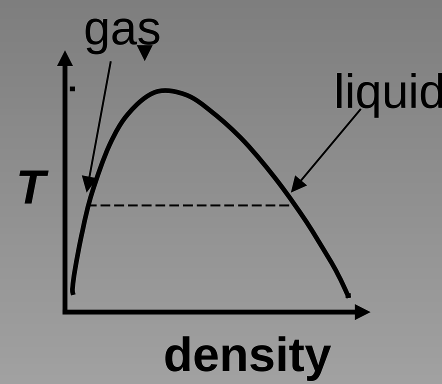


Contribution to **free energy (*E – TS*)**?

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

Phase transition – charged gels - schematic:

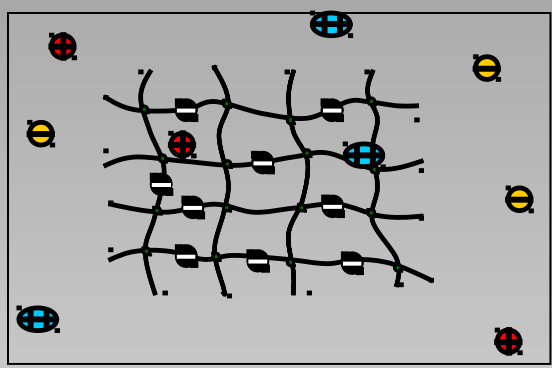




Issues:

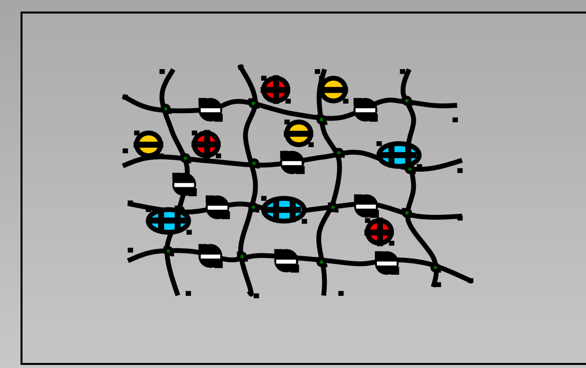
A. Coexistence in charged polymer gels,

B. Interplay of hydrophobic and electrostatic interactions



Repulsion - monomers

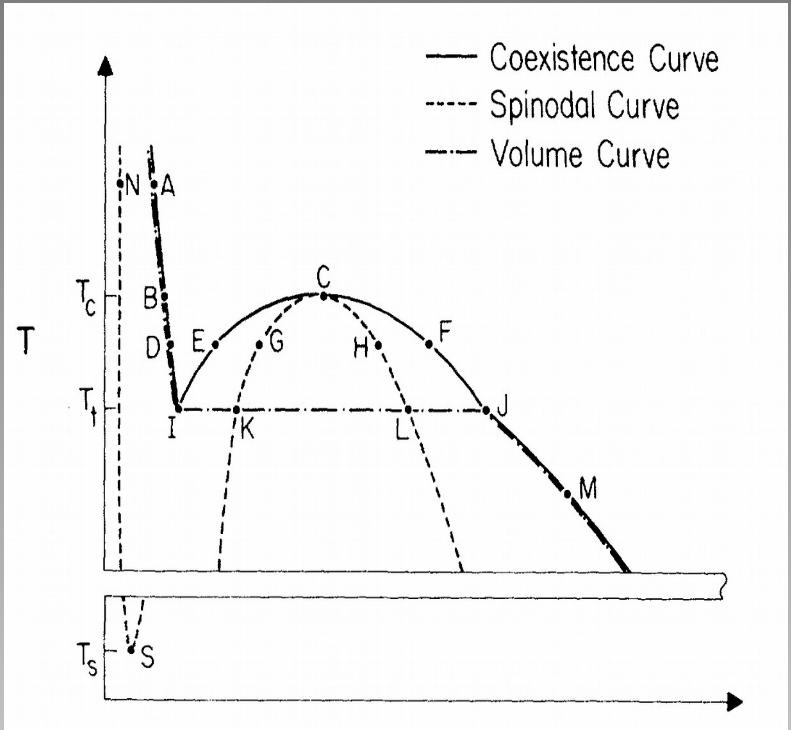
What does swell the gel? Electrostatics or free ion entropy?

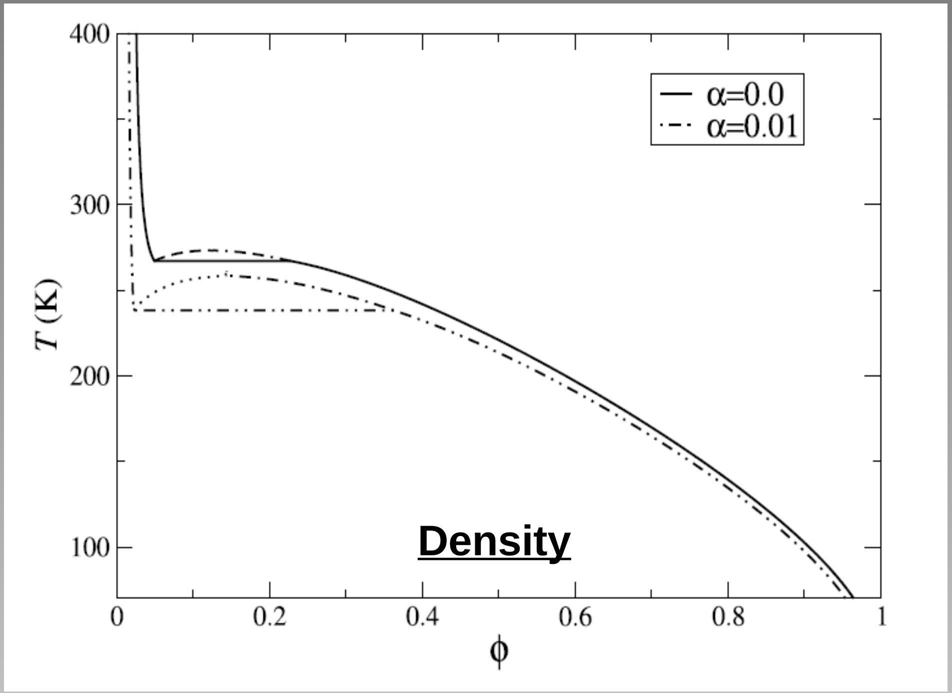


Entropy - counterions

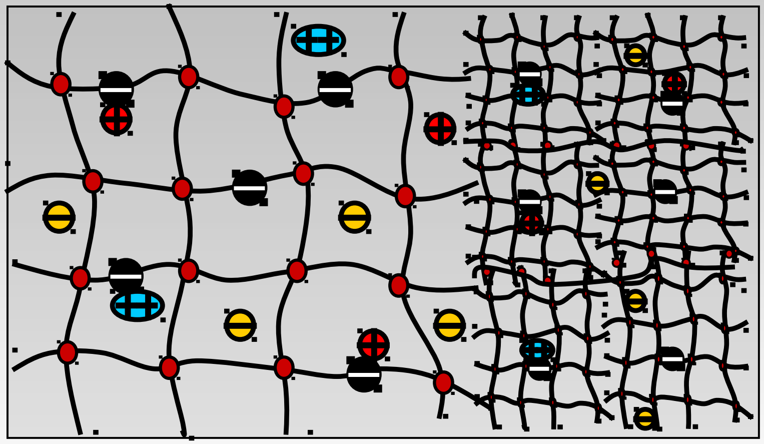
1. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press
2. Jing Hua, Mithun K. Mitra, and M. Muthukumar JCP, 136, 134901 (2012).

Phase behaviour – charged gels - theory:

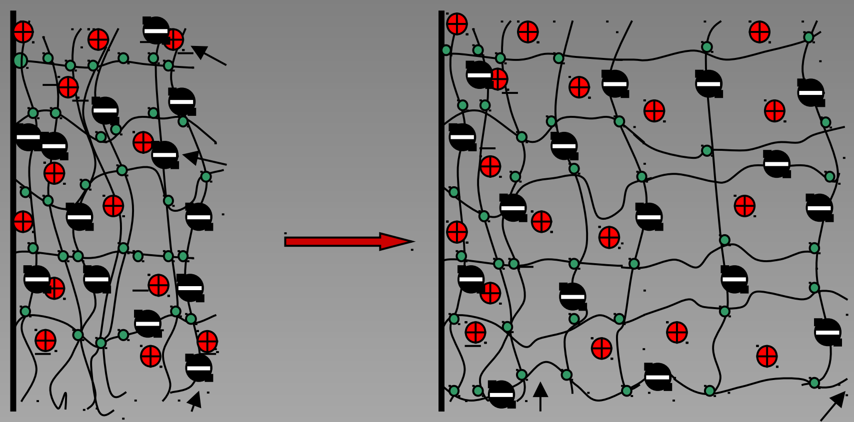




Swati Sen and A. Kundagrami,
JCP, 143, 224904 (2015)

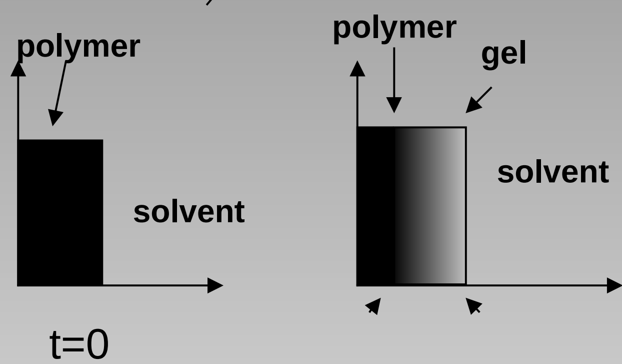


Swelling kinetics of a charged gel – Aim of study:



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

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

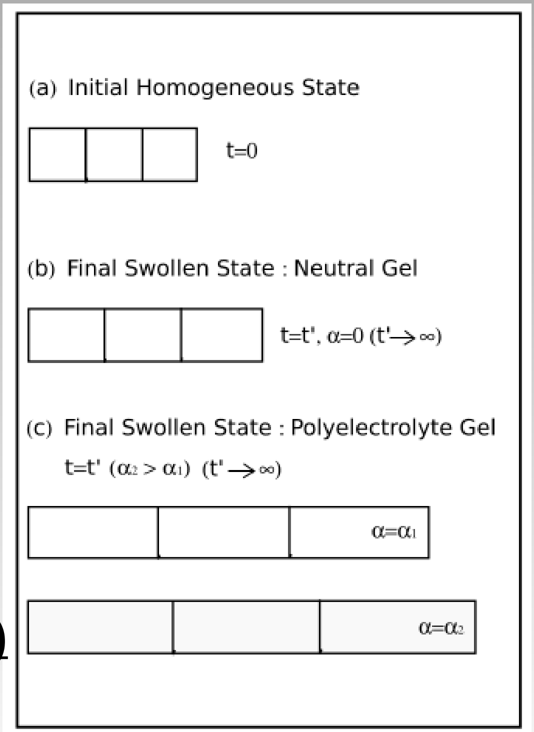


We want to find:

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)

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

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

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

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

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

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

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

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)

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

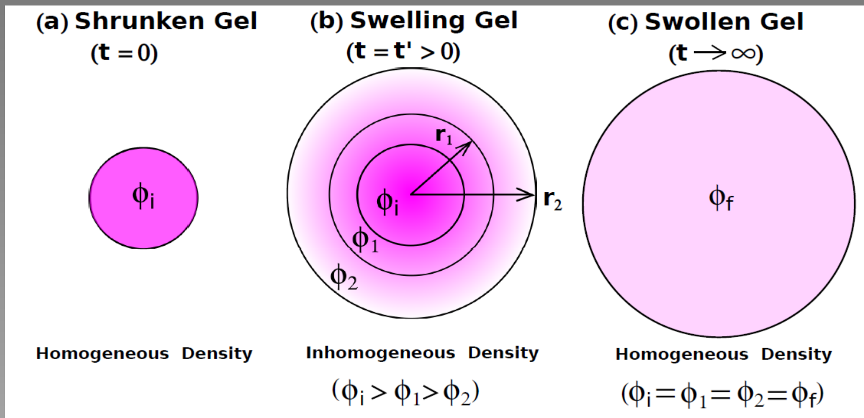
$$\sigma_{xx} = \frac{K_B T}{\nu_c}\Bigg[-\phi - ln(1-(1+\alpha)\phi) - \chi\phi^2(1+\alpha) + S\phi_0^3\left(\frac{\phi}{2\phi_0} - \left(\frac{\phi}{\phi_0}\right)^{\frac{1}{3}}\right) + \frac{1}{4\pi}\left\{ ln(1+\tilde{\kappa}) - \frac{\tilde{\kappa}}{2(1+\tilde{\kappa})} - \frac{\tilde{\kappa}}{2}\right\}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

Polymer (uncharged) gel

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

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

Swelling of PE gels – variable degree of ionization:



Schematic of swelling

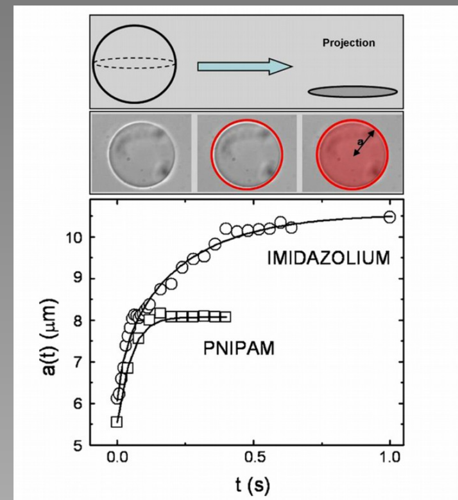
$$\frac{\partial u}{\partial t} = \frac{K}{f}\frac{\partial}{\partial r}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 u_r\right)\right)$$ **BMM**

$$\frac{\partial u}{\partial t} = \frac{1}{f}\frac{\partial}{\partial r}\Pi_{rr}$$ **SRM w/ charge-regularization**

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

$$\Pi = \Pi_0 + K\left(\frac{\partial u}{\partial r} + 2\frac{u}{r}\right)$$

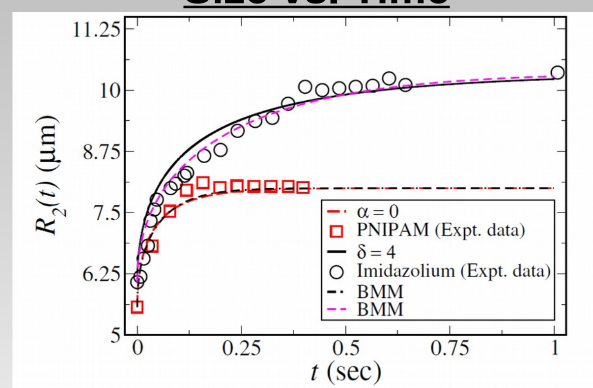
→ $K(\phi, \alpha, \chi, S)$



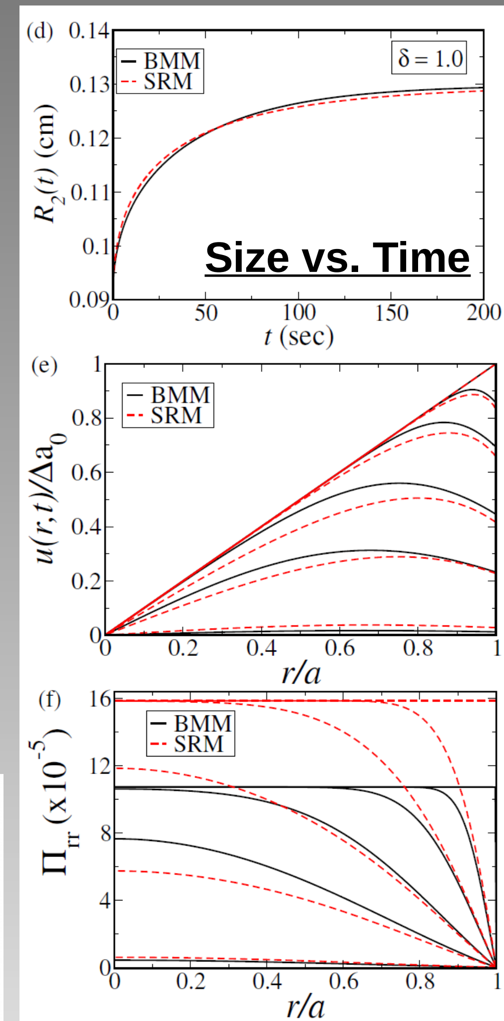
Matching of gel-front w/ Experiments: BMM

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

Size vs. Time



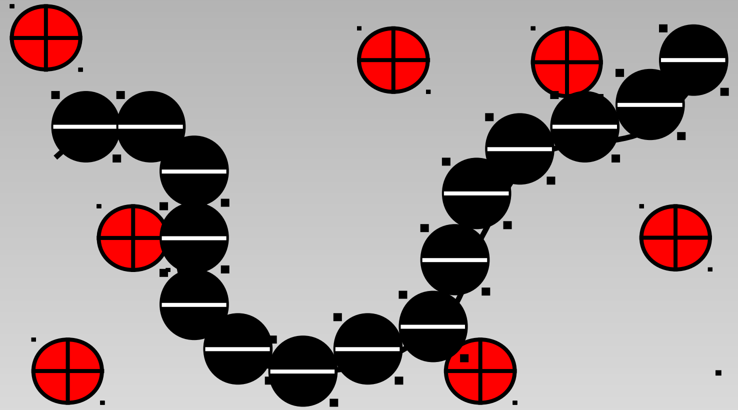
Matching of gel-front w/ Experiments: SRM



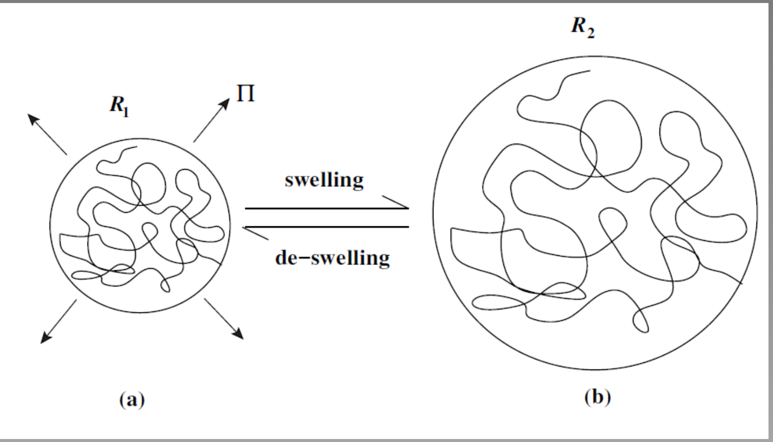
Matching between BMM & SRM: Size & Osmotic Pressure

Swati Sen and A. Kundagrami, *to be submitted*

Kinetics of swelling and collapse of a single polymer chain



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

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

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, *under revision in* Macromolecules

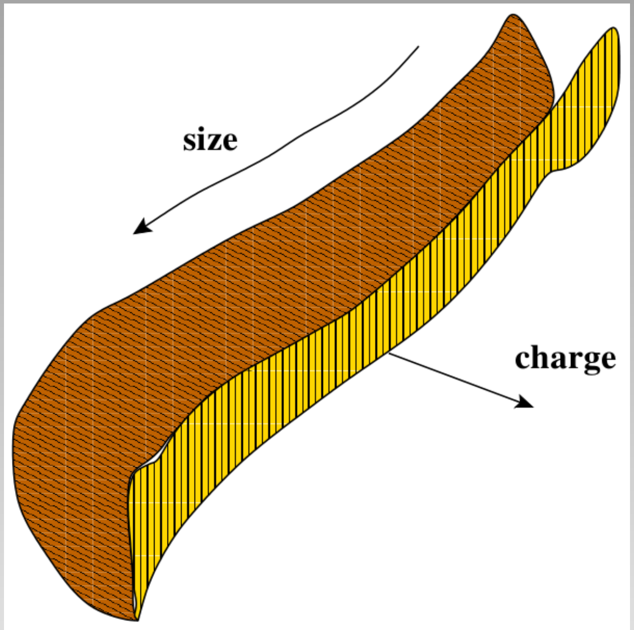
Charge regularization:

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!

A free-energy to derive the osmotic pressure:

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

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

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

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

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

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

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

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

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

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

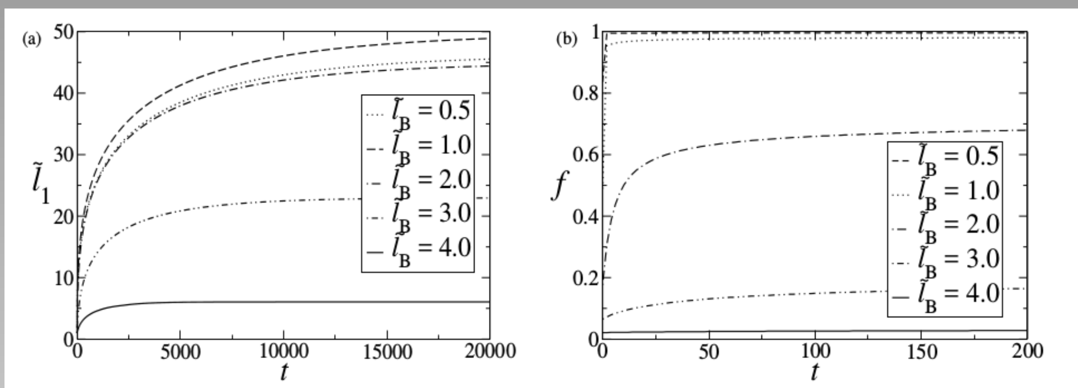
Swelling profiles:

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

Expression of charge – expanded state

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

Size vs. Time **Charge vs. Time**



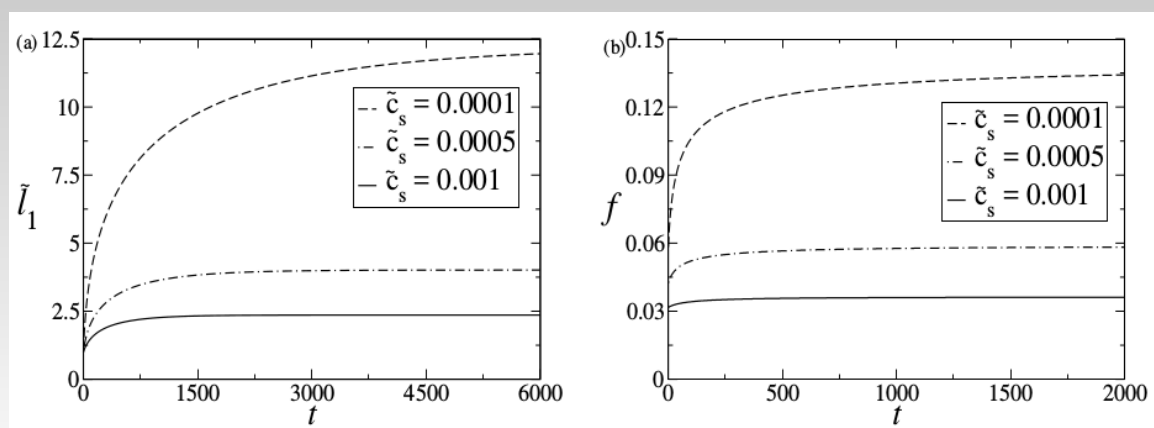
Swelling at different temperatures:

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

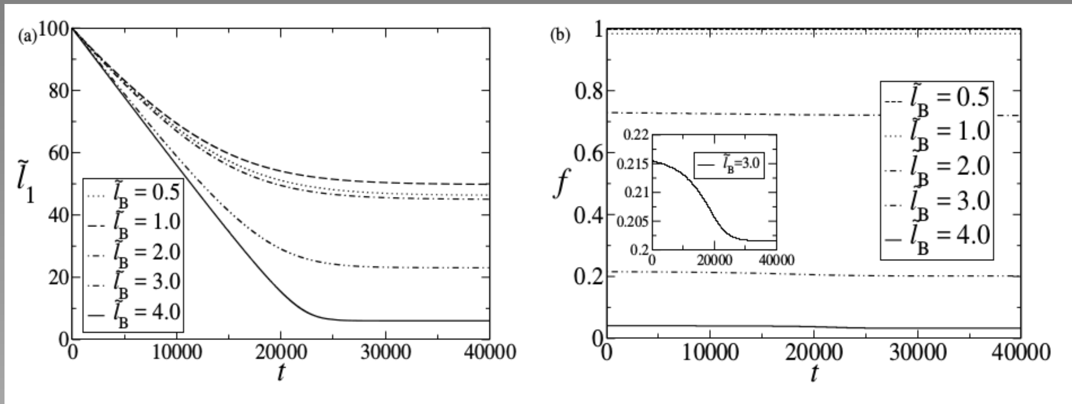
Size vs. Time **Charge vs. Time**

Swelling at different salt:

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



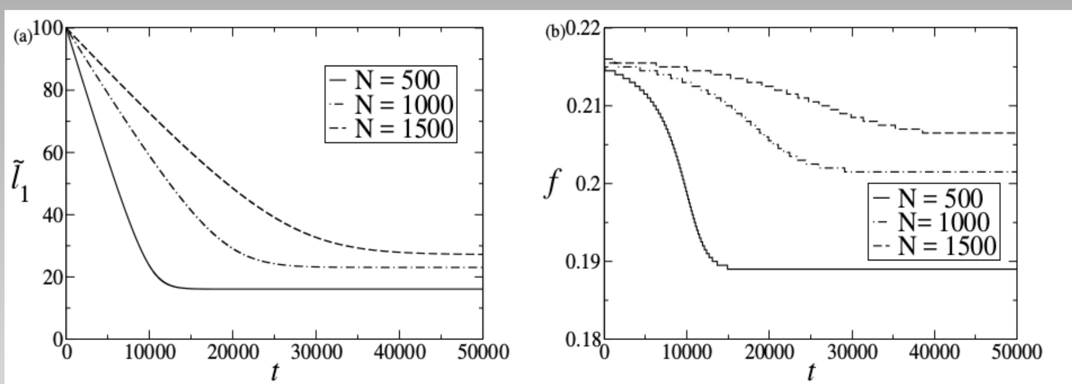
De-swelling profiles:



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

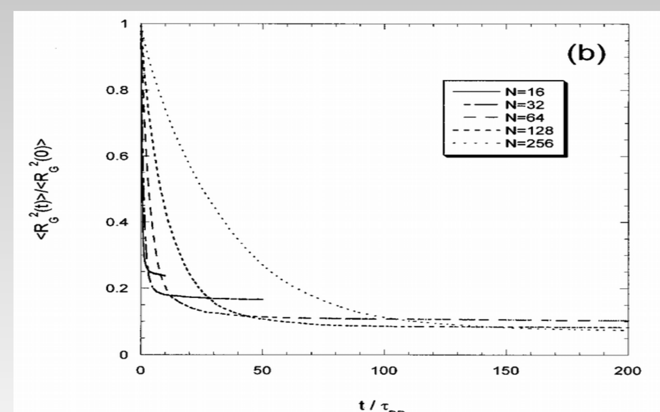
Size vs. Time **Charge vs. Time**



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)

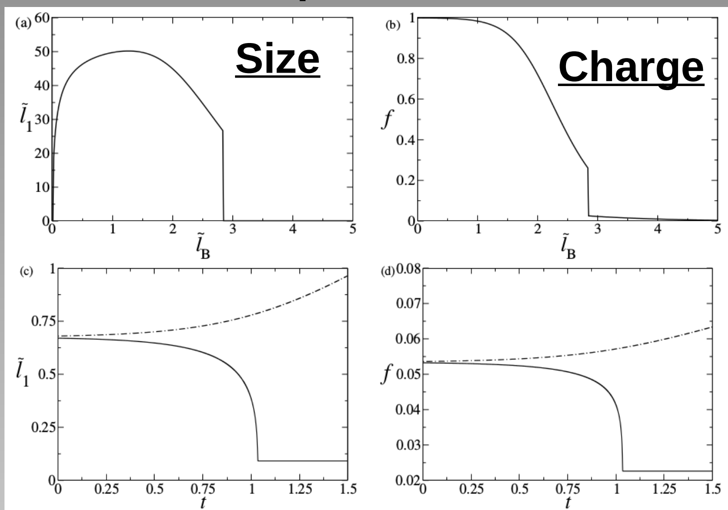


Size vs. Time

Collapse profiles:

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

Equilibrium

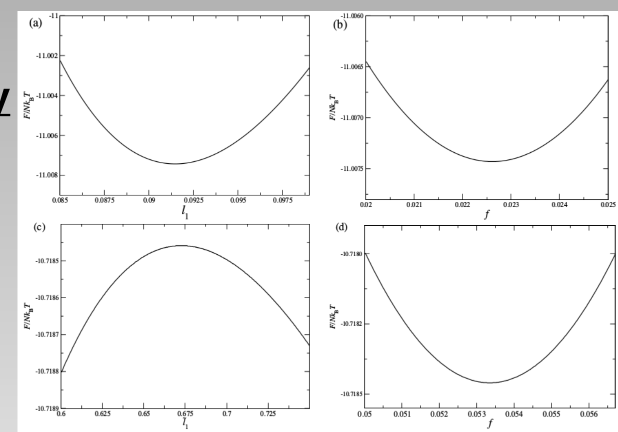


Kinetics

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

Local maximum prohibits direct collapse to the global minimum

Free energy

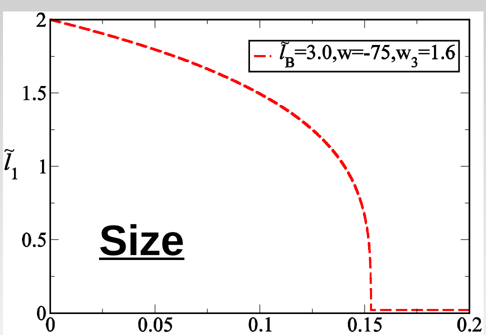


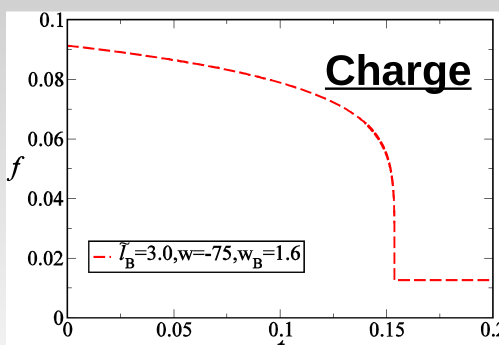
Size **Charge**

Local maximum

Global minimum

Direct collapse: extended to globule





Time

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:

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

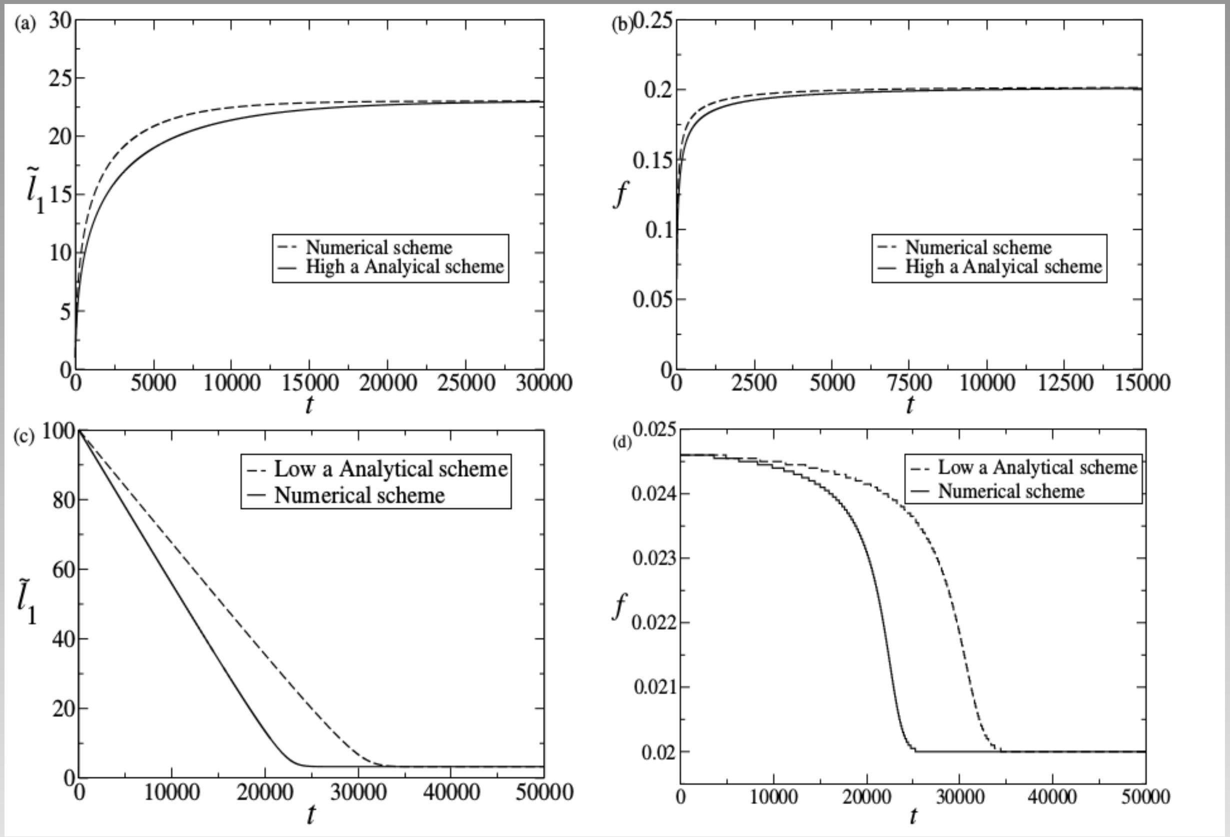
$$w' = w + \frac{f^2}{(f\tilde{\rho} + 2\tilde{c}_s)}$$

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**

Limiting results – comparison to full numerical results:

High-salt

Low-salt



Size vs. Time **Charge vs. Time**

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

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

High-salt

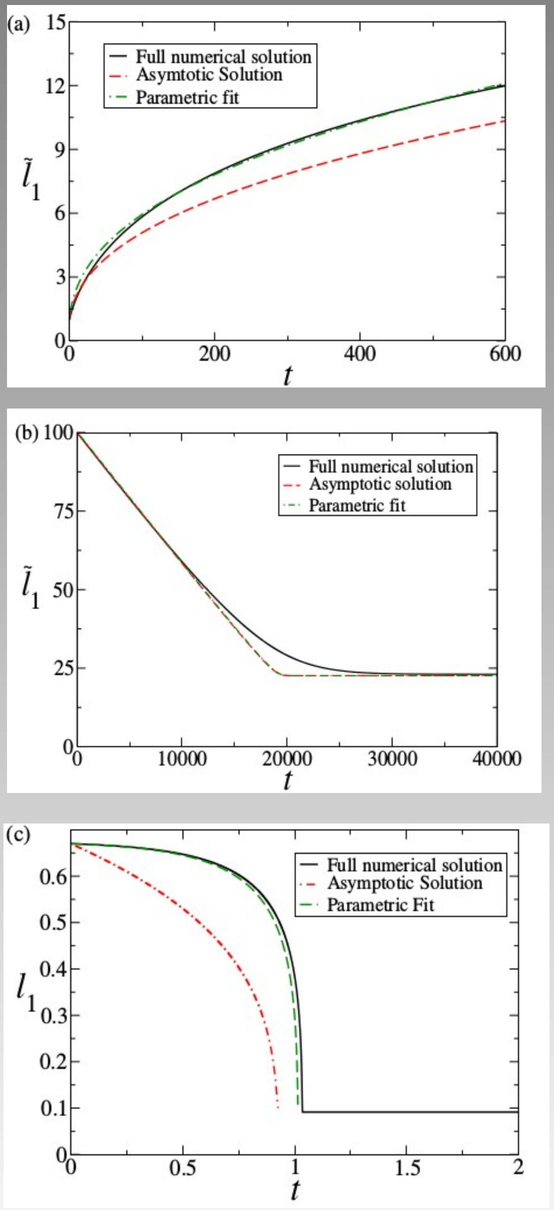
De-swelling:

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

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



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

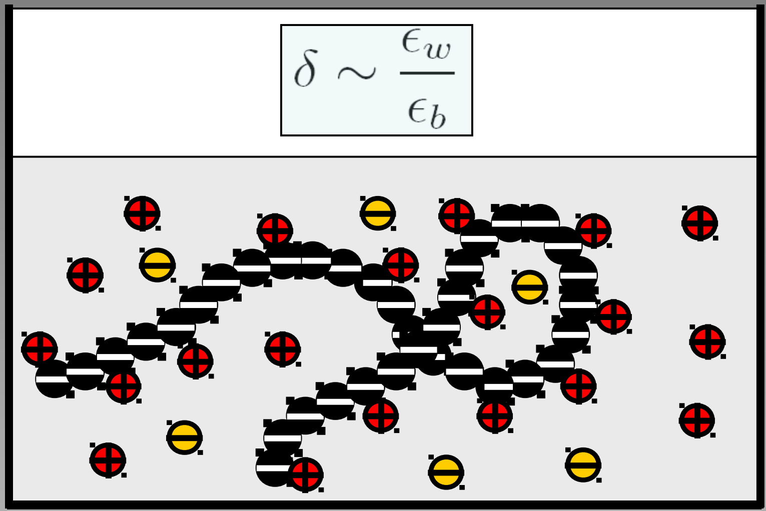
4. Single polyelectrolyte chain:
   a) swells faster and farther for higher temperature
   b) de-swells faster and deeper for higher salt
   c) kinetics is slower for higher molecular weight
   d) self-consistent dependency between size and charge strong in the vicinity of the Gaussian size

Charged polymers – energy and entropy:

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

Counterion condensation. **WHY?**

Effective ϵ low close to backbone



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

Condense → **gain in Coulomb energy**

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

Let's predict qualitatively:

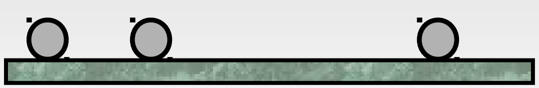
Remember: *E - TS*

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

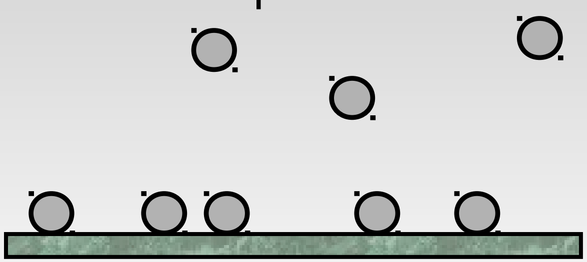
1. ***T*** ↓ → ***S*** fixed, ***E***/ion-pair fixed → more ion-pairs → less charge
2. ϵ ↓ → ***S*** fixed, ***T*** fixed, ***E***/ion-pair increases → more ion-pairs
3. ***V*** ↑ → ***S*** increases, ***T*** fixed, ***E***/ion-pair fixed → less ion-pairs

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

SALT ⟷ **WET WEATHER**

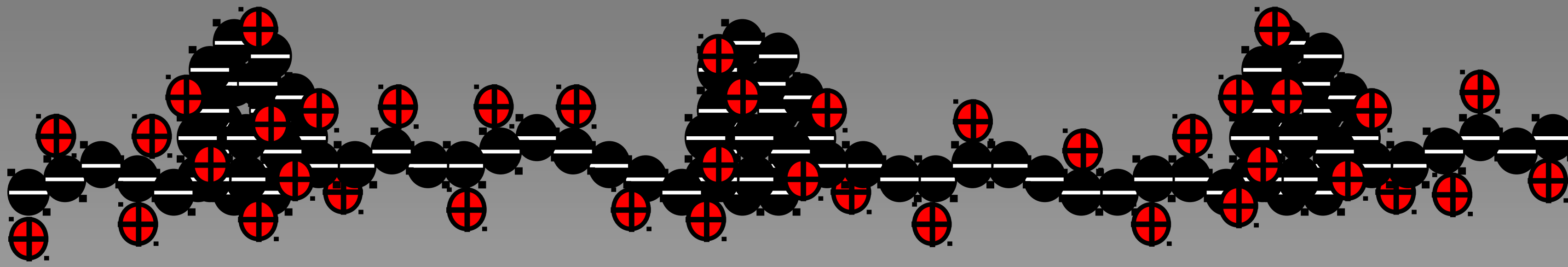


Cold surface

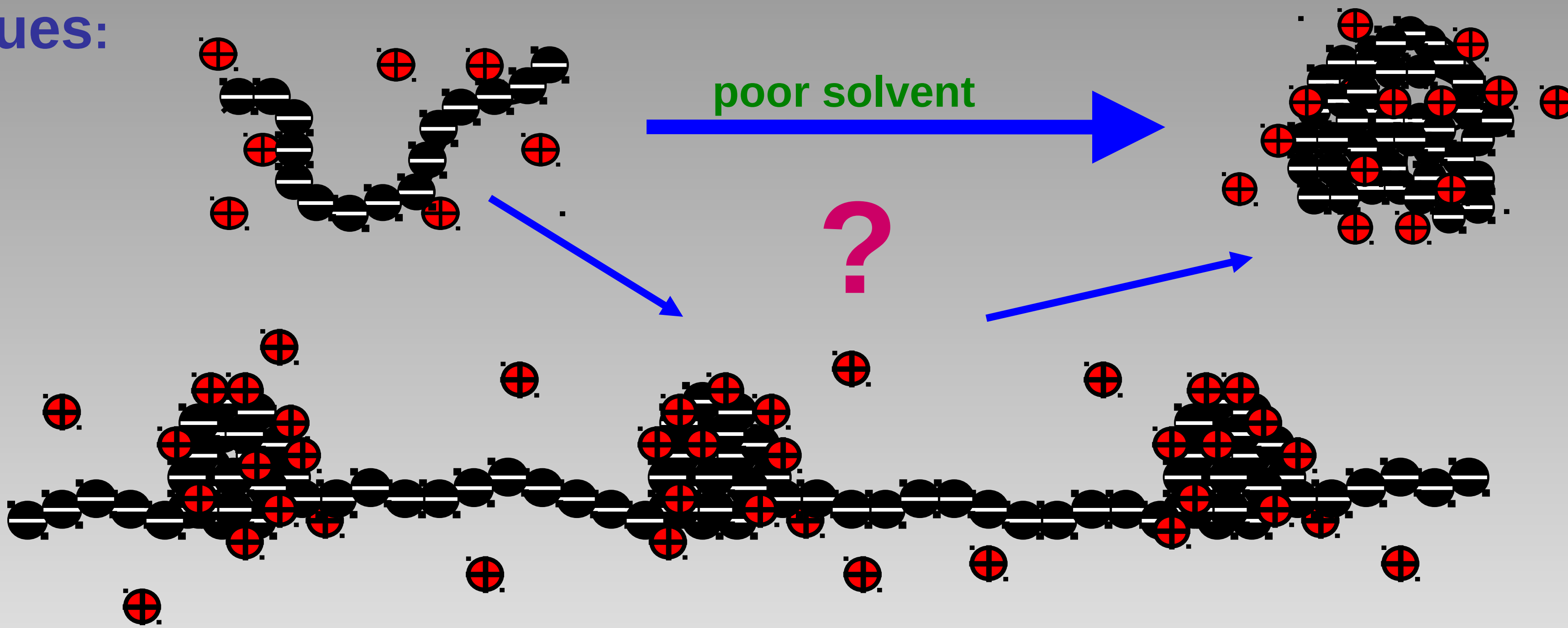


Cold surface

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



Issues:

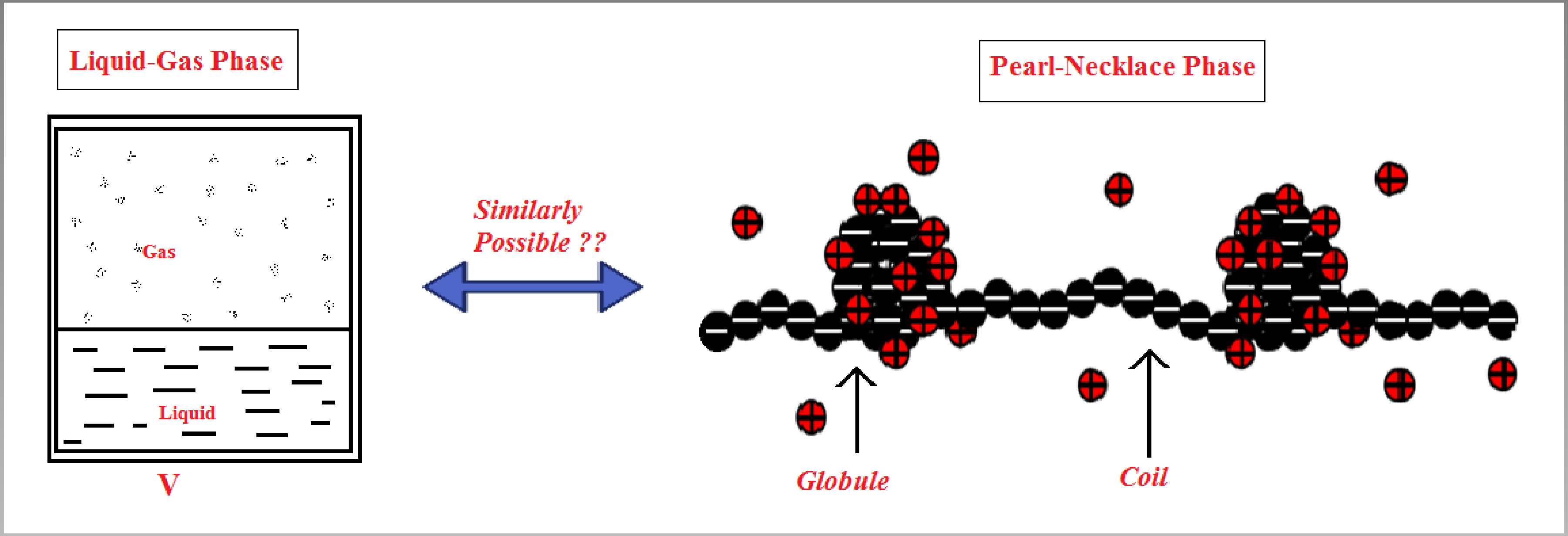


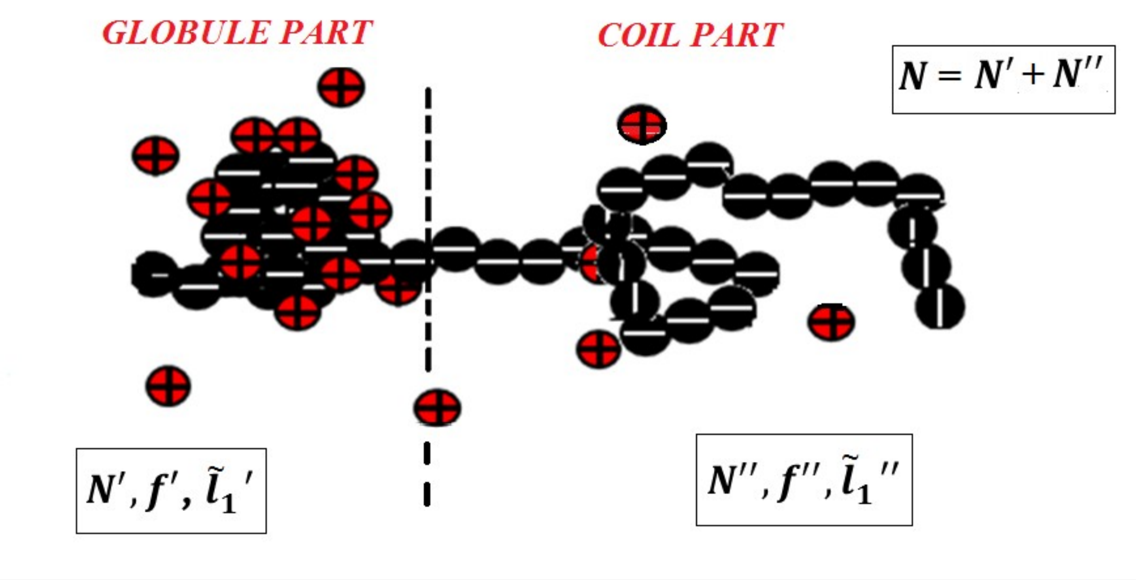
Simulations do not consider oily backbone → Low dielectric constant

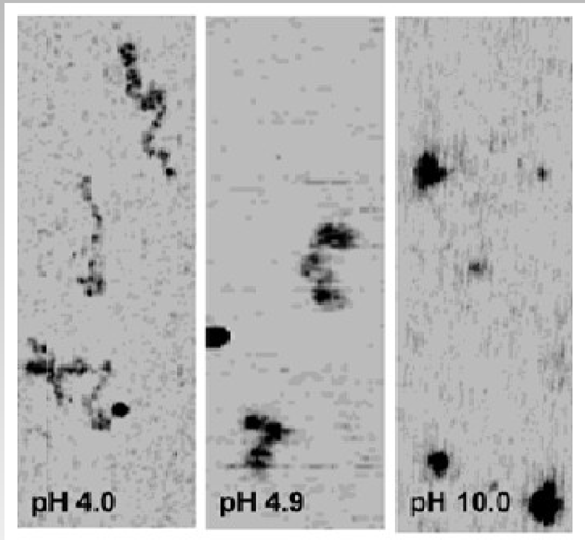
Can free ion entropy win over electrostatic energy gain of bound pairs?

IPhD student: Sourav Sadhukhan (joined August 2014)

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

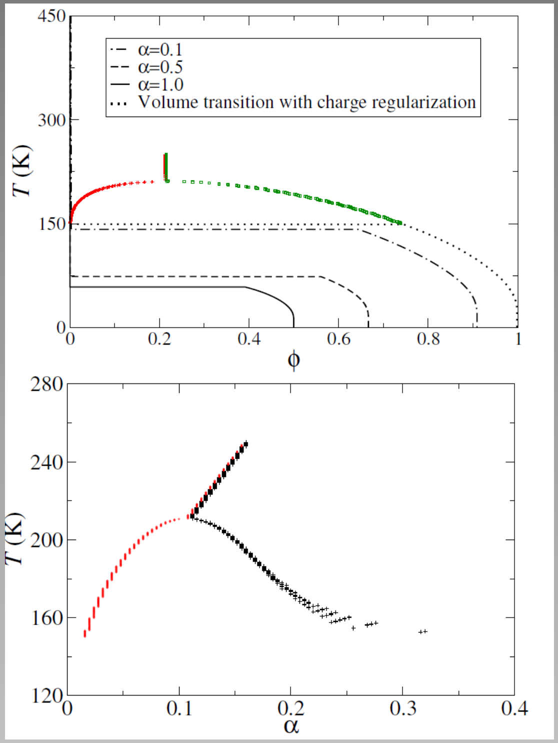




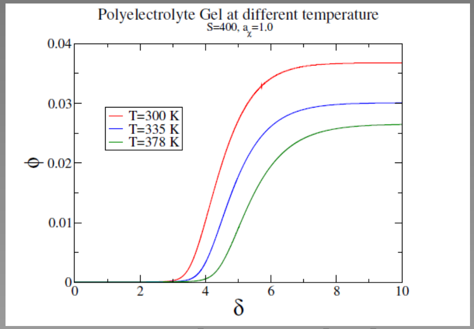


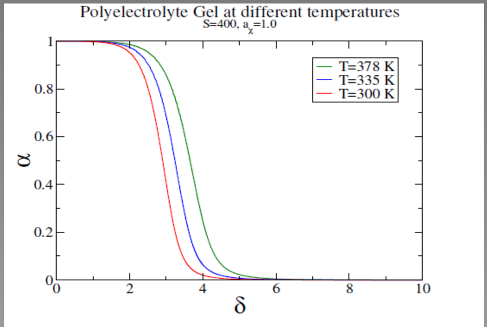
L. J. Kirwan, G. Papastavrou, M. Borkovec, Nano Lett., 4, 149 (2004)

Polyelectrolyte gels: equilibrium results:

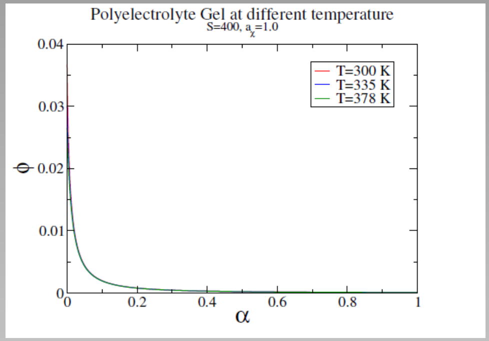


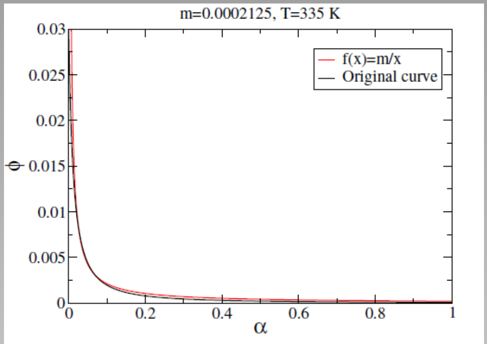
Coexistence curves:
Density and charge





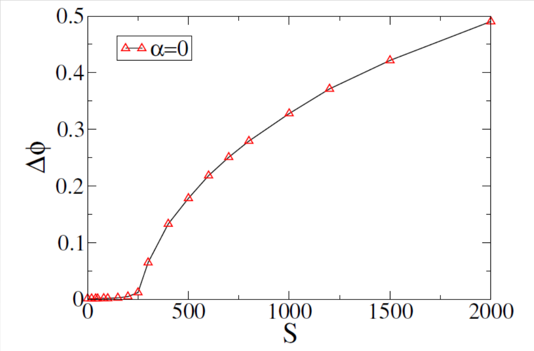
Density and charge vs. Coulomb strength





Density vs. charge:
invariant with Coulomb strength;

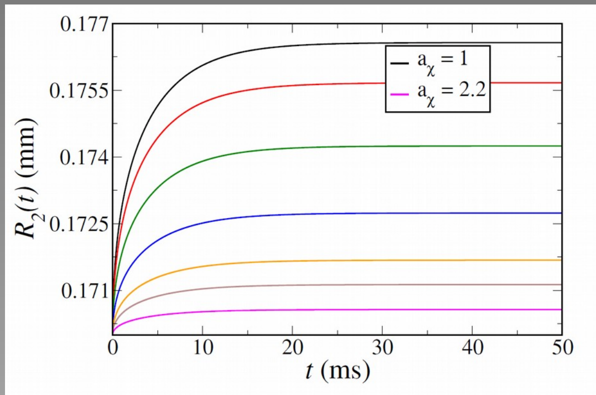
Density vs. charge:
product is constant

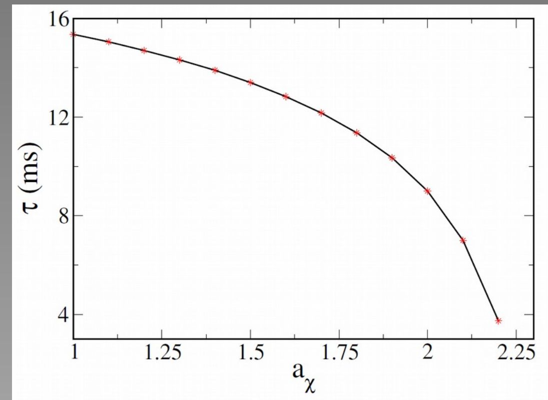


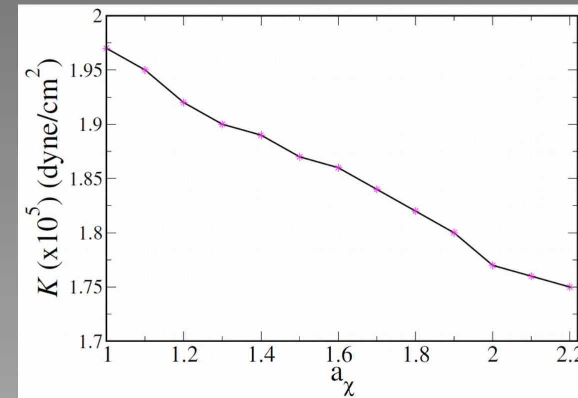
Collapse volume change with crosslink density:
Critical exponent?

PhD student: Swati Sen (SRF)

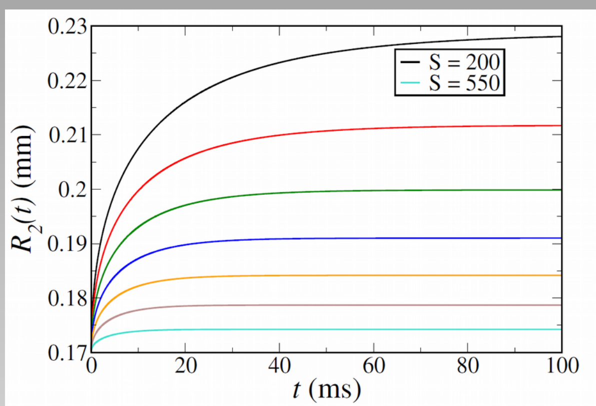
Swelling: solvent quality, crosslink density, critical dynamics:

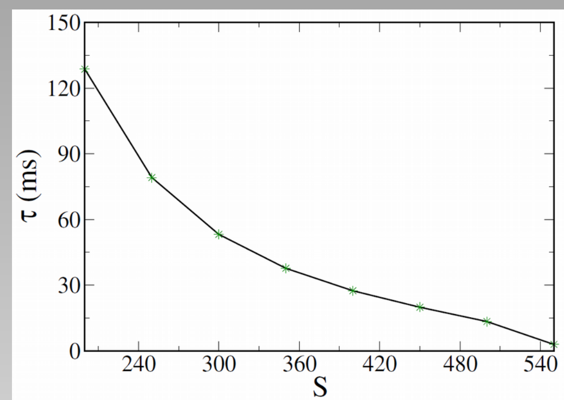


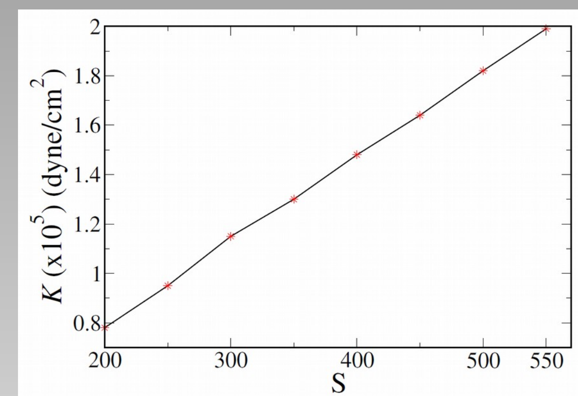




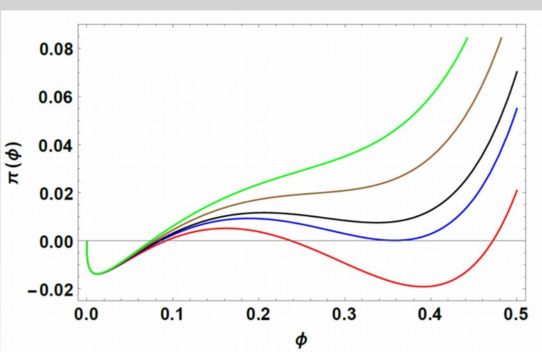
Swelling characteristics: solvent quality



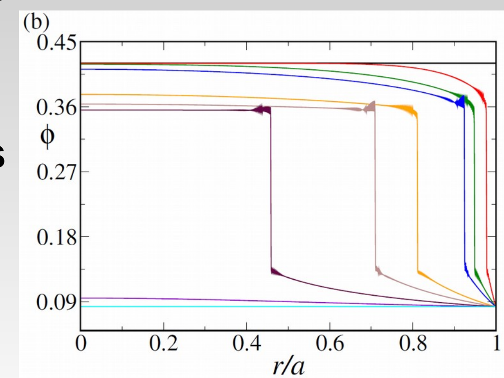




Swelling characteristics: crosslink density



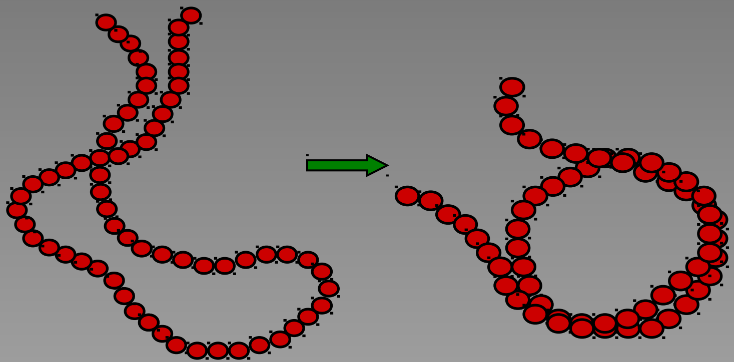
Critical dynamics



PhD student: Swati Sen (SRF)

Future Directions

Collapse of a semi-flexible chain - toroids:

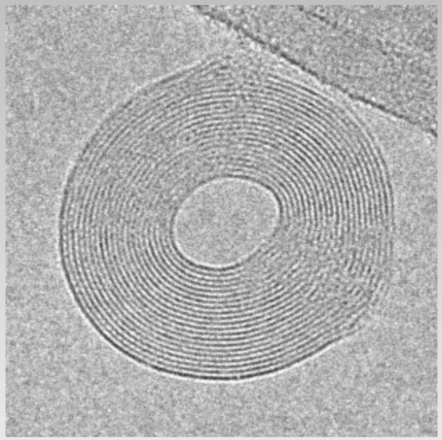


Issues:

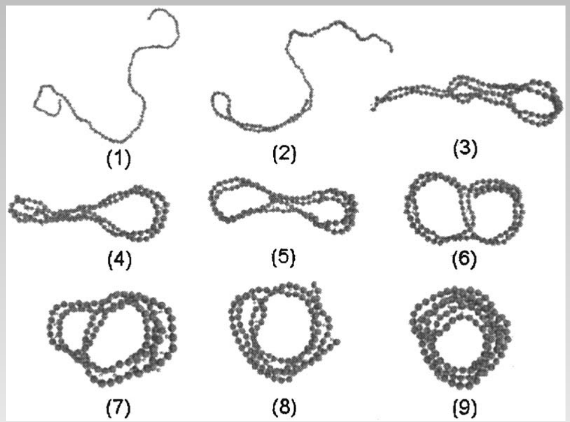
stiff chain —condensing agent→ no globules
toroids

Kinetics of nucleation and growth of toroids

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

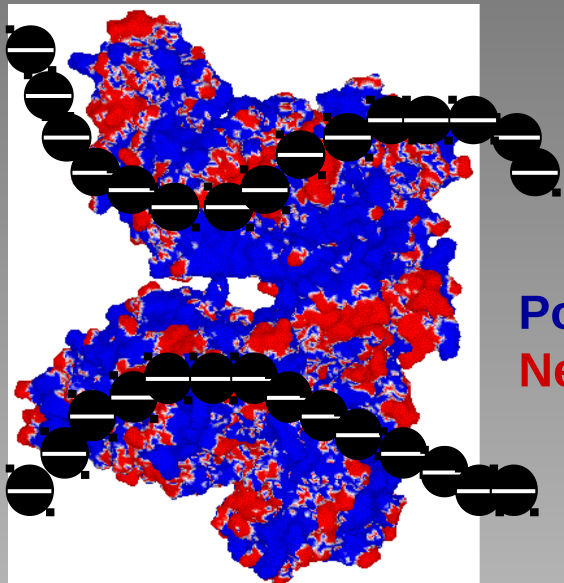


Experiments: Nick Hud, Georgia Tech.



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?

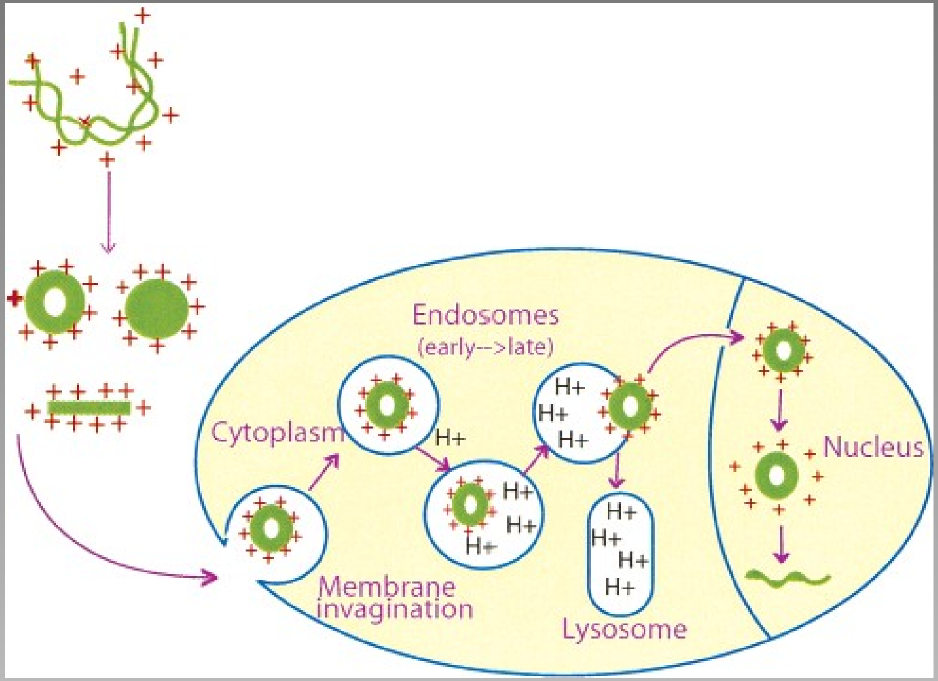
Simple theories of overcharging inapplicabl

Possible aggregation and detachment depending on salt

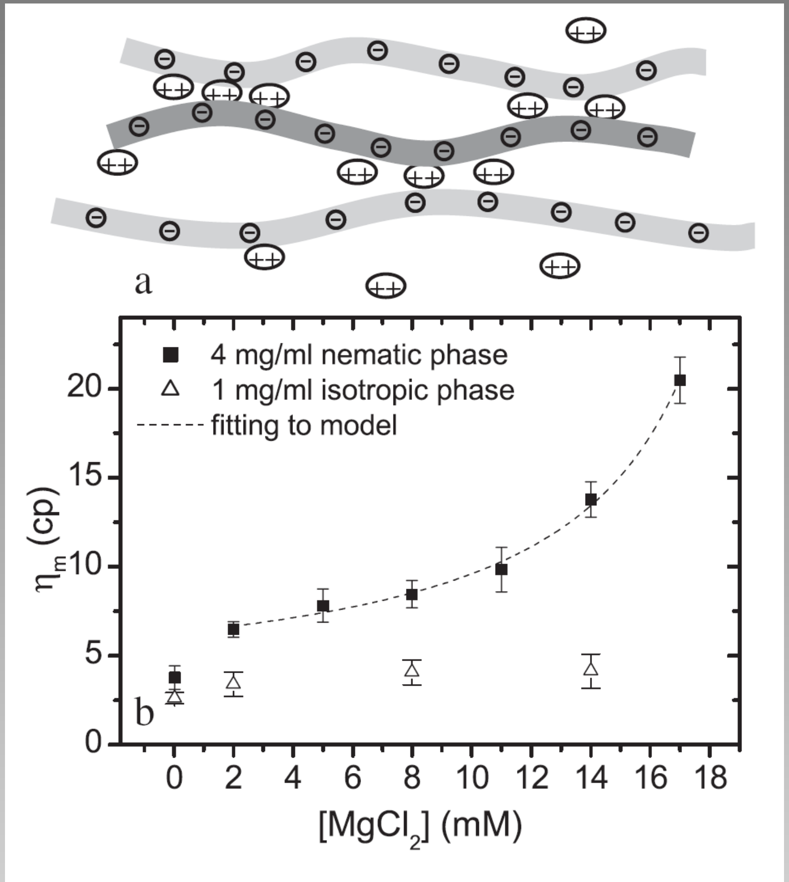
Examples: aggregation of flexible anionic polyion (sodium polyacrylate) and DOTAP lipids

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

Charge inversion and ion-bridging – applications, effects:



V. Vijayanathan ***et al*****., Biochemistry, <u>41</u>,** 14085 (2002)



J. He ***et al.*** **PRL <u>99</u>,** 068103 (2007)

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

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