Entropy in Charged Polymers – A Theoretical Perspective

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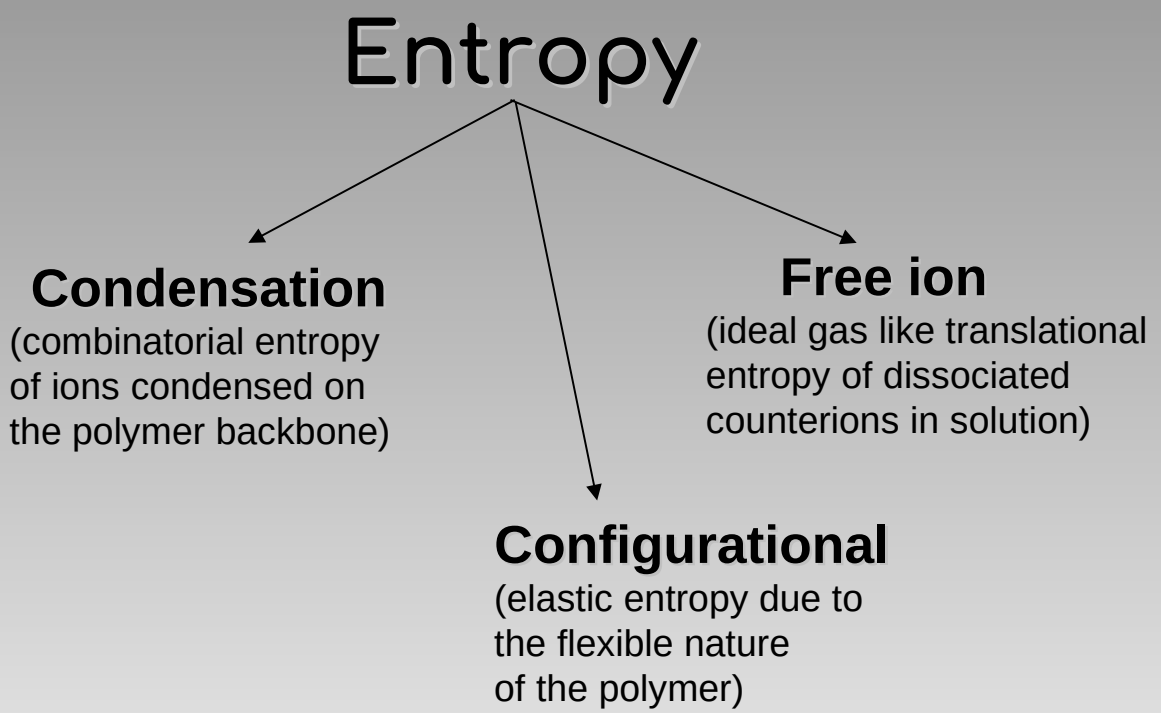
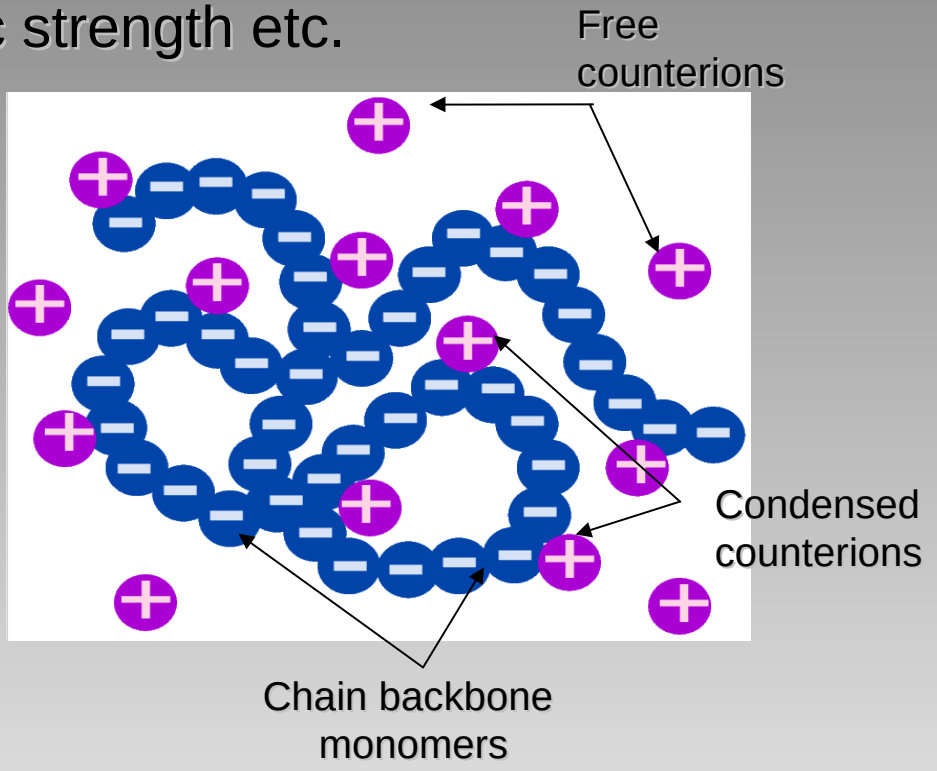
Entropy in charged polymer systems:

Monomers dissociate in solution to release *counterions*

The counterions can stay *released* in solution, or *condense* on polymer backbone depending on temperature, ionic strength etc.





Single polyelectrolyte chain: idea of counterion condensation

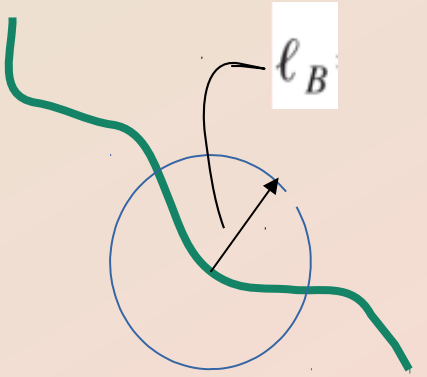
"…*there is a balance between the binding energy and the dissociation entropy of ions*…",

- *G. S. Manning*, J Biomol Struct Dyn. (1988)

Size of the chain: $\tilde{l}_1 = \left(\frac{6}{Nl^2}\right) R_g^{\,2}$

f - degree of chain ionisation

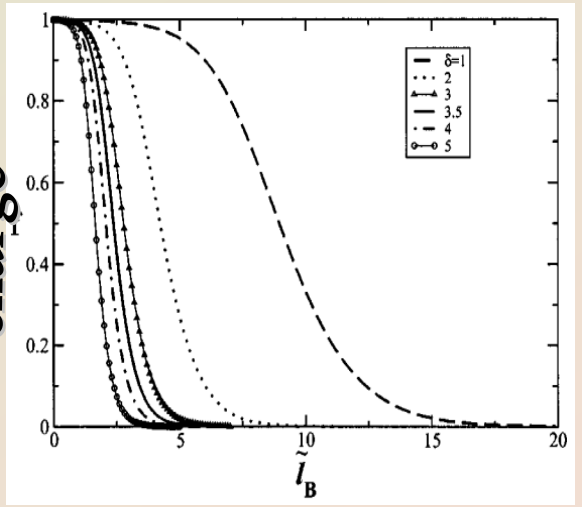
l=Kuhn segement length

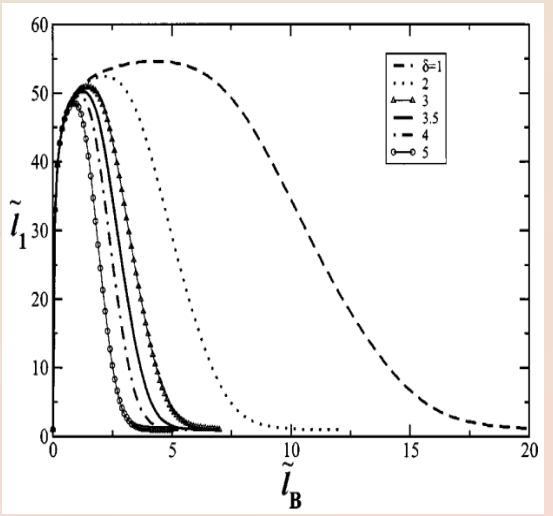


Bjerrum length

$$\ell_B = \frac{e^2}{4\pi\epsilon_0\epsilon k_B T}$$

ℓ_B ↑ , higher condensation





$\tilde{l}_B = l_B / l$

Bjerrum length →

Free energy of a single polyeletrolyte

$$F = F(f, \tilde{l}_1, \delta, \tilde{l}_B, \tilde{c}_s, \ldots)$$

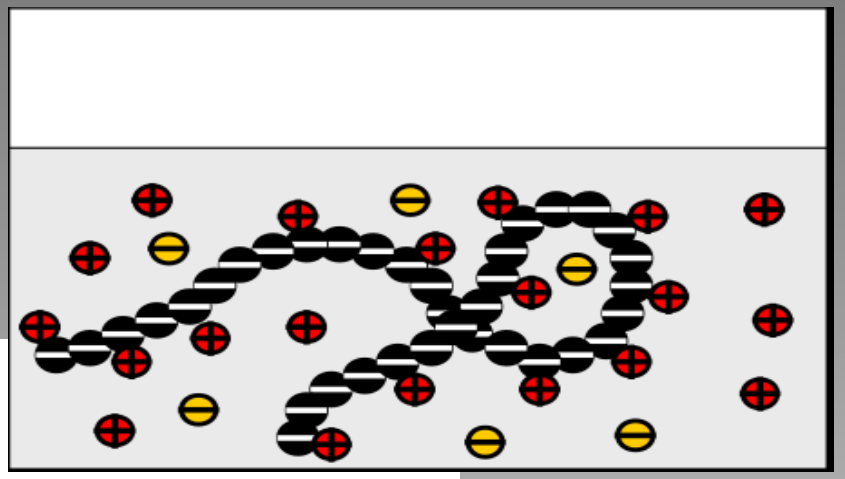
"…*there is a compromise between the translational entropy of the counterions and the electrostatic attraction of the counterions by the polymers*…"

- *Muthukumar*, J Chem Phys (2004)

A free-energy for a single polyelectrolyte in solution:

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

In units of $k_B T$ nd per monomer:



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

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

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

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

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

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

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

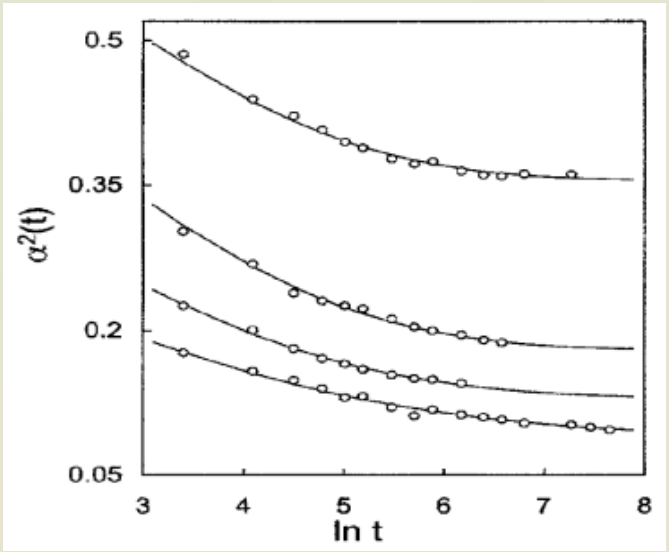
$$a = \tilde{\kappa}^2 N\tilde{l}_1/6 \qquad \tilde{\kappa}^2 = 4\pi\tilde{l}_B(f\tilde{\rho} + 2\tilde{c}_s) \qquad \tilde{l}_B = e^2/4\pi\epsilon\epsilon_0 l k_B T$$

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

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

Role of entropy and energy in the Kinetics of conformational changes of a single, isolated polyelectrolyte chain

Experiments and simulations on kinetics of single PE chain



Experiment:

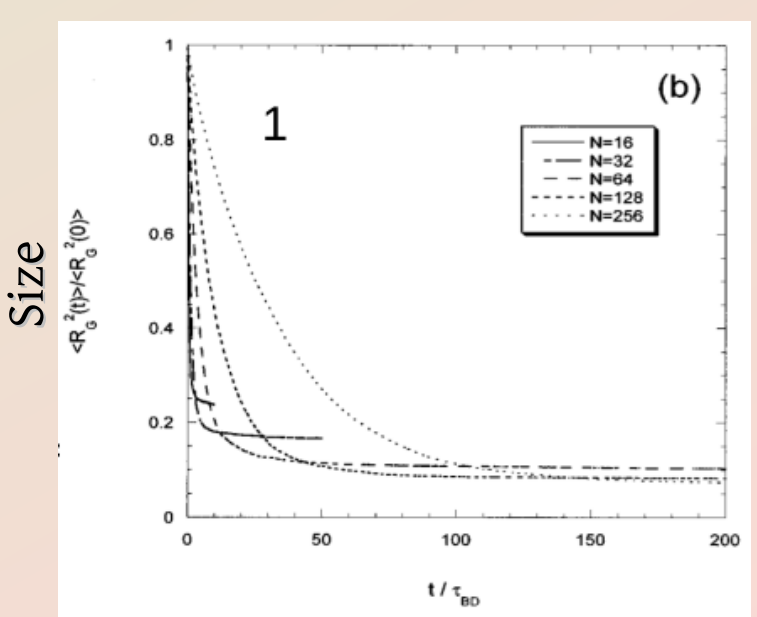
Light scattering study of collapse of PMMA poly(methyl methacrylate)-temporal profiles Of chain size for different temperature quench

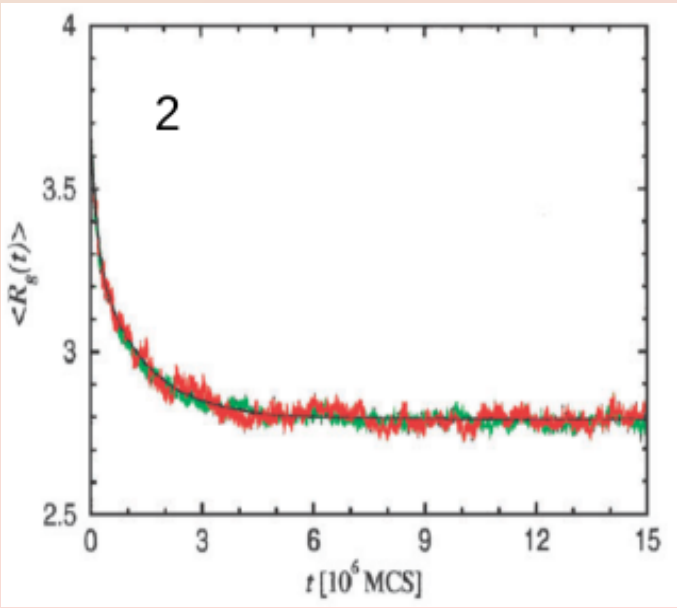
-Yasuyuki Maki et. al. *J. Chem. Phys.* (2007)

Simulations:

1. Brownian dynamics for neutral polymer deswelling; for various chain lengths

2. Temporal variation of size of a folding protein





time

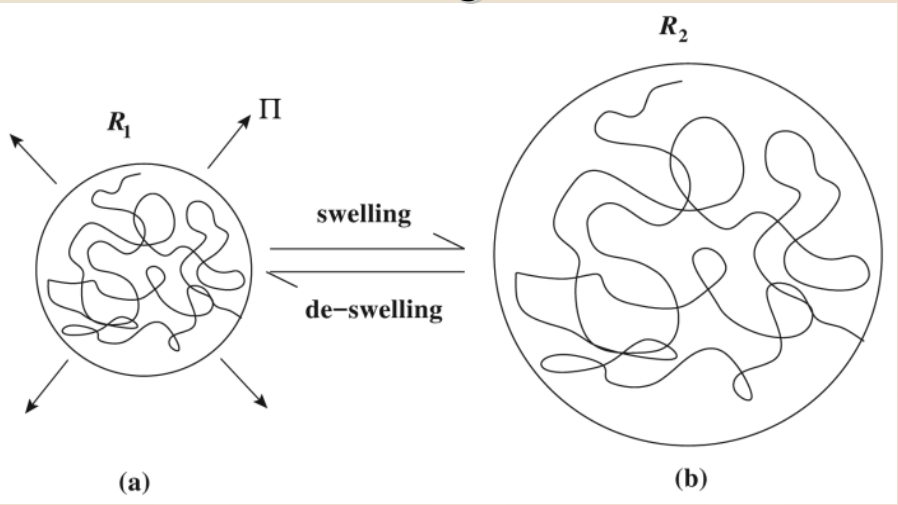
[1] Yethiraj, *J. Chem. Phys.* (2001)
[2] Guy Ziv, *Phys. Chem. Chem. Phys.* (2009)

Kinetics of a single polyelectrolyte

Equation of motion, for surface element of sphere;
Osmotic and viscous forces

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

Isolated, single PE in solution



Uniform spherical expansion model

Osmotic pressure

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

Free energy of the single PE chain

$$F(\tilde{l}_1, f, N, T) = N k_B T \Sigma_i F_i$$

Final equation of motion:

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

Size of the chain: $\tilde{l}_1 = \left(\frac{6}{Nl^2}\right) {R_g}^2$

f - degree of chain ionisation

Soumik Mitra, Arindam Kundagrami, *Macromolecules* (2017)

Free energy of a single Polyelectrolyte

$$F(\tilde{l}_1, f, N, T) = N k_B T \Sigma_i F_i$$

F_1 - *entropy of condensed counterions*

F_2 - *entropy of free counterions*

F_3 - *Debye-Hückel fluctuation energy of dissociated ions*

F_4 - *electrostatic energy of bound ion pairs*

F_5 - *configurational energy due to the flexibility and charged nature of the polymer backbone*

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

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

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

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

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

where,

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

and,

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

Soumik Mitra, Arindam Kundagrami, *Macromolecules* (2017)

Kinetics of a single polyelectrolyte(contd.)-Swelling

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

Configurational entropy — excluded volume — **electrostatic interaction**

- Swelling beyond *Gaussian* size ⟶ w=0 (*good solvent*)
- Swelling is dominantly driven by the *Coulomb interaction* among monomers and the pressure from contained ions (to *maximise entropy*)

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

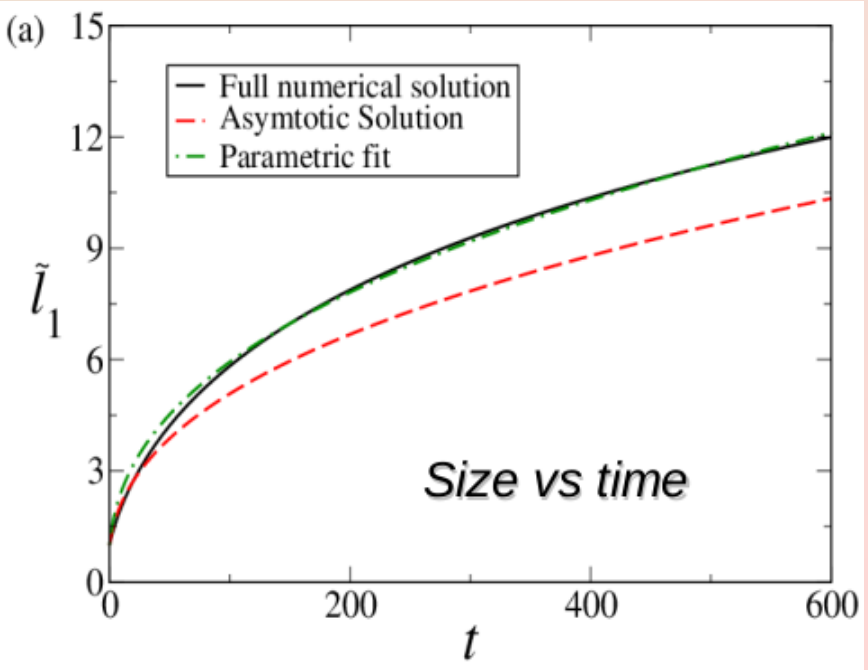
High-salt:
$$\tilde{l}_1^{7/2} - \tilde{l}_{10}^{7/2} = \frac{7}{8\zeta'}\left(\frac{6}{N\pi}\right)^{3/2} \frac{Tf^2}{f\tilde{\rho} + 2\tilde{c}_s} t$$

Low salt case:

➡ **Fit parameter: α**

$$\alpha = \frac{5}{2}\frac{T}{N\zeta'}\frac{2}{15}\sqrt{\frac{6}{\pi}} f^2 \tilde{l}_B N^{1/2}$$

➡ From **α-value**, charge(***f***) of PE chain can be determined, if chain length is known.



Soumik Mitra, Arindam Kundagrami, *Macromolecules* (2017)

Kinetics of a single polyelectrolyte(contd.)-De-swelling

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

Configurational entropy excluded volume electrostatic interaction

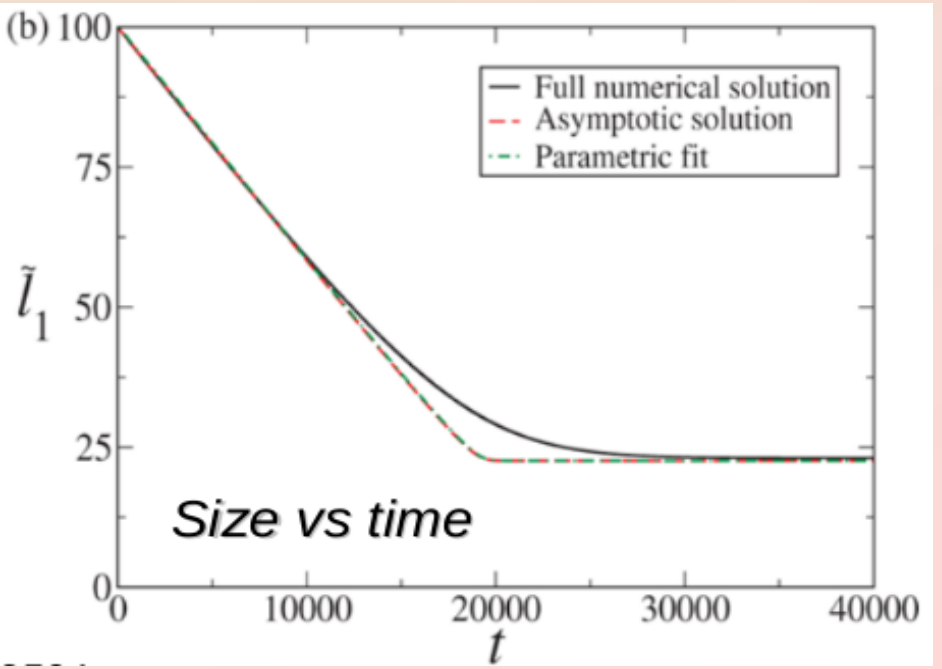
- Initial size higher than Gaussian ⟶ like-charge repulsion negligible
- Kinetic process predominantly driven by the configurational entropy of the polymer

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

➡ Fit parameter: **β**

$$\beta = \frac{3T}{2N^2\zeta'}$$

➡ From β the molecular weight(chain length N) of PE chain can be determined



Soumik Mitra, Arindam Kundagrami, *Macromolecules* (2017)

Kinetics of a single polyelectrolyte(contd.)-Collapse

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

Configurational entropy — **excluded volume** — electrostatic interaction

Sub-Gaussian sizes ⟶ Configurational entropy minimal

Charge on PE chain is nominal ⟶ electrostatics negligible

Major kinetic drive from attractive two-body interaction

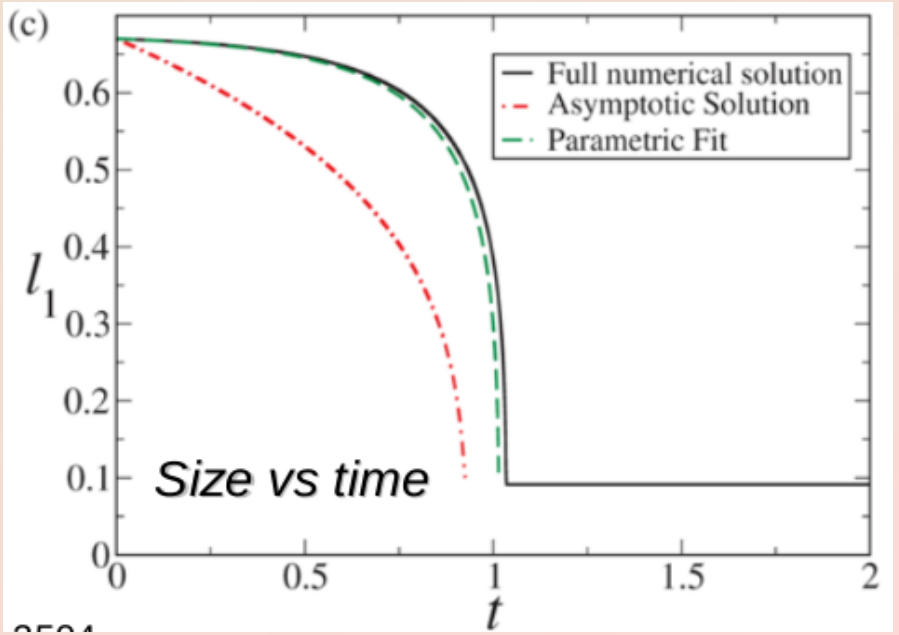
$$\tilde{l}_1^{7/2} - \tilde{l}_{10}^{7/2} = \frac{7}{2}\frac{2T}{N\zeta'}\left(\frac{3}{2\pi}\right)^{3/2}\frac{wt}{\sqrt{N}}$$

➡ Fit parameter: ***γ***

$$\gamma = \frac{7}{2}\frac{2T}{N\zeta'}\left(\frac{3}{2\pi}\right)^{3/2}\frac{w}{\sqrt{N}}$$

➡ From *γ* the hydrophobicity(***w***) of the polymer can be determined

➡ Confirms the unusual temporal profile for collapse as the effect coming purely from the ***negative two-body interaction***



Soumik Mitra, Arindam Kundagrami, *Macromolecules* (2017)

Interaction between two oppositely charged polyelectrolytes: Complexation

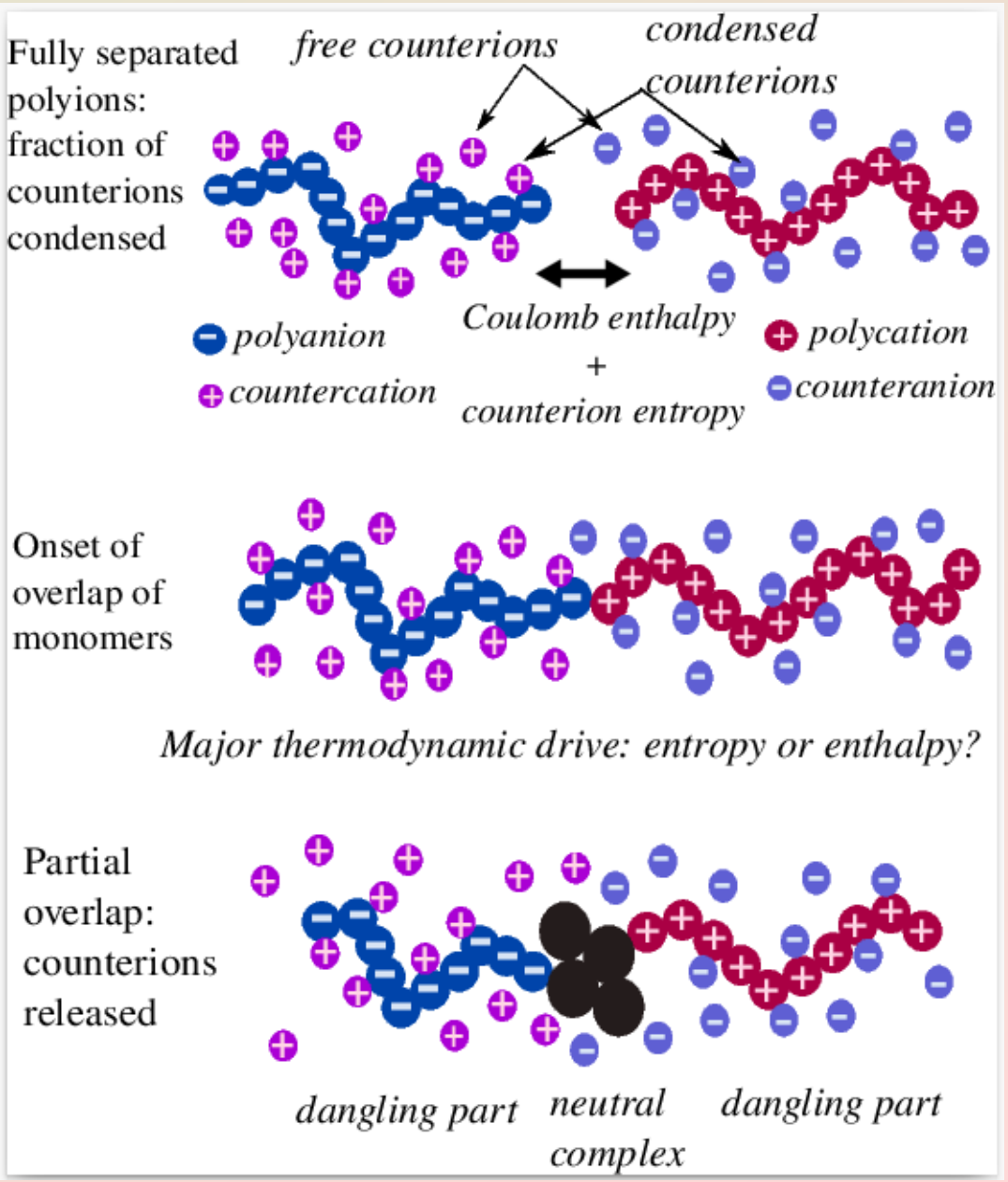
What drives the Complexation between two oppositely charged PEs?

Two oppositely *charged polymers (symmetric in size), fully ionised*

Competing driving forces:
Role of free ***counterion entropy*** and ***bound ion-pair enthalpy***:
Which one dominates?

Is the process always favorable? following a ***downhill free energy***??

How does the process of complexation trend in the system for parameters like ***temperature***, ***salt*** etc.?



Complexation between two oppositely charged polyelectrolytes

Free energy

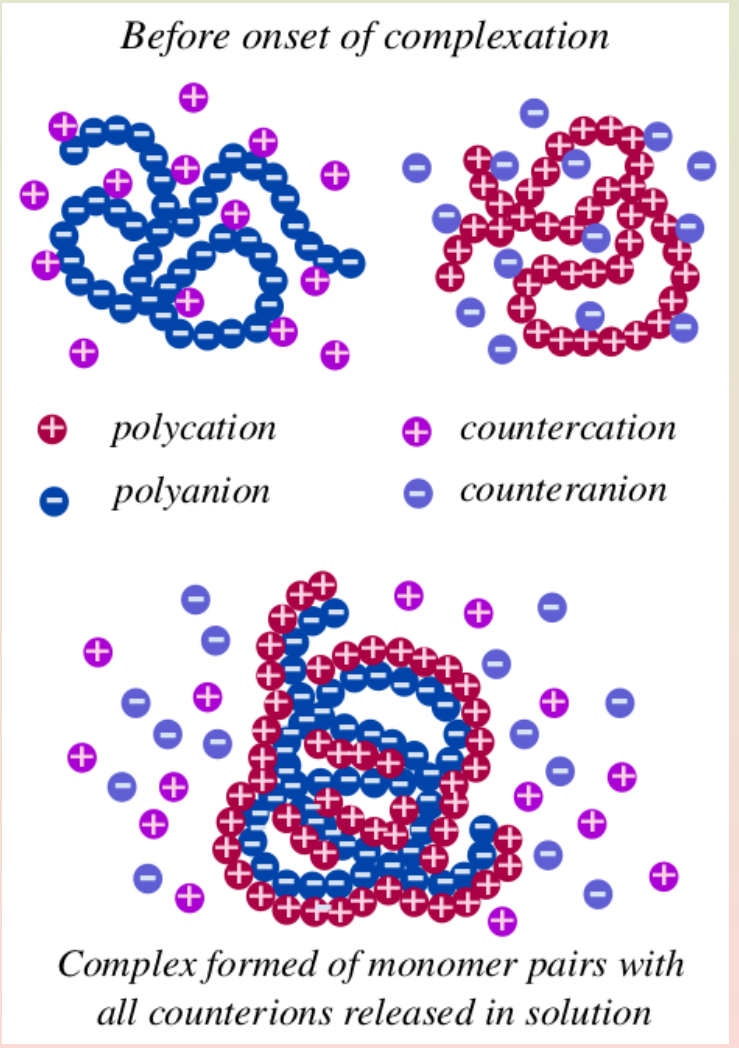
$$F = F(f, \tilde{l}_1, \delta, \tilde{l}_B, \tilde{c}_s, \ldots)$$

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

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

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

$$\frac{F_4}{k_B T} = -\left[2\delta(N-n)(1-f) + n\delta_{12}\right]\tilde{l}_B$$



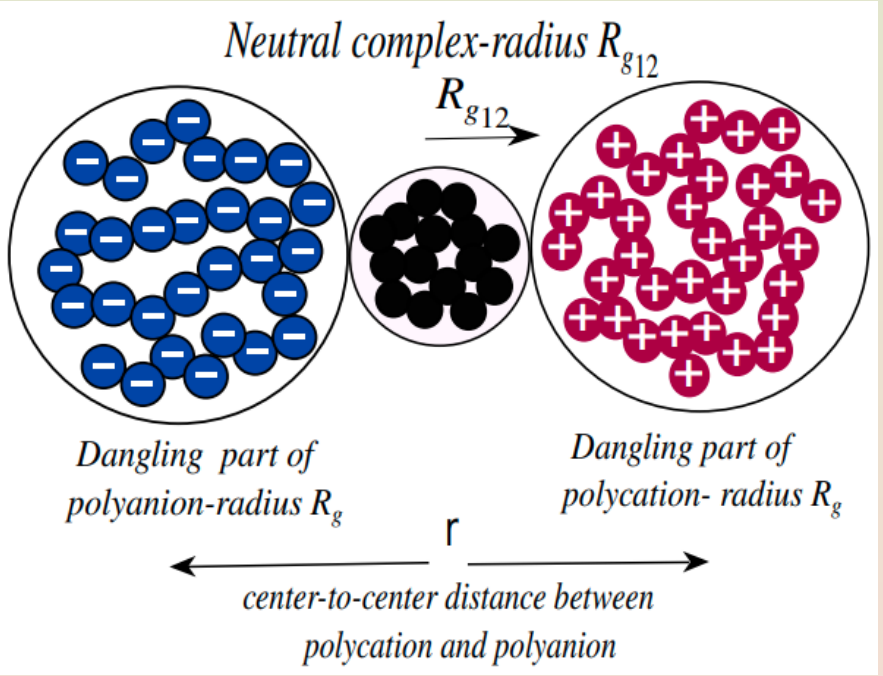
Soumik Mitra, Arindam Kundagrami, JCP (2022),

Complexation between two oppositely charged polyelectrolytes

Free energy(contd.)

$$\frac{F_5}{k_BT} = 3[\tilde{l}_1 - 1 - \log\tilde{l}_1] + \frac{8}{3}\left(\frac{3}{2\pi}\right)^{3/2} w\frac{(N-n)^{1/2}}{\tilde{l}_1^{3/2}} + 4\sqrt{\frac{6}{\pi}} f^2\tilde{l}_B\frac{(N-n)^{3/2}}{\tilde{l}_1^{1/2}}\Theta_0(a) + \frac{3}{2}[\tilde{l}_{13} - 1 - \log\tilde{l}_{13}] + \frac{4}{3}\left(\frac{3}{2\pi}\right)^{3/2} w_{12}\frac{n^{1/2}}{\tilde{l}_{13}^{3/2}},$$

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



Schematic of the two overlapping Polyelectrolyte chains

Where,

$$\tilde{r} = 2\left\{\left[\frac{(N-n)}{6}\tilde{l}_1\right]^{1/2} + \left[\frac{n}{6}\tilde{l}_{13}\right]^{1/2}\right\}$$

n-number of monomers overlapped

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Tracking the dominance of entropy and enthalpy

Conjecture: free ion entropy & bound pair enthalpy consitutes significant free energy contribution

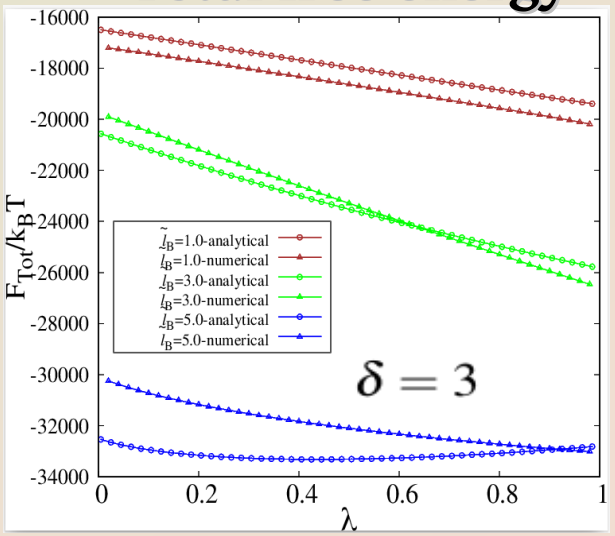
$$F_{tot} = F_1 + F_2 + F_4$$

$$f = -\frac{1}{2\tilde{\rho}}\left[\frac{\lambda\tilde{\rho}}{1-\lambda} + \tilde{c}_s + \exp\left(-\delta\tilde{l}_B\right)\right] + \frac{1}{2\tilde{\rho}}\sqrt{\left(\frac{\lambda\tilde{\rho}}{1-\lambda} + \tilde{c}_s + \exp\left(-\delta\tilde{l}_B\right)\right)^2 + 4\tilde{\rho}\exp\left(-\delta\tilde{l}_B\right)}$$

(δl_B)- Coulomb strength

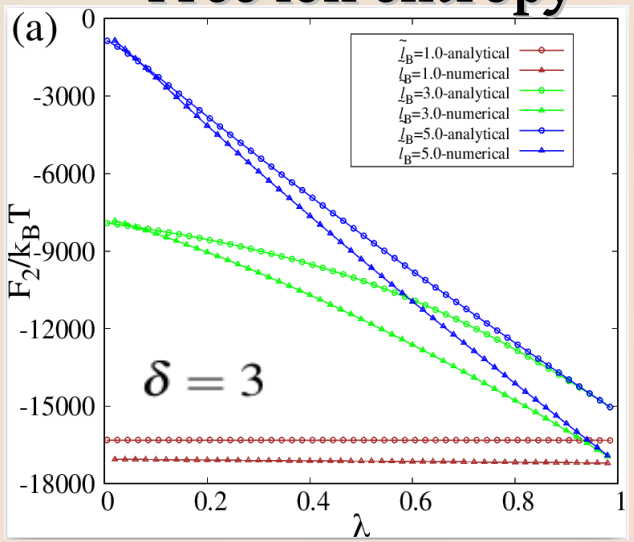
λ = no. of monomer pairs formed/no. of monomers in PE chain

Total free energy



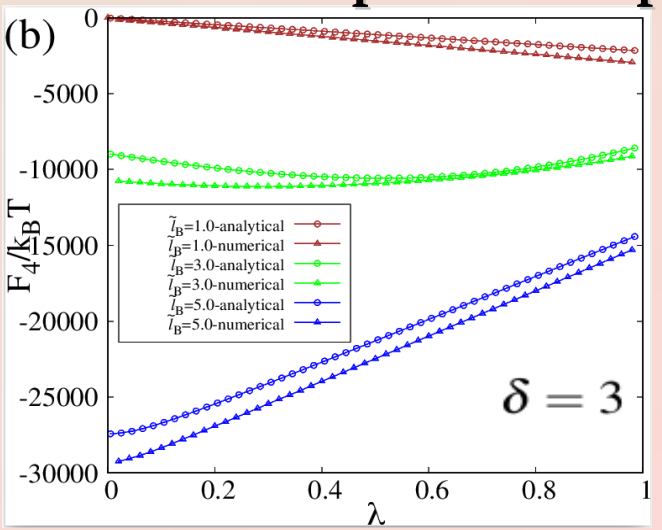
overlap

Free ion entropy



overlap

Bound ion-pair enthalpy



overlap

- Free energy gain ~ $6k_BT$
  - reported by simulations

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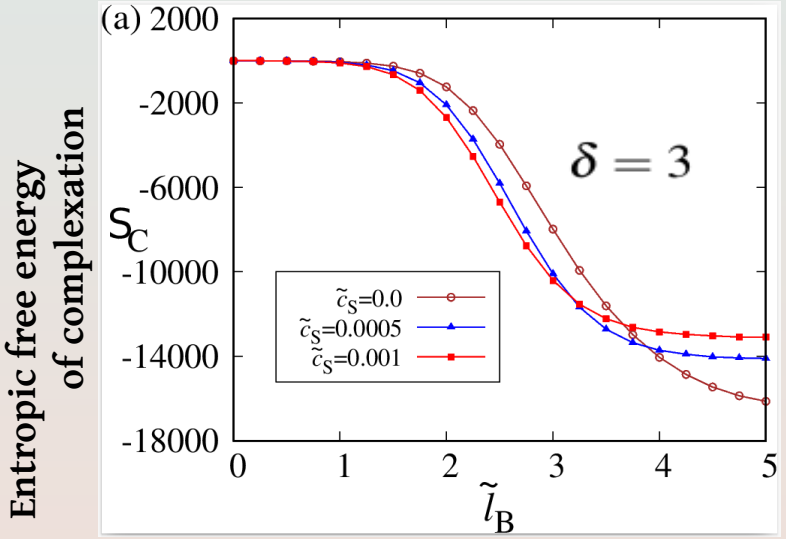
Entropy, Enthalpy and Free energy of Complexation



Entropy: $S_c = S_{final} - S_{initial}$

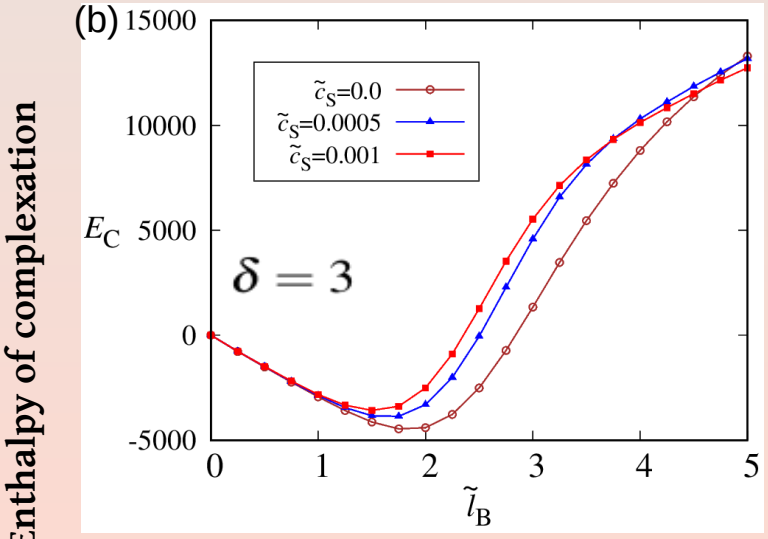
$(S = S_{condensation} + S_{translational} + S_{configurational})$

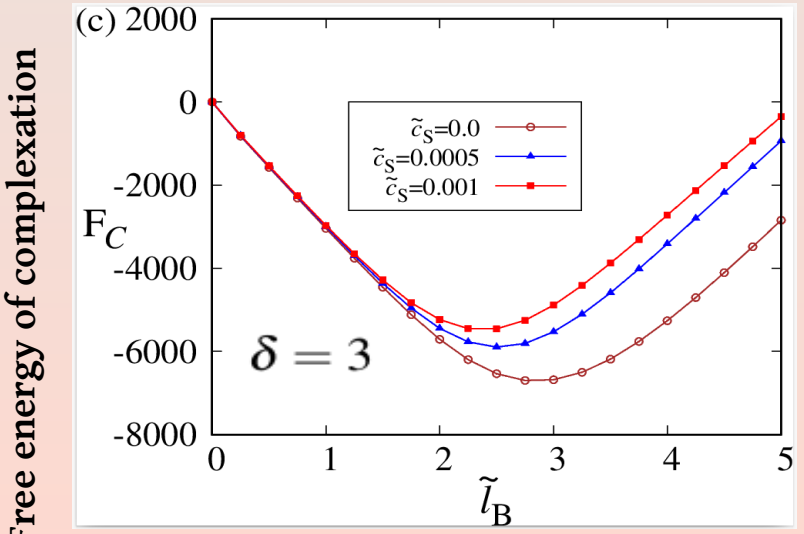
Enthalpy : $E_c = E_{final} - E_{initial}$

$(E = E_{bound\text{-}pair} + E_{inter\text{-}chain} + E_{intra\text{-}chain})$

Free Energy : $F_c = F_{final} - F_{initial}$

$(F = F_{Total})$





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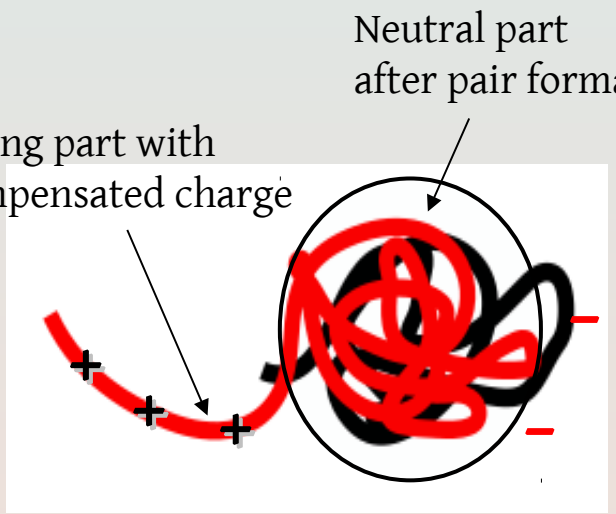
What happens for two asymmetric chains & partial charge density?

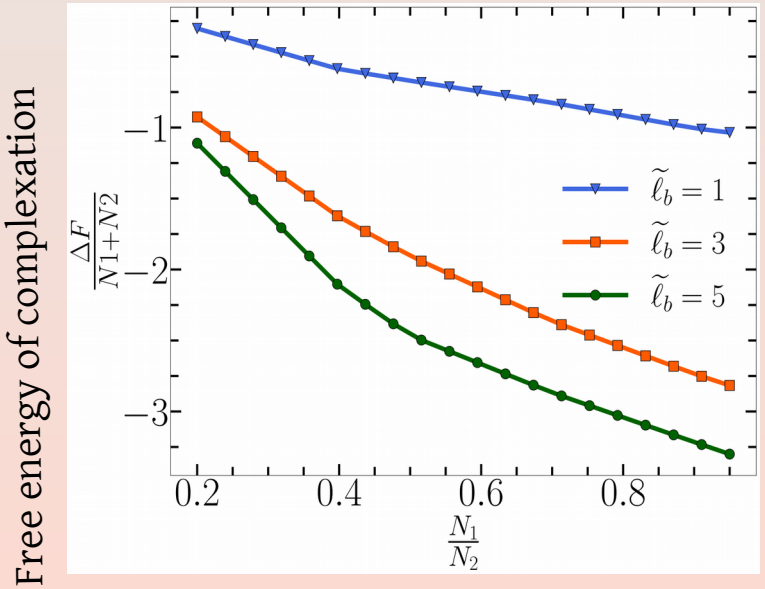
- Unequal number of monomers On the two PE chains

$$N_1 \neq N_2,\ N_{1c} \neq N_{2c}$$

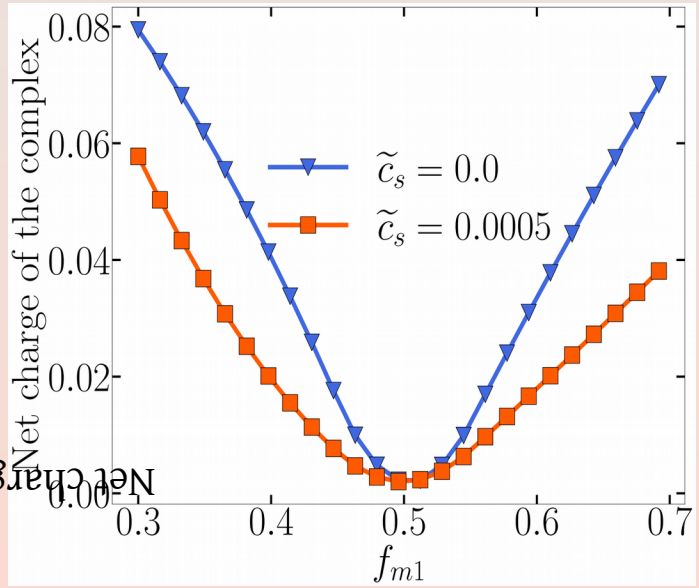
- All monomers are not ionisable

$$f_{m1} = N_{c1}/N_1 \qquad f_{m2} = N_{c2}/N_2$$





Asymmetry in chain length = N_1/N_2



Net charge of complex

Charge density

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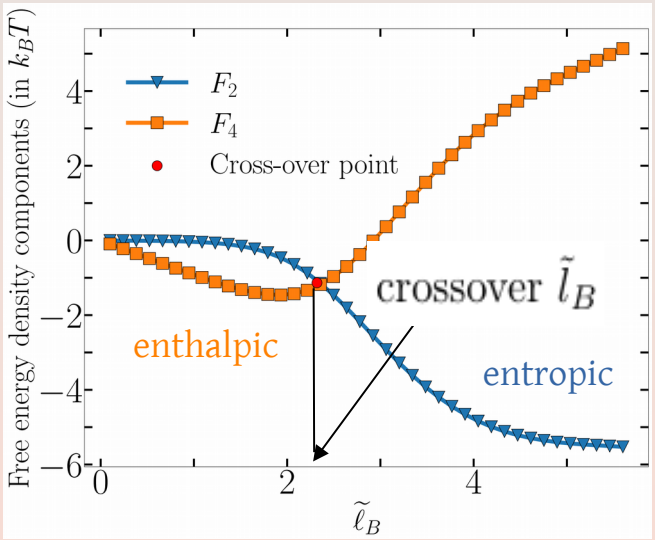
What happens for two asymmetric chains & partial charge density?

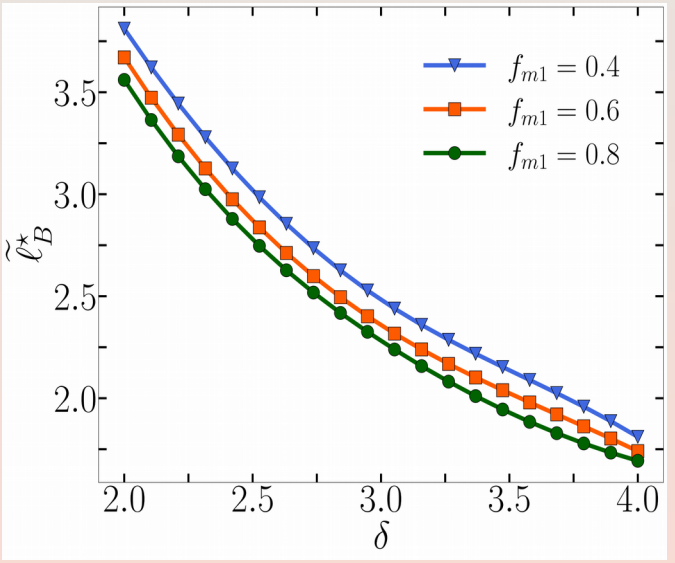
- Polyelectrolytes can be either weak or strong, depending on their backbone charge density
- Does the drive for complexation(entropy or enthalpy) depend on the charge density??

Free ion entropy
Bound ion pair enthalpy



Bjerrum length

crossover $\tilde{l}_B$



Dielectric mismatch

thermodynamic drive for complex formation is characterized by $\tilde{l}_B$ which in turn is coupled to δ and f_{m1}; complexation can be driven by entropy or enthalpy depening on δ , f_{m1} and l_B..

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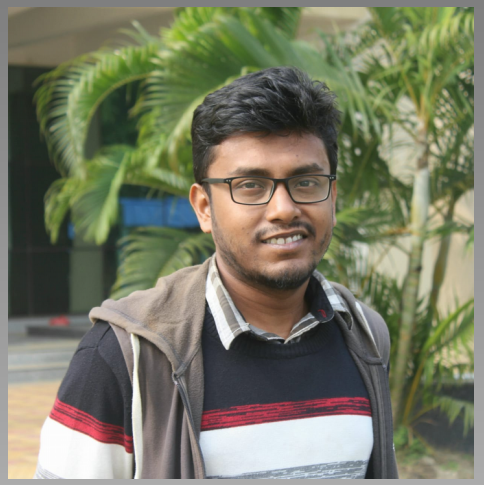

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