

# Effective interactions between macro-ions: valence-dependence of condensed counter-ions ...dealing with counter-ions in polyelectrolyte solutions

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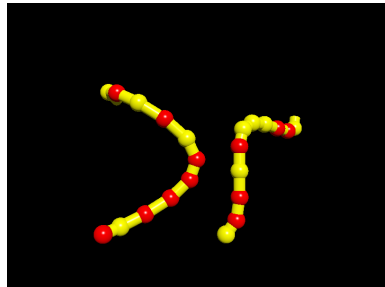
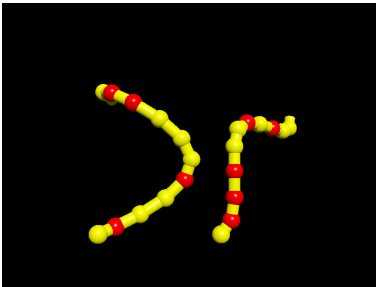
KITP, 18 November 2008



# Pectin



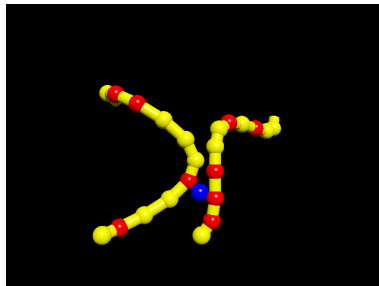
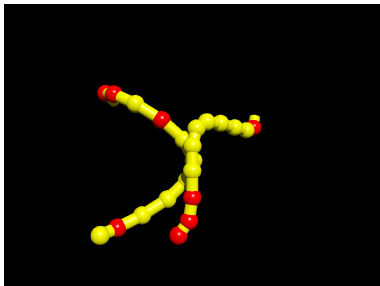
Pectin in the fruit or additional pectin is responsible for some of the particular mechanical properties of certain types of jam.



Chemistry of the chain and acidity of the environment control the degree of dissociation.



# Linking by two methods



Gelation is thought to occur in different ways: hydrogen bonding with hydrophobicity and salt bridging by divalent ions (typically  $\text{Ca}^{2+}$ ). Purification can be done with  $\text{Cu}^{2+}$ .

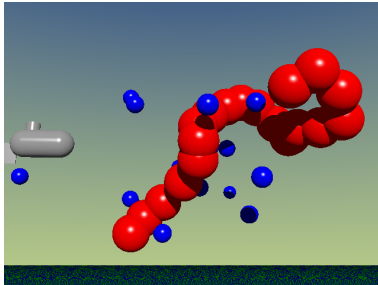


# The ingredients

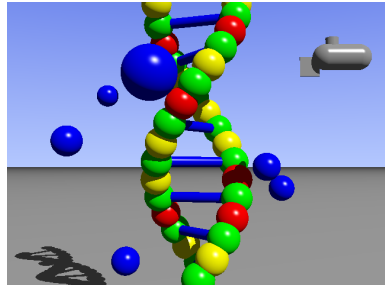
- Polymer chain
- Charge (and associated interactions)
- Gelation — the formation of a (temporary) network of chains
- One needs at least **divalent** ions



# Polyelectrolytes



(movie)



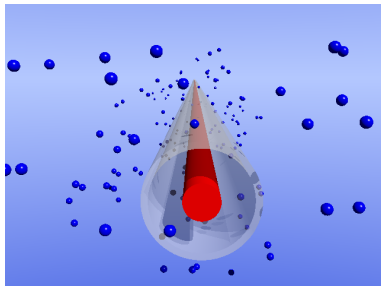
(movie)

- Macro-ions with charged groups that dissociate in polar solvent
- Macro-ions themselves have complicated behaviour of their conformations
- A variety of properties that have been difficult to understand



# Counter-ion condensation (Manning & Oosawa)

(movie)



- Non-interacting counter-ions in potential of an infinite rod
- Bjerrum length

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

- Potential  $\propto \ln r$
- Boltzmann weight

$$w \exp[-2\lambda\ell_B r] = wr^{-2\lambda\ell_B}$$

$$\Rightarrow N_{<r_0} = 2\pi \int_0^{r_0} dr r^{1-2\lambda\ell_B}$$

- Condensation when  $\ell_B\lambda > 1$ .
- $f = 1 - 1/(\lambda\ell_B)$ .



# Screening of electrostatic charge (Debye-Hückel)

- Poisson's equation  $\nabla^2\phi = -\rho/\epsilon$
- Estimating the density by the Boltzmann weight for charges in an electric field leads to the Poisson-Boltzmann equation:

$$\nabla^2\phi = - \sum_s c_{0,s}(ez_z)e^{ez_s\phi(r)/k_B T}$$

- Linearised to approximate gives **Debye-Hückel screened** potential:

$$V_{\text{DH}}(r) = \frac{1}{\epsilon|r|} e^{-\kappa|r|}$$

where  $\kappa^2 = 4\pi\ell_B (\sum_s c_{0,s}z_s^2)$



# Experimental and theoretical situation

- A long history.
- Debye-Hückel theory is the typical first approach to these systems.
- Nishida & Kanaya *JCP* (2001) phase diagram of salt-free polyelectrolytes; Zhang *et al JCP* (2001) and Dubois & Boué *Macromol* (2001) effects of counterion valences; Das *et al PRL* (2003) condensation profiles; Qiu *et al PRL* (2006) effective interaction as function of valence.
- Simulations have also addressed multivalence (e.g. Chang and Yethiraj *JCP* 2003).
- Counterion correlations in polyelectrolyte solutions, gelation, e.g. Ermoshkin & Olvera de la Cruz *Macromol, PRL* (2003)
- Strong coupling theory Netz and coworkers (e.g. Naji & Netz *EPJE* (2004))
- Two-fluid models, e.g. Lau, *et al PRE* (2002)





# The questions

- How much condensation of counter-ion occurs on other objects (including flexible polymer chains)?
- Does the valence of counter-ions play a role here?
- In which ways would condensed counter-ions alter the pure Coulomb repulsion between macro-ions?



# The strategy

- Polymer + Counter-ions MIXED WITH Coulomb interaction
- Calculate the partition function.

... Only in principle

$$\begin{aligned}
 Z &= \sum_{\text{polymers}} \sum_{\text{counter-ions}} e^{-\beta H(\text{polymers, counter-ions with Coulomb})} \\
 &= \sum_{\text{polymers}} e^{-\beta H_{\text{effective}}(\text{polymer})}
 \end{aligned}$$

we do this in three stages:

- Stage 1: counter-ions as continuum
- Stage 2: counter-ions as discrete
- Stage 3: aspects of continuum discrete

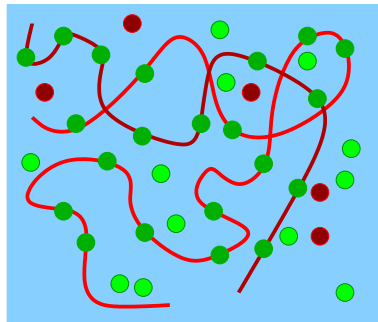


# Charge condensation on flexible, linear chains

Work with Tannie Liverpool (Bristol)

TB Liverpool & KKMN *J. Phys. Condens. Matter* (2006)

- $\mathcal{N}$  flexible polyelectrolyte chains of with linear charge density  $-\lambda e$
- neutralized by  $N$  counterions of charge  $ze$
- additional salt
- A fraction  $f$  of the number of counter-ions  $N$  is presumed to be condensed on the chain —  
counter-ions split up into two species!



# Seeing this...



There is much important work related to such ideas: Ha & Liu (late 1990's), Golestanian, *et al.*



# Method

$$\begin{aligned}
 Z(f) = & C(N, M, f) J_\phi \int [d\tilde{\mathbf{r}}(s)] [d\tilde{\phi}(\mathbf{x})] \prod_{i=1}^{(1-f)N+M} d^3 z_i \prod_{k=1}^M d^3 z'_k \prod_{j=1}^{fN} ds_j \\
 & \times \exp \left\{ -\frac{3}{2} \sum_{i=1}^{\mathcal{N}} \int_0^{L/\ell} ds \left( \frac{\partial \mathbf{r}_i}{\partial s} \right)^2 - \frac{1}{8\pi z^2 \tilde{\ell}_B} \int_{\tilde{V}} d^3 x \left( \nabla \tilde{\phi}(\mathbf{x}) \right)^2 \right\} \\
 & \times \exp \left\{ +i \int_{\tilde{V}} d^3 x \left[ \left( -\tilde{\lambda}/z + \tilde{c}_0 \right) \varrho(\mathbf{x}) + \tilde{n}^+(\mathbf{x}) - \tilde{n}^-(\mathbf{x}) \right. \right. \\
 & \left. \left. + \sum_{i=1}^{\mathcal{N}} \int_0^{L/\ell} ds \delta(\mathbf{x} - \tilde{\mathbf{r}}_i(s)) \tilde{c}(s) \right] \tilde{\phi}(\mathbf{x}) \right\}.
 \end{aligned}$$

where  $C(N, M, f) = \frac{1}{M!} \frac{1}{[(1-f)N+M]!} \frac{1}{(fN)!}$



# Method (2): Quadratic order in density

$$\begin{aligned}
 Z_q(f) = & \frac{1}{(fN)!} \frac{1}{[(1-f)N + M]!} J_\phi J_\varrho e^{[(1-f)N + M] \ln \tilde{V} + fN \ln(L/\ell)} \\
 & \times \int [d\varrho] [d\phi] \exp \left\{ -\frac{1}{2} \int d^3x d^3x' \varrho G_0^{-1} \varrho + i \int d^3x \phi \left( -\frac{\tilde{\lambda}}{z} + \tilde{c}_0 \right) \varrho \right\} \\
 & \times \exp \left\{ -\frac{1}{2z^2 \tilde{\ell}_B} \int d^3x \left[ \frac{(\nabla \phi)^2}{4\pi} + z^2 \tilde{\ell}_B \left( \frac{\tilde{\lambda}}{z} \Phi_0 + 2\tilde{n}_0^- \right) \phi^2 \right] - \frac{1}{2} \tilde{c}_0 \int d^3x \phi^2 \varrho \right\}.
 \end{aligned}$$

**Red parts:** entropic counter-ion contribution  
Debye-Hückel interaction contribution to  $(1-f)^2$   
contribution to  $f^2$

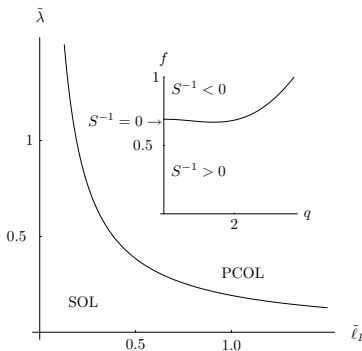
Leads to an **effective interaction** between macro-ions:

$$V_{\text{eff}} \equiv \left( \frac{\tilde{\lambda}}{z} \right)^2 \left[ (1-f)^2 V_{\text{DH}} - \frac{f^2}{2} V_{\text{DH}}^2 \right].$$

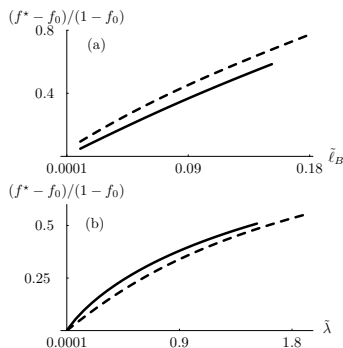
with Debye-Hückel interaction  $V_{\text{DH}}(\mathbf{r}) = z^2 \tilde{\ell}_B e^{-\tilde{\kappa}|\tilde{\mathbf{r}}|}/|\tilde{\mathbf{r}}|$  where  
 $\tilde{\kappa}^2 = 4\pi z^2 \tilde{\ell}_B \left[ 2\tilde{n}_0^- + \frac{\tilde{\lambda}}{z} \Phi_0 \right]$



# Results (1): Degree of condensation



**Figure:**  $\tilde{\ell}_B$  and  $\tilde{\lambda}$  where chains always in solution (SOL). Outside — possible chain collapse (PCOL). Inset: PCOL —  $S_f^{-1}(q)$  break down of formalism. ( $\tilde{R}_g^2 = 10.0$ ,  $\Phi_0 = 0.05$ . Main graph:  $n_0 = 0.0$ , Inset:  $\tilde{\lambda} = 8.0$ ,  $\tilde{\ell}_B = 0.5$  and  $n_0 = 0.01$ .)



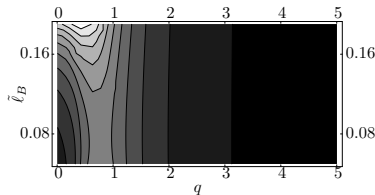
**Figure:** Numerical solutions of  $f^*$ : (a) for  $\tilde{n}_0 = 0.0$  (solid) and  $\tilde{n}_0 = 0.03$  (dashed), with  $\Phi_0 = 0.1$ ,  $\tilde{\lambda} = 1.0$ ,  $\tilde{R}_g^2 = 10.0$ . In (b) for  $\Phi_0 = 0.1$  (solid) and  $\Phi_0 = 0.05$  (dashed) where  $\tilde{\ell}_B = 0.1$ ,  $\tilde{n}_0 = 0.0$ ,  $\tilde{R}_g^2 = 10.0$ .



## Results (2): Valence

**Table:** We list values of  $f^*$  for increasing valences in systems where  $\tilde{\ell}_B = 0.05$ ,  $\tilde{\lambda} = 1.0$ ,  $\tilde{R}_g^2 = 10$ ,  $\Phi_0 = 0.1$ , and  $\tilde{n}_0 = 0.0$ . As expected the results indicate that increasing valence causes stronger condensation (and by implication, in our model, a significant increase in the attraction of the effective chain-chain interaction.)

$z$	1	2	3
$f^*$	0.292	0.556	0.884
$q_{\text{peak}}$	0.743	0.507	0.0



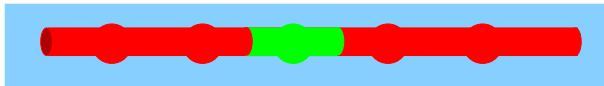
**Figure:** Contour plot of structure factor as  $\tilde{\ell}_B \propto 1/T$  varies. Shows the polyelectrolyte peak (lighter areas — greater scattering intensity).  $\tilde{\lambda} = 1.0$ ,  $\Phi_0 = 0.1$ ,  $\tilde{n}_0^+ = 0.0$ , and  $\tilde{R}_g^2 = 10.0$ .





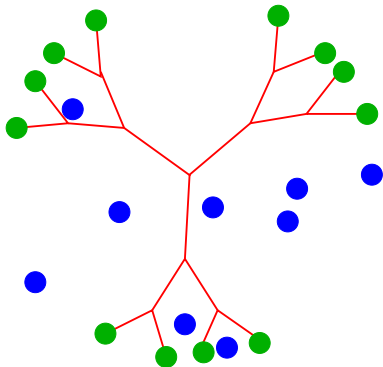
# Introduction: discrete condensing counter-ions

Related to ideas by Aurenzoni et al. *Eur. Phys. J B* (1999)



Condensed charge, valence 2

Dendrimer without a linear charge:



# The model

Work done with Thomas Vilgis, Max-Planck-Institut für Polymerforschung, Mainz.

- Fixed sites with labels

$$i \in \{1, \dots, N\} \text{ with positions } \{\mathbf{r}_1, \dots, \mathbf{r}_N\} \subset \mathbb{R}^3.$$

- Two-state** variables at sites

$$\tau_i = \begin{cases} 1, & \text{counter-ion on site } i \longrightarrow \text{charge at site} = e(1 - z) \\ 0, & \text{no counter-ion on site } i \longrightarrow \text{charge at site} = e \end{cases}, \forall i$$

- Coulomb interaction  $q_i \times q_j \frac{1}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|}$ .
- Partition function** for counter-ions condensing at the sites

$$Z(\{\mathbf{r}_i\}) = \sum_{\{\tau_i\}} \exp(-\beta H(\{\tau_i\}))$$

$$\text{with } -\beta H(\{\tau_i\}) = \mu \sum_{i=1}^N \tau_i - \ell_B \sum_{i < j} (1 - z\tau_i)(1 - z\tau_j) V_{ij}.$$



# Effective potential

Interaction potential may be expanded in a systematic, virial technique.

$$Z = Z_\mu \exp \left\{ \sum_{i < j} \left[ -\tilde{V}_{ij} + \ln \left( 1 + \overset{\text{solid}}{\underset{i}{\bullet}} \overset{\text{solid}}{\underset{j}{\bullet}} + \overset{\text{dashed}}{\underset{i}{\circ}} \overset{\text{dashed}}{\underset{j}{\circ}} + \overset{\text{solid-dashed}}{\underset{i}{\bullet}} \overset{\text{dashed}}{\underset{j}{\circ}} \right) \right] \right. \\ \left. + \sum_{i < j < k} w_{ijk}^{(3)} \right\}$$

The **effective potential**

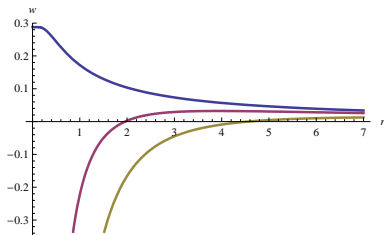
$$w_{ij}^{(2)} \equiv \tilde{V}_{ij} - \ln \left[ (1-f)^2 + 2f(1-f)e^{z\tilde{V}_{ij}} + f^2 e^{-(z^2-2z)\tilde{V}_{ij}} \right]$$



# Effective potential (2)

- Limiting behaviour

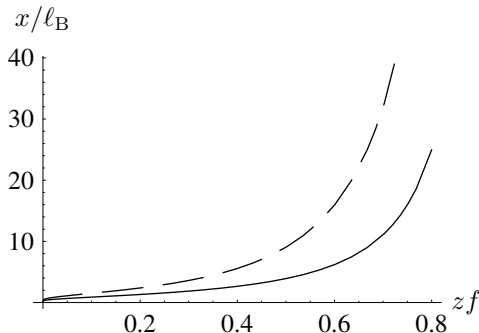
$$w^{(2)}(r) = \frac{1}{2} - \ln \left[ (1-f)^2 + 2f(1-f)e^{z/r} + f^2 e^{(-z^2+2z)/r} \right]$$
$$\approx \begin{cases} \frac{(1-zf)^2}{r}, & r \text{ large} \text{ — repulsion} \\ \frac{1-z}{r} - \delta_{z,1} \ln(2f-f^2) & r \text{ small} \text{ — attraction for } z > 1 \end{cases}$$



blue — monovalent  
purple — divalent  
brown — trivalent



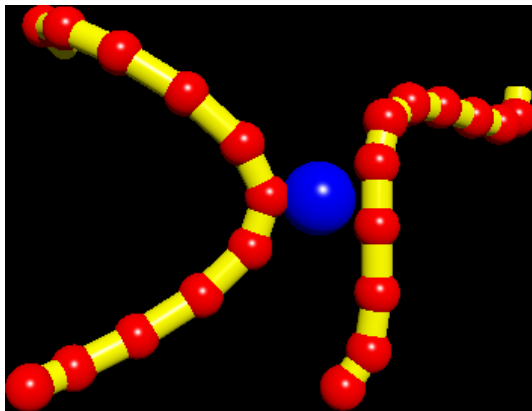
# Effective potential (3)



**Figure:** Where the sign changes as a function of **distance** and **neutralized charge** (in noninteracting system).  $\frac{\partial w_{ij}^{(2)}}{\partial x} = 0$  indicating crossover for 2nd virial contribution from repulsion at large distances to attraction at closer distances;  $z > 1$ . Dashed line: trivalent case. Solid line: divalent case.  $zf = 1$  neutrality in *non-interacting* system.



# Reversible networking

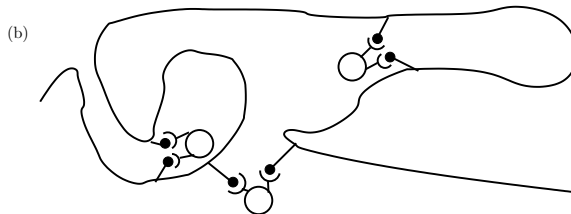
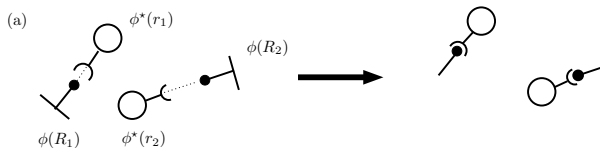


- Kornyshev & Leikin *PRL* 1999 — zipping of DNA
- Salt bridges
- Also suggested by experiments (Dubois & Boué; Zhang)



# Networking by means of crosslinkers

- crosslinkers — with some functionality
- places where they can stick



# Basic model

- **Reversible** networking, with **crosslinkers** as the high valence counter-ion.
- Competition
  - Crosslink reduces translational freedom of polymer chains
  - Potentially is of energetic advantage
  - However closer chains also bring about energetic penalty (like charges). However, with the condensation renormalising the charge and the much weakened interactions, this can become feasible.
- Need a suitable formalism: Edwards developed a field theory formulation for polymer networks: linking by cross-linkers of some functionality. *J Phys France* (1988)

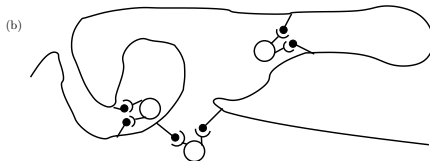
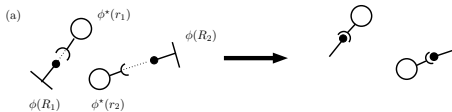




# Counting the number of ways in which one can link

Based on two Gaussian field and appropriate grouping. Produces crosslinkers and we do the “statistical physics thing” by counting all the possible ways to do this via the field theory

$$\mathcal{N}'' \int [d\phi] [d\phi^*] \left\{ \prod_i^M \phi(\mathbf{R}_i) \right\} \left[ \int d^3r (\phi^*(\mathbf{r}))^f \right]^{M'} \exp \left( - \int \phi \phi^* \right).$$



# The model

- Take **polymer** and **counter-ions** with **Coulomb** interaction

$$Z(\{\mathbf{R}_i\}) = \frac{1}{M!} \int d^3r_1 \dots d^3r_M \int [d\psi] \exp \left\{ +\frac{1}{2\ell_B} \int d^3r \psi(\mathbf{r}) \nabla^2 \psi(\mathbf{r}) - i \sum_{i=1}^N \psi(\mathbf{R}_i) + iz \sum_{j=1}^M \psi(\mathbf{r}_j) \right\}$$

- A model for the polymer

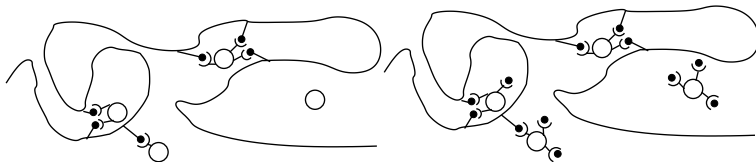
$$P(\mathbf{R}_i) = G(\mathbf{R}_1, \mathbf{R}_2) G(\mathbf{R}_2, \mathbf{R}_3) \dots G(\mathbf{R}_{N-1}, \mathbf{R}_N).$$

- Allow for linking (there are some options here)



# Linking options

- with different functionality
- with caps



# Grand canonical partition function

The following partition function now applies

$$\begin{aligned}
 Z_{||} &= \frac{\mathcal{N}}{M!} \int [d\phi] [d\phi^*] [d\psi] d^3 R_1 \dots d^3 R_M \\
 &\quad (1 + \phi(\mathbf{R}_1)) e^{-i\psi(\mathbf{R}_1)} G(\mathbf{R}_1, \mathbf{R}_2) (1 + \phi(\mathbf{R}_2)) e^{-i\psi(\mathbf{R}_2)} G(\mathbf{R}_2, \mathbf{R}_3) \times \dots \\
 &\quad \times \left( \int d^3 r (\phi^*(\mathbf{r}))^z e^{iz\psi(\mathbf{r})} \right)^M e^{\int d^3 r \phi(\mathbf{r})} \\
 &\quad \times \exp \left[ +\frac{1}{2} \int d^3 r \psi(\mathbf{r}) \nabla^2 \psi(\mathbf{r}) - \int d^3 r \phi(\mathbf{r}) \phi^*(\mathbf{r}) \right].
 \end{aligned}$$

In the grand canonical formalism for the counter-ions

$$\begin{aligned}
 \Xi_{||} &= \int [d\phi] [d\phi^*] [d\psi] \left\{ \prod d^3 R \right\} \left\{ \prod G \right\} \\
 &\quad \times \exp \left\{ + \int \phi - i \int \psi \rho + \int \rho \ln(1 + \phi) - \int \phi \phi^* + \frac{1}{2} \int \psi \nabla^2 \psi + \int e^{iz\psi} \phi^{*z} \right\} \\
 &= \int [d\phi] [d\phi^*] [d\psi] \left\{ \prod d^3 R \right\} \left\{ \prod G \right\} \exp \{ +\mathcal{F}_{||}[\phi, \phi^*, \psi] \}
 \end{aligned}$$



# Saddle point approximation

Determine saddle point

$$\left. \frac{\delta \mathcal{F}_{II}}{\delta \phi(\mathbf{x})} \right|_{\bar{\phi}, \bar{\phi}^*, \bar{\psi}} = 0, \quad \left. \frac{\delta \mathcal{F}_{II}}{\delta \phi^*(\mathbf{x})} \right|_{\bar{\phi}, \bar{\phi}^*, \bar{\psi}} = 0 \quad \text{and} \quad \left. \frac{\delta \mathcal{F}_{II}}{\delta \psi(\mathbf{x})} \right|_{\bar{\phi}, \bar{\phi}^*, \bar{\psi}} = 0.$$

such that

$$\begin{aligned} \frac{\rho}{1 + \bar{\phi}} + 1 &= \bar{\phi}^* \\ z_3 e^{iz\bar{\psi}} \bar{\phi}^{*z-1} &= \bar{\phi} \\ -i\rho + iz_3 e^{iz\bar{\psi}} \bar{\phi}^{*z} + \nabla^2 \bar{\psi} &= 0 \quad (\text{Poisson-Boltzmann of sorts}) \end{aligned}$$

A little rearrangement of “Poisson-Boltzmann”-like term

$$-i \left( \frac{1}{1 + \bar{\phi}} \right) \rho + i\bar{\phi} + \nabla^2 \bar{\psi} = 0.$$

— a bulk contribution and renormalisation of polymer charge.



# Monovalent solution

- Linearise Poisson-Boltzmann equation (remember this gives a screened interaction in general — also here)
- Substitute, keep terms quadratic in  $\rho$
- Effective polymer-polymer interaction term

$$-\frac{1}{2} \int \frac{\rho}{1+\zeta} V_{\text{DH}} \frac{\rho}{1+\zeta}$$

- We find: charge renormalised and screened interaction



# Divalent solution

- Two solutions of fields, one is physical.
- Linearise as before
- Substitute
- Effective polymer-polymer interaction term

$$\int \rho \left[ \frac{z}{(1+2z)^2} - \frac{1}{2} \left( \frac{1-2z}{1+2z} \right)^2 V_{\text{DH}} \right] \rho.$$

- We find: charge renormalised, screened interaction **and short-ranged attraction**
- counter-ion density profile more subtle



# Quadratic fluctuations, $z = 2$

- Quadratic fluctuations  $\Delta\phi$ ,  $\Delta\phi^*$  and  $\Delta\psi$  around  $\bar{\phi}$ ,  $\bar{\phi}^*$  and  $\bar{\psi}$
- Leads to

$$\begin{aligned} \Xi &\approx \int [d\Delta\psi] \exp \left\{ -\frac{1}{2} \text{Tr} \ln \left[ 1 + 2\mathfrak{z} \frac{\rho}{(1+\bar{\phi})^2} e^{2i\bar{\psi}} \right] \right\} \\ &\exp \left\{ -\frac{1}{2} \int \Delta\psi \left[ -\nabla^2 + 4\mathfrak{z}\bar{\phi}^{*2} e^{2i\bar{\psi}} \left( 1 + \frac{4e^{4i\bar{\psi}} \mathfrak{z}^2 (1+\bar{\phi})^2}{2e^{2i\bar{\psi}} \mathfrak{z} \rho + (1+\bar{\phi})^2} \right) \right] \Delta\psi \right\} \end{aligned}$$





# Conclusions and outlook

- Condensation of counter-ions on non-cylindrical objects.
- Self-consistent calculation with fluctuating counter-ion density along chain backbone.
- Discrete model: role of valence becomes very clear.
- Formalism for bridging provides a combination of discrete nature and continuum formalism.
- Field theory allows far more intricate and subtle dependencies on polymer shape to be investigated.
- Other work: counter-ions in restricted geometries around a macro-ion. (With L Boonzaaier, F Scholtz)



# Acknowledgements

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