



**The Abdus Salam  
International Centre for Theoretical Physics**



**2038-6**

**Conference: From DNA-Inspired Physics to Physics-Inspired Biology**

*1 - 5 June 2009*

**Generalizations and ramifications induced by counterion structure in the strong  
and weak-coupling electrostatic interactions between macromolecules**

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# Generalizations and ramifications induced by counterion structure in the strong and weak-coupling electrostatic interactions between macromolecules

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Part of a broader study of image and counterions structure effects.

- M. Kanduč and R. Podgornik: Electrostatic image effects for counterions between charged planar walls, EPJ E - Soft Matter (2007).
- Y. S. Jho, M. Kanduč, A. Naji, R. Podgornik, M. W. Kim, and P. A. Pincus: Strong-Coupling Electrostatics in the Presence of Dielectric Inhomogeneities, PRL 101, 188101 (2008).
- M. Kanduč, A. Naji, Y.S. Jho, P.A. Pincus, R. Podgornik: Role of Multipoles in Counterion-Mediated Interactions between Charged Surfaces: Strong and Weak Coupling (in press 2009).

## Outline:

1. Counterions and condensation of biomolecules
2. Weak and strong ES coupling dichotomy
3. Stiff multipoles with weak and strong ES coupling
4. Flexible polyelectrolytes
5. Polyelectrolyte bridging interactions

# DNA-INSPIRED ELECTROSTATICS

Not just the repository of our genetic information, DNA is also a fascinating, shape-shifting molecule whose behavior in solution counters our intuition and challenges our physical understanding.

William M. Gelbart, Robijn F. Bruinsma, Philip A. Pincus, and V. Adrian Parsegian

## PHYSICS TODAY

SEPTEMBER 2000



DNA-INSPIRED ELECTROSTATICS

### Poisson-Boltzmann Mean-Field Theory of Macro-Ions

Let us approximate the free energy of a solution of macro-ions, counterions, and added salt by the following simple functional of the ion concentrations:

$$F_{\text{FB}}(\{n_i\}) = \int d\mathbf{r} \left\{ \frac{1}{2} \rho^2 \Psi + kT \sum_i n_i \ln(n_i/n_0) \right\}. \quad (1)$$

The second term is the mean-field entropic free energy of the ions, with  $n_i$  being the concentration of the  $i$ th ion species carrying charge  $z_i e$  ( $n_0$  sets the zero of the potential—see the following). The first term is the electrostatic energy, with the charge density  $\rho(\mathbf{r})$  being the sum of charge densities of the macro-ions and the mobile ions:

$$\rho(\mathbf{r}) = \rho_{\text{macro}}(\mathbf{r}) + \sum_i z_i e n_i(\mathbf{r}). \quad (2)$$

The local electrostatic potential is  $\Psi(\mathbf{r})$ . The charge density and the potential are related by Poisson's equation,  $-\nabla^2 \Psi = (4\pi/\epsilon)\rho(\mathbf{r})$ , where  $\epsilon$  is the dielectric constant of the continuum—the aqueous medium in which the ions are dissolved. Minimization of equation 1 with respect to the ion concentrations leads to the condition that they obey the Boltzmann distribution. More explicitly, using Poisson's equation, we obtain the relation

$$\nabla^2 \Psi = -\frac{4\pi e n_0}{\epsilon} \sum_i z_i \exp(-z_i e \Psi / kT) \quad (3)$$

for the potential outside the surface of the macro-ions. This nonlinear differential equation, which is known as the Poisson-Boltzmann (PB) equation, must be solved under the boundary condition (Gauss's law) that the electric field  $\mathbf{E} = -\nabla \Psi$  at the surface of a macro-ion be consistent with its fixed charge density  $\sigma$ . That is,  $-\nabla \Psi = (4\pi/\epsilon)\sigma$ .

The electrostatic self-energy of a macro-ion is computed by inserting the solution of the PB equation into equation 1 for an isolated macro-ion, and then subtracting the free energy with all charges set equal to zero. When this calculation is carried out

for a charged rod, the self-energy is found to be positive; the increase in entropic free energy induced by the confinement of the ions near the rod exceeds the lowering of their electrostatic energy.

The force acting between macro-ions is found by integrating the stress tensor

$$\sigma_{ij} = -kT \left( \sum_i n_i \right) \delta_{ij} + (\epsilon/4\pi)(E_i E_j - (E^2/8)\delta_{ij})$$

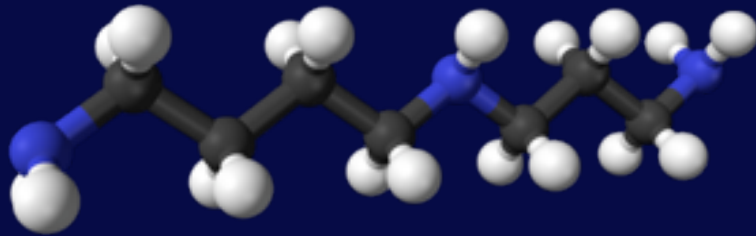
across a surface surrounding each macro-ion. For large distances  $r$ , the dimensionless electrostatic potential  $e\Psi(r)/kT$  in between the macro-ions is small compared to one and the PB equation reduces to the well-known Debye-Hückel (DH) equation:

$$\nabla^2 \Psi = z^2 \kappa^2 \Psi. \quad (4)$$

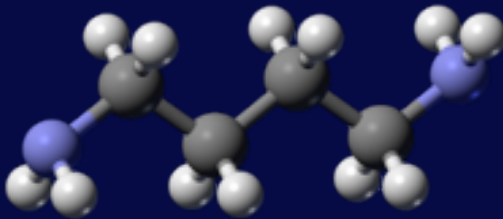
The Debye screening length is  $\kappa^{-1}$  ( $\kappa^2 = 8\pi\lambda_D n_0$ ),  $\lambda_D = e^2/\epsilon kT$  is the Bjerrum length, and  $z$  is the magnitude of the  $z_i$ . It is straightforward to solve equation 4 for two parallel line charges each with a charge per unit length  $\lambda$  and separated by a distance  $r$ . We can then use this solution to compute the force on a rod provided we integrate the stress tensor over a cylindrical surface located outside the rod with a radius big enough compared to  $\kappa^{-1}$  for the DH approximation to be valid. The effective interaction computed in this way is  $V(r) \approx (2\lambda^2/\epsilon)(\pi/2\kappa r)^{1/2} \exp(-\kappa r)$ ,  $\kappa r \gg 1$ . Here,  $\lambda^*$  is an effective or renormalized charge per unit length whose relation to the bare charge density  $\lambda$  must come from a complete solution of the PB equation. For  $b < \lambda_D$ ,  $\lambda^*/\lambda$  is found to equal the Manning-Oosawa parameter  $\xi \equiv \lambda_D/b$  and to equal one otherwise ( $b$  is the distance between fixed charges on the rod). A similar calculation for spherical macro-ions shows that the effective charge  $z^* e$  of an isolated sphere equals the bare charge  $ze$ , consistent with there being no counterion condensation in this case. For any nonzero concentration of spheres, however,  $z^* e$  is of order  $R/\lambda_D$ , with  $R$  being the sphere radius. For charged planar surfaces, on the other hand, the renormalized charge per unit area is effectively zero.



It is also known that DNA condensation is effectively driven by short stiff polyamines such as spermine and spermidine which can be viewed as rodlike ions. In this respect, ion structure is anticipated to play a crucial role in the interactions between charged bodies.



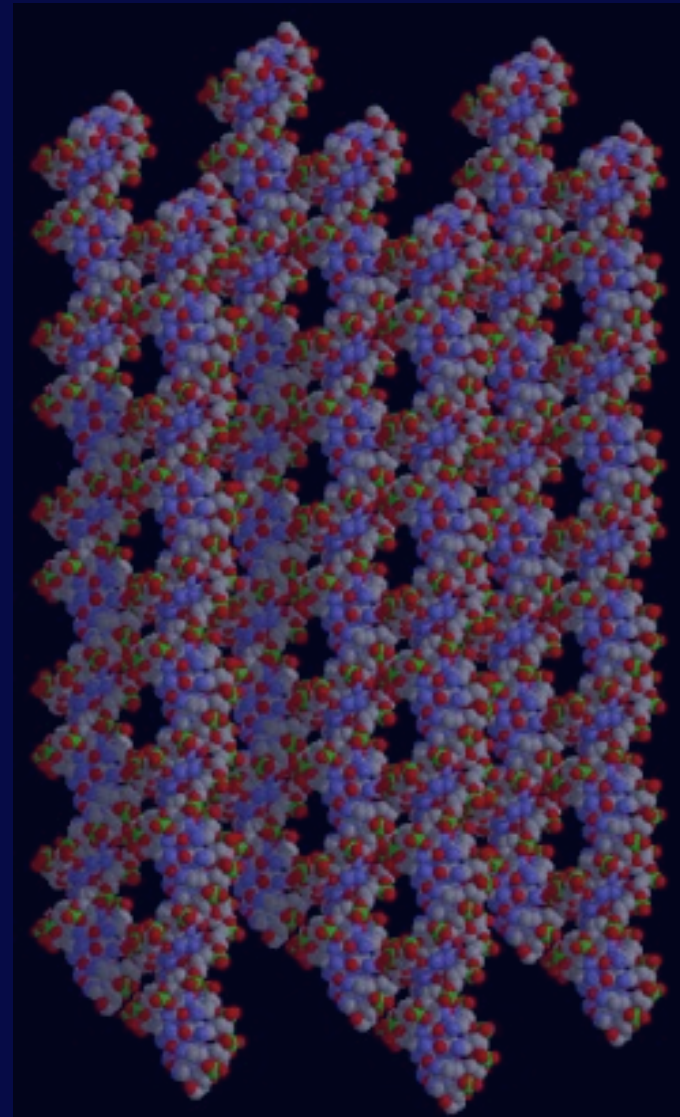
Spermidine (charge 3+)



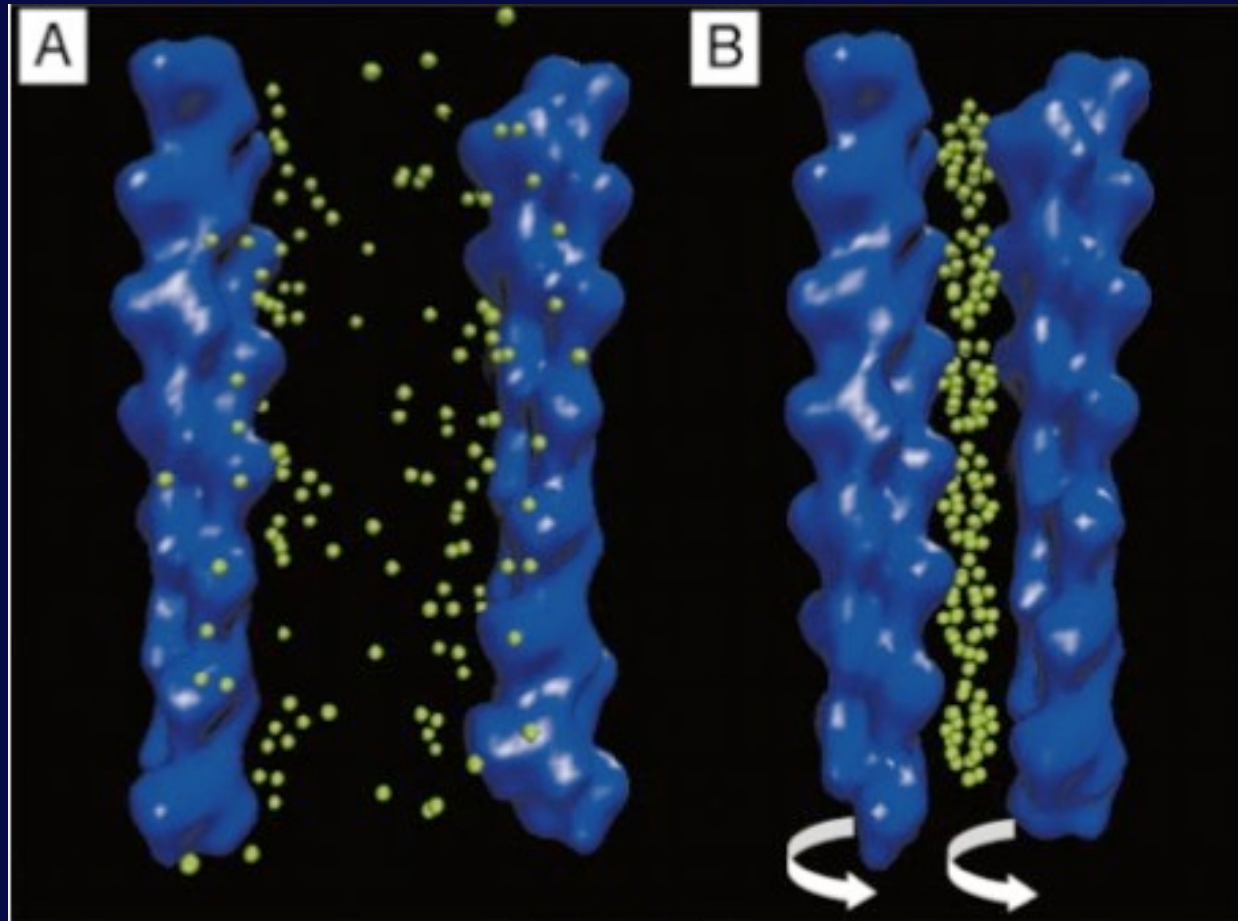
Putrescine (charge 2+)

The DNA-DNA interactions can be measured directly in osmotic stress experiments.

Attraction energies:  
~ 0.1 kT/ base pair.

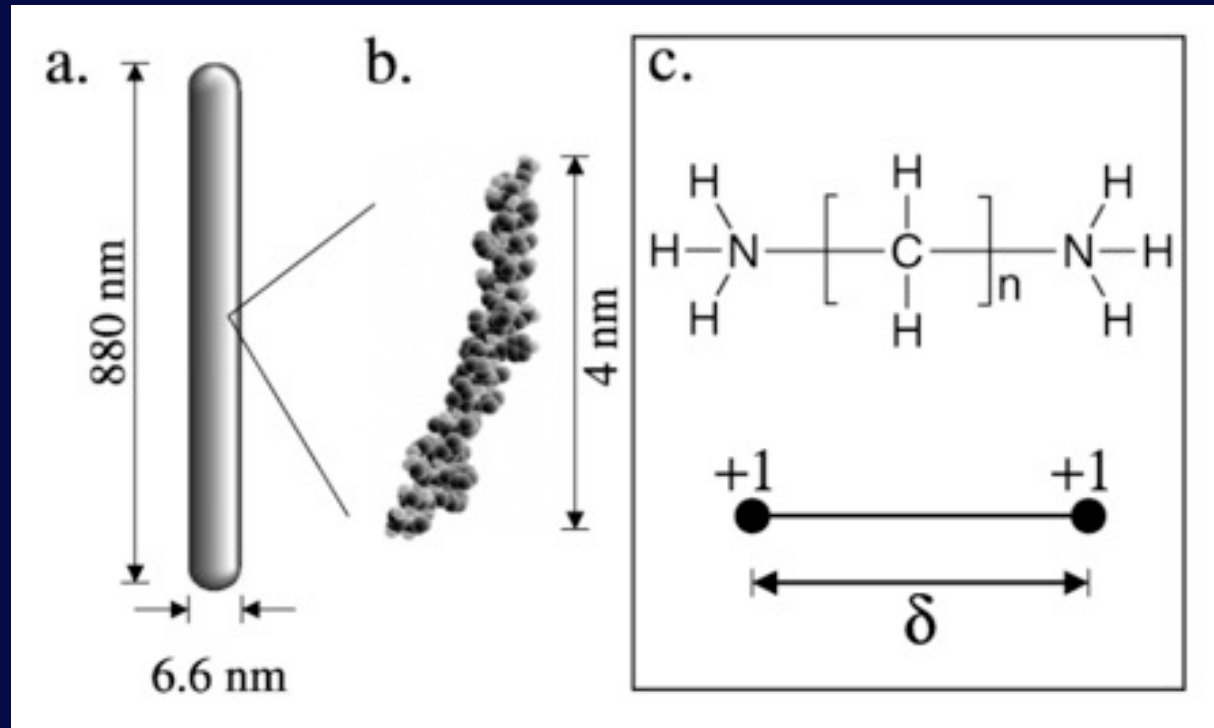


Rau et al., 1997.



Schematic representations of uncondensed and condensed F-actin. (A) At low multivalent ion concentrations, two F-actin filaments maintain their native  $13/6$  symmetry and are unbound. (B) At high multivalent ion concentrations, the ions collectively form a CDW and bundle F-actin filaments. Moreover, the CDW forms a coupled mode with torsional distortions of the F-actin and has overtwisted it by  $3.8^\circ$  per monomer to a new  $36/17$  symmetry.

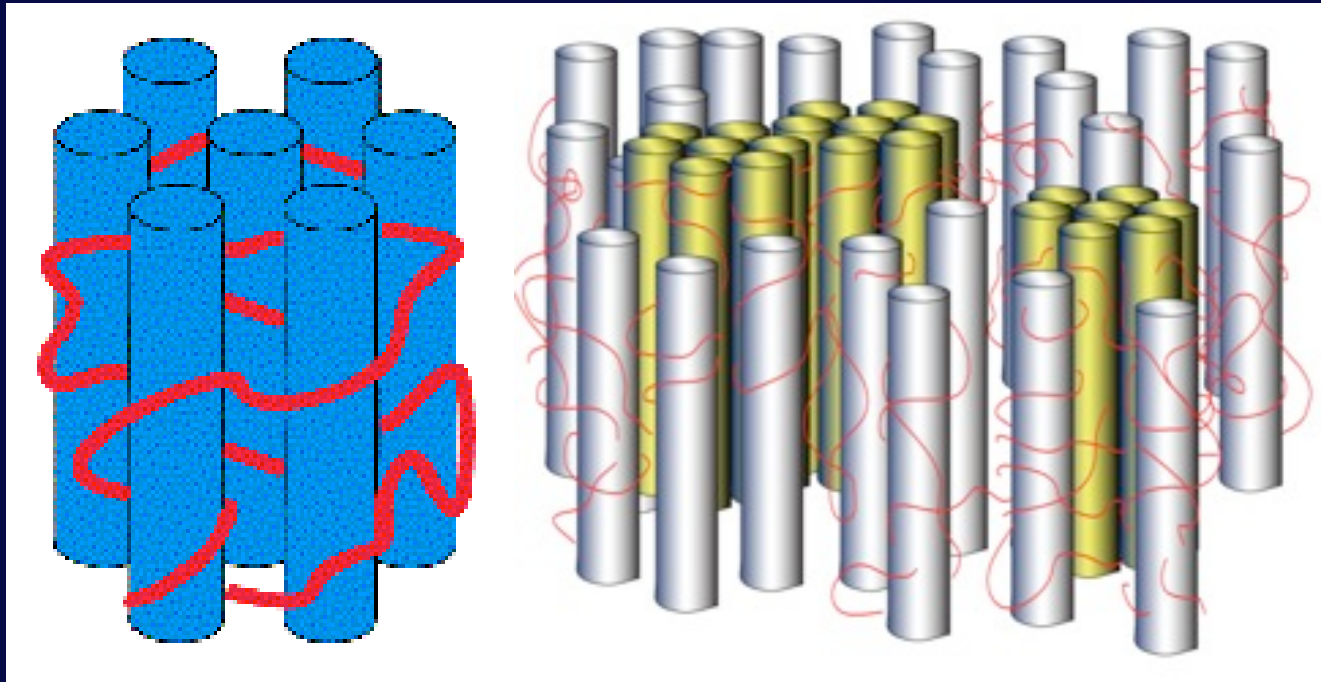
Polyelectrolyte condensation using the anionic rodlike M13 virus, and a series of “tunable” divalent cat ions,  $\text{H}_3\text{N}^+-(\text{CH}_2)_n-\text{NH}_3^+$ , where  $n = 1, 2, 3, 4$ . These diamine ions consist of two amine groups separated by  $n$   $\text{CH}_2$  groups (for  $n = 1$  and  $2$  the size is  $0.29$  and  $0.37$  nm).



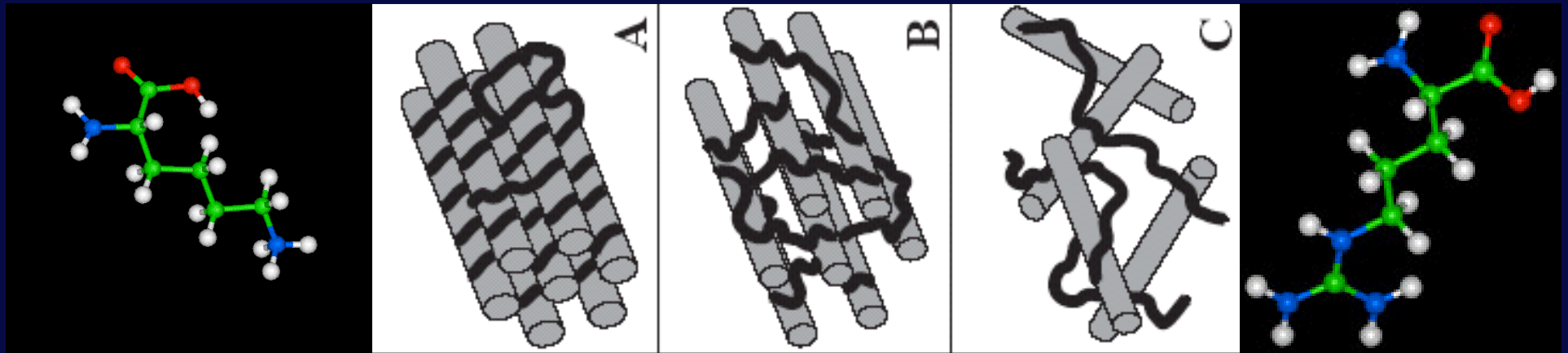
John C. Butler, Thomas Angelini, Jay X. Tang, and Gerard C. L. Wong, PRL 91, 028301-1 (2003).

The surface of each filamentous bacteriophage M13 virus is comprised of approximately 2700 copies of a major coat protein which package the single-stranded circular viral DNA into a rod ( persistence length of 2 microns) with a total length of 880 nm and a diameter of 6.6 nm. This major coat protein is a charged helix consisting of 50 residues, and constitutes the bulk of the total charge on the virus. Smooth charge density compared to other biopolymers such as DNA and F-actin.





Complexes of DNA and cationic PE. poly-L-lysine (PL), poly-L-arginine (PA), spermine (Sp), and linear and branched polyethyleneimine (IPEI and bPEI). SAXS on PL-DNA and PA-DNA. Tight bundle, loose bundle and isotropic. de Rouchey et al. 2004.



# Coulomb and Boltzmann

Bjerrum length

$$\ell_B = e_0^2 / 4\pi\epsilon\epsilon_0 kT.$$

$$V(\mathbf{r}_1, \mathbf{r}_2) = \frac{e_1 e_2}{4\pi\epsilon\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|},$$

Coulomb's law  
and  
kT

Gouy - Chapman length

$$\lambda_{GC} = \frac{2 kT \epsilon\epsilon_0}{e_0 \sigma}.$$

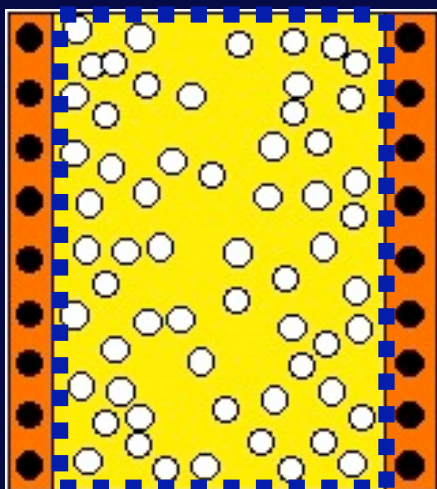
Ratio between the Bjerrum and the Gouy - Chapman lengths. Bulk versus surface interactions.

**Weak coupling limit**  
(Poisson - Boltzmann)  
 $\Xi \rightarrow 0$

Coupling parameter

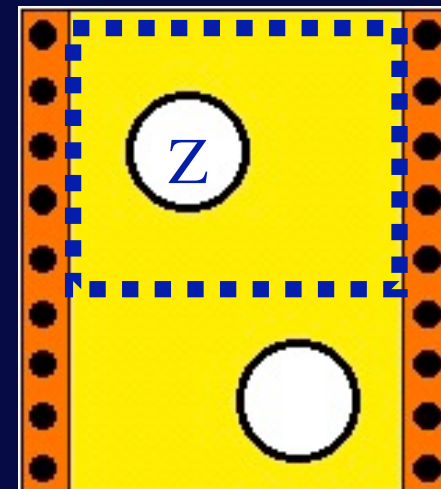
$$\Xi = 2\pi Z^3 \ell_B^2 \sigma$$

**Strong coupling limit**  
(Netz - Moreira)  
 $\Xi \rightarrow \infty$

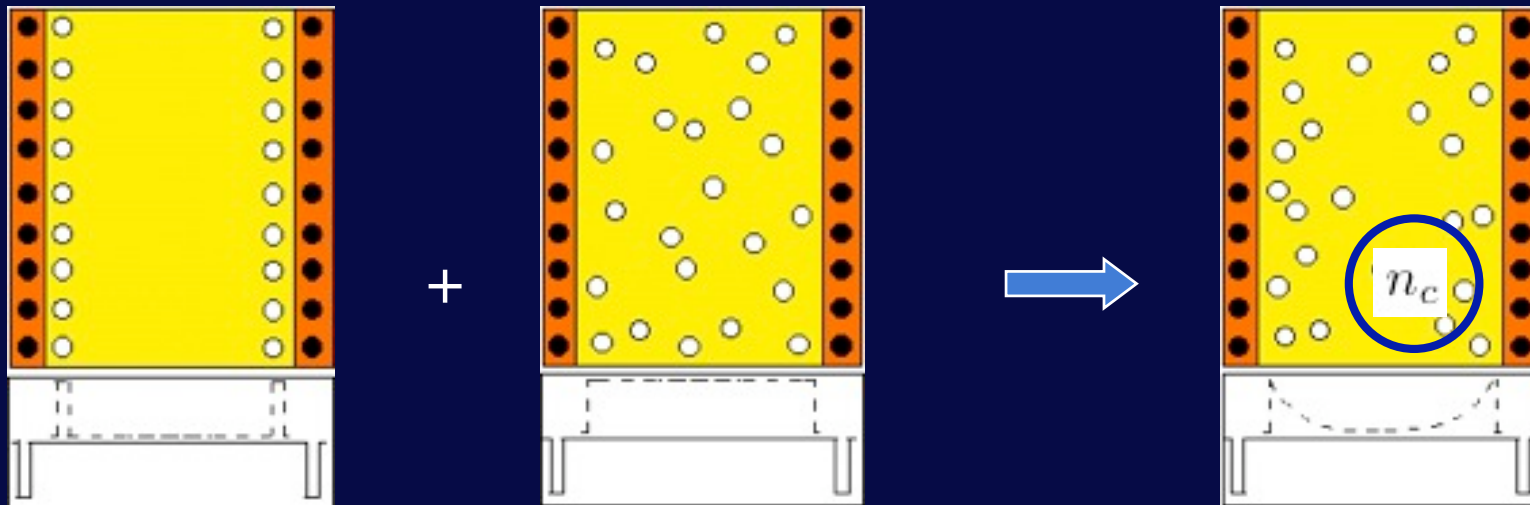


Collective description  
(Poisson - Boltzmann "N" description)  
Screened Debye-Hueckel

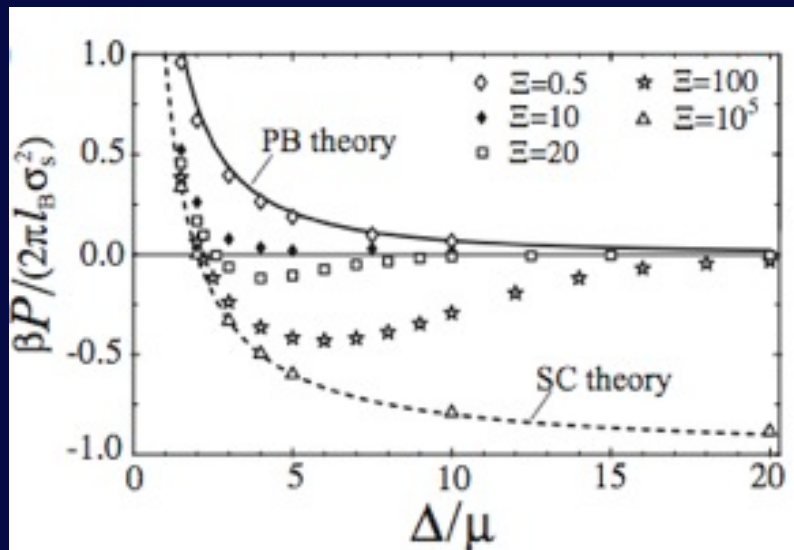
vs.  
Single particle description  
(Strong Coupling "1" description)



# The weak coupling (PB) theory: collective description



Non-equilibrium free energy = (electrostatic energy) - k (ideal gas entropy)

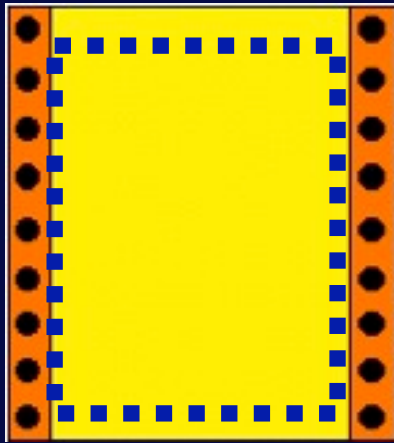


$$\mathcal{F} = \Delta\mathcal{E} - T\Delta\mathcal{S}$$

Electrostatic energy: collaps to the surface  
 Entropy: uniform distribution of charges  
 The two together: non-homogeneous ionic profile

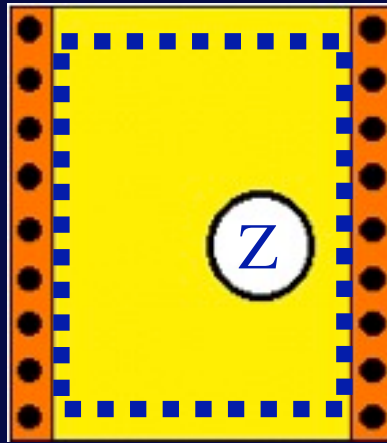
Weak coupling limit = minimization of the collective free energy.

# Strong coupling theory: one particle description



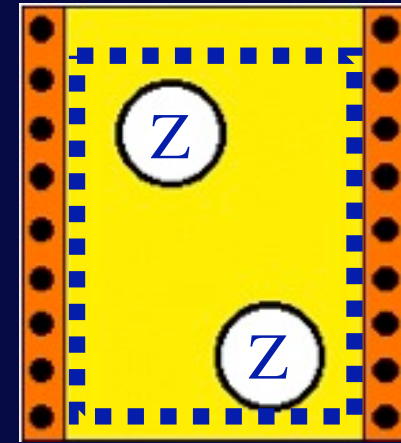
Electrostatic energy without mobile counterions

+



Electrostatic energy of a single counterion

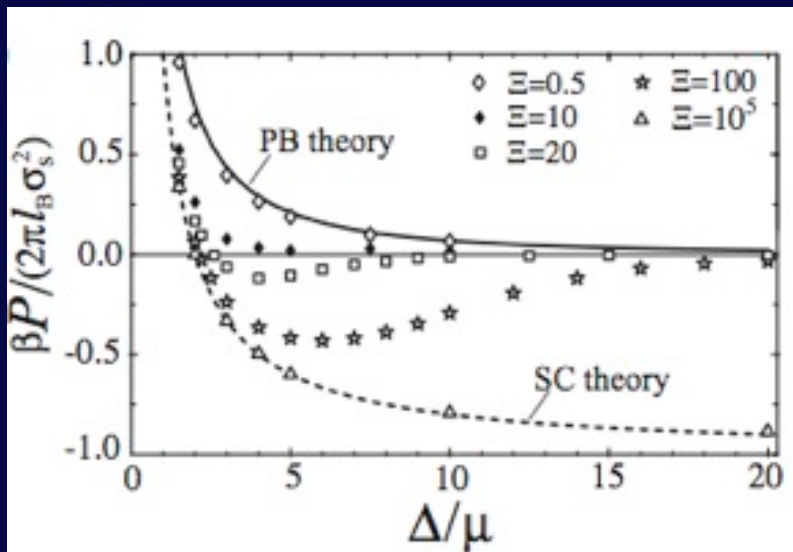
+



Electrostatic energy of two counterions

+

...



Electrostatic energy of a single counterion plus entropy of a trapped counterion.

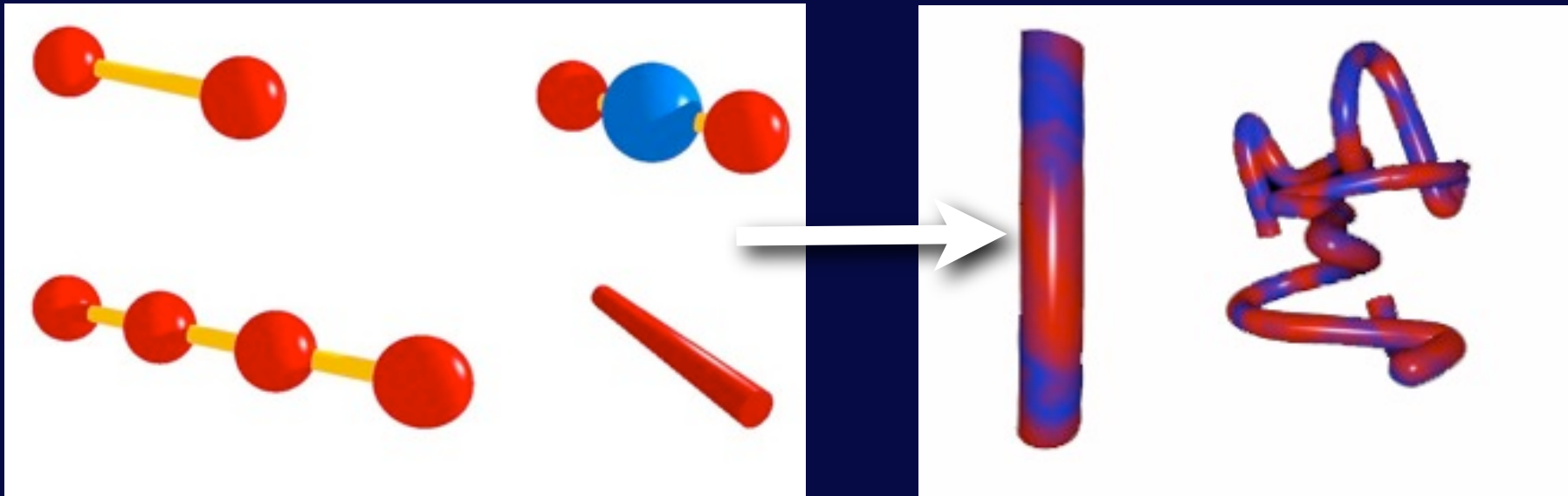
$$\mathcal{F} = \mathcal{E}_0 - kT \Xi N \log \int_{(V)} d^3 \mathbf{r} \exp -\frac{\mathcal{E}_1(\mathbf{r})}{kT}.$$

Netz (2000)

Strong coupling limit = virial expansion to first order.

# Weak and strong coupling theory: multipoles and polyelectrolytes

We investigate completely general distribution of charges in counterions.



From stiff to flexible counterions.

$$\hat{\rho}(\mathbf{r}; \mathbf{R}_i, \boldsymbol{\omega}_i) = e_0 q \delta(\mathbf{r} - \mathbf{R}_i) - p_0 (\mathbf{n}_i \cdot \nabla) \delta(\mathbf{r} - \mathbf{R}_i) + t_0 (\mathbf{n}_i \cdot \nabla)^2 \delta(\mathbf{r} - \mathbf{R}_i) + \dots,$$

When the multipoles become large enough the flexibility effects can not be ignored any more. multipolar effects should merge into polyelectrolyte effects.

Later we will also deal with flexible counterions.

large stiff multipoles



long flexible polyelectrolytes

Both will be analysed.

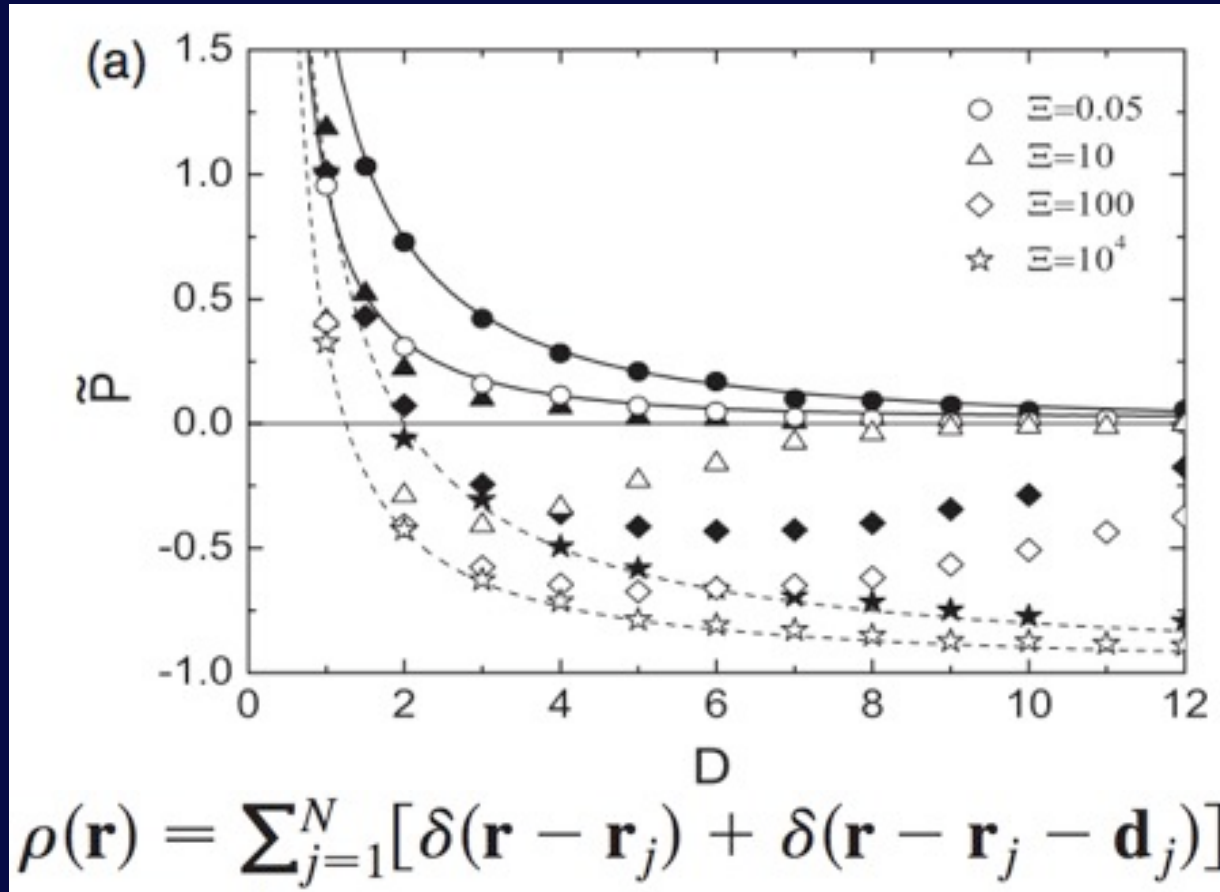


For certain multivalent ions, the separations between charges in an ion are too large to be ignored, leading to breakdown of the pointlike picture of ions assumed in the PB theory.

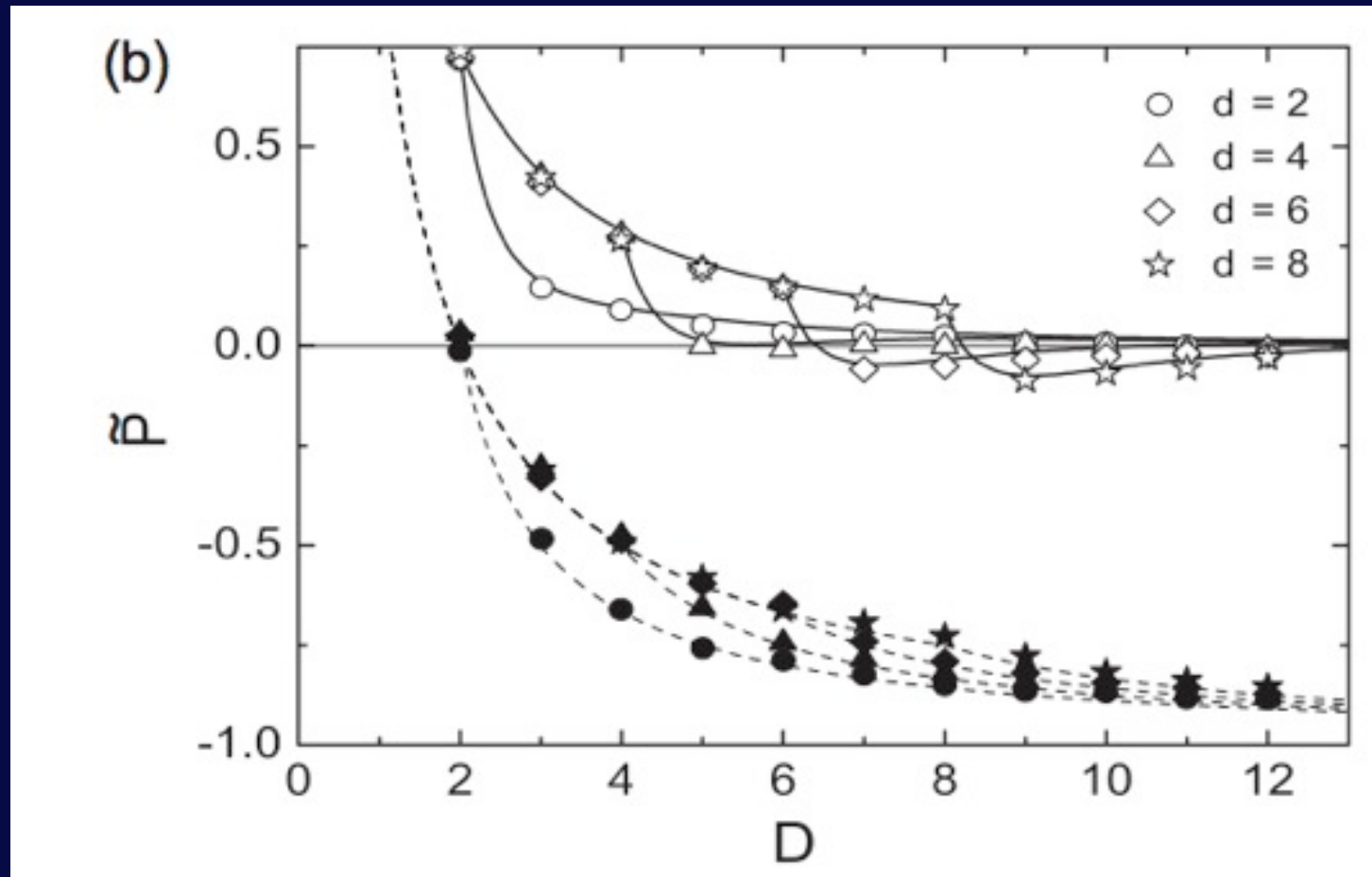
Yong Woon Kim, Juyeon Yi and P. A. Pincus PRL 101, 208305(2008)



Stiff dumbbells.



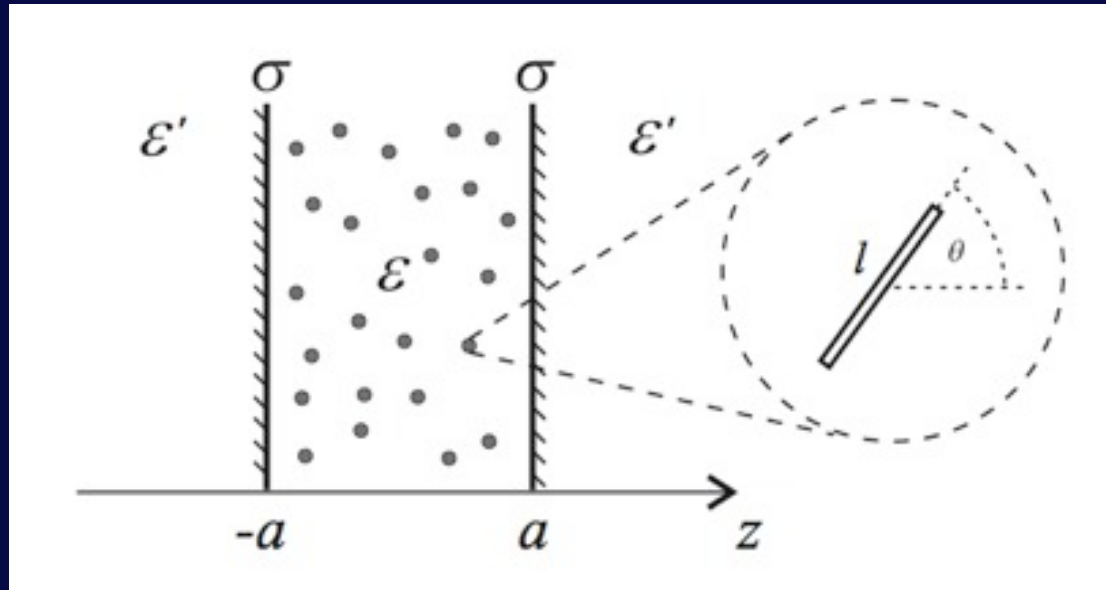
Pressure as a function of the plate separation  $D$  (a) for small dumbbell ions of  $d$  0:5 with various values of  $\Xi$ . Solid and dashed lines denote SC predictions for respective dumbbell sizes. For comparison, pressures for the equivalent system consisting of pointlike ions and having the same surface charge are plotted together in (a): MC simulations (filled symbols), PB (solid), and SC (dashed) solutions.



Pressure as a function of the plate separation  $D$  for large dumbbell ions at  $0.05$  (open symbols) and at  $10^{-4}$  (filled symbols). Solid and dashed lines denote PB and SC predictions for respective dumbbell sizes. For comparison, pressures for the equivalent system consisting of pointlike ions and having the same surface charge are plotted together: MC simulations (filled symbols), PB (solid), and SC (dashed) solutions.

# Multipolar counterions

A reformulation of the model of the electrostatic interactions between (bio)colloids.



Multipole expansion for charge density of pointlike counterions (plus dielectric inhomogeneities):

$$\hat{\rho}(\mathbf{r}; \mathbf{R}_i, \omega_i) = e_0 q \delta(\mathbf{r} - \mathbf{R}_i) - p_0 (\mathbf{n}_i \cdot \nabla) \delta(\mathbf{r} - \mathbf{R}_i) + t_0 (\mathbf{n}_i \cdot \nabla)^2 \delta(\mathbf{r} - \mathbf{R}_i) + \dots,$$

$$t_0 = e_0 q l^2 / 24. \quad (\text{quadrupolar moment for a rod})$$

First part is just the standard primitive model. Point counterions.

Dipolar part: Abrashkin A, Andelman D and Orland H, PRL 99 077801 2007.

Quadrupolar part: Maset S and Bohinc K J. Phys. A 40 11815 2007.

## Interactions and dielectric images.

The interaction potential is:

$$u(\mathbf{r}, \mathbf{r}') = u_0(\mathbf{r}, \mathbf{r}') + u_{\text{im}}(\mathbf{r}, \mathbf{r}').$$

And contains the bare as well as the image contributions due to dielectric inhomogeneity.

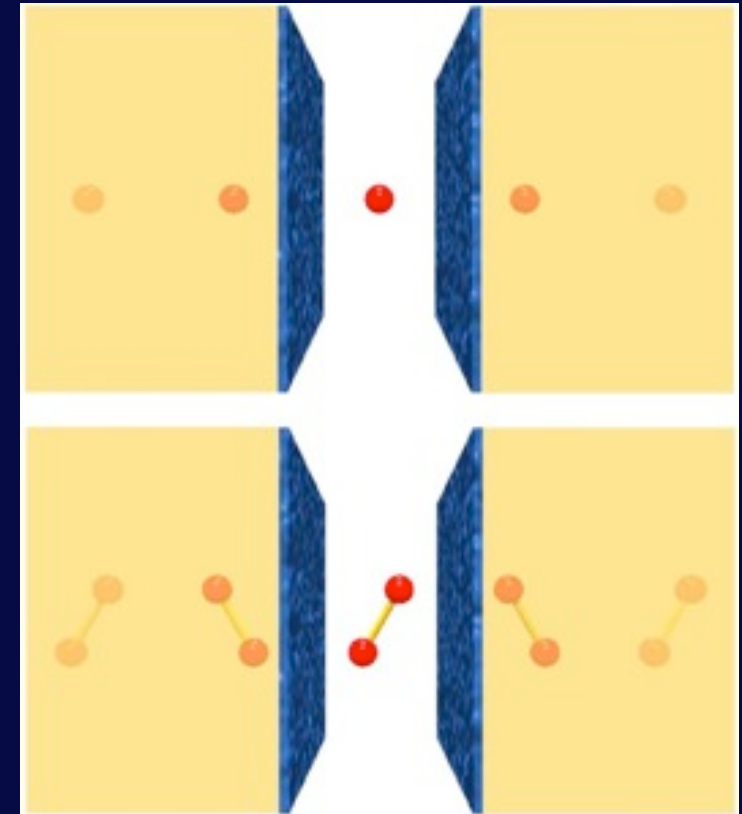
### Planar Green's function.

$$u(\mathbf{r}, \mathbf{r}') = \frac{1}{4\pi\epsilon\epsilon_0} \left[ \sum_{n \text{ even}} \frac{\Delta^{|n|}}{|\mathbf{r}' - \mathbf{r} - 2na \hat{\mathbf{k}}|} + \sum_{n \text{ odd}} \frac{\Delta^{|n|}}{|\mathbf{r}' - \mathbf{r} + (2na - 2z') \hat{\mathbf{k}}|} \right]$$

$$\Delta = (\epsilon - \epsilon') / (\epsilon + \epsilon').$$

The external charge is assumed to be of the form:

$$\rho_0(\mathbf{r}) = \sigma\delta(a - z) + \sigma\delta(a + z).$$



There are two types of effects: those due to the multipolar charge distribution of counterions, the entropy effects of finite size of the counterions, image effects of the dielectric discontinuities in the system.

# The Poisson - Boltzmann theory

The generalized PB equation for the case of counterions with multipolar structure.

$$\psi'' = -\frac{1}{2} \int_{-1}^{+1} dx \Omega(x, z) (u(z) - pxu'(z) + tx^2u''(z)),$$

$$u(z) = C \exp(-\psi - px\psi' - tx^2\psi'')$$

$$p = p_0/e_0q\mu \quad \text{and} \quad t = t_0/e_0q\mu^2,$$

Just as in the standard PB theory there exists a pressure equation  
(first integral of the B equation)

$$\tilde{P} = -\frac{1}{4}\psi'^2 + \frac{1}{4} \int_{-1}^1 dx [u + pxu\psi' + tx^2(u\psi'' - u'\psi')].$$

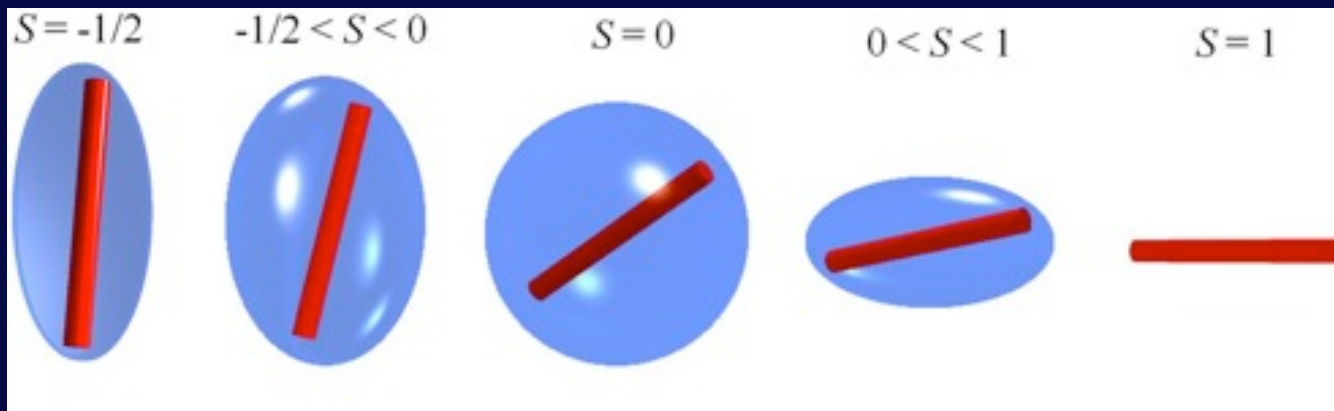
Positional as well as orientational profile:

Orientalional OP.

$$S = \frac{1}{2} (3 \langle x^2 \rangle - 1).$$

$$\langle x^2 \rangle = \frac{\int x^2 u(x) dx}{\int u(x) dx}.$$

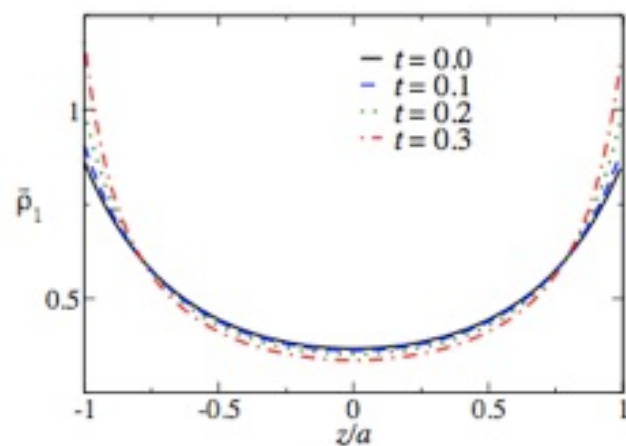
$$x = \cos \theta,$$



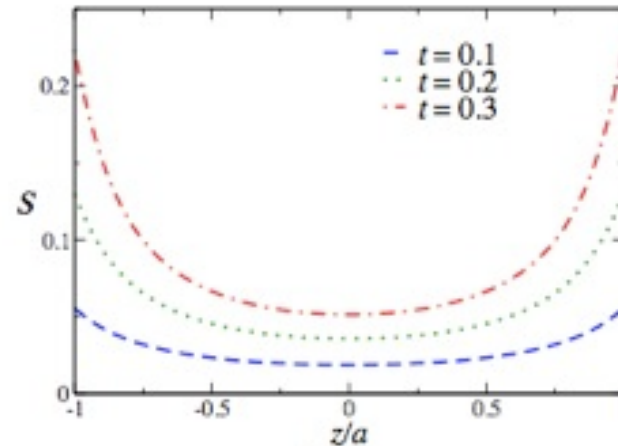


# The Poisson - Boltzmann theory: numerics

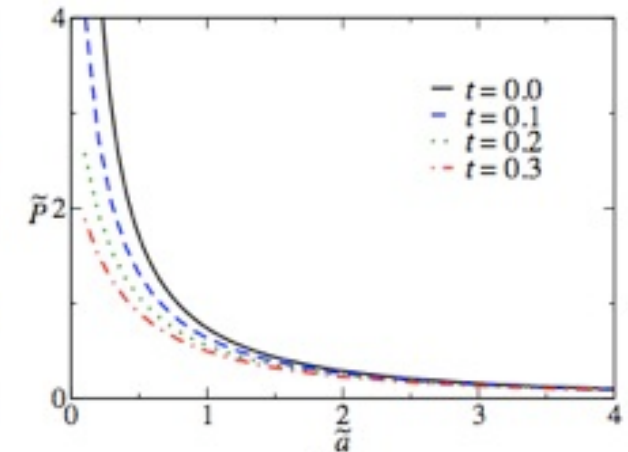
An approximate (perturbation) solution.



(a)



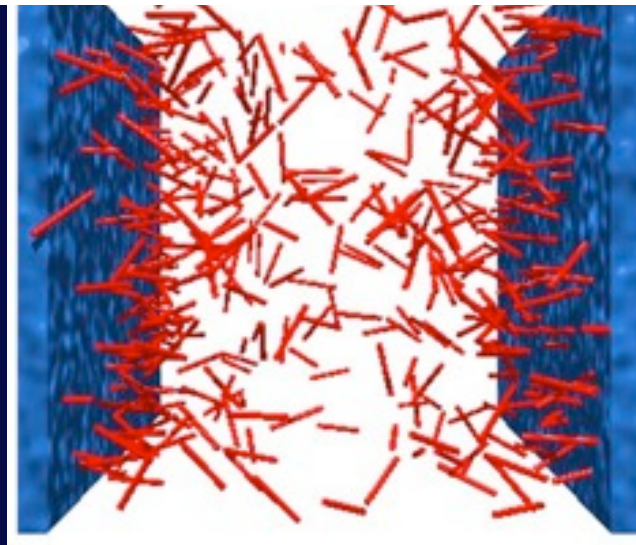
(b)



(c)

Mean-field results for various  $t$  in first-order approximation.

(a) Counterion density profile. By increasing  $t$  in the mean-field limit counterions are depleted from the center toward both surfaces. (b) Order parameter profile.



(c) Dimensionless pressure-distance curves obtained from the first-order approximation. Quadrupolar contributions are attractive. No image effects! (planar geometry)

This is all for point quadrupoles. Thus only multipolar and not steric and entropic effects which are easy to understand in terms of bridging and steric hindrance (Maset S and Bohinc K J. Phys. A 40 11815 2007).

## The strong coupling theory

The free energy for multipoles with dielectric images derived exactly.

$$\tilde{F}/\tilde{A} = 2\tilde{a} - 2 \ln \int_{-\tilde{a}}^{\tilde{a}} d\tilde{z} \int_{-1}^1 dx \exp\left(-\sum_{i=1}^9 \tilde{w}_i(\tilde{z}, x)\right).$$

$$\tilde{w}_1(\tilde{z}, x) = \frac{1}{2}\Xi \sum_{n \text{ odd}} \frac{n\tilde{a}\Delta^n}{(n\tilde{a})^2 - \tilde{z}^2} - \frac{\Xi}{4\tilde{a}} \ln(1 - \Delta^2),$$

$$\tilde{w}_2(\tilde{z}, x) = \frac{1}{2}\Xi p x \tilde{z} \sum_{n \text{ odd}} \frac{n\tilde{a}\Delta^n}{[(n\tilde{a})^2 - \tilde{z}^2]^2},$$

$$\tilde{w}_3(\tilde{z}, x) = -\frac{1}{8}\Xi t(1 - 3x^2) \left\{ \sum_{n \text{ even}} \frac{\Delta^n}{(n\tilde{a})^3} + \sum_{n \text{ odd}} n\tilde{a} \frac{(n\tilde{a})^2 + 3\tilde{z}^2}{[(n\tilde{a})^2 - \tilde{z}^2]^3} \Delta^n \right\},$$

$$\tilde{w}_5(\tilde{z}, x) = \frac{1}{8}\Xi p^2 \left\{ (1 - 3x^2) \sum_{n \text{ even}} \frac{\Delta^n}{(n\tilde{a})^3} + (1 + x^2) \sum_{n \text{ odd}} n\tilde{a} \frac{(n\tilde{a})^2 + 3\tilde{z}^2}{[(n\tilde{a})^2 - \tilde{z}^2]^3} \Delta^n \right\},$$

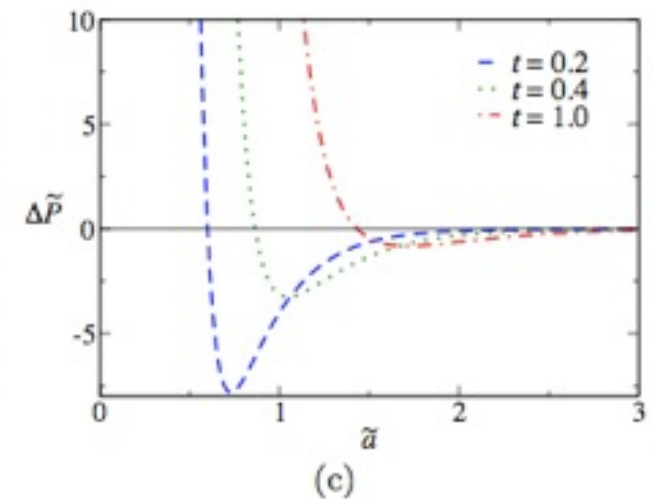
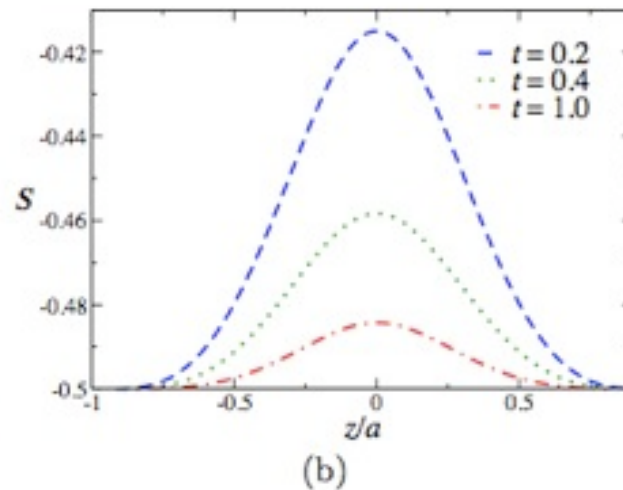
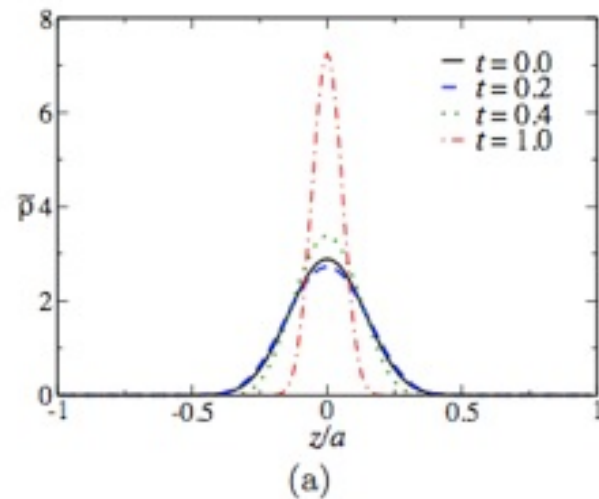
$$\tilde{w}_6(\tilde{z}, x) = \frac{3}{4}\Xi p t(1 + x^2)x \tilde{z} \sum_{n \text{ odd}} n\tilde{a} \frac{(n\tilde{a})^2 + \tilde{z}^2}{[(n\tilde{a})^2 - \tilde{z}^2]^4} \Delta^n,$$

$$\tilde{w}_9(\tilde{z}, x) = \frac{3}{32}\Xi t^2 \left\{ (3 - 30x^2 + 35x^4) \sum_{n \text{ even}} \frac{\Delta^n}{(n\tilde{a})^5} + (3 + 2x^2 + 3x^4) \sum_{n \text{ odd}} n\tilde{a} \frac{(n\tilde{a})^4 + 10(n\tilde{a}\tilde{z})^2 + 5\tilde{z}^4}{[(n\tilde{a})^2 - \tilde{z}^2]^5} \Delta^n \right\}.$$

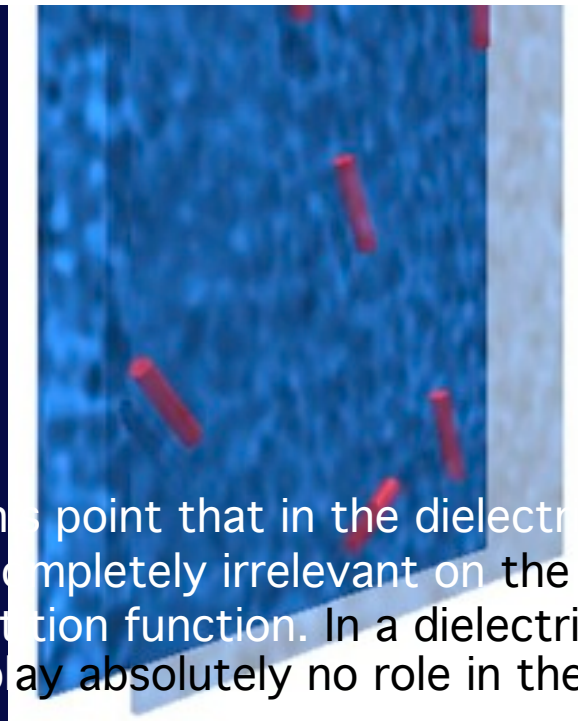
Without the images higher order multipoles thus make NO direct contribution to the strong coupling interaction free energy or forces between the bounding charged surfaces without dielectric inhomogeneities!

# The strong coupling theory: numerics

An exact solution.



Strong coupling results for  $\Xi=50$  and  $\Delta=0.95$  and various  $t$ . (a) Counterion density profile. (b) Order parameter profile. Counterions are less ordered at the center. Order is increased with increasing  $t$ .

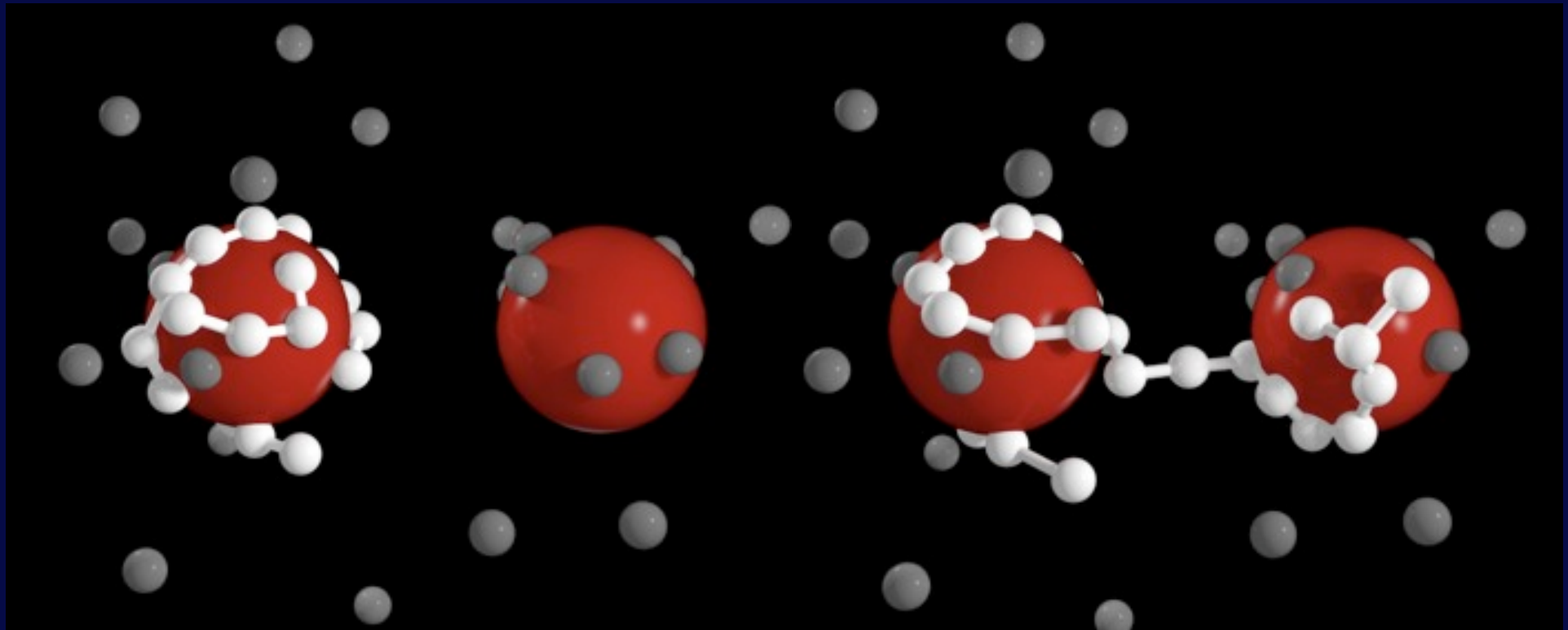


(c) Quadrupolar pressure difference. Contribution is repulsive at small separations and becomes attractive at larger separations. At very large separations it goes to zero.

Thus one can conclude at this point that in the dielectrically homogeneous case the higher order multipoles are completely irrelevant on the SC level. Only the monopolar term survives in the partition function. In a dielectrically homogeneous case multipolar moments play absolutely no role in the strong coupling limit!

# Polyelectrolyte bridging

Definition of polyelectrolyte bridging interactions. Flexible counterions.



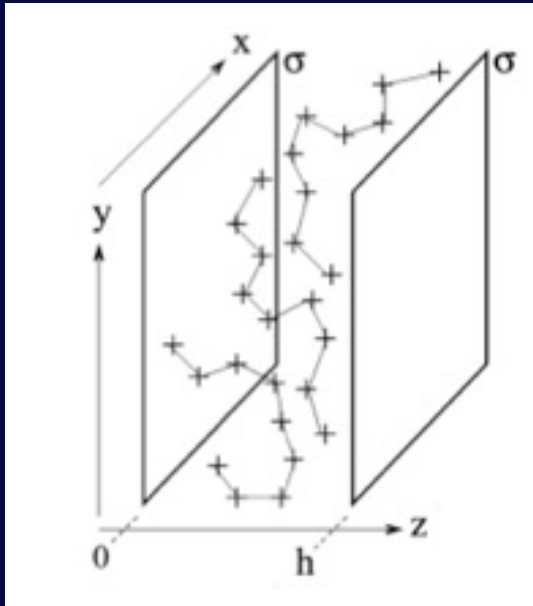
Electrostatic interactions effect  
polymer **structural parameters**  
(persistence length, stretching modulus)  
as well as **conformations**  
(DNA condensation).

**Polyelectrolyte bridging:**  
a case of coupling between  
conformations and interactions.

Podgornik and Licer (2007)

Model system: a charged flexible chain  
and oppositely charged macroions.

# Polyelectrolyte chain between charged surfaces



M. Turesson

On large lengthscales the mesoscopic Hamiltonian can be taken as Edwards model (flexible chain) plus electrostatic interactions.

$$\mathcal{H}[\mathbf{r}(s), \mathbf{r}_i] = \frac{3}{2\ell} \int_0^L \dot{\mathbf{r}}(s)^2 ds + \frac{1}{2} \int_0^L \int_0^L V(|\mathbf{r}(s) - \mathbf{r}(s')|) ds ds'$$

Chain entropy

Chain interactions

$$L = N\ell.$$

$$V(\mathbf{r}_1, \mathbf{r}_2) = \frac{e_1 e_2}{4\pi\epsilon\epsilon_0|\mathbf{r}_1 - \mathbf{r}_2|},$$

The WC limit in this case should lead to a form of the PB equation. The polyelectrolyte PB equation (PEPB). What is it?

$$-\epsilon\epsilon_0 \nabla^2 \phi = e_0 n_0 e^{-\frac{e_0 \phi}{kT}}.$$

$$\epsilon\epsilon_0 \frac{\partial \phi}{\partial \mathbf{n}} + \sigma = 0.$$

The standard PB equation for mobile counterions. Is it changed?



# Polyelectrolyte Poisson - Boltzmann theory

The Poisson - Boltzmann equation for PE.  
Boltzmann distribution is modified by the connectivity of the polycounterion.

$$-\epsilon\epsilon_0 \nabla^2 \phi = \rho_\phi = \langle \exp(-\beta e_\tau \phi) \rangle$$

vs.

$$-\epsilon\epsilon_0 \nabla^2 \phi = e_0 n_0 e^{-\frac{e_0 \phi}{kT}}.$$

Polyelectrolyte PB equation (Podgornik, 1990. Akesson et al. 1989.)  
Connectivity implies the Edwards equation for the monomer density field.

Monomer density.

$$\rho_\phi(\mathbf{r}) = e_\tau \psi(\mathbf{r})^2$$

... that satisfies ...

Edwards equation.

$$\left[ \frac{\ell^2}{6} \nabla^2 + (E_N - \beta e_\tau \phi) \right] \psi(\mathbf{r}) = 0.$$

Ground state dominance ansatz for long chains  $N \gg 1$ .

$$\mathcal{G}_\phi(\mathbf{r}, \mathbf{r}'; N) = \psi(\mathbf{r})\psi(\mathbf{r}') e^{-E_N N}$$

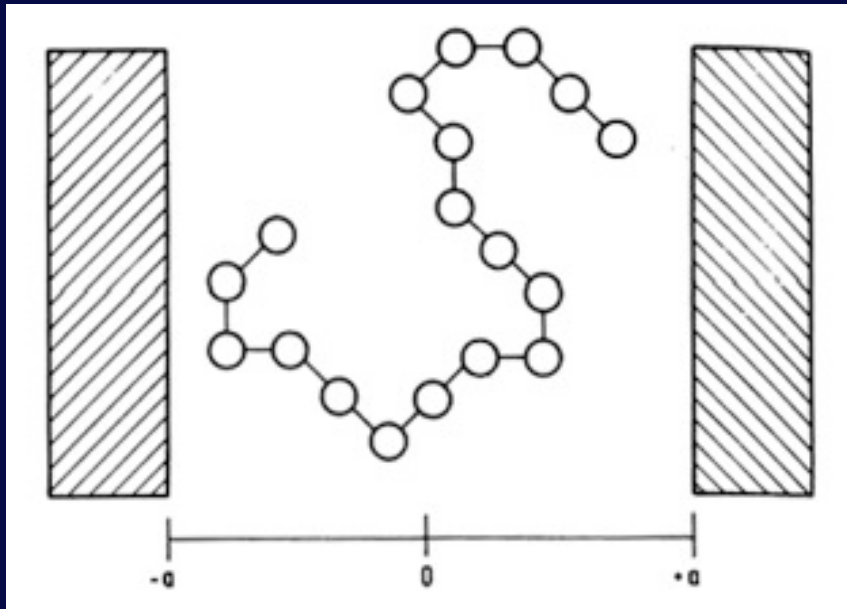
Only the first term in eigenfunction expansion.

$$\mathcal{F} \cong k_B T E_0 N.$$

Free energy.

# Polyelectrolyte Poisson - Boltzmann theory: explicit formulation

Combination of the standard PB equation and the Edwards equation of polymer statmech.



$$\epsilon\epsilon_0 \frac{d^2\phi(z)}{dz^2} + e_\tau \psi(z)^2 = 0.$$

$$\frac{\ell^2}{6} \frac{d^2\psi(z)}{dz^2} + (E_N - \beta e_\tau \phi) \psi(z) = 0.$$

A **coupled** set of two equations.

Podgornik 1991, Varoqui 1993,  
Chattelier and Joanny, 1996, Borukhov et al.  
1998

$$\lambda_B = \frac{24\pi\ell_B e_\tau \sigma}{e_0^2 \ell^2} \longrightarrow \lambda^{1/3} a = \frac{a}{a_0} = \Xi.$$

Polyelectrolyte Poisson - Boltzmann equation.

$$\epsilon\epsilon_0 \frac{d\phi(z = -a)}{dz} = \sigma \quad \epsilon\epsilon_0 \frac{d\phi(z = 0)}{dz} = 0.$$

$$\int_{-a}^{+a} dz \psi^2(z) = \frac{N}{S}.$$

Boundary condition, symmetry condition (just like PB) plus total number of polymer units.

# Single polyelectrolyte chain: solutions

Can be done explicitly and analytically.

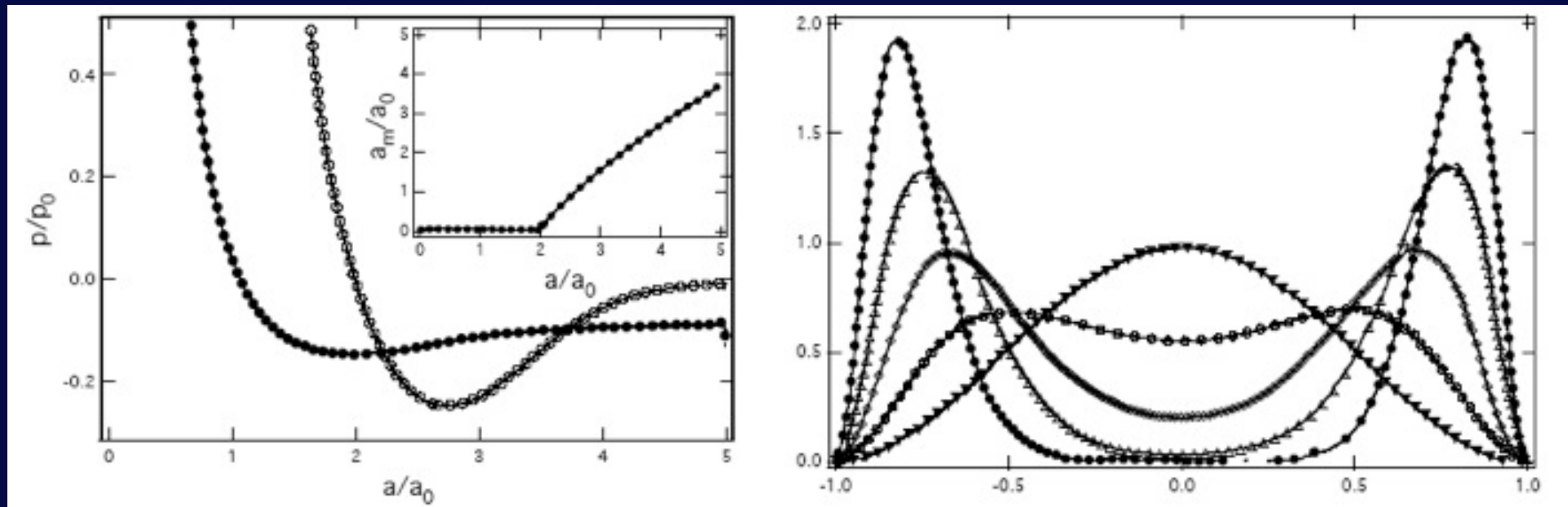
Small separation limit:

$$E_N = \frac{\ell^2}{6} \left( \left( \frac{\pi^2}{2a} \right)^2 + \frac{1}{2} \lambda_B a \right)$$

Large separation limit:

$$E_N = \frac{\ell^2}{6} \left( -\lambda_B^{1/3} a + ai_0 - \frac{1}{2} C(ai_0) \exp\left(-\frac{4}{3} \sqrt{\lambda_B a^3}\right) \right)$$

Interaction pressure and monomer density distribution.

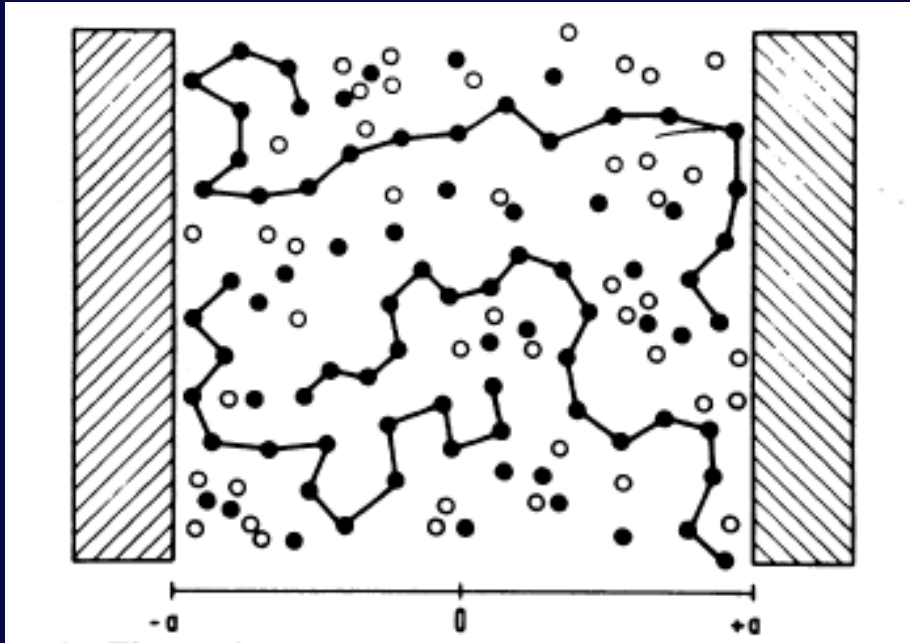


Monomodal-bimodal transition

Coupling between chain conformation and interactions: bridging - no-bridging.

# PE chain plus mobile salt ions

Uni valent salt plus polyelectrolyte chains. A lot richer and more complicated.



Polyelectrolyte plus mobile salt ions.  
Ground-state dominance:

$$\mathcal{G}_\phi(\mathbf{r}, \mathbf{r}'; N) = \psi(\mathbf{r})\psi(\mathbf{r}')e^{-E_N N}$$

Polyelectrolyte PB equation:

$$\frac{\ell^2}{6} \frac{d^2 \psi(z)}{dz^2} + (E_N - \beta e_\tau \phi) \psi(z) = 0.$$

Large parameter space

$$\epsilon \epsilon_0 \frac{d^2 \phi(z)}{dz^2} - 2n_0 e_0 \sinh(\beta e_e \phi(z)) + e_\tau \psi(z)^2 = 0.$$

Dimensionless formulation

$$\kappa \ell.$$

$$\Gamma = \frac{\beta e_0 \sigma}{\epsilon \epsilon_0 \kappa}$$

Surface charge

$$\lambda = \frac{\beta e_0^2 N}{\epsilon \epsilon_0 \kappa S}$$

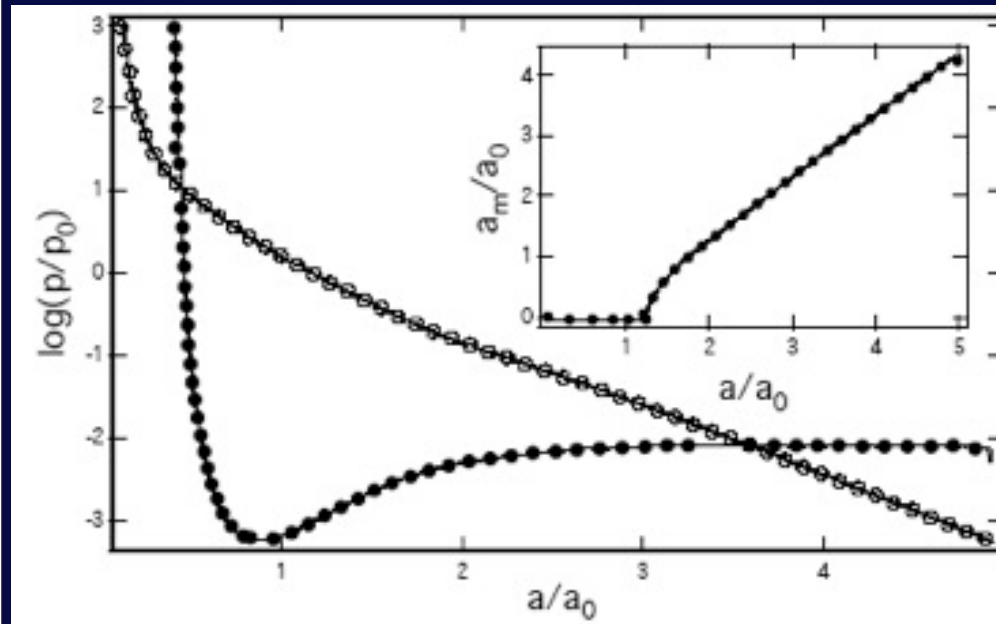
Monomer density

$$w_0 = \kappa a$$

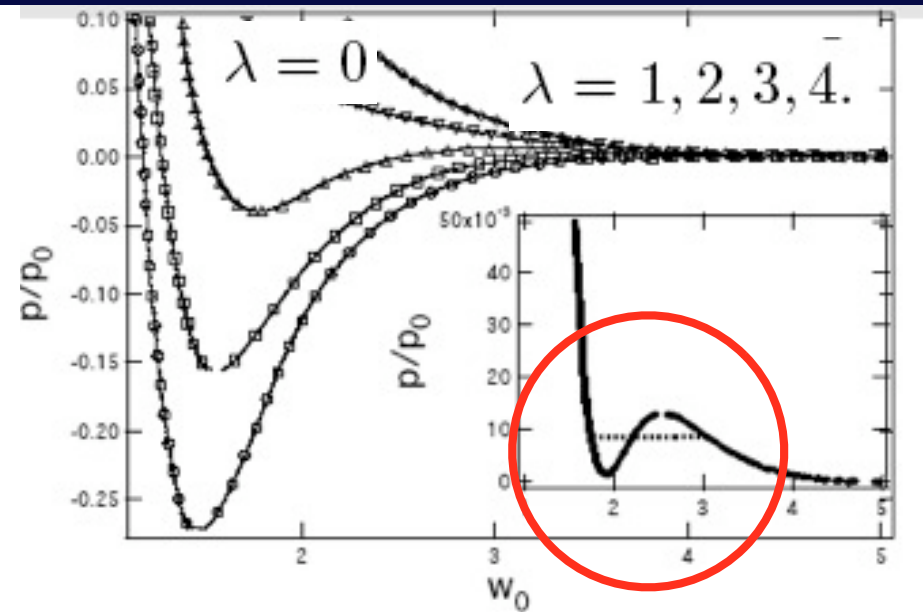
Separation

# Polyelectrolyte bridging with salt ions

Competition between two types of electrostatic interactions. **Multiple phase equilibria.**



$\Gamma = 5.4, \lambda = 1$  and  $\kappa l = 1$ .



$\lambda = 2.5$  and  $\Gamma = 5.45$

$\Gamma = 5.45, l = 2.5$  (corresponding to 1 charge per  $2 \text{ nm}^2$  and Debye length of 1.2 nm).

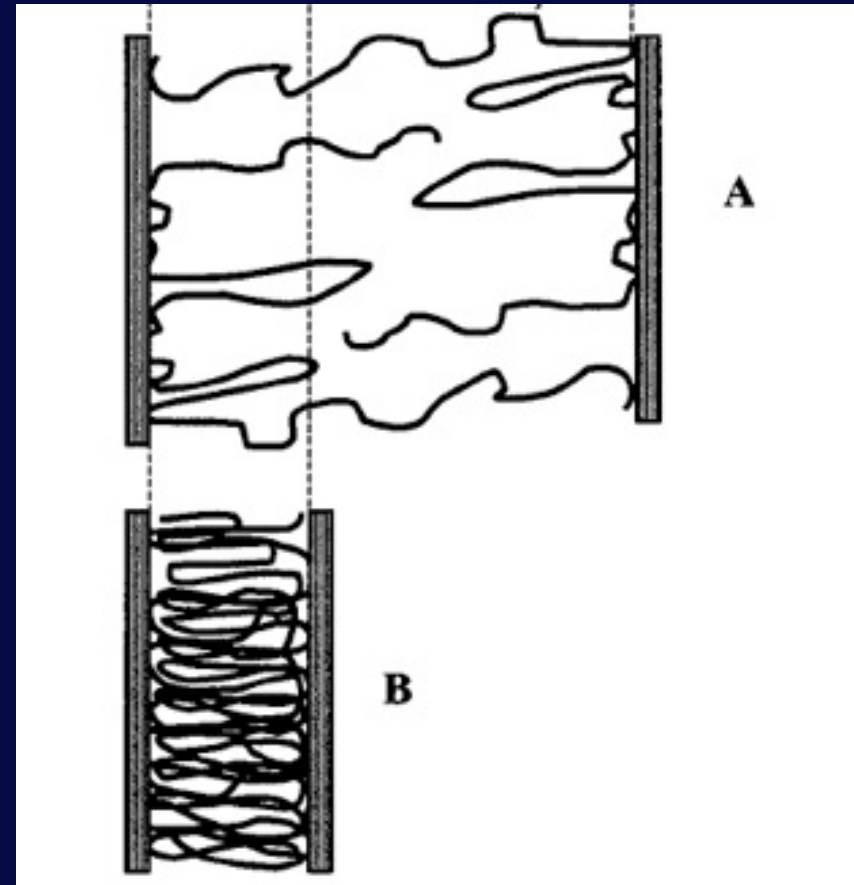
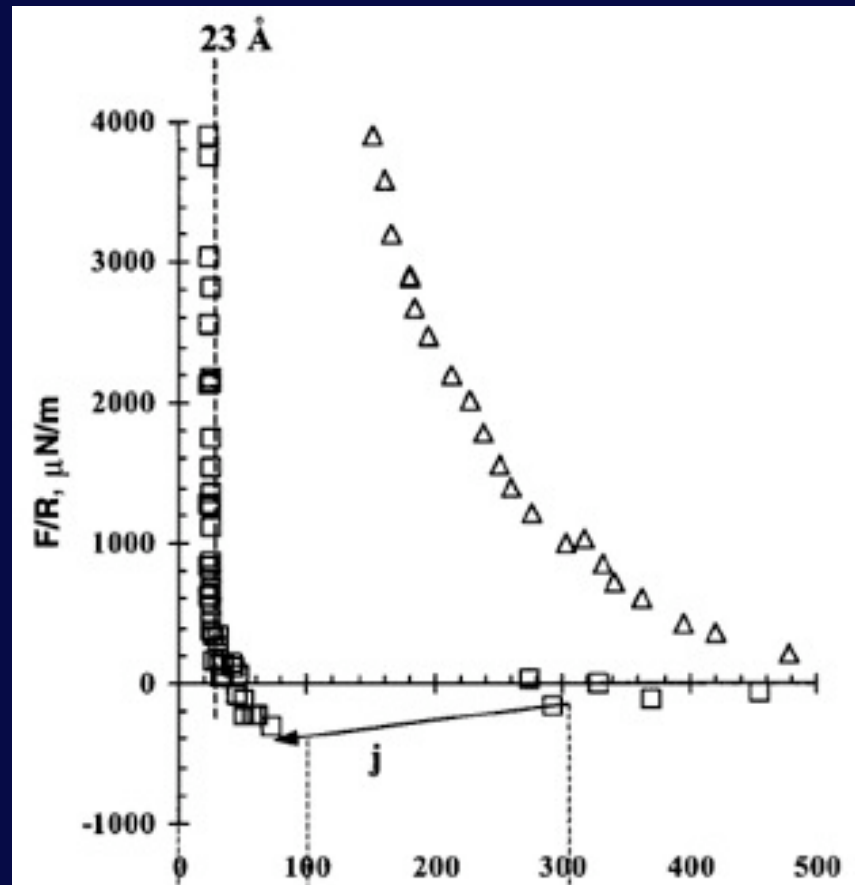
Polyelectrolyte conformation and interactions are not directly correlated.  
Bridging attraction has to **compete** with PB repulsion.

PE chains in equilibrium with a bulk reservoir, interacting with Coulomb as well as hard core potentials. Borukhov, Andelman, Orland (1999)



# Charged surfaces with PE chains (SFA between mica surfaces)

Experimental results with poly acrylic acid.



Abraham et al. (2001) 3 mM  $\text{MgCl}_2$  salt (promotes adsorption of PAA onto mica) with low (squares) and high (triangles) concentration of PAA.

PAA (polyacrylic acid) and mica. Small concentration of PAA gives long range attractive bridging interaction. Qualitatively described by the PE-PB theory.

# Charged surfaces with PE chains (AFM between silica particles)

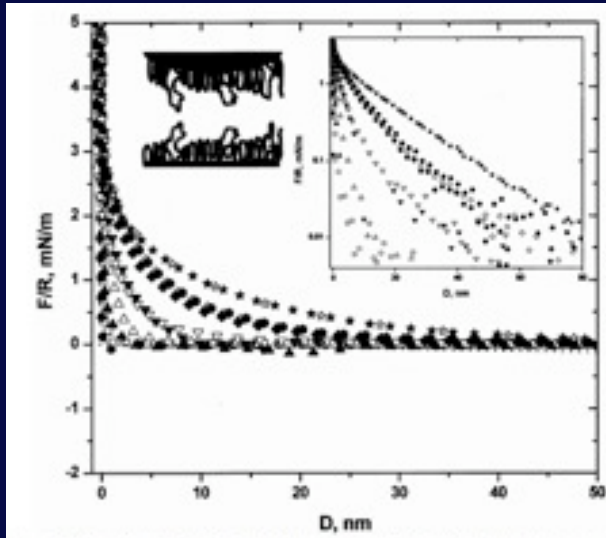


Figure 4. Measured forces (FIR) as a function of distance of separation (D) between two silica surfaces in an aqueous solution containing 20 mM KCl at pH ~ 8.0 at various AMAC-14 concentrations. Inset shows force profiles on approach (open circles) and retraction (filled circles), respectively. Keys: (□) 0.1, (▲) 0.2, (●) 0.3, (▼) 0.4, (◇) 0.5, (○) 0.6, (○) 0.7, (○) 0.8, (○) 0.9, (○) 1.0 ppm AMAC-14.

AMAC-14

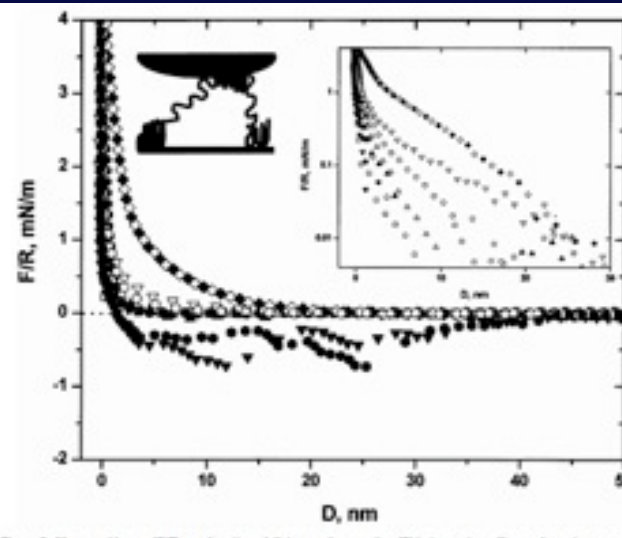


Figure 5. Measured forces (FIR) as a function of distance of separation (D) between two silica surfaces in an aqueous solution containing 20 mM KCl at pH ~ 8.0 at various AMAC-40 concentrations. Inset shows force profiles on approach (open circles) and retraction (filled circles), respectively. Keys: (□) 0.1, (▲) 0.2, (●) 0.3, (▼) 0.4, (◇) 0.5, (○) 0.6, (○) 0.7, (○) 0.8, (○) 0.9, (○) 1.0 ppm AMAC-40.

AMAC-40

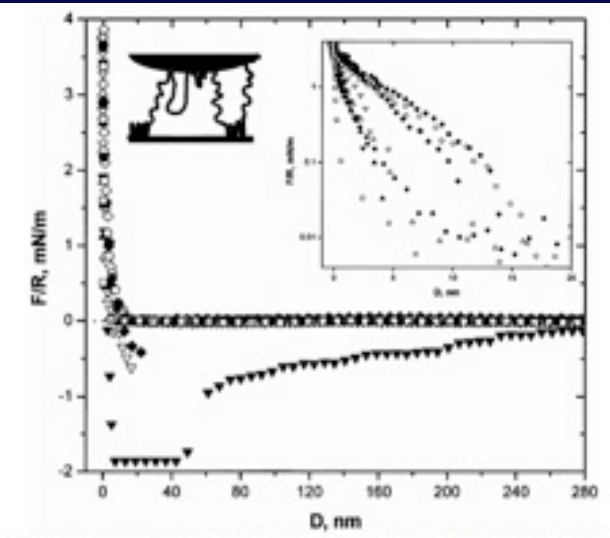


Figure 6. Measured forces (FIR) as a function of distance of separation (D) between two silica surfaces in an aqueous solution containing 20 mM KCl at pH ~ 8.0 at various AMAC-70 concentrations. Inset shows force profiles on approach (open circles) and retraction (filled circles), respectively. Keys: (□) 0.1, (▲) 0.2, (●) 0.3, (▼) 0.4, (◇) 0.5, (○) 0.6, (○) 0.7, (○) 0.8, (○) 0.9, (○) 1.0 ppm AMAC-70.

AMAC-70

$$\Pi(D) = \frac{\sigma^2}{\epsilon\epsilon_0} \left\{ \left( \frac{\pi}{2} \right)^2 \left[ \frac{kT\epsilon\epsilon_0}{6\sigma \left( \frac{\tau}{l^2} \right)} \right] \frac{1}{D^3} + \frac{1}{4} \right\}$$

SCF result (Podgornik and Licer 2007).

AMAC random copolymer of neutral acrylamide and positively charged acrylic sedments. Control the linear charge density (14, 40 and 70% charged). Abraham et al. (2004).

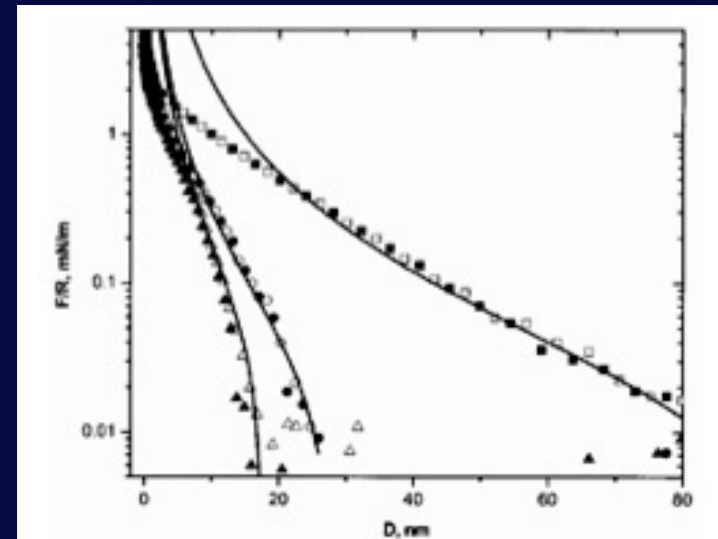


Figure 10. Comparison of measured forces between two silica surfaces in an aqueous solution containing 20 mM KCl at pH ~ 8.0 at 50.0 ppm polymer concentration.

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