Electrostatic Effects in Soft Matter and Biophysics

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SOFT CONDENSED MATTER PHYSICS IN MOLECULAR AND CELL BIOLOGY
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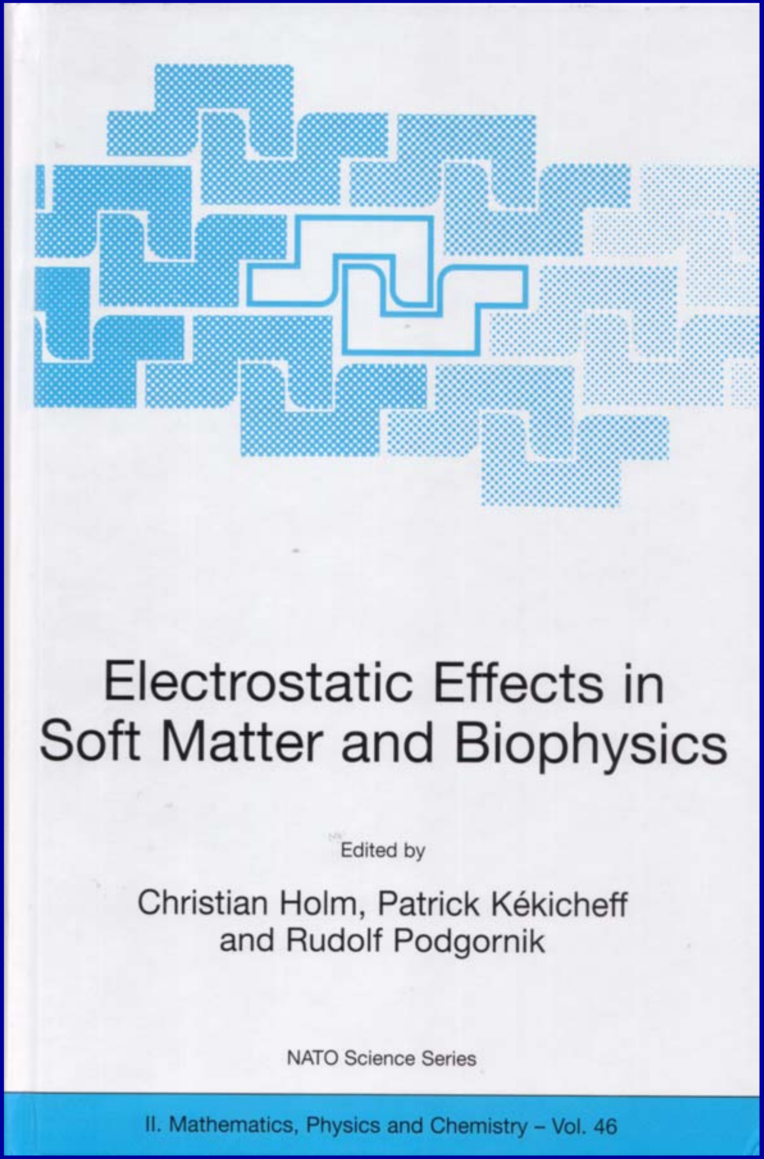
PLAN:

- the two faces of electrostatics
- weak- coupling electrostatics
- strong-coupling electrostatics
- DNA equation of state - low salt
- electrostatics and conformational fluctuations
- DNA equation of state - high salt
- electrostatics and elasticity
- DNA persistence length - weak-coupling (OSF result)
- DNA persistence length - strong-coupling (DNA condensation)
- DNA stretching modulus - weak-coupling
- polyelectrolyte bridging
- interactions between nucleosomal core particles



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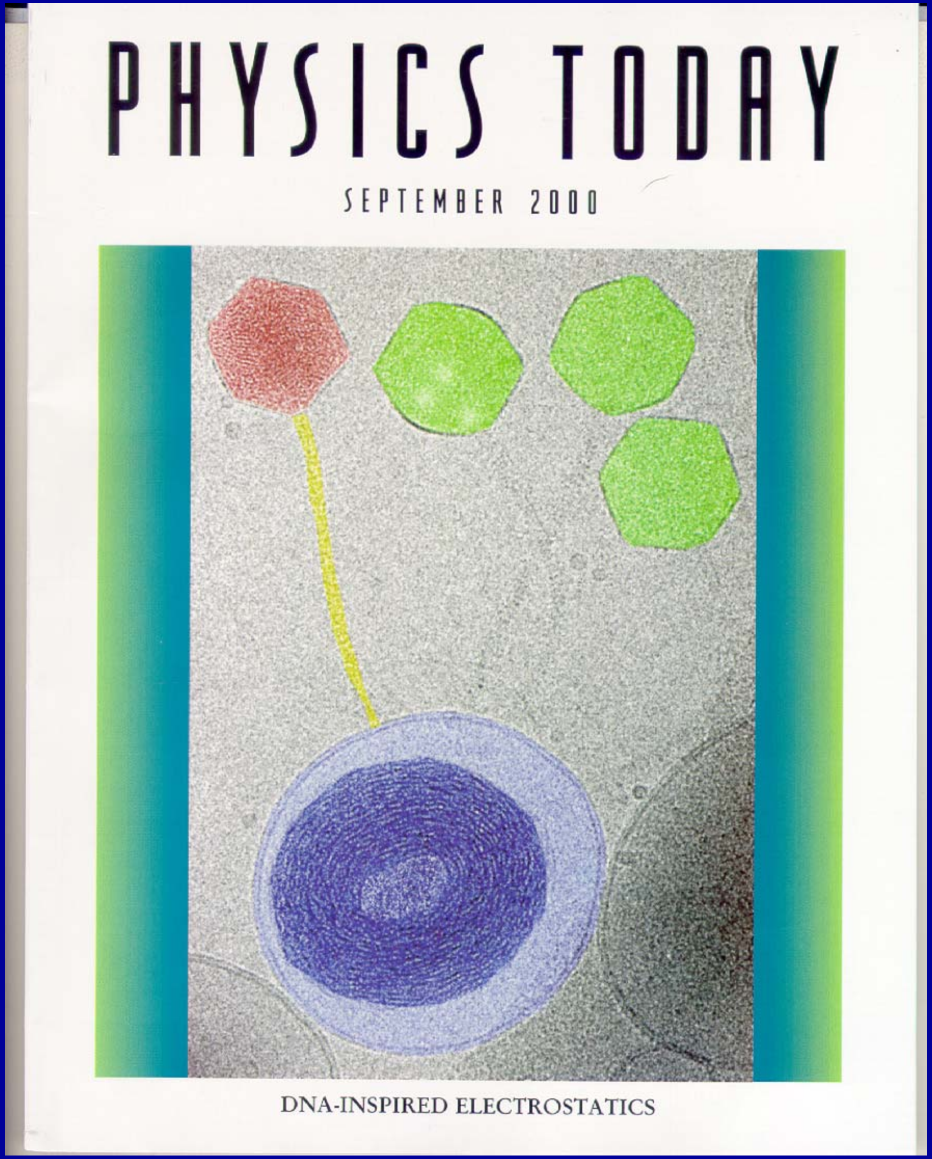


PHYSICS TODAY

SEPTEMBER 2000

DNA-INSPIRED ELECTROSTATICS

The ominous correlation effect

Developments in the 80’s colloid science:

- Oosawa derives attractive interactions between DNAs (late 60’s)
- Simulation of DLVO interactions (early 80’s - el. bilayer Torrie and Valleau (1980))
- Fundamental paper by Gulbrand, Jonsson, Wennerstrom and Linse (1984)

Established that for planar surfaces the Interactions with divalent counterions can be attractive!

They dubbed it the correlation effect because it stemms from a correlation term in the stress tensor.

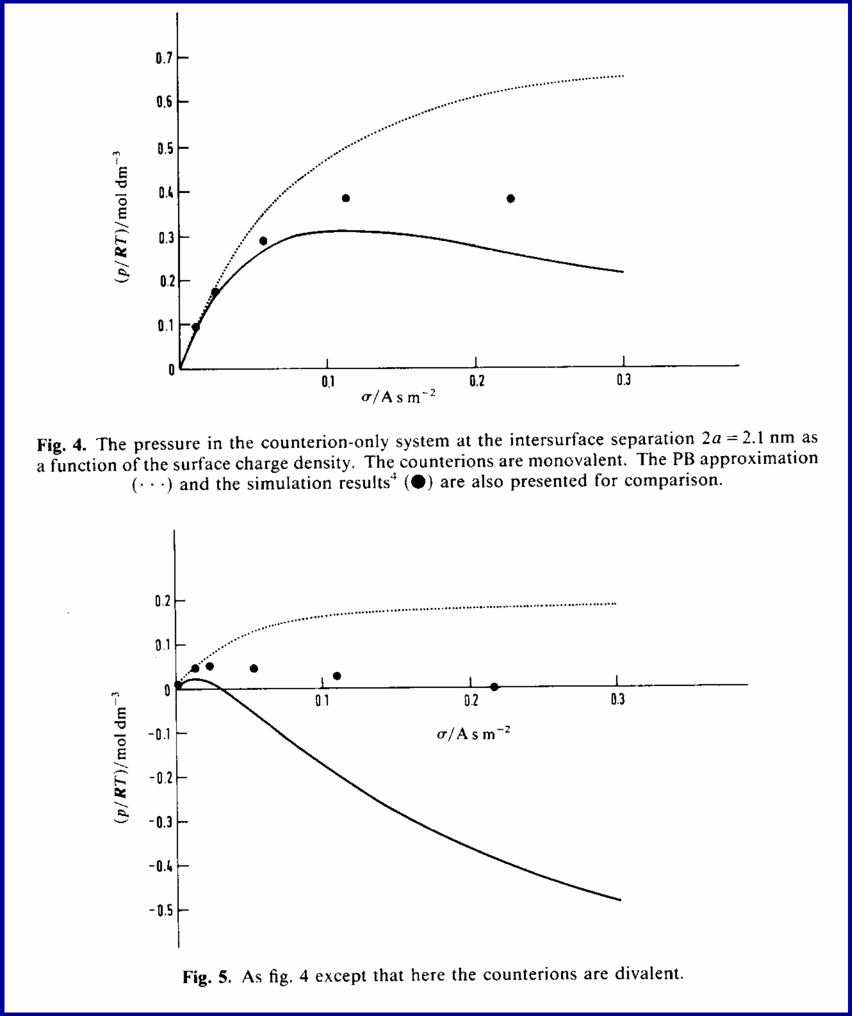


Fig. 4. The pressure in the counterion-only system at the intersurface separation $2a = 2.1$ nm as a function of the surface charge density. The counterions are monovalent. The PB approximation (· · ·) and the simulation results[4] (●) are also presented for comparison.

Fig. 5. As fig. 4 except that here the counterions are divalent.

Probably the biggest advance in colloid science since DLVO.

The great electrostatic divide

The (Netz) dimensionless coupling parameter

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

$$\Xi = 2\pi Z^3 \ell_B^2 \sigma \longrightarrow 0$$

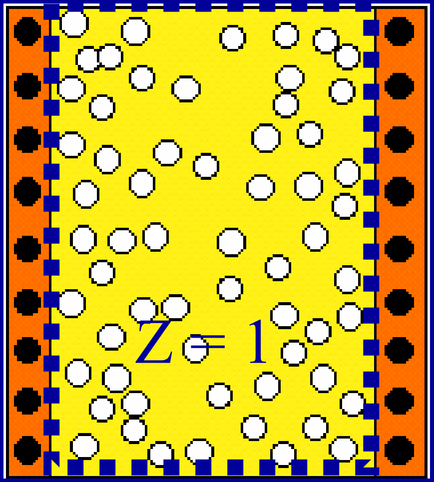
Weak coupling limit
(Poisson - Boltzmann)

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

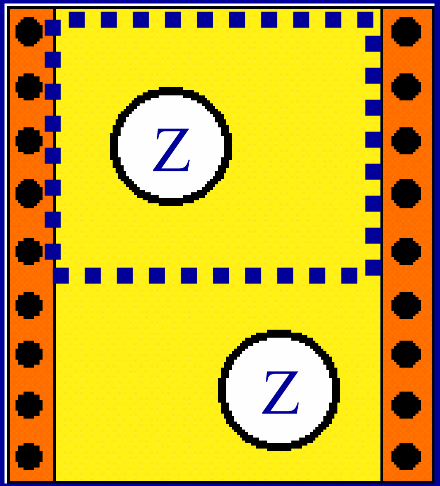
$$\Xi = 2\pi Z^3 \ell_B^2 \sigma \longrightarrow \infty$$

Strong coupling limit
(Netz - Moreira)

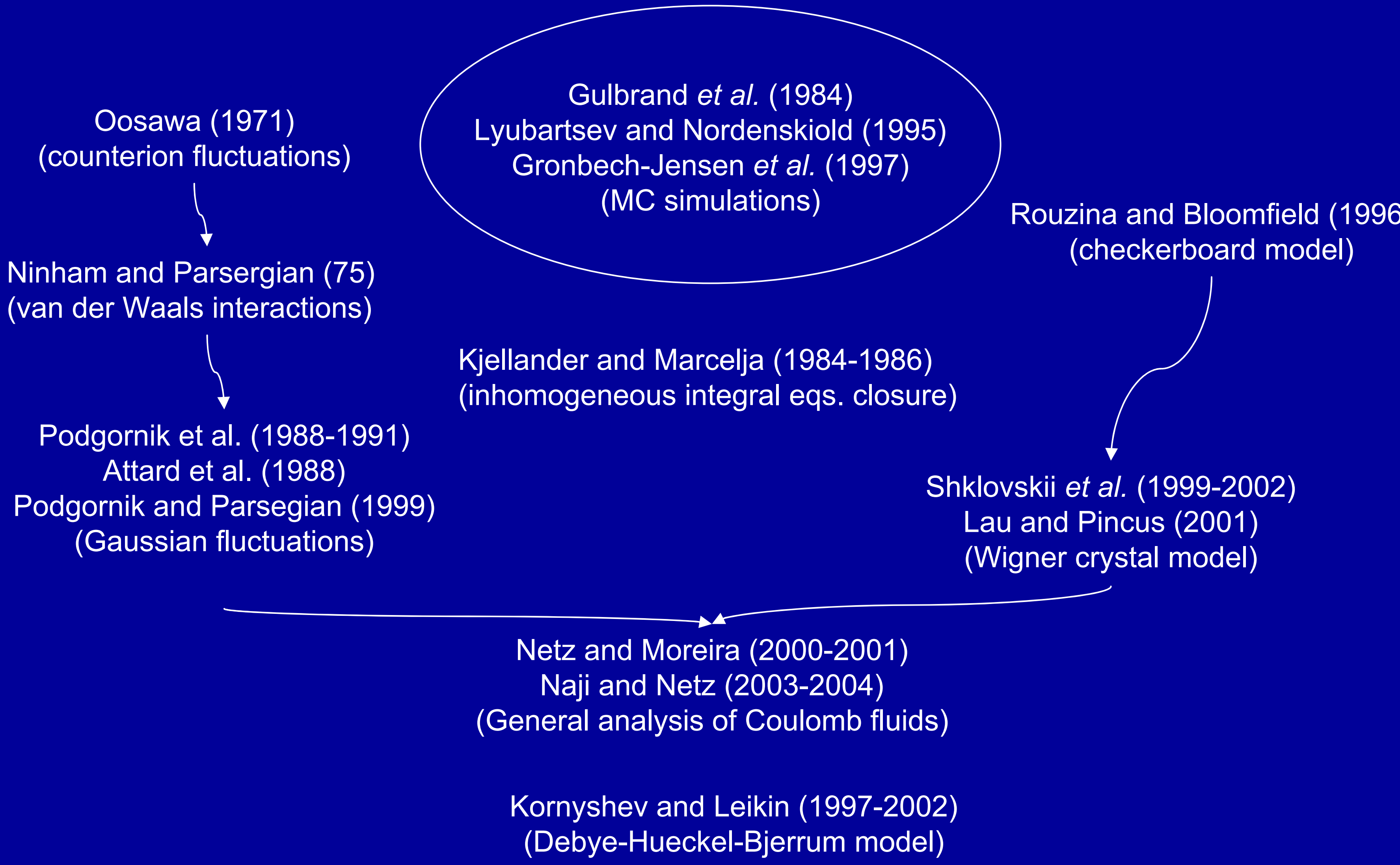
$$N Z e_0 = \int_{(V)} \rho(\mathbf{r})\ d^3\mathbf{r} = \oint_{(S)} \sigma(\mathbf{r})\ d^2\mathbf{r}.$$



Collective description
("N" description)
vs.
Single particle description
("1" description)



A historical guide to the correlation effect



Oosawa (1971)
(counterion fluctuations)

Ninham and Parsergian (75)
(van der Waals interactions)

Podgornik et al. (1988-1991)
Attard et al. (1988)
Podgornik and Parsegian (1999)
(Gaussian fluctuations)

Gulbrand *et al.* (1984)
Lyubartsev and Nordenskiold (1995)
Gronbech-Jensen *et al.* (1997)
(MC simulations)

Kjellander and Marcelja (1984-1986)
(inhomogeneous integral eqs. closure)

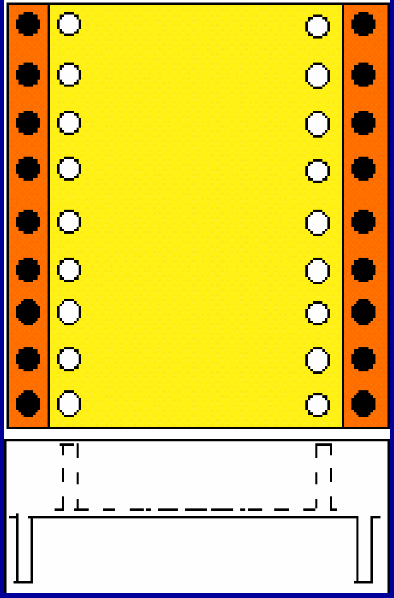
Rouzina and Bloomfield (1996
(checkerboard model)

Shklovskii *et al.* (1999-2002)
Lau and Pincus (2001)
(Wigner crystal model)

Netz and Moreira (2000-2001)
Naji and Netz (2003-2004)
(General analysis of Coulomb fluids)

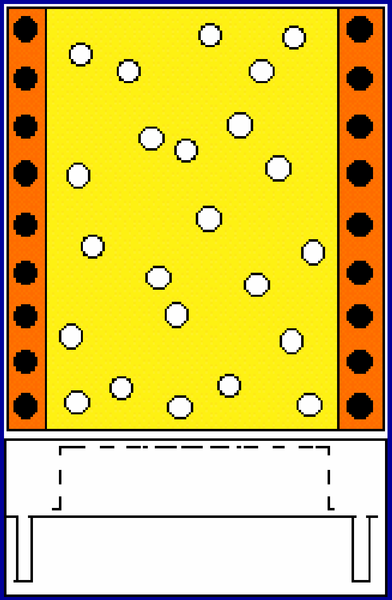
Kornyshev and Leikin (1997-2002)
(Debye-Hueckel-Bjerrum model)

The weak coupling limit I
(collective description)

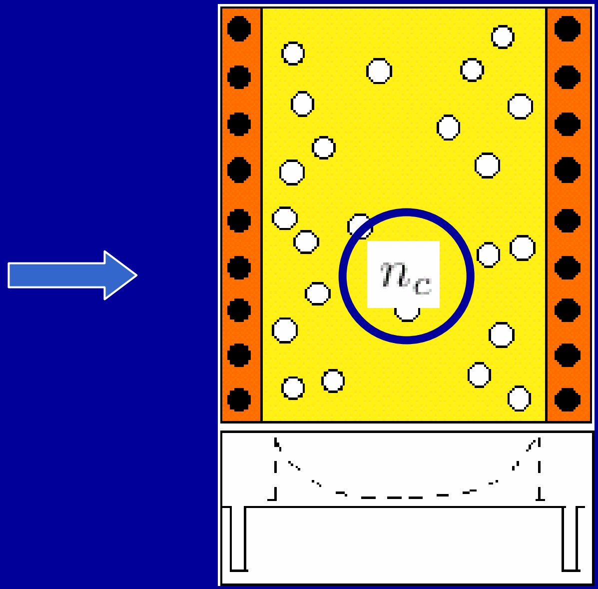


electrostatic energy

+



ideal gas entropy



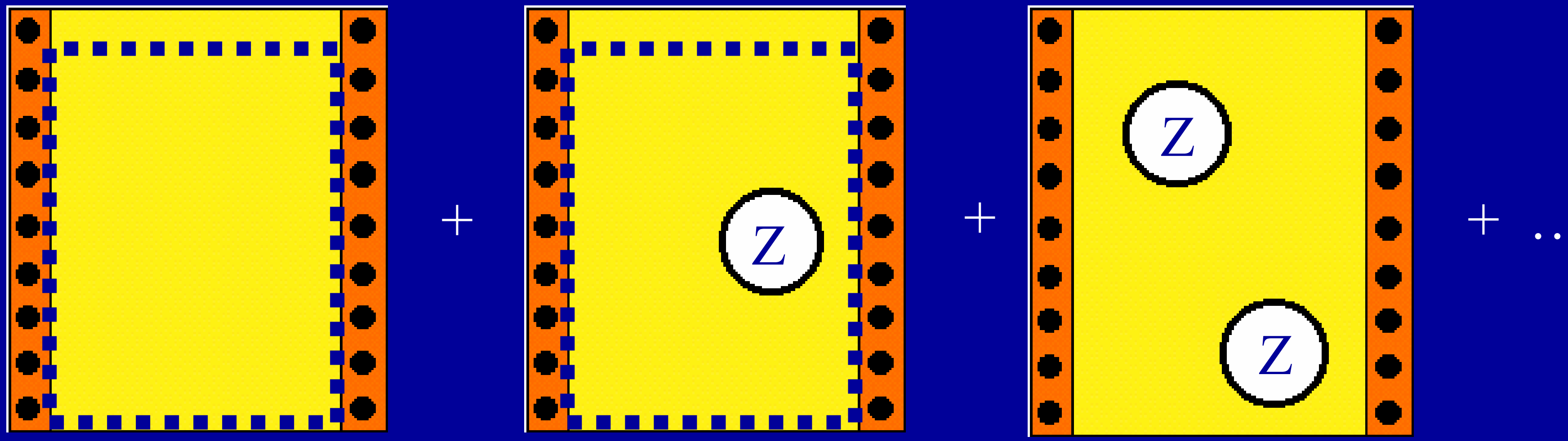
minimize to get equilibrium

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

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

$$\mathcal{F} = -\tfrac{1}{2}\epsilon\epsilon_0\int_V(\boldsymbol{\nabla}\phi)^2 d^3\mathbf{r} + \int_V e_0 n_c\,\phi\,d^3\mathbf{r} + \int_{\partial V}\sigma\phi\,d^2\mathbf{r} + kT\int_V\left(n_c\ln\tfrac{n_c}{n_0} - (n_c - n_0)\right)d^3$$

The strong coupling limit I
(virial expansion)



Electrostatic energy
without mobile counterions

Electrostatic energy
of a single counterion

Electrostatic energy
of two counterions

$$N Z e_0 = \oint_{(S)} \sigma(\mathbf{r})\ d^2\mathbf{r}.$$

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

Gouy-Chapman length
(scaling lengths)

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

Virial expansion to first order

The weak coupling limit II

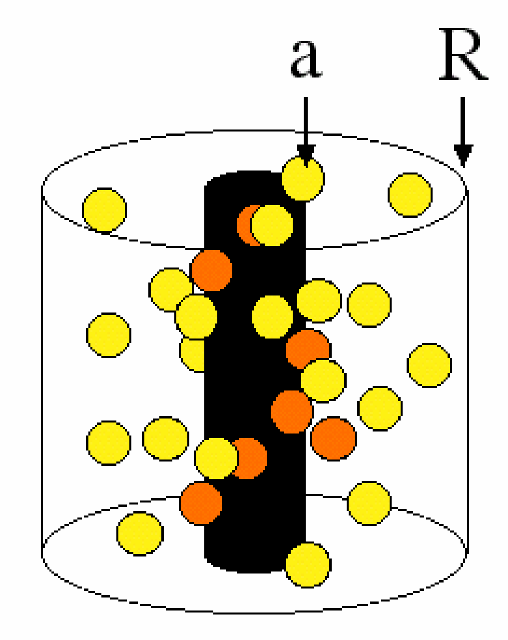
Minimization of the free energy

$$\mathcal{F} = -\frac{1}{2}\epsilon\epsilon_0 \int_V (\boldsymbol{\nabla}\phi)^2 d^3\mathbf{r} + \int_V e_0 n_c\, \phi\, d^3\mathbf{r} + \int_{\partial V} \sigma\phi\, d^2\mathbf{r} + kT \int_V \left(n_c \ln \frac{n_c}{n_0} - (n_c - n_0) \right) d^3$$

The Poisson - Boltzmann equation and the electroneutrality BC

$$-\epsilon\epsilon_0 \nabla^2 \phi = e_0 n_0\, e^{-\frac{e_0 \phi}{kT}}. \qquad \epsilon\epsilon_0 \frac{\partial \phi}{\partial \mathbf{n}} + \sigma = 0.$$

$K^2 = 4\,\pi\, l_B\, n_0$



To solve the Poisson - Boltzmann eq. in cylindrical geometry one has to introduce a neutralizing cell. Fuoss, Katchalsky, Lifson (1951)

$$u(r) = \ln \left(\frac{(\kappa r)^2}{4z^2} \cos^2 (z \ln(\frac{r}{R_M})) \right)$$

$$\frac{du(r)}{dr}\Big|_{r=a} = \frac{e_0 \sigma}{\epsilon\epsilon_0\ kT} = \frac{2Q}{a}$$

$$Q = \frac{\ell_B}{h},$$

Has to satisfy BC at both boundaries. The Manning parameter.

The weak coupling limit III
(osmotic pressure)

The force equilibrium in the cell

$$\mathbf{F} = \int_V \rho_f(\mathbf{r})\mathbf{E}(\mathbf{r})\ d^3\mathbf{r}_{;} = \oint \left[\epsilon\epsilon_0\mathbf{E}(\mathbf{E}\cdot\mathbf{n}) - \frac{1}{2}\epsilon\epsilon_0 E^2\mathbf{n} - kT\ n_0 e^{-\frac{e_0\phi}{kT}}\mathbf{n}\right] dS,$$

Maxwell electrostatic stresses plus van't Hoff counterion pressure

The contact theorem (normal pressure)

$$p = \frac{F_n}{S} = kTn(\partial V) - \frac{1}{2}\frac{\sigma^2}{\epsilon\epsilon_0}.$$

Inner boundary

$$p = \frac{F_n}{S} = kTn(\partial V)$$

Outer boundary

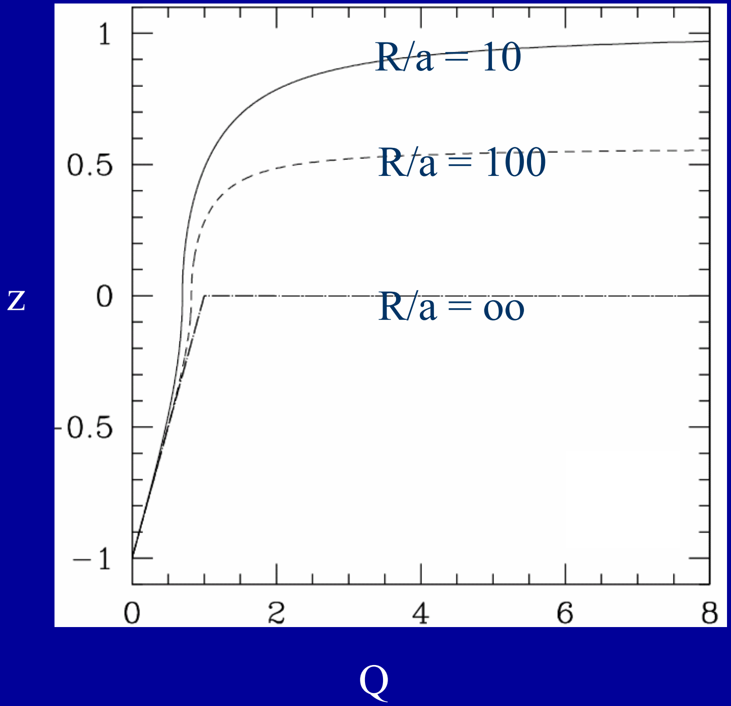
$$p(Q > 1) = kTn_0 = \frac{kT}{2\pi\ell_b R^2}(1 + z^2)$$

$$p(Q < 1) = kTn_0 = \frac{kT}{2\pi\ell_b R^2}(1 - z^2).$$

Z from the FKL solution

The concentration of counterions at the outer cell boundary gives the osmotic pressure in the system. A fundamental insight of the weak coupling theory.

The weak coupling limit VI (conterion condensation)



z = z (Q, a/R) (Borukhov, 2003)

Onsager-Oosawa-Manning counterion condensation

$$
\begin{aligned}
u(r) &= -2Q\log\frac{r}{a} \qquad Q<1\\
u(r) &= -2\log\frac{r}{a} - 2\log\left(1+(Q-1)\log\frac{r}{a}\right) \qquad Q >
\end{aligned}
$$

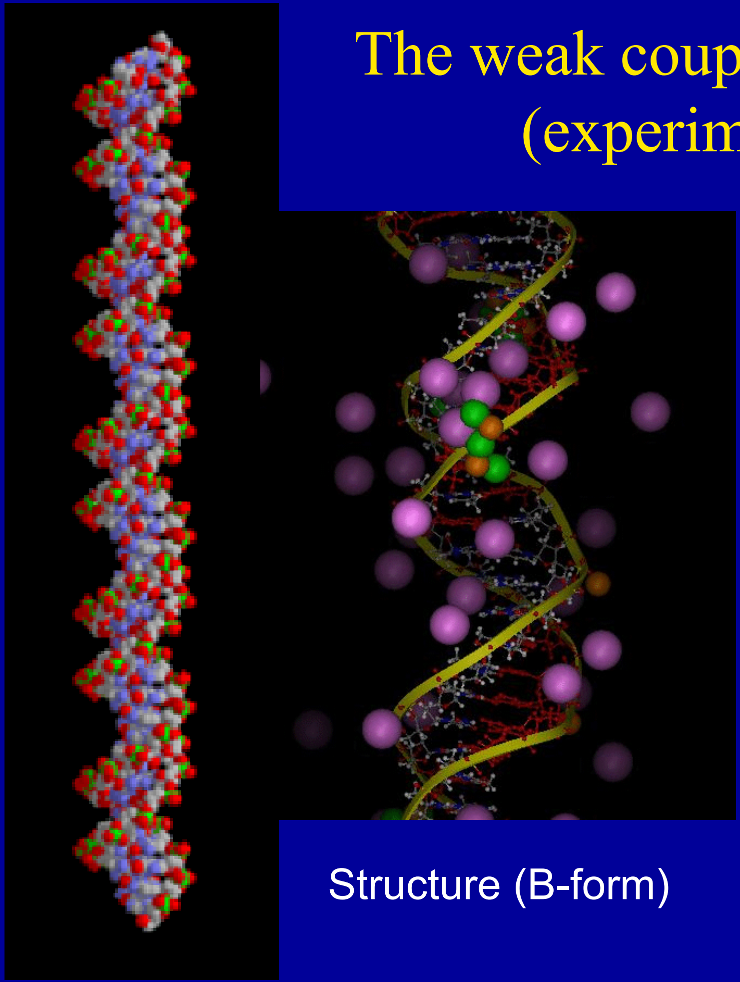
For infinite dilution If Q >1 the counterions “condense” on the macroion untill it has the charge Q=1. In terms of the osmotic coefficient:

$$\phi = \frac{kT\kappa^2}{8\pi\ell_B}\frac{\pi R^2 h}{kT} = \frac{1}{2Q}(1 \pm z^2),$$

$$
\begin{aligned}
\phi(Q>1) &= \frac{1}{2Q}\left(1+\frac{\pi^2}{\log^2\frac{R}{a}}\right)\\
\phi(Q<1) &= (1-\frac{Q}{2})\left(1+\left(\frac{1-Q}{1-\frac{Q}{2}}\right)^2\left(\frac{a}{R}\right)^{2(1-Q)}\right)
\end{aligned}
$$

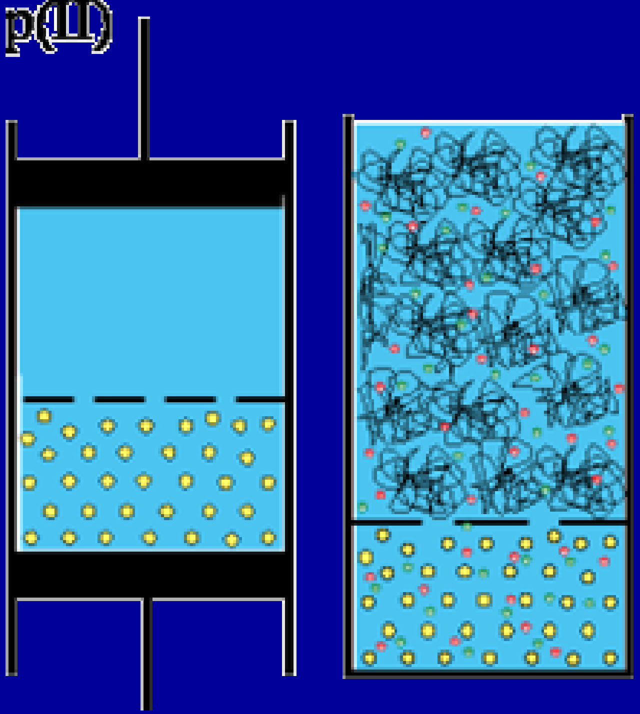
The infinite dilution limit might be difficult to reach.

The weak coupling limit V (experiments)

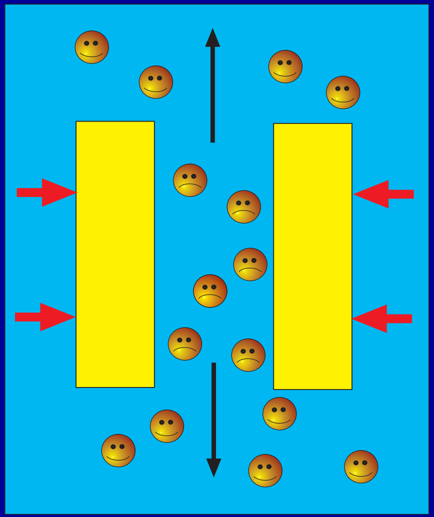


Structure (B-form)

- 0.34 nm /bp
- a ~ 1 nm
- Q ~ 4.35
- DNA length from 50 nm to ~ μm



The Boyle experiment



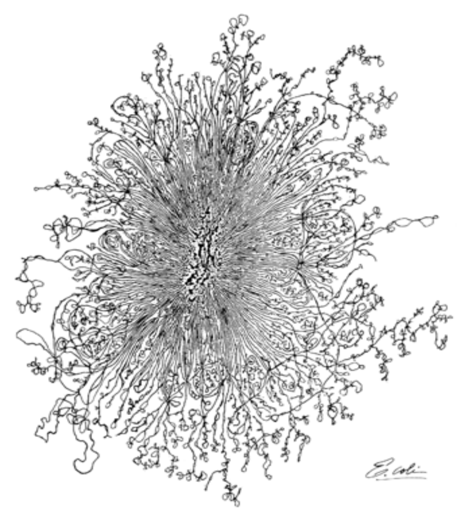
$\Pi\, dV$

$-\mu\, dN$

Osmotic stress method (Parsegian & Rand)

Why study DNA at high densities?

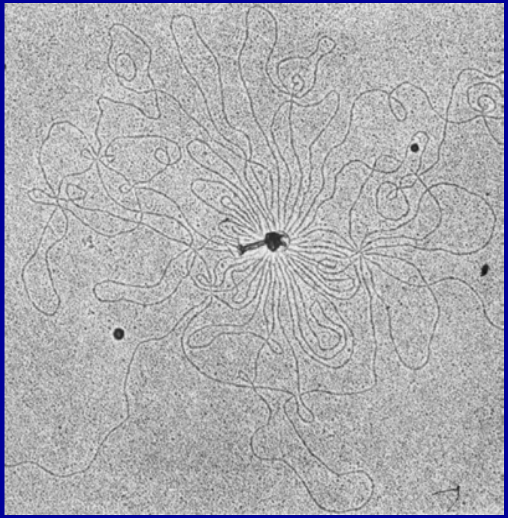
~ 630 m long
~1 mm thick
~ 25 cm



(R. Cavenoff (1995))

E.Coli

T2

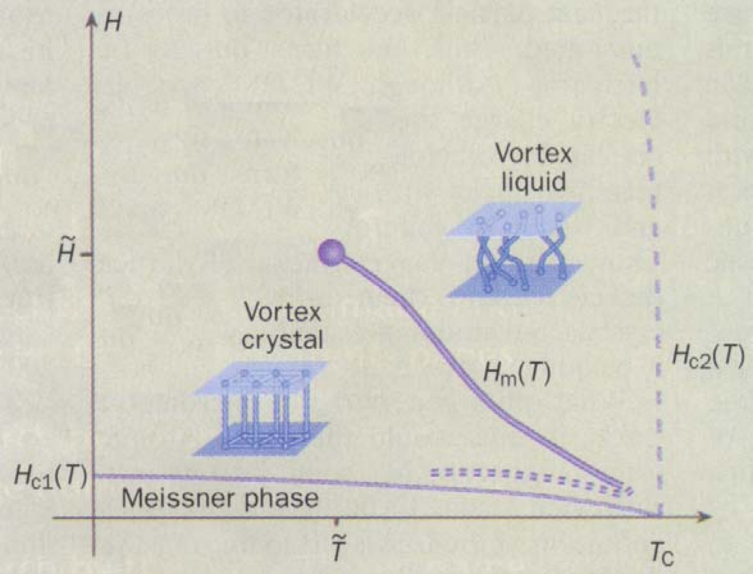


(Kleinschmidt *et al.* (1962))

P~100 atm
ρ~100 mg/m

Vortex lines in II sc

Tension
Non-chiral
Magnetic field
Temperature
London repulsion

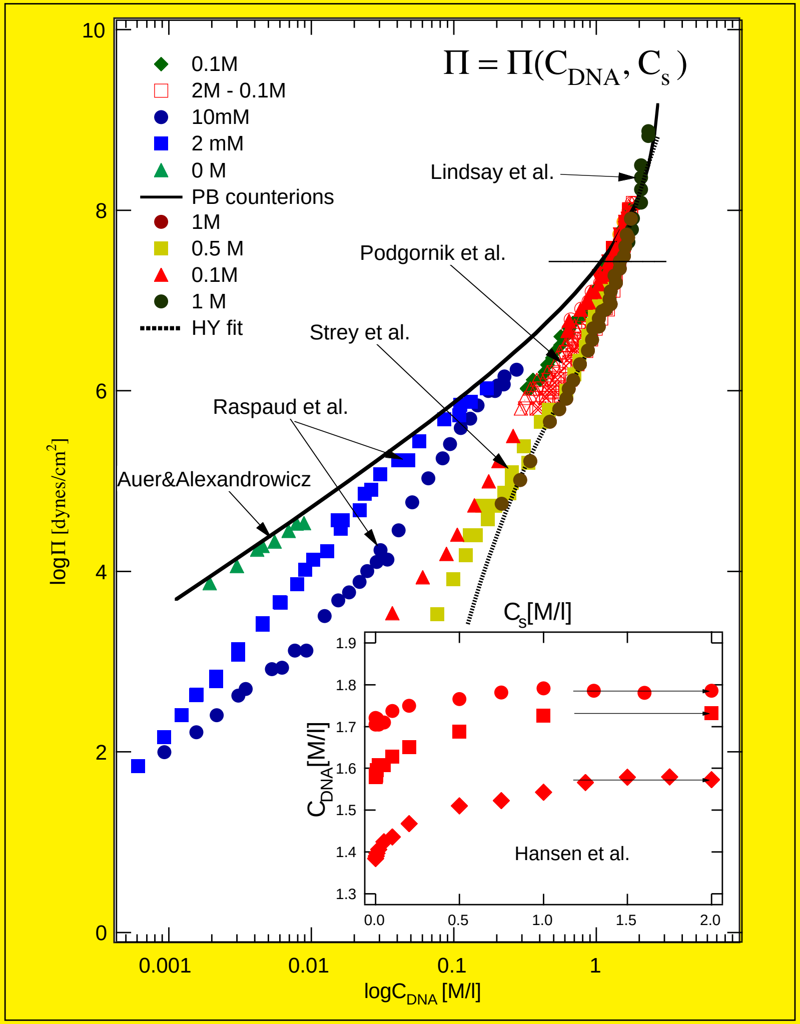


(D. Nelson. (1995))

Bending
Chiral
density
Ionic strength
Debye-Huckel repulsion

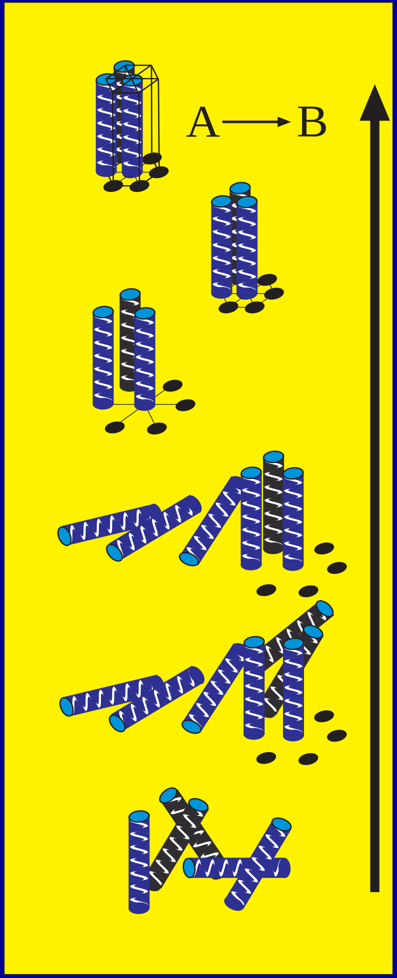
DNA equation of state (experiments)

Equation of State Na-DNA



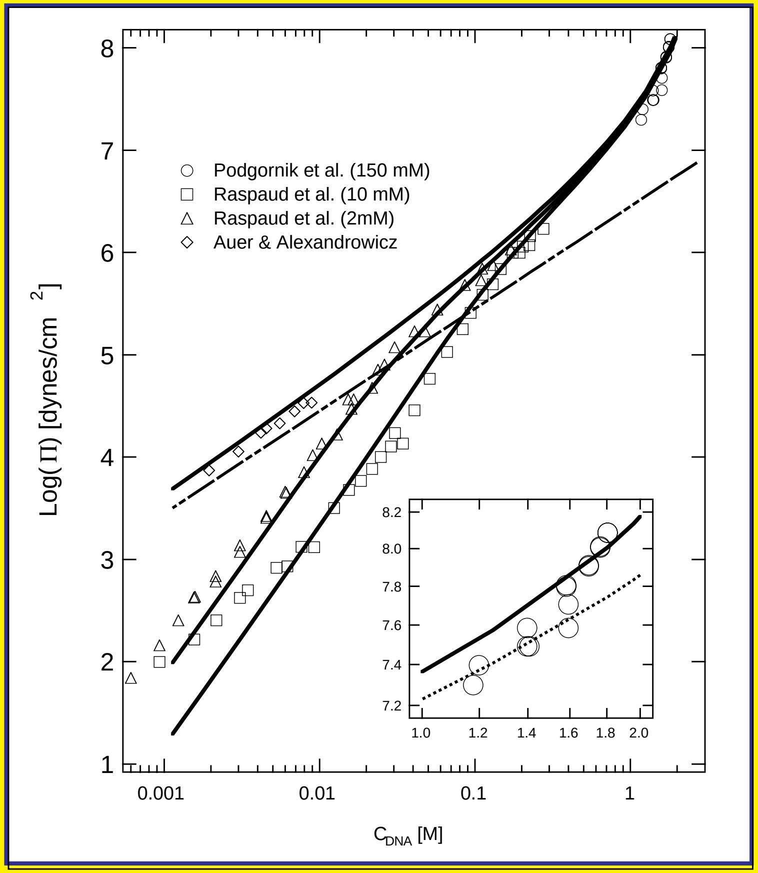
(Rau, Parsegian, Podgornik, Strey, Lindsay, Raspaud, Livolant …)

(Livolant, Leforestier, Rill, Robinson, Strzelecka …)



The weak coupling limit VI

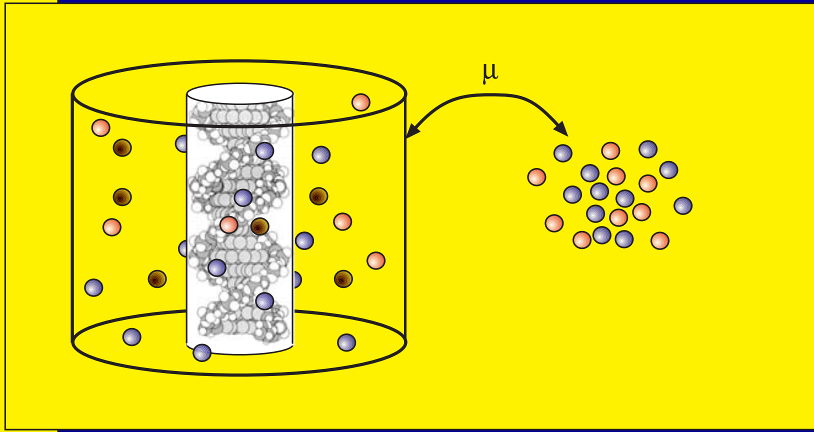
Poisson - Boltzmann for no salt plus
Donnan equilibrium for salt (Hansen et al. 2000)



Data from Raspaud et al. (PRL 2000), Auer and Alexandrowicz (Biopol. 1969), Podgornik et al. (Macromol 1989)

Comparison between the experiment
(SF DNA) and theory.

No salt and low salt.

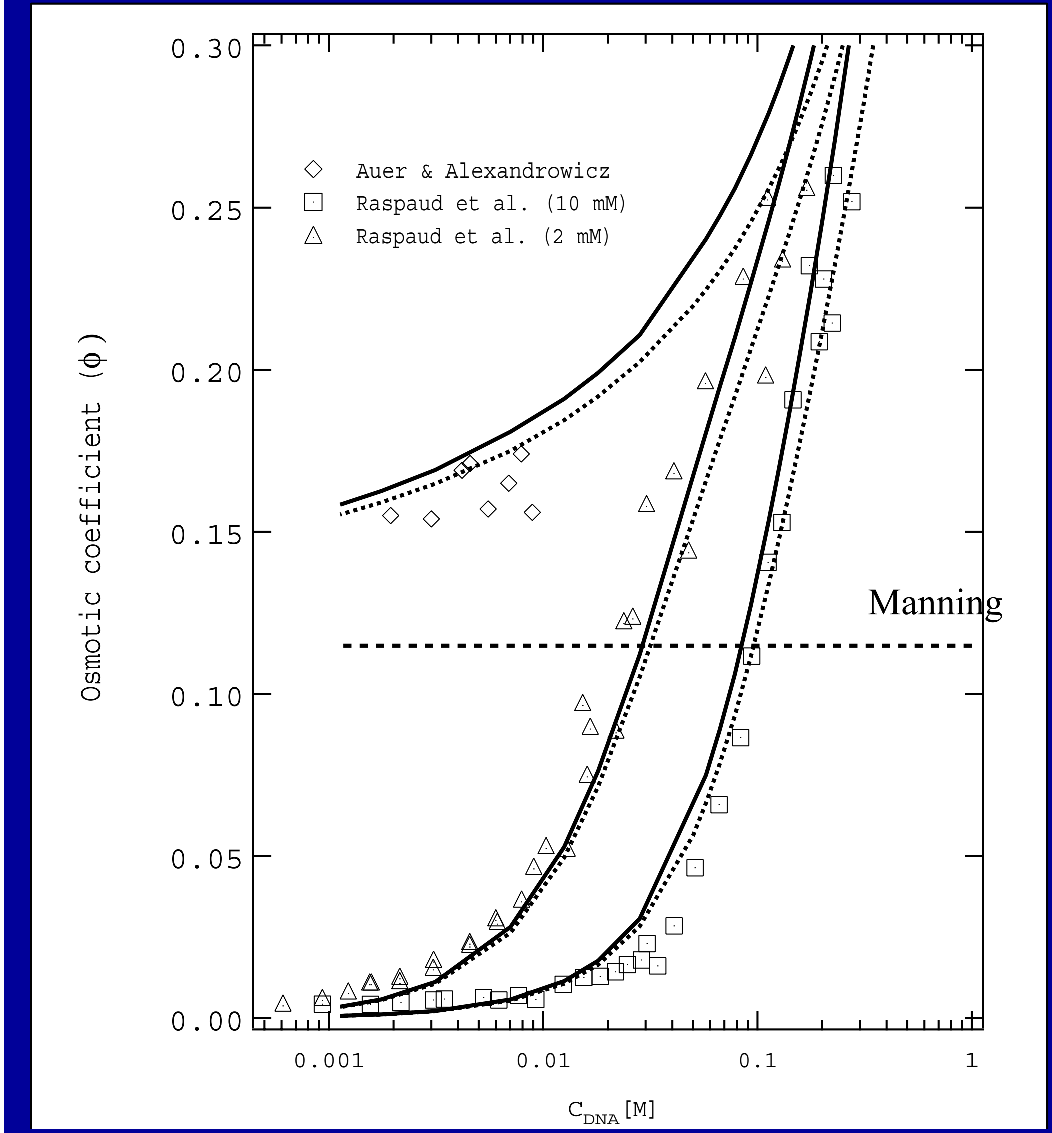


For low salt one approximates

$$n_i(n(R)+n_i)=n_0^2,$$

$$\pi \simeq k_B T[n(R)+2(n_i-n_o)].$$

The weak coupling limit VII



Short fragment nucleosomal DNA + buffer + salt.

Osmotic coefficient is never really Independent of the DNA density, it has a long range tail:

$$\phi \simeq \frac{1}{2Q_o}\left(1+\frac{\pi^2}{\ln^2\left(\frac{R}{a}\right)}\right).$$

Onsager-Oosawa-Manning does not wor
It really is a limiting law.

The weak coupling limit for monovalent salts works almost perfectly (quantitatively).

Raspaud *et al.* 2001.

The weak coupling limit VII
(effect of salt)

Assume now we have counterions and uni-univalent salt in equ. with a reservoir.

$$\begin{aligned}\mathcal{F} &= \mathcal{E} - T\mathcal{S} = \\ &= -\int_V \tfrac{1}{2}\epsilon\epsilon_0 \boldsymbol{\nabla}\phi^2 \; d^3\mathbf{r} + \int_V \rho \; \phi \; d^3\mathbf{r} + kT \int_V \sum_{i=1}^{3} \left(n_i \ln \tfrac{n_i}{n_{i0}} - (n_i - n_{i0}) \right) d^3\mathbf{r}\end{aligned}$$

The total charge density is now

$$\rho = \sum_{i=1}^{3} e_i n_i = e_0 n_c + e_0 n_+ - e_0 n_- . = Z e_0 n_M e^{-\beta e_0 \phi} + e_0 n_{+0} e^{-\beta e_0 \phi} - e_0 n_{-0} e^{+\beta e_0}$$

Minimizing the free energy we again derive the PB equation

Introduce a transformed potential (Hansen and Podgornik, 2004)

$$\beta e_0 \phi = \beta e_0 \phi' - \tfrac{1}{2} \log \tfrac{n_{-0}}{n_{+0} + Z n_M} .$$

But we also have to take into account the electrochemical equilibrium between the cell and the bulk.

The weak coupling limit VIII
(Poisson-Boltzmann-Donnan equation)

Take into account the electrochemical equilibrium of all charged species between the boundary of the cell (zero potential) and the bulk reservoir

$$(n_{+0} + Zn_M)n_{-0} = n_+^{(0)} n_-^{(0)}.$$

Where superscipt 0 stands for the values in the bulk reservoir. The "local" Donnan potential (at the outer wall) is defined as

$$\beta e_0 \phi_D = \frac{1}{2} \log \frac{n_{-0}}{n_{+0} + Zn_M}.$$

and thus

$$\nabla^2(\beta e_0 \phi') = \kappa_0^2 \ \sinh \beta e_0 \phi',$$

$$\phi' = \phi + \phi_D.$$

$$\kappa_0^2 = \frac{2\beta e_0^2}{\epsilon\epsilon_0} \sqrt{(n_{+0} + Zn_M)n_{-0}} = \frac{2\beta e_0^2}{\epsilon\epsilon_0} \sqrt{n_+^{(0)} n_-^{(0)}} = \frac{2\beta e_0^2}{\epsilon\epsilon_0} n^{(0)}.$$

The weak coupling limit IX
(Poisson-Boltzmann-Donnan equation)

In cylindrical cell geometry there are no analytical solutions at finite dilution.
At infinite dilution: Tracy - Widom (1997) analytical solution.
At best we remain with the linearized solution or the complete numerical solution.

$$u(r) = 2QK_0(\kappa_0 r).$$

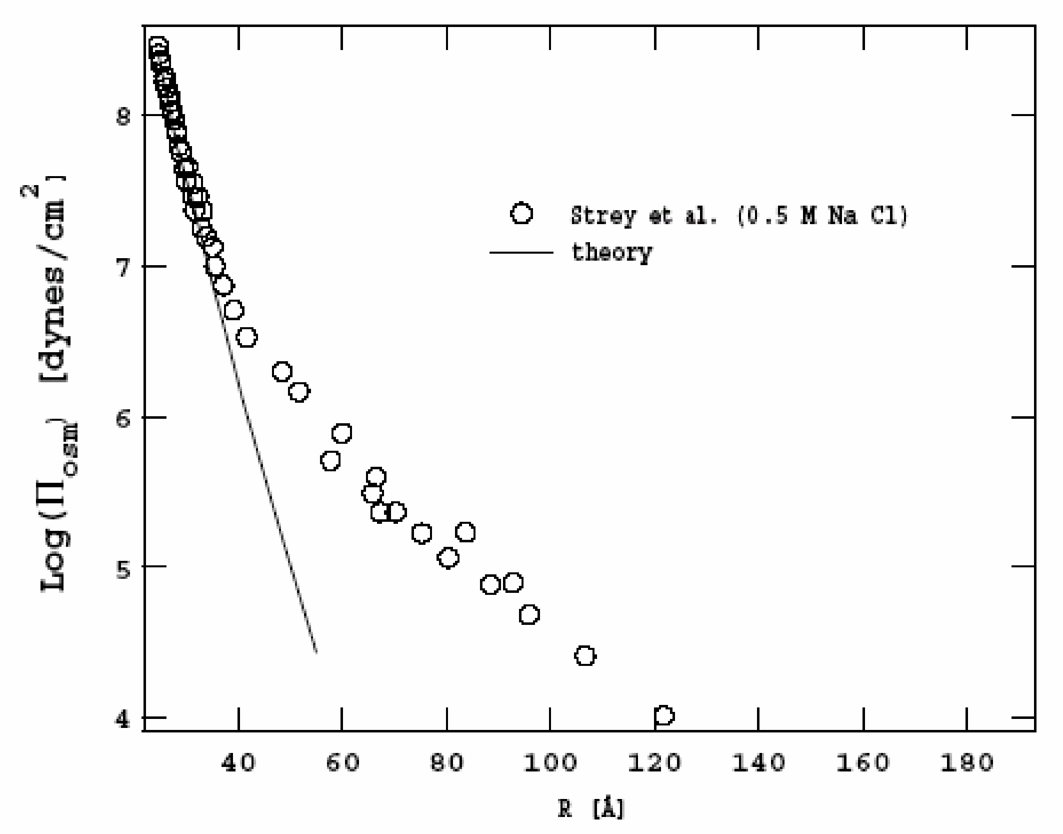
In cylindrical cell geometry just as in the counterion-only case:

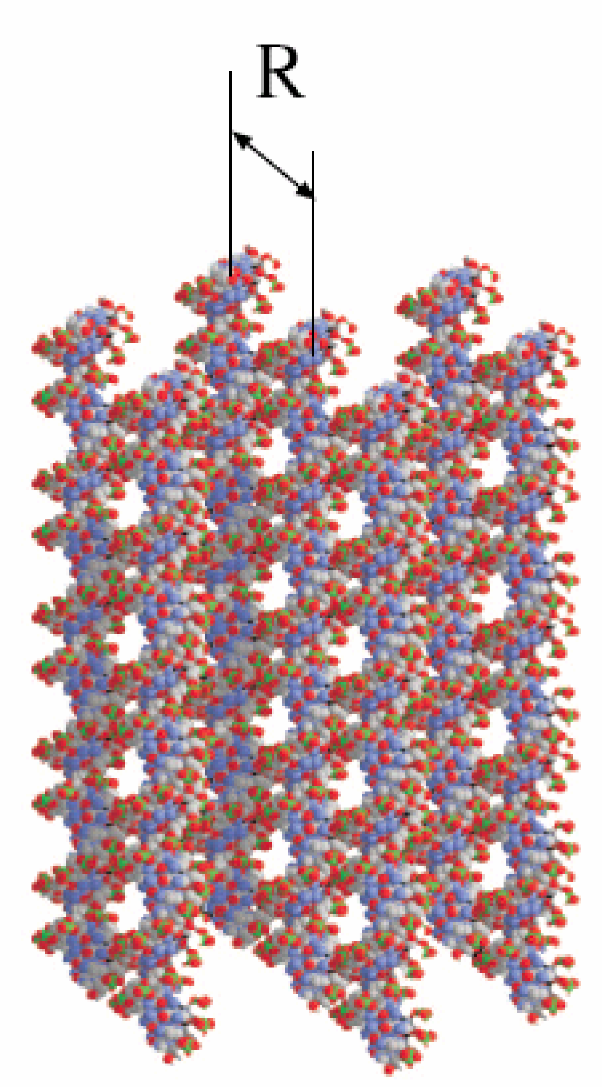
$$\Pi = \frac{\sigma^2}{2\epsilon\epsilon_0 K_1^2(\kappa_0 a)}\; K_0^2(\kappa_0 R/2)\; p^2(\kappa_0 R/2, \kappa^0 a),$$

$$p(\kappa_0 R/2, \kappa_0 a) = \frac{1 - \dfrac{K_1(\kappa_0 R/2) I_0(\kappa_0 R/2)}{I_1(\kappa_0 R/2) K_0(\kappa_0 R/2)}}{1 - \dfrac{K_1(\kappa_0 R/2) I_1(\kappa_0 a)}{I_1(\kappa_0 R/2) K_1(\kappa_0 a)}}.$$

The dominant behavior is exponential with Debye screening length (inverse κ_0).

The weak coupling limit X (comparison with experiment)





DNA in monovalent (NaCl) salt solution.

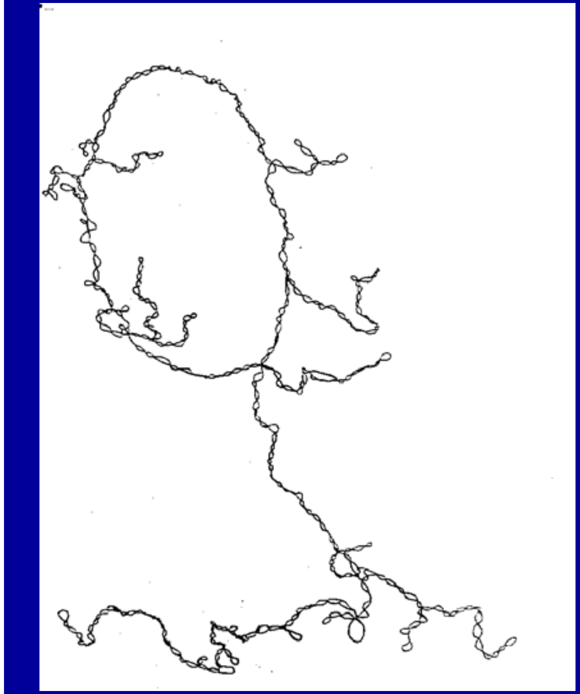
$$\Pi(\rho) = -\left(\frac{\partial(\mathcal{F}(D)/L)}{\sqrt{3}\ R\partial R}\right)_T$$

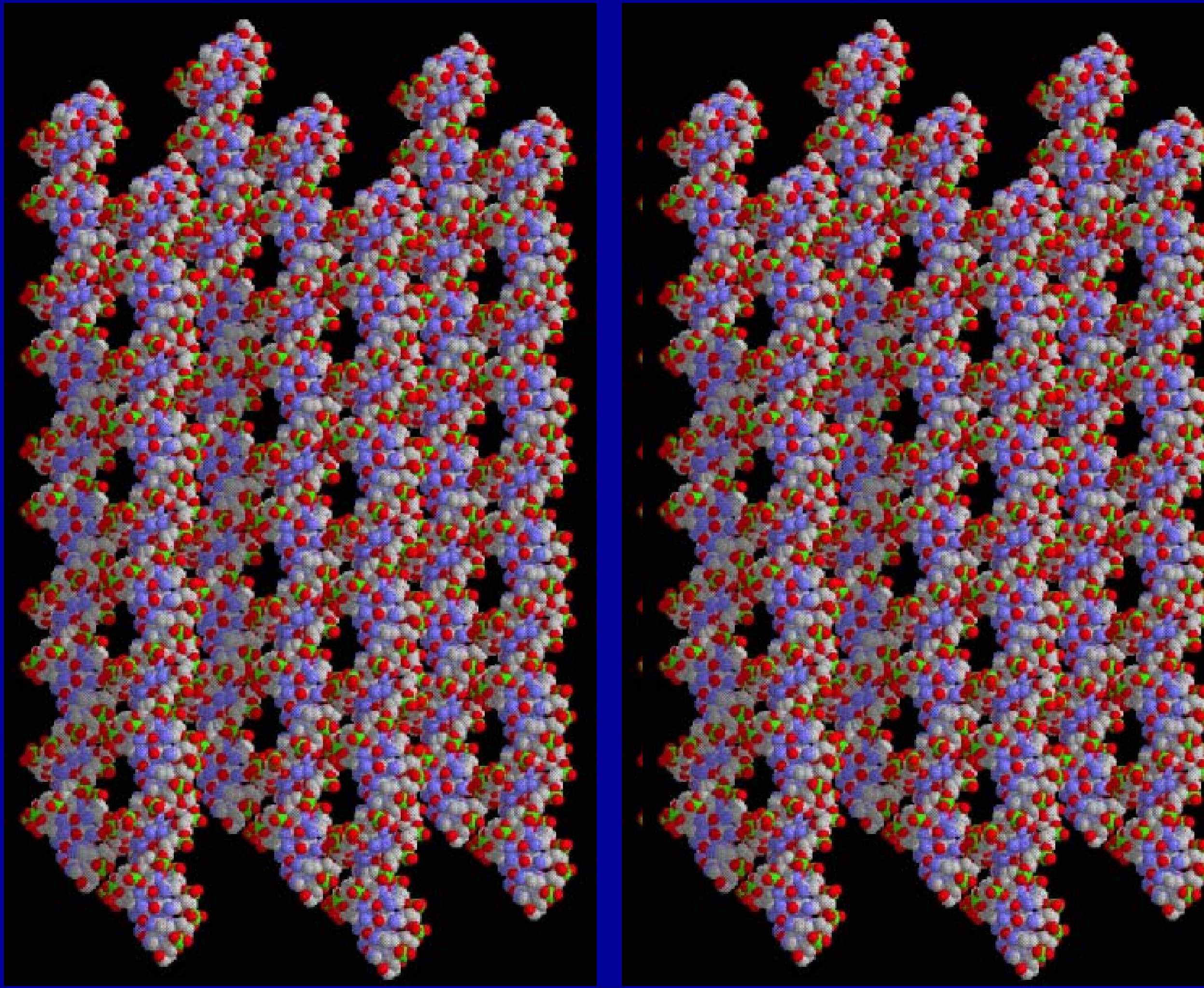
Osmotic pressure
For a 2D hex. array

$$\rho = \frac{2}{\sqrt{3}\ R^2}.$$

Conformational fluctuations I

Surprisingly the weak coupling limit for finite salt does not work.
What are we missing in this picture? Orientational order…





- $L_p \sim 50$ nm
- $K_C = k_B T\, L_p$

DNA is a flexible molecule.

At room temperature big conformational fluctuations.

Conformational fluctuations II
(mesoscopic Hamiltonian)

Treat DNA nematic phase with a mesoscopic Hamiltonian.

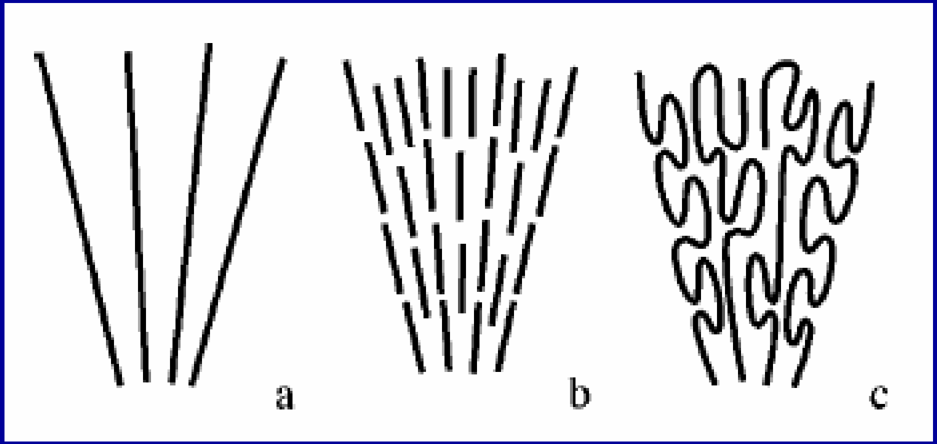
$$(\delta n_x(\mathbf{r}), \delta n_y(\mathbf{r}), 1) \qquad \mathbf{r} = (z, \mathbf{r}_\perp)$$

Nematic part:

$$\mathcal{F}_N = \frac{1}{2} \int d^2\mathbf{r}_\perp dz \left[K_1 \left(\nabla_\perp . \delta\mathbf{n} \right)^2 + K_2 \left(\nabla_\perp \times \delta\mathbf{n} \right)^2 + K_3 \left(\partial_z \delta\mathbf{n} \right)^2 \right]$$

$$\partial_z \delta\rho + \rho_0 \nabla_\perp . \delta\mathbf{n} = 0.$$

In long nematic polymers there is coupling between orientational order and density!



Conformational fluctuations III
(macroscopic free energy)

The effective mesoscopic Hamiltonian is therefore:

$$\mathcal{H} = \mathcal{F}_0(\rho_0) + \frac{1}{2}\int d^2\mathbf{r}_\perp dz \left[\mathcal{B}\left(\frac{\delta\rho}{\rho_0}\right)^2 + G\left(\partial_z\delta\rho + \rho_0\nabla_\perp.\delta\mathbf{n}\right)^2\right] + \mathcal{F}_N$$

density variation, density-nematic coupling, nematic variation

$$G = \frac{k_B T \ell}{2\rho_0},$$

Coupling strength (Kamien *et al.* 1992)

$$\mathcal{F} = -kT\ln\!<e^{-\beta\mathcal{H}}> = \frac{1}{2}\,k_B T \iint \frac{d^2q_\perp dq_z}{(2\pi)^3}\ln\left(K_1 q_\perp^2 q_z^2 + K_3 q_z^4 + \mathcal{B}q_\perp^2\right).$$

The integral depends on the cutoff in the perpendicular direction set by the 2D density of the polymer chains. At the DNA densities under consideration we are always at the small cutoff limit.

$$\mathcal{F} \simeq \frac{k_B T\ V}{5\times 2^{3/2}\pi}\sqrt[4]{\frac{\mathcal{B}}{K_3}}\,q_{\perp max}^{5/2} + \dots \qquad ; \quad q_{\perp max} \ll 2\sqrt{\frac{\mathcal{B}K_3}{K_1^2}} \quad q_{\perp max} \simeq$$

This is the free energy that should give us the osmotic pressure (Strey et al. 1998).

Conformational fluctuations IV (renormalized screening)

The macroscopic free energy depends on the microscopic elastic moduli. (Prost and de Gennes, 1997).

$$
\begin{aligned}
K_1 &= K_2 \simeq U(R)/R \\
K_3 &\simeq \rho_0 K_c + U(R)/R \\
\mathcal{B} &\simeq V \frac{\partial^2 \mathcal{F}_0(V)}{\partial V^2} = \frac{\sqrt{3}}{4} \left(\frac{\partial^2 (\mathcal{F}/L)}{\partial^2 R} - \frac{1}{R} \frac{\partial (\mathcal{F}/L)}{\partial R} . \right)
\end{aligned}
$$

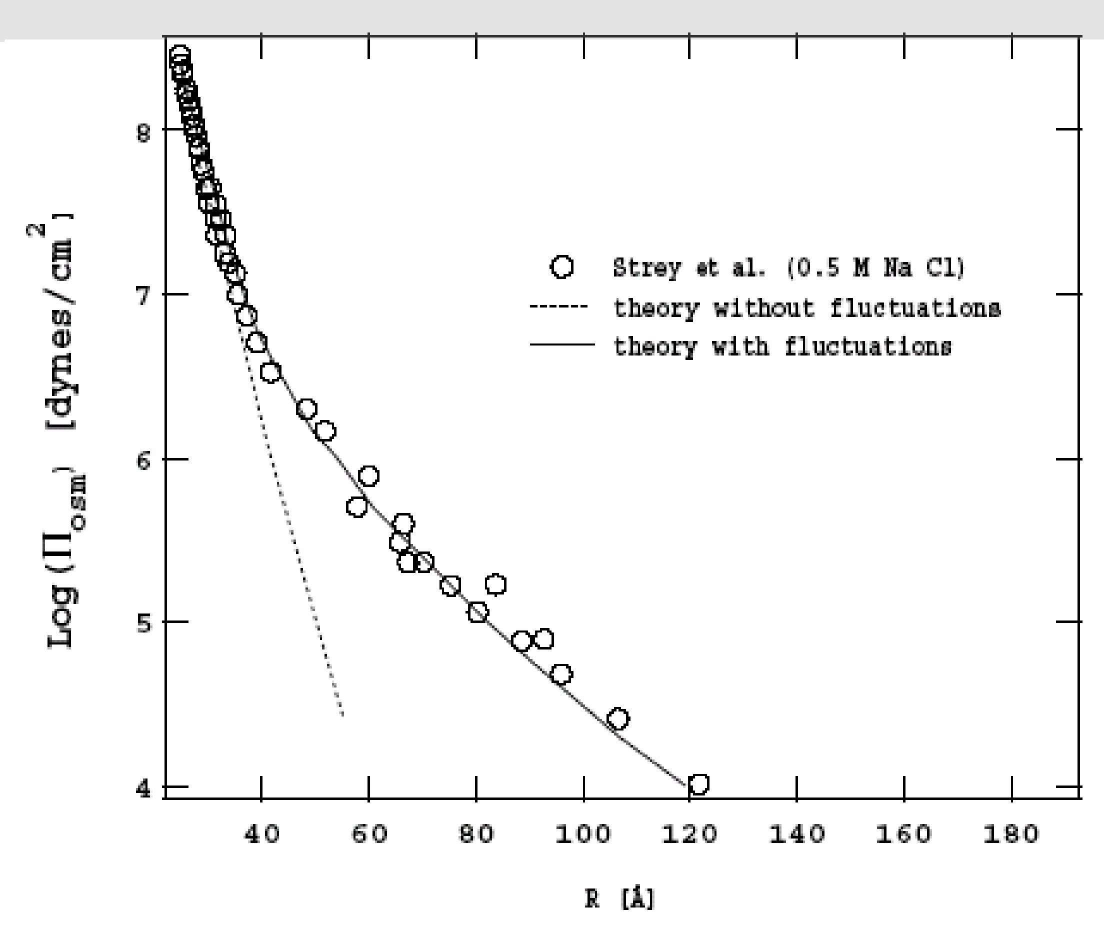
For DNA $K_C = k_B T\ L_p$ and is thus linearly dependent on the persistence length. The compressibility modulus B is obtained from the linearized PB equation.

$$
\mathcal{F} \simeq \frac{k_B T\ V}{5 \times 2^{3/2} \pi} \sqrt[4]{\frac{\mathcal{B}}{K_3}}\ q_{\perp max}^{5/2}
$$

Renormalied screening length (Strey *et al.* 1998)

$$
\text{if} \qquad \mathcal{B} \sim \exp \boxed{(-\kappa^{(0)} R)} \qquad \text{then} \qquad \mathcal{F} \sim \exp \boxed{(-\frac{\kappa^{(0)} R}{4})}
$$

Conformational fluctuations V (comparison with experiment)



DNA in monovalent (NaCl) salt solution. Paradigmatic behavior for all monovalent salts.

Electrostatics can only be seen indirectly, as modified by the presence of conformational fluctuations.

Only for counterion-only case does one see direct effects of electrostatics.

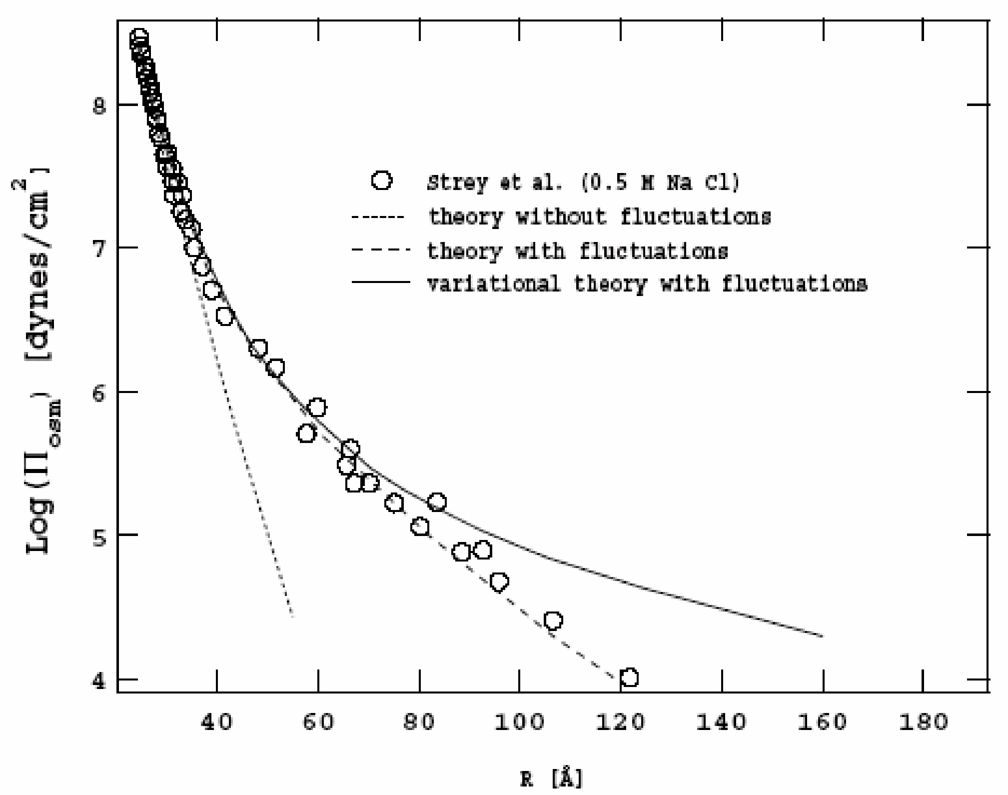
Renormalized value of λ.

$$\lambda^{(r)} = 4\,\lambda_D.$$

Factor 4 due to elasticity (fourth derivative).

Conformational fluctuations VI
(variational theory)

$$\mathcal{H} = \tfrac{1}{2}K_C \sum_{n,m=1}^{\infty} \int dz \left(\frac{\partial^2 \mathbf{r}_\perp{}^{(n,m)}(z)}{\partial z^2}\right)^2 + \tfrac{1}{2}\sum_{n,m\neq n'm'}^{\infty} \int dz\, V\left(\mathbf{r}_\perp{}^{(n,m)}(z) - \mathbf{r}_\perp{}^{(n',m')}(z)\right)$$



$$\mathbf{r}_\perp{}^{(n,m)}(z) \quad = \quad \mathbf{R}_{nm} + \mathbf{u}^{(n,m)}(z$$

$$\mathbf{R}_{nm} \quad = \quad n\mathbf{a}_1 + m\mathbf{a}_2,$$

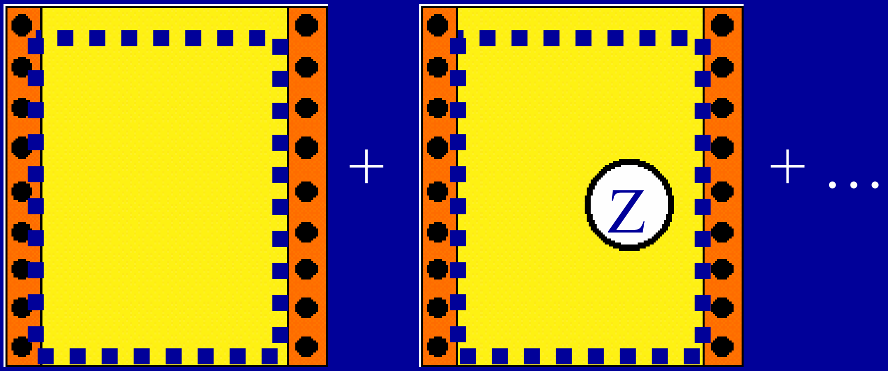
Harmonic fluctuations around mean positions $R_{n,m}$.

Odijk's (1993) theory applied to DNA data by Kassapidou and van der Maarel (1998).

Worse fit to data. DNA at this densities is not a crystal.

Continue…

The strong coupling limit I (asymptotics)



Electrostatic energy
of a single counterion

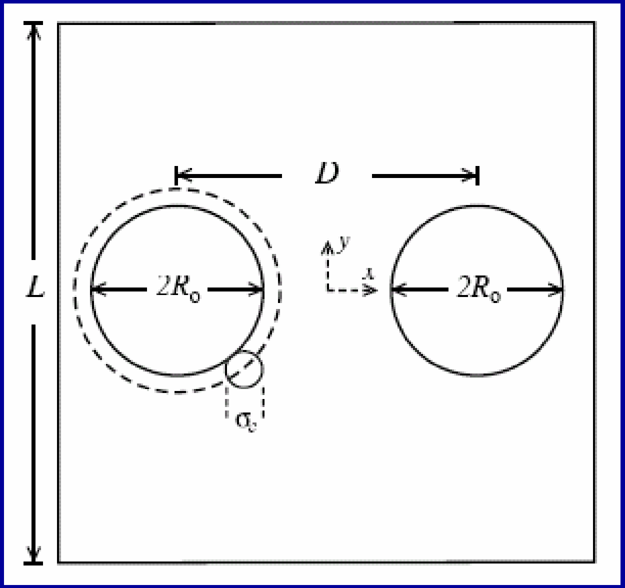
Electrostatic energy
without mobile counterions

$$Q = \frac{\ell_B}{h},$$

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

$$Q_c = \frac{2}{3}.$$

Critical Manning parameter.



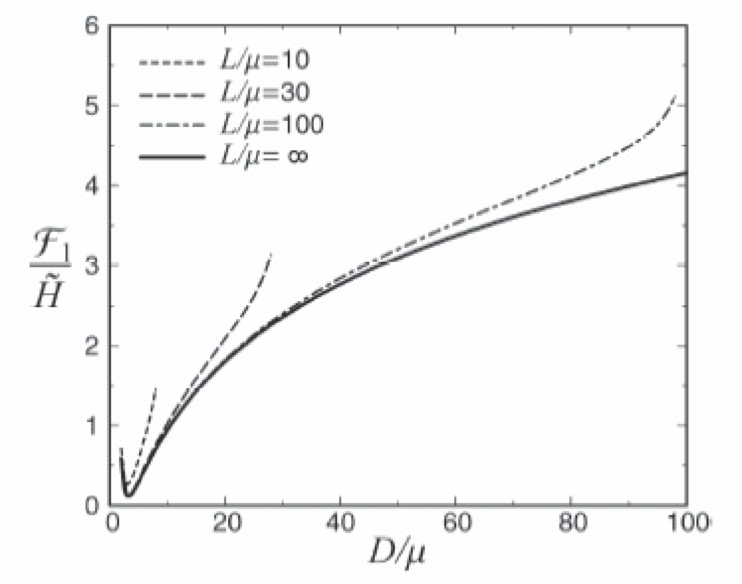
Asymptotic forms of the free energy:

$$\mathcal{F}(Q < 1)\frac{\lambda_{GC}}{h} \sim -6Q(Q_c - Q)\log\frac{D}{\lambda_{GC}}$$

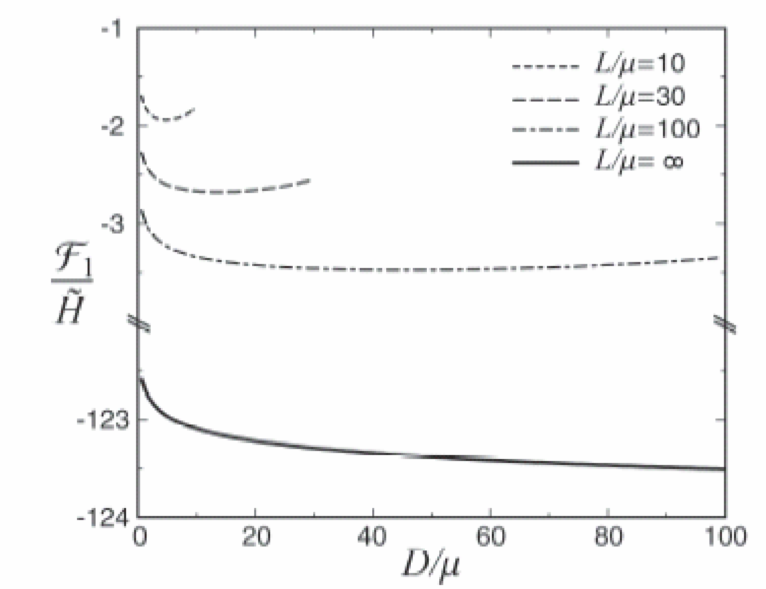
$$\mathcal{F}(Q > 1)\frac{\lambda_{GC}}{h} \sim 2Q^2 \log\frac{D}{\lambda_{GC}}$$

Naji and Netz, 2004.

The strong coupling limit II



Q = 1.



Q = 0.3

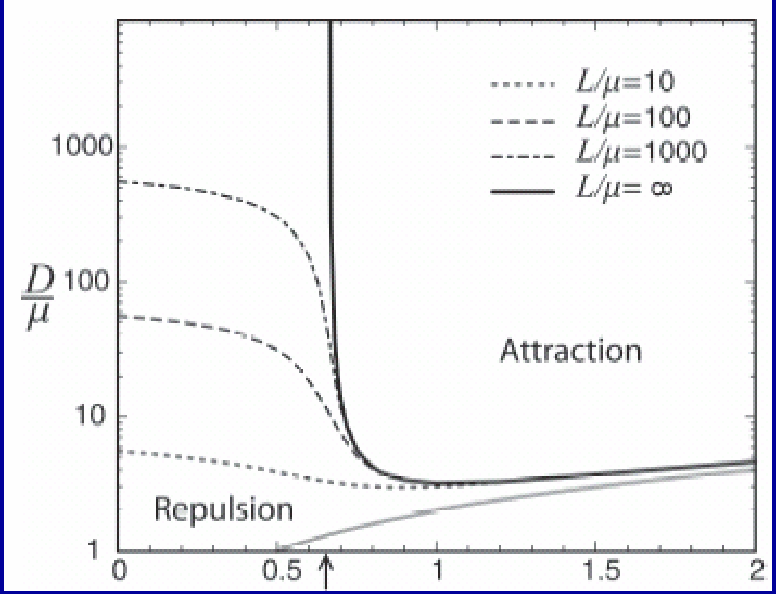
Equilibrium spacing.

$$D_*(Q \gg 1) \sim 2R + \frac{2}{3}\lambda_{GC} + \ldots$$

Close to the critical value of Q

$$D_*(Q \rightarrow Q_c) \sim (Q - Q_c)^{-3/2}$$

Naji and Netz, 2004.



The strong coupling limit III
(simulations)

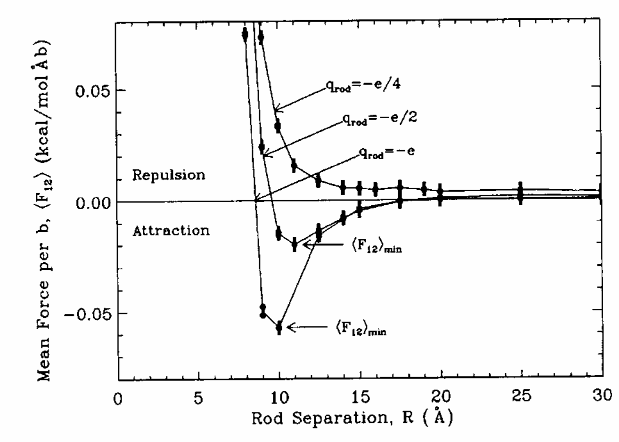
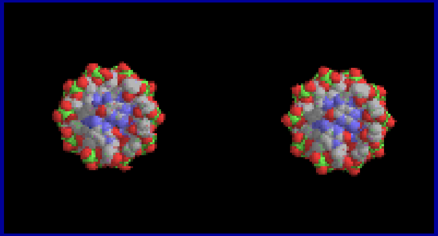


FIG. 1. Mean force $\langle F_{12}\rangle$ (per length b) between two parallel charged rods, with divalent counterions, as a function

A pair of DNAs with poly-counterions:
(Gronbech-Jensen *et al.* 1997)



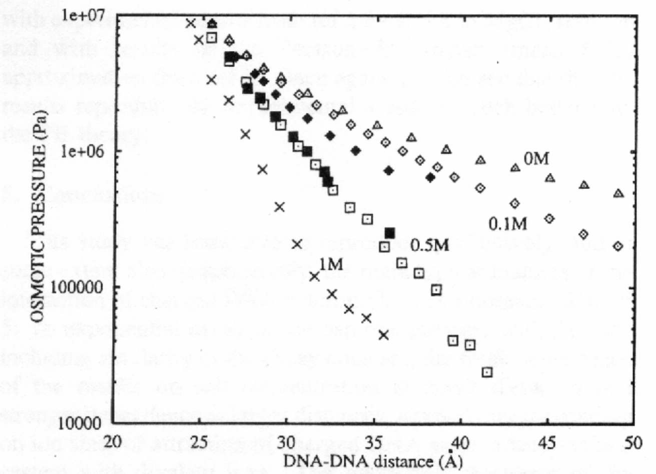
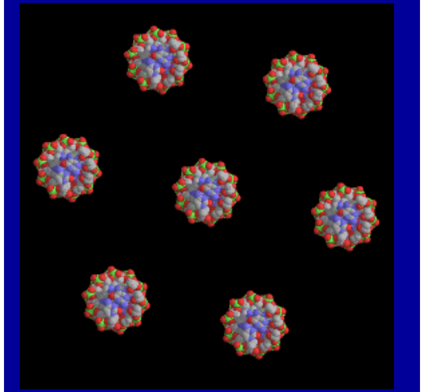


Figure 8. Osmotic pressure in the ordered DNA system in equilibrium with a 1:1 electrolyte bulk phase at different salt concentrations. Ion diameter is 4 Å. Filled squares are experimental results² for 0.1 and 0.5 M equilibrating bulk salt solutions.



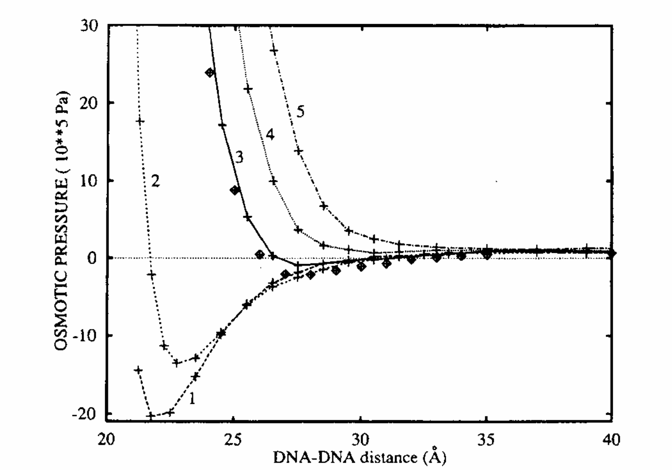
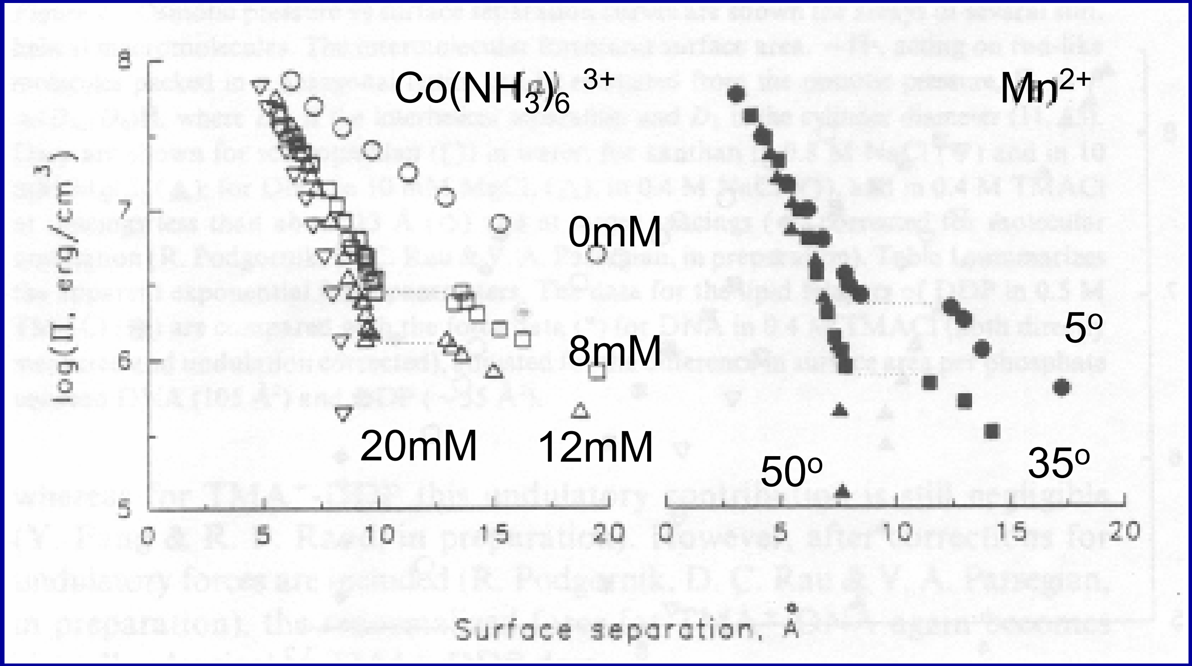
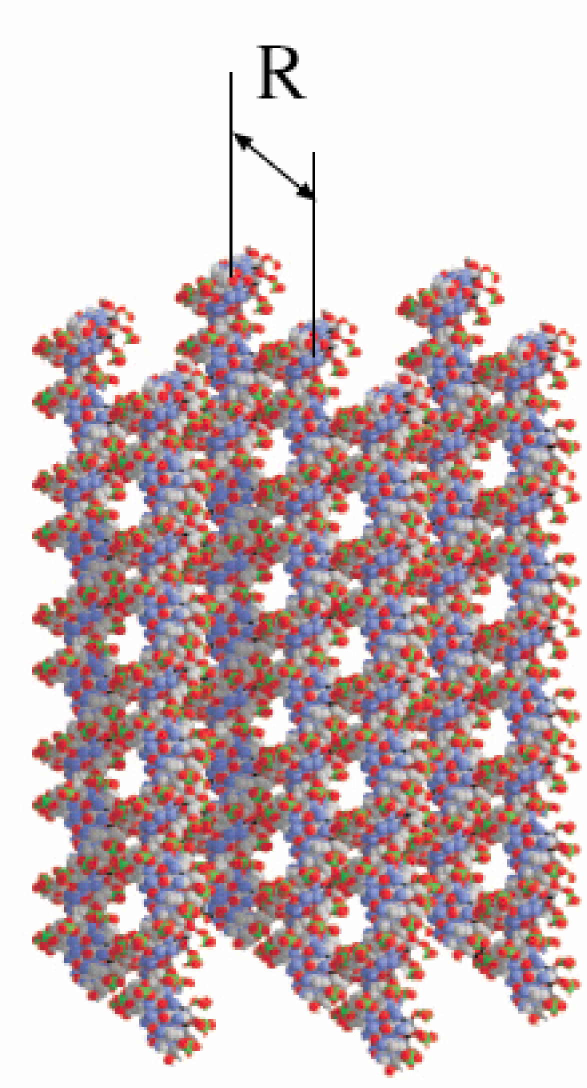


Figure 7. Osmotic pressure in the ordered DNA system with +2 counterions. Lines: one DNA in the cell and ion diameter $\sigma = 0$ (1), $\sigma = 1$ Å (2), $\sigma = 4$ Å (3), $\sigma = 5$ Å (4), $\sigma = 6$ Å (5). Points: seven DNA's in the cell and $\sigma = 4$ Å.

Hexagonal array of DNA poly-counterions: (Lyubartsev and Nordenskiold, 1995)

The strong coupling limit IV
(comparison with experiment)





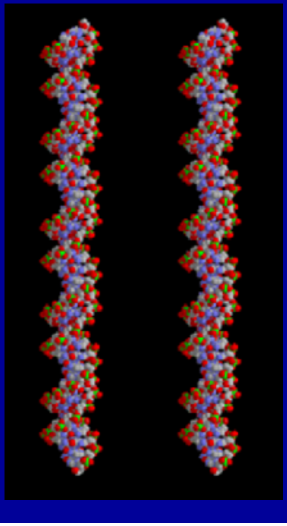
Polyvalent counterions + NaCl at 0.25 M:

- $Co(NH_3)_6Cl_3$ counterion $Co(NH_3)_6{}^{3+}$ (Z = 3)
- $MnCl_2$ counterion Mn^{2+} (Z = 2)

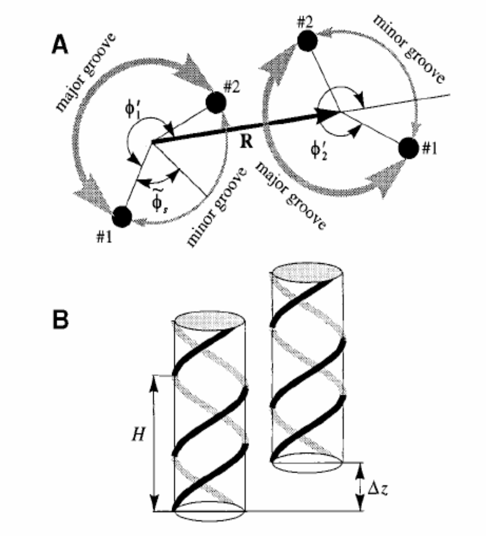
Attraction is obviously there.
Quantitative comparison still difficult.
Monovalent salt + polyvalent counterions

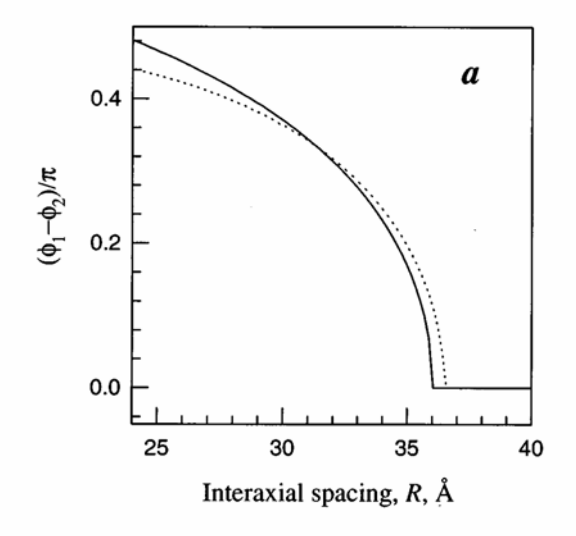
Molecular theories of electrostatics

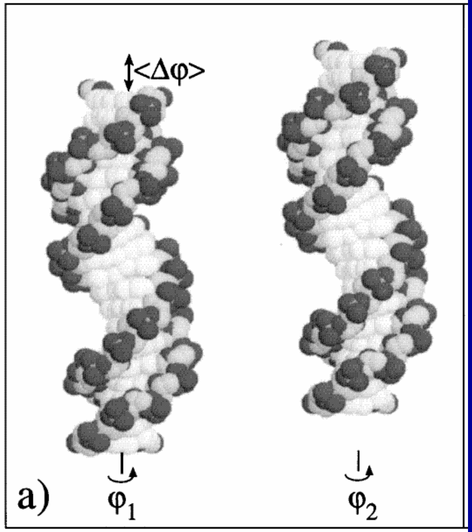
Debye-Hueckel interaction:
- smeared charge
- smeared counterions
- Manning condensation



Kornyshev-Leikin interaction:
- explicit charge
- explicit counterions
- DH-Bjerrum level



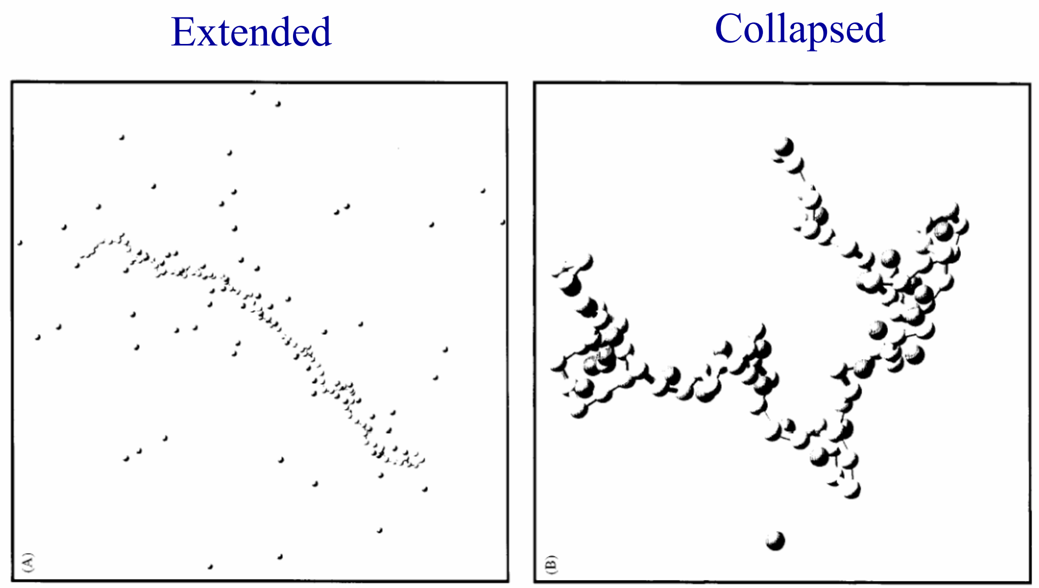




Kornyshev - Leikin, 1998, 2000, 2002.

The strong coupling limit V
(flexible polyelectrolyte)

Swedish polyelectrolyte (no hard cores etc).



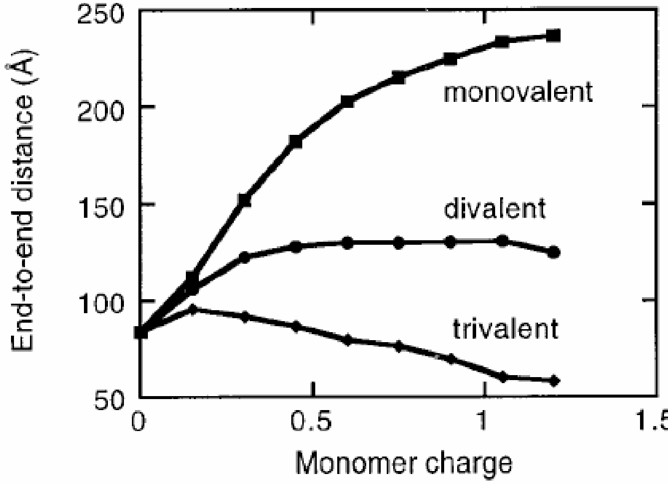
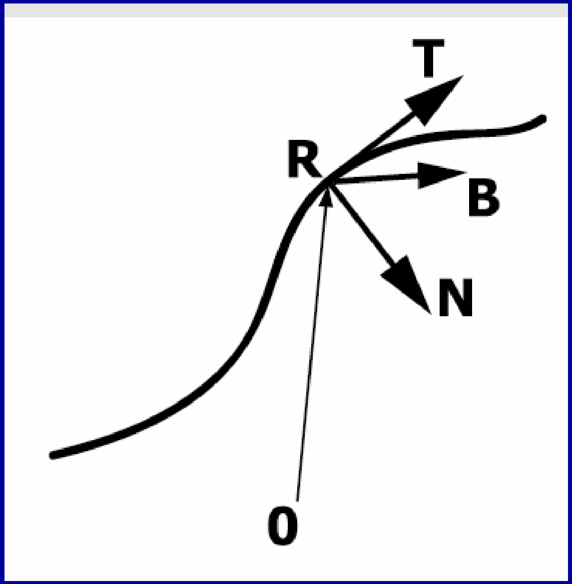


FIGURE 1 The end-to-end distance is shown as a func
tion of monomer charge, for different valency of the cour
terions. No salt was added (N = 80, c_m = 5.4 mM, and
= 6 Å).

Khan and Jonsson, (1999): polyvalent counterions can collapse a flexible chain.
A new problem: interactions and polyelectrolyte flexibility.

Semiflexible chain
(a digression I)



After Kamien (2002).

$$\mathbf{T}(s) = \frac{\mathbf{R}'(s)}{||\mathbf{R}'(s)||},$$

Tangent vector

Arclength parametrization: $||\mathbf{R}'(s)|| = 1$

$$\mathbf{T}'(s) = \kappa(s)\mathbf{N}(s)$$

Normal vector

Elastic energy of the curve can thus be written as (no torsion, no extensibility)

$$E_{\text{curv}} = \frac{1}{2}K_C \int_0^L \left[\frac{d\mathbf{T}(s)}{ds}\right]^2 ds,$$

Elastic constants has the unites of energy X length, thus

$$K_C = kT\ \ell_P^{(0)}$$

Persistence length

Semiflexible chain
(a digression II)

$$Z\left(\mathbf{T}_L\right) = \int_{\mathbf{T}(0)=\hat{z}}^{\mathbf{T}(L)=\mathbf{T}_L} [d\mathbf{T}] e^{-E_{\mathrm{curv}}[\mathbf{T}]/k_{\mathrm{B}}T}$$

Partition function is analogous to the probablity amplitude in QM.

$$\frac{\partial Z(\mathbf{T}, s)}{\partial s} = \frac{1}{2L_p} \hat{\mathbf{L}}^2 Z(\mathbf{T}, s).$$

L^2 is the angular momentum operator..

$$\langle\, \mathbf{T}(s) \cdot \mathbf{T}(s')\,\rangle \;=\; \langle \cos\theta(S)\,\rangle = \frac{\int_{-1}^{1} d(\cos\theta)\cos\theta\, Z(\cos\theta, S)}{\int_{-1}^{1} d(\cos\theta) Z(\cos\theta, S)}$$

$$\frac{d\langle \cos\theta(S)\,\rangle}{dS} = \frac{1}{2L_p}\langle\, \hat{\mathbf{L}}^2 \cos\theta(S)\,\rangle = -\frac{1}{L_p}\langle \cos\theta(S)\rangle$$

with

$$\hat{\mathbf{L}}^2 \cos\theta = -2\cos\theta$$

$$\langle \cos\left[\theta(s) - \theta(s')\right]\rangle = e^{-|s-s'|/L_p}.$$

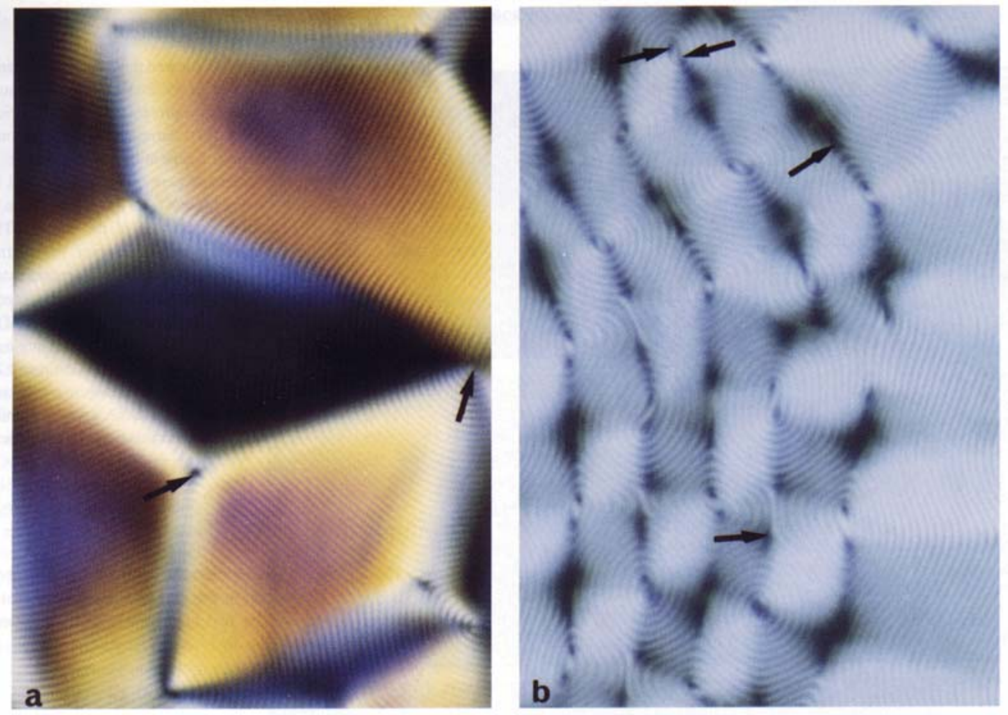
Persistence length sets scale of angular correlations.

Elasticity and interactions I (persistence length)

Persistence length of a semiflexible polymer

$$K_C = kT\ \ell_P^{(0)}$$

μ–tubules	0.1 M NaCl	10^7	Spectrin	0.1 M NaCl	15
TMV	0.1 M NaCl	10^6	Cellulose trinitrate	acetone	17
F-actin	0.1 M NaCl	10000	ss-DNA	0.2 M NaCl	3
Schizophyllan	water	200	Hyaluronic acid	0.2 M NaCl	1
Xanthan	0.1 M NaCl	120	Long Alkanes		0.5
ds-DNA	0.2 M NaCl	50			



cholesteric

Livolant et al. (97)

line hexatic

Elasticity and interactions II
(Kratky-Porod result)

Size of the chain.

$$<\cos(\theta(s)-\theta(s'))> = \exp\left(-\frac{s-s'}{\ell_P^{(0)}}\right)$$

Angular correlations give directly the size of the chain.

$$<(\mathbf{r}(L)-\mathbf{r}(0))^2> = \int_0^L\int_0^L ds ds' <\dot{\mathbf{r}}(s)\cdot\dot{\mathbf{r}}(s')> = \int_0^L\int_0^L ds ds' <\cos(\theta(s)-\theta(s'))>.$$

$$<(\mathbf{r}(L)-\mathbf{r}(0))^2> = 2(\ell_P^{(0)})^2\left(\frac{L}{\ell_P^{(0)}} - (1-\exp-\frac{L}{\ell_P^{(0)}})\right)$$

Kratky - Porod result.

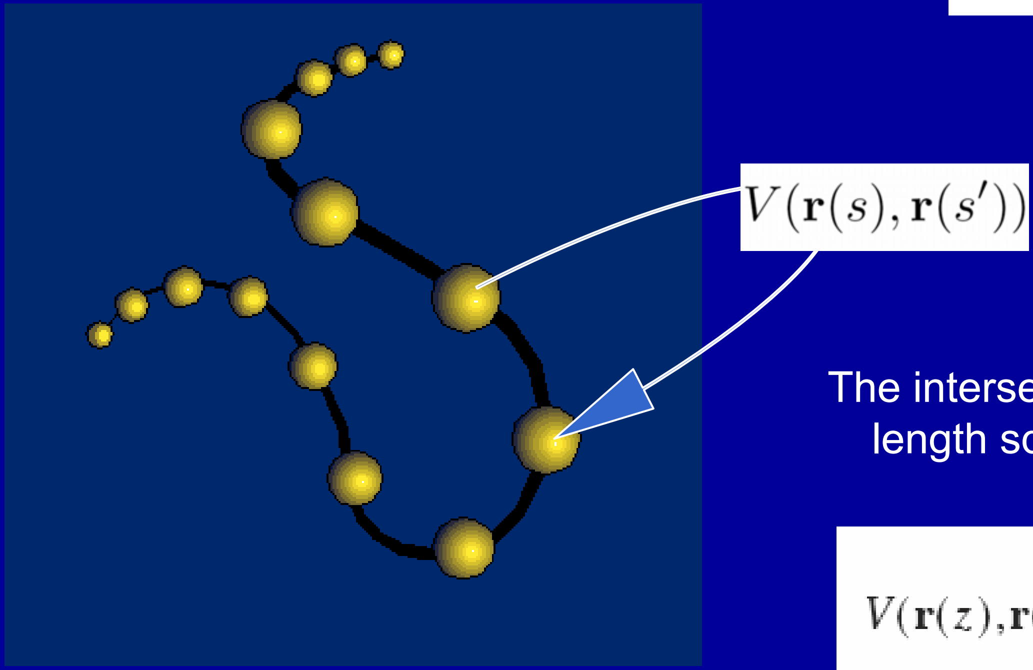
The real problem is however:

$$\mathcal{H} = \frac{k_B T \ell_p^{(0)}}{2}\int ds\left(\frac{\partial^2\mathbf{r}}{\partial s^2}\right)^2 + \frac{1}{2}\int\int ds ds' V(|\mathbf{r}(s)-\mathbf{r}(s')|),$$

Elasticity and interactions III
(interaction potential)

The total interaction energy of the chain:

$$\frac{1}{2}\int_0^L\int_0^L V(\mathbf{r}(s),\mathbf{r}(s'))ds\,ds'$$



Interactions mediated by salt
as well as polyvalent counterions.

The intersegment interaction potential per unit length squared in the weak coupling limit:

$$V(\mathbf{r}(z),\mathbf{r}(z'))=\frac{kTl_B}{a^2}\frac{\exp(-\kappa|\mathbf{r}(z)-\mathbf{r}(z')|)}{|\mathbf{r}(z)-\mathbf{r}(z')|},$$

We do not know the explicit form of the total interaction potential when the bathing solution contains uni-univalent salt (weak coupling) as well as polyvalent counterions (strong coupling).

Elasticity and interactions V
(first repulsive interaction potential)

$$\mathcal{H}=\frac{k_BT\ell_p^{(0)}}{2}\int ds\left(\frac{\partial^2\mathbf{r}}{\partial s^2}\right)^2+\frac{1}{2}\int\int ds\,ds'\,V(|\mathbf{r}(s)-\mathbf{r}(s')|),\quad V(\mathbf{r}(z),\mathbf{r}(z'))=\frac{kTl_B}{a^2}\frac{\exp(-\kappa|\mathbf{r}(z)-\mathbf{r}(z')|)}{|\mathbf{r}(z)-\mathbf{r}(z')|},$$

In addition to this: unstretchable chain plus the form of interactions.

$$\delta\mathcal{H}_1=\frac{1}{2}\int ds\,\lambda^{(0)}(s)((\partial_s\mathbf{r}(s))^2-1).$$

$$\mathbf{t}(s)\cdot\mathbf{t}(s)=1.$$

$$\delta\mathcal{H}_2=\frac{1}{2}\int ds\,ds'\,g(s,s')((\mathbf{r}(s)-\mathbf{r}(s'))^2-B(s,s')).$$

$$V(\mathbf{r}(s),\mathbf{r}(s'))=V(|\mathbf{r}(s)-\mathbf{r}(s')|$$

The partition function can be thus cast into the form

$$Z=\int \mathbf{D}[\mathbf{r}(s)]\mathbf{D}[\lambda^{(0)}(s)]\mathbf{D}[g(s,s')]\mathbf{D}[B(s,s')]$$
$$\times\exp(-\beta(\mathcal{H}+\delta\mathcal{H}_1+\delta\mathcal{H}_2)).$$

Integrate out the harmonic degrees of freedom, and minimize the rest.

Elasticity and interactions VI
(Odijk-Skolnick-Fixman result)

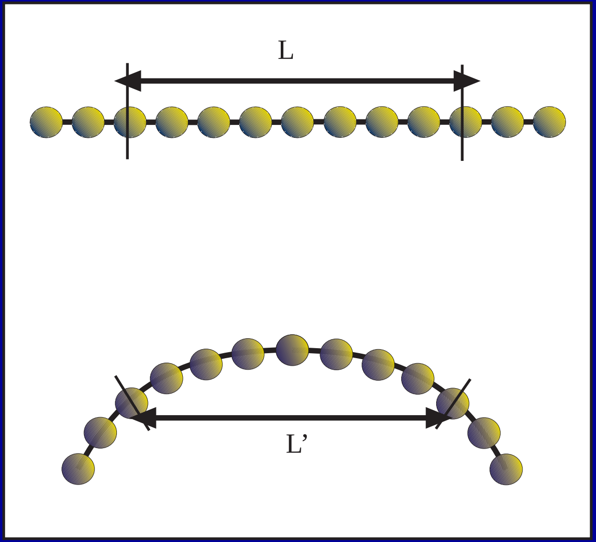
Fundamental insight that this calculation leads to:

$$\boxed{\delta K_c = -2\int_{-\infty}^{\infty} ds \frac{s^4}{4!} V'(B).}$$

$$B(s) = \frac{d k_B T}{2K_c^{(R)}}[\xi^2 s + \xi^3(e^{-s/\xi} - 1)],$$

For screened electrostatics (weak coupling):

$$V(\mathbf{r}(z),\mathbf{r}(z')) = \frac{kT l_B}{a^2}\frac{\exp(-\kappa|\mathbf{r}(z)-\mathbf{r}(z')|)}{|\mathbf{r}(z)-\mathbf{r}(z')|},$$



$$\delta\ell_p = -2\frac{l_B}{A^2}\int_0^{\infty} ds \frac{s^4}{12}\partial_B\left(\frac{e^{-\kappa_0\sqrt{B}}}{\sqrt{B}}\right)_{B=s^2} = \frac{1}{4}\frac{l_B}{A^2}\frac{1}{\kappa_0^2}.$$

$$\ell^{(R)} = \ell^{(0)} + \delta\ell_p.$$

A fundamental insight: Renormalized bending modulus depen
on the parameters of the interaction potential.

Th. Odijk (1977). J. Skolnick and M. Fixman (1977)

Elasticity and interactions IV
(interaction potential)

We assume that the simple salt and the polyvalent counterion interaction potentials are additive and pick a model for the spatial dependence of the latter:

The box model (1):

$$V(r)=\begin{cases}-V_0 & \text{if} \quad r<r_0,\\ 0 & \text{otherwise,}\end{cases}$$

The exponential- inverse r model (2):

$$V(r)=-V_0 e^{-r/r_0},$$

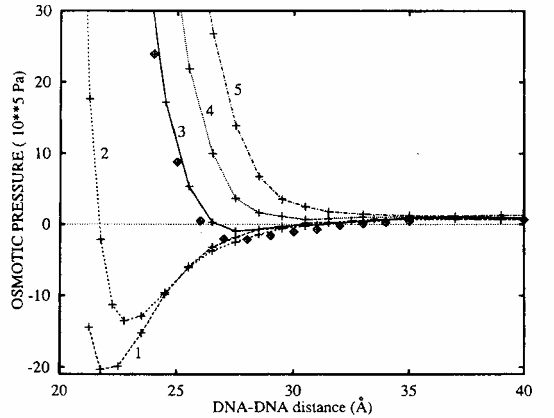


Figure 7. Osmotic pressure in the ordered DNA system with +2 counterions. Lines: one DNA in the cell and ion diameter $\sigma = 0$ (1), $\sigma = 1$ Å (2), $\sigma = 4$ Å (3), $\sigma = 5$ Å (4), $\sigma = 6$ Å (5). Points: seven DNA's in the cell and $\sigma = 4$ Å.

Reality check

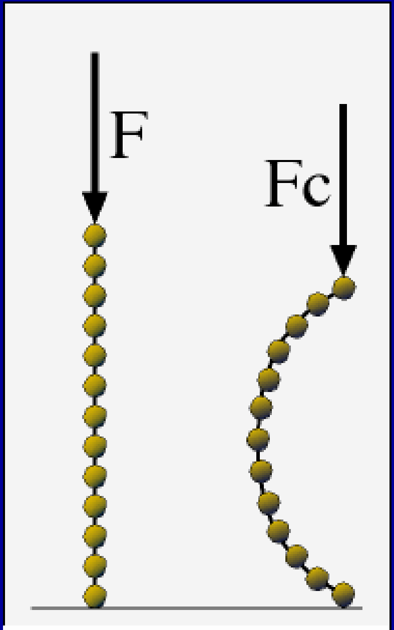
The exponential-inverse r² model (3):

$$V(r)=-V_0 a^2\left(\frac{e^{-r/r_0}}{r}\right)^2 \equiv -|v_0|\frac{e^{-\kappa r}}{r^2}.$$

Refrain from details, concentrate on the salient features of models (1), (2), and (3).

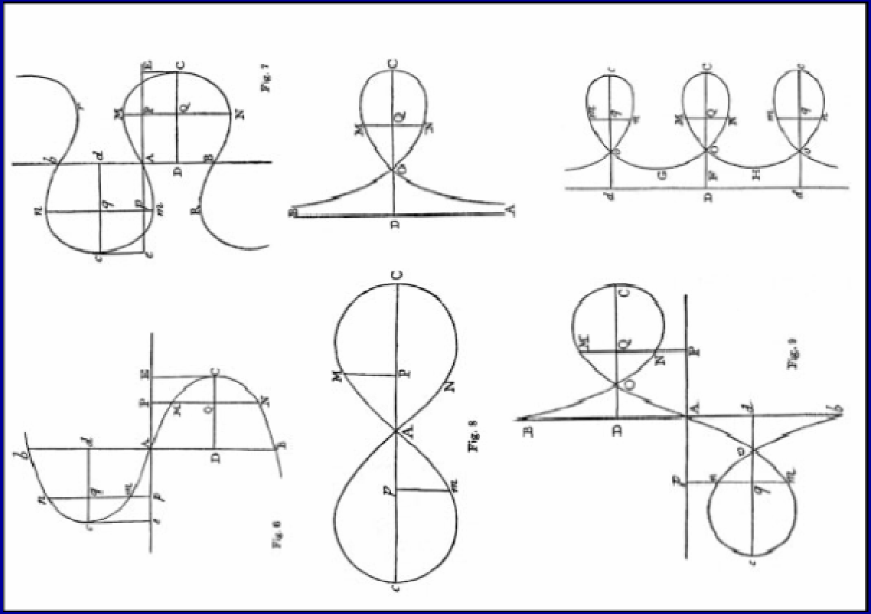
Hansen *et al.* 1999.

Elasticity and interactions VII
(Euler instability)



$$\frac{L^2 F}{K_c} \sim \frac{\pi^2}{2}$$

Press on an elastic filament hard enough and it buckles



Kirchhoff kinematic analogy

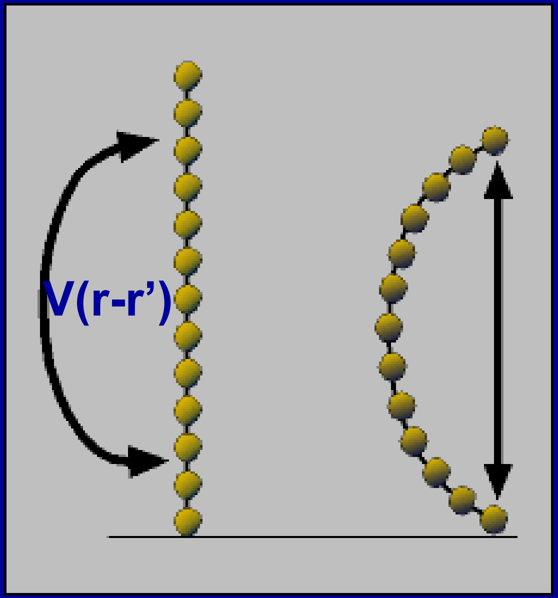
The role of the external force can be played by attractive interactions.
Euler-Kirchhoffian elasticity gives in this case:

$$K_c \rho^{(iv)}(z) - \int_0^L dz' V(|z-z'|)\rho''(z) \simeq 0.$$

$$(z, \rho(z))$$

Manning (1985): Euler buckling due to self-interactions (?).

Elasticity and interactions VIII
(Manning buckling)



$$K_c\rho^{(iv)}(z)-\int_0^L dz'V(|z-z'|)\rho''(z)\simeq 0.$$

$$\int_0^L dz\sqrt{\left|\int_0^L dz'\beta V(|z-z'|)\right|}=\sqrt{\beta K_c}\pi.$$

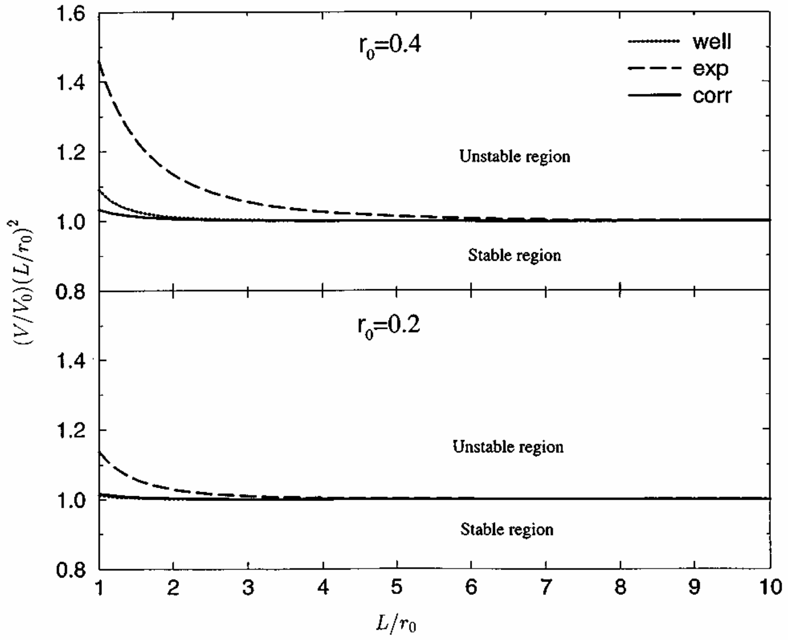


FIG. 2. Critical strength of the interaction potential, in terms of the dimensionles parameter $(V_{\mathrm{cr}}/V_0)(L/r_0)^2$, with $V_0=K_c/r_0^3$, as a

Models (1), (2) and (3) give similar results.

This is a mean-field like calculation. No thermal fluctuations. Just elasticity.

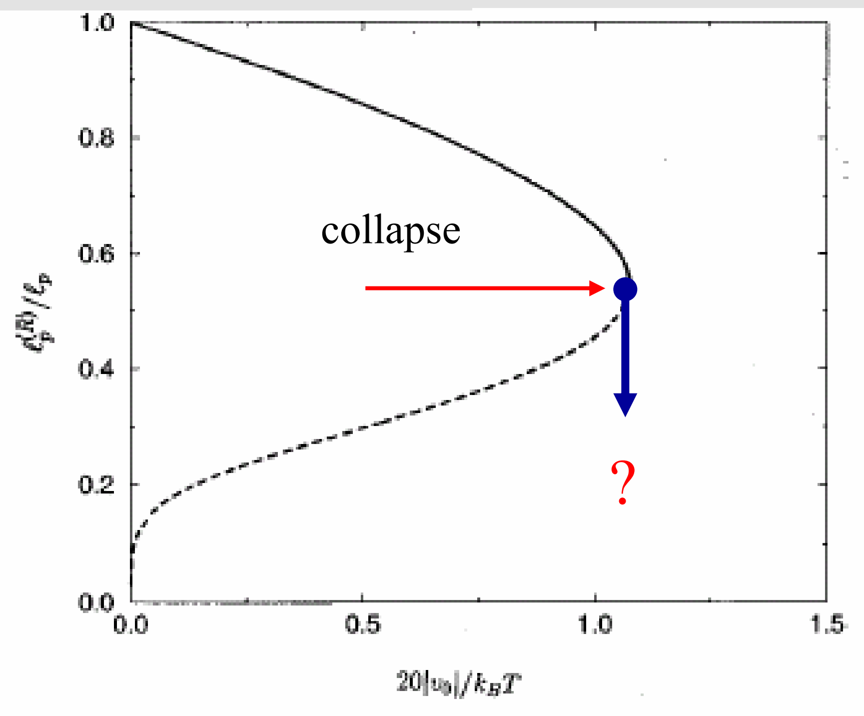
Elasticity and interactions IX
(Buckling and thermal fluctuations)

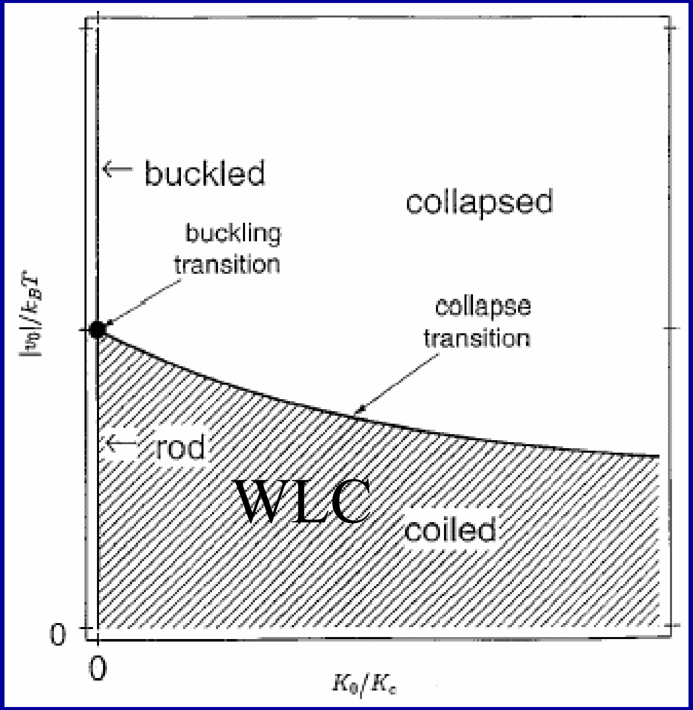
How to include thermal fluctuations? Odijk (1998) proposes a harmonic theory. It leads to a renormalization of the bending rigidity. A full non-linear theory takes us back right to:

$$\delta K_c = -2\int_{-\infty}^{\infty} ds \frac{s^4}{4!} V'(B).$$

Hansen *et al.* 1999.

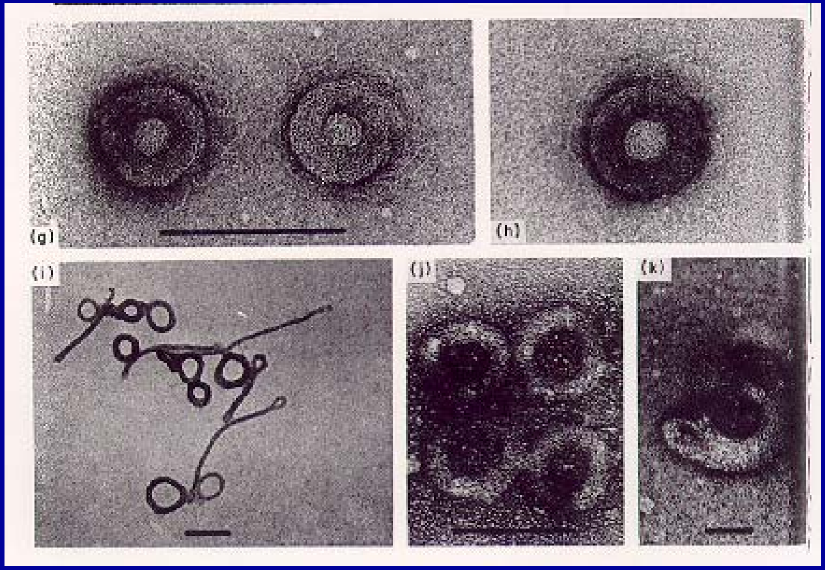
But now the interaction has a repuslive (WC) and an attractive part (SC).

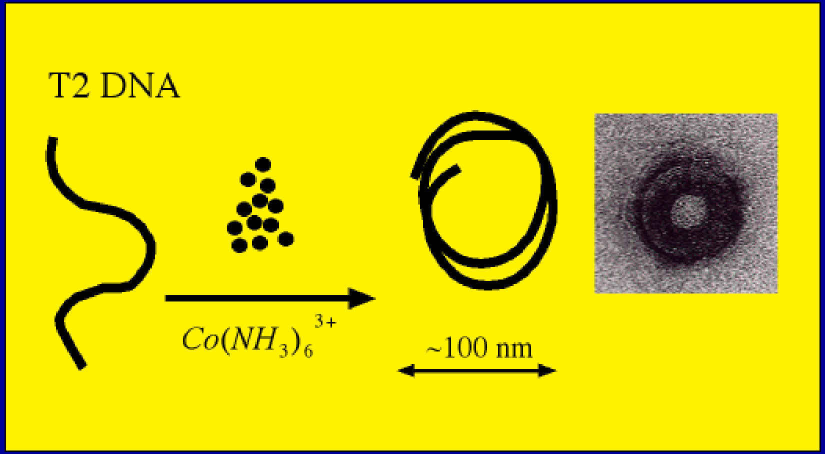




Liverpool, Golestanian, Kardar (2000). Ha and Thirumalai (2002), Nguyen, Rouzina and Shklovski (1999).

Elasticity and interactions X
(Buckling and DNA condensation)



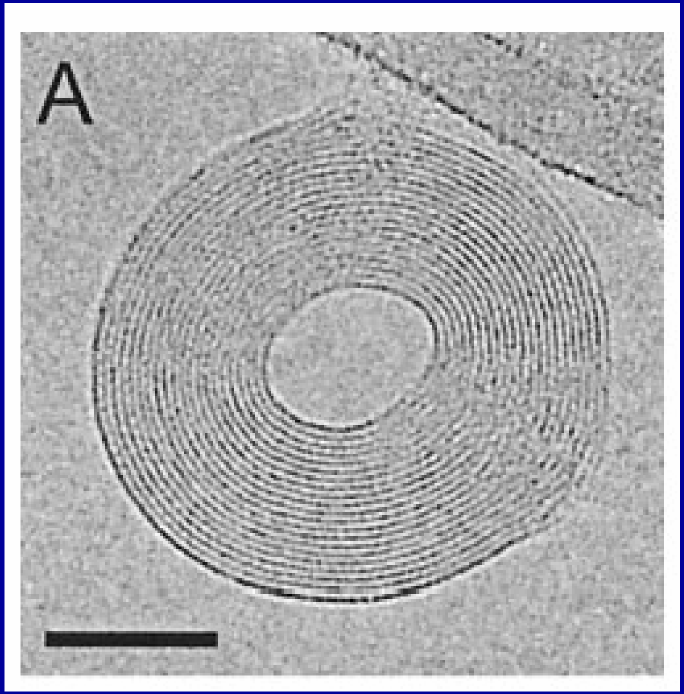

T2 DNA

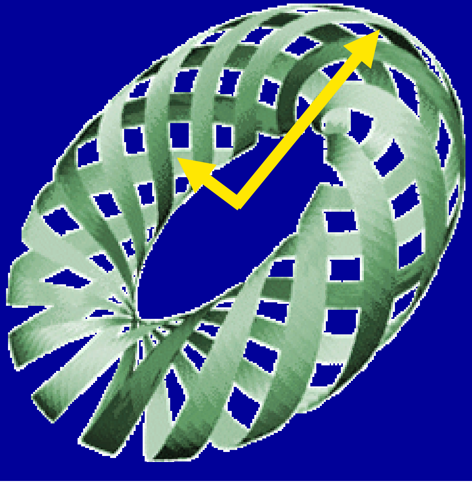
$Co(NH_3)_6^{3+}$

~100 nm

Chattoraj *et al.* (1978).

Hud & Downing (2001)



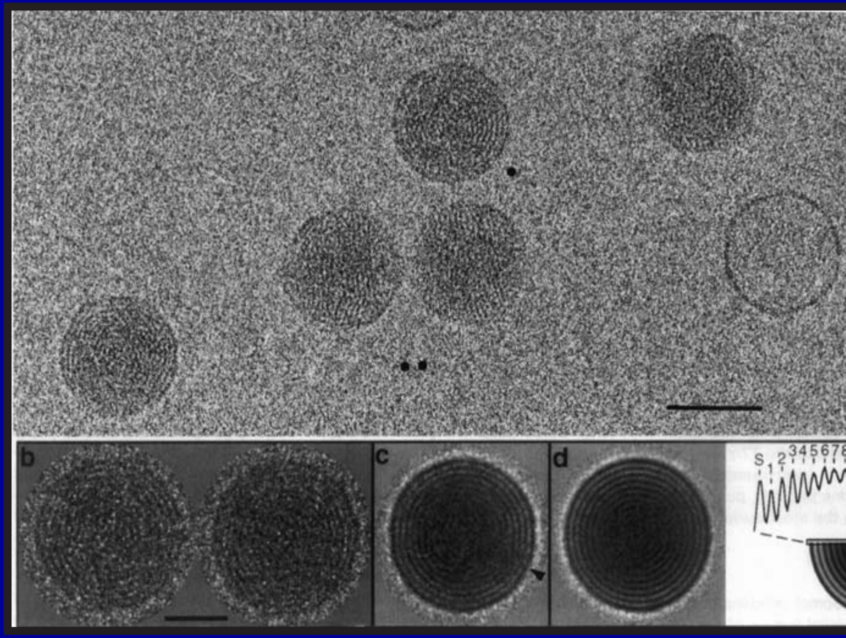


95-185 nm
35-85 nm
2.4 nm

DNA condensation

In most vertebrate sperm cells DNA is condensed by arginine-rich proteins into thousands of toroidal structures, each measuring ~ 100 nm in outside diameter. The DNA of some bacteriophages also is packaged into a single toroid, or spool, with similar dimensions. Thus, the toroid represents a fundamental morphology selected by nature for the high-density packaging of DNA (Hud & Downing 2001).

- Very few - luckily for us - (cat)ions induce DNA condensation. Mn^{2+}, Cd^{2+}, $Co(NH_3)^{3+}$, polyamines such as sperimidine $^{3+}$, spermine $^{4+}$, protamine $^{21+}$, polylysine^{N+}
- Condensation is a complex phenomenon still not completely understood.
- Axial charge separation along DNA seems to be necessary for condensation
- Best condensing agents bind into the major or minor groove.
- Almost all divalent cations condense ssDNA but not dsDNA.
- Electrostatics is an important but not the only factor in DNA collapse (CoHex more efficient then spermidine!).

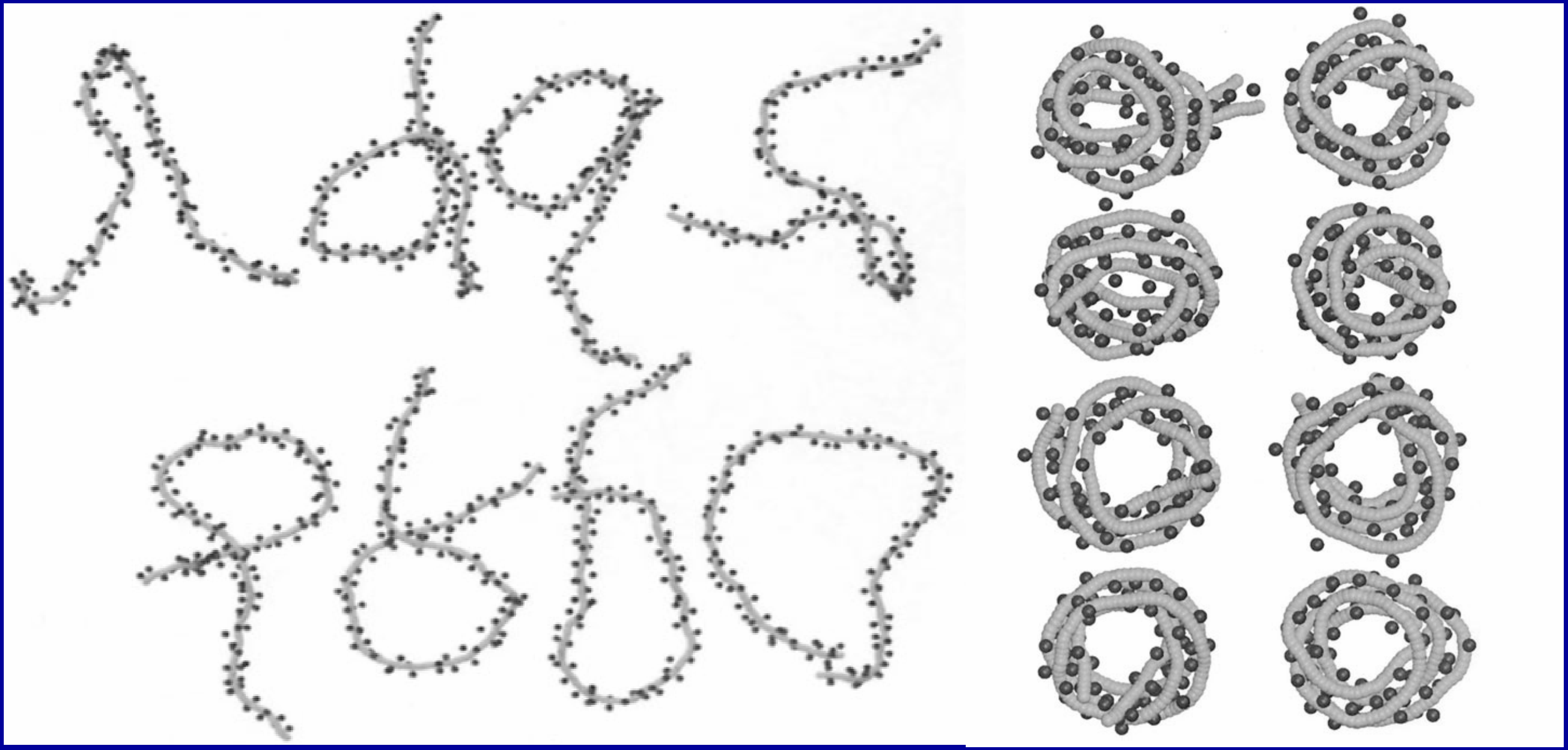


Cerritelli et al.(1997). T7 DNA.

Elasticity and interactions XI
(DNA condensation simulations)

Elastic, Euler-like, states are important for DNA collapse. Stiff polymers have a different Collapse pathway (originates in the buckling transition) then flexible polymers.

There might be a whole slew of Euler-like intermediate states that lead to DNA collapse. Much more ordered collapsed state then in Khan and Jonsson.



Stevens BJ (2001). This collapse is very different from a flexible chain.

Elasticity and interactions XII
(DNA condensation simulations)

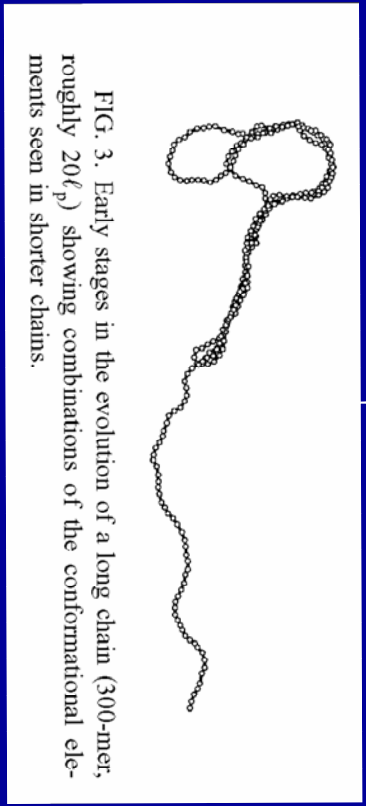


FIG. 3. Early stages in the evolution of a long chain (300-mer, roughly $20\ell_p$) showing combinations of the conformational elements seen in shorter chains.

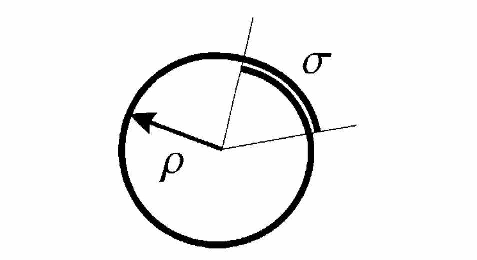


FIG. 5. Sketch of a generic torus (here a 1+ in our labeling scheme) of radius ρ and overhang σ.

toroidal

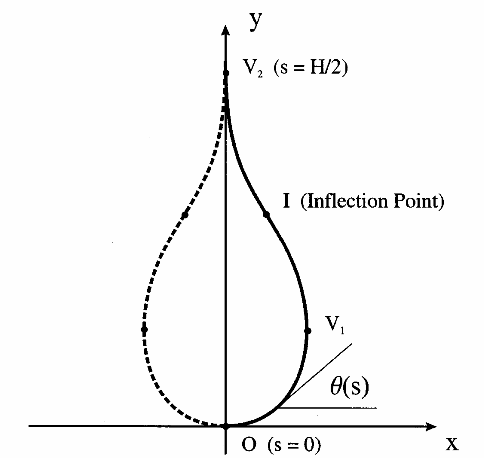
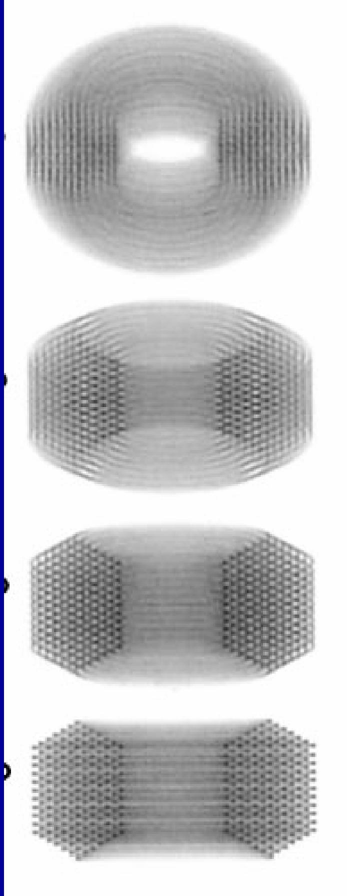


FIG. 10. Schematic figure of a racquet head with axes appropriate for our calculation. Local tangent angles θ are measured from the x axis. Symmetrical regions along the contour s are delimited by solid circles.

racquet-like

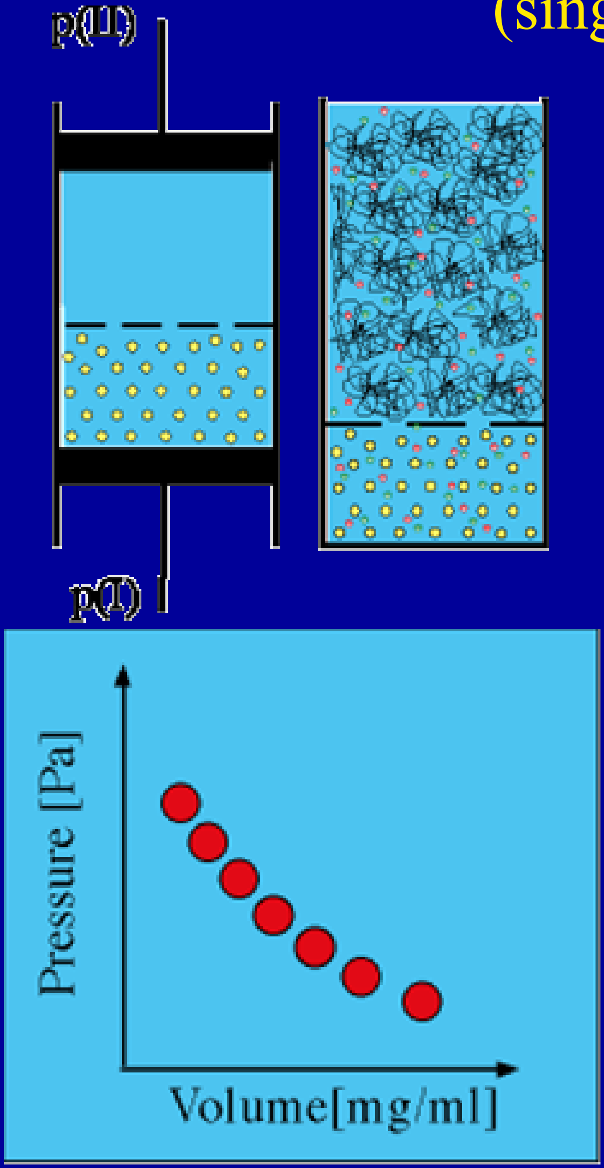
?



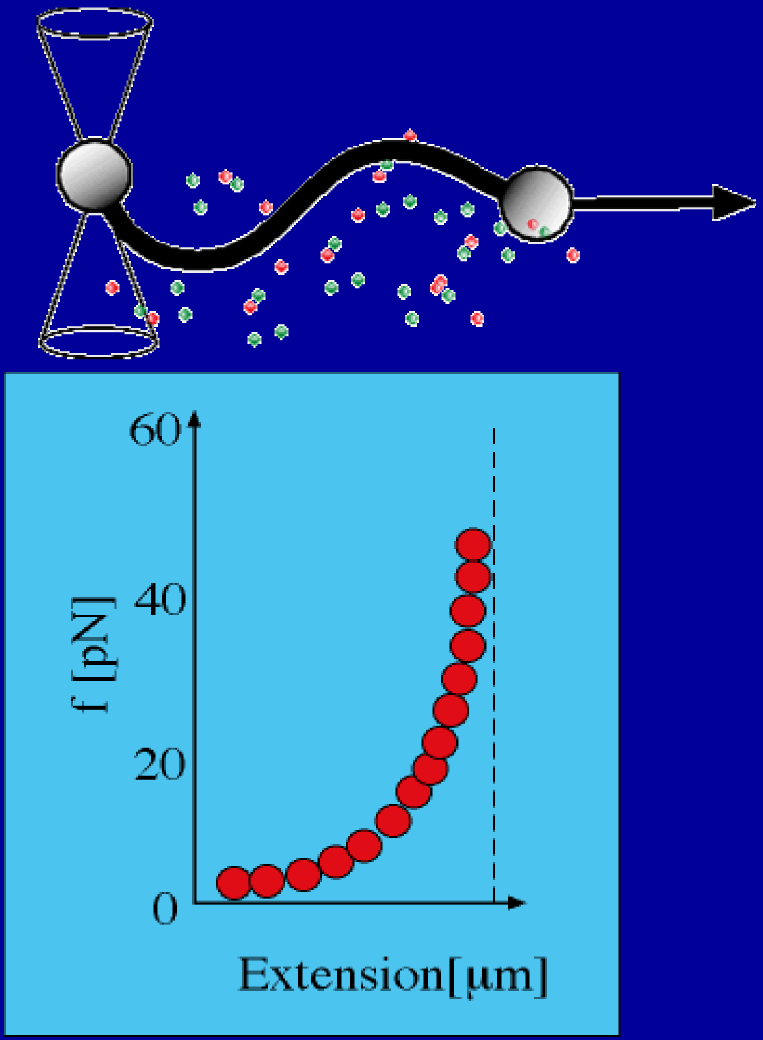
Euler (elastic) intermediates are clearly seen also in simulations of Schnurr, Gittes and MacKintosh PRE (2002).

We understand “well” only one side of the transition. The destabilization of the persistence length leading to a 1st order transition.

Elasticity and interactions XIII
(single molecule physics)



Many chains



Single chain

Elasticity and interactions XIII
(elastic equation of state)

A mesoscopic model of a chain under external traction

$$\mathcal{H} = \tfrac{1}{2} K_C \int_0^L \dot{\mathbf{t}}(s)^2 ds + \mathbf{f} \cdot (\mathbf{r}(L) - \mathbf{r}(0)) = \tfrac{1}{2} K_C \int_0^L \dot{\mathbf{t}}(s)^2 ds + \int_0^L \mathbf{f} \cdot \mathbf{t}(L).$$

Equation of state

$$\mathcal{F}(f) = -kT \ \log \int \ \mathcal{D}[\mathbf{t}(s)] \exp\left(-\beta \mathcal{H}[t(s)]\right)$$

Pincus, 1975, de Gennes, 1975 Marko & Siggia 1994 Vologodskii 1994 Odijk 1995 Moroz & Nelson 1997 Ha & Thirumalai 1997 Bouchiat *et al*. 1999 Podgornik *et al*. 2000 Netz 2001

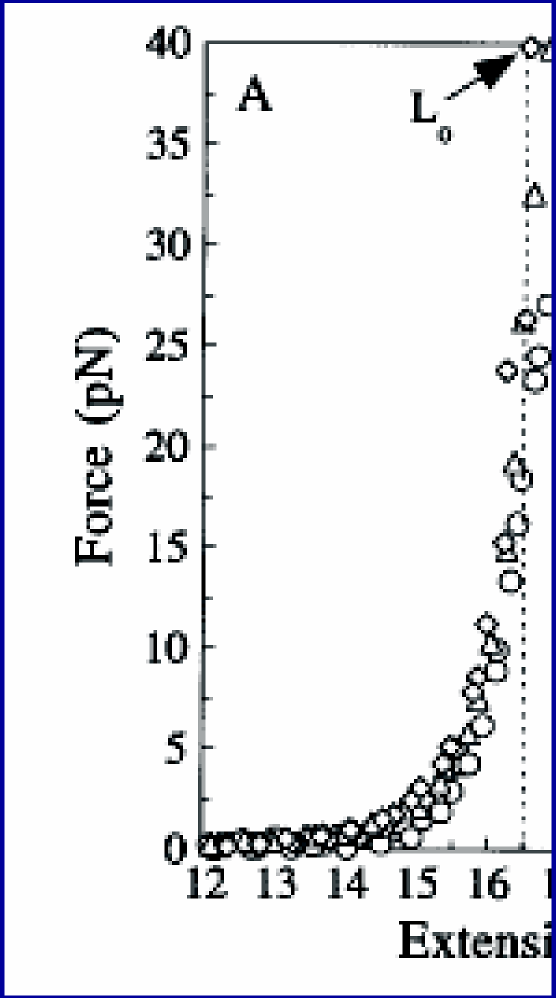
$$f = \frac{kT}{4\ell_P^{(0)}} \left(\frac{1}{1 - \zeta^2} - 1 + 4\zeta \right) + \frac{kT}{\ell_P^{(0)}} \sum_{N=1}^{N_m} \alpha_N \zeta^N .$$

$$\frac{\ell^{(0)}}{kT} f = \zeta + \mathcal{O}(\zeta)$$

Limiting forms

$$\frac{4\ell^{(0)}}{kT} f = \frac{1}{(1 - \zeta)^2} + \mathcal{O}(1 - \zeta$$

Elasticity and interactions XIV (bending and stretching)



$$\zeta \longrightarrow \zeta - \frac{f}{\lambda^{(0)}}$$

Entropic plus enthalpic Hookeian elasticity

$$\zeta = 1 + \frac{f}{\lambda^{(0)}} + \frac{1}{2}\sqrt{\frac{kT}{\ell^{(0)} f}} + \mathcal{O}(1/f)$$

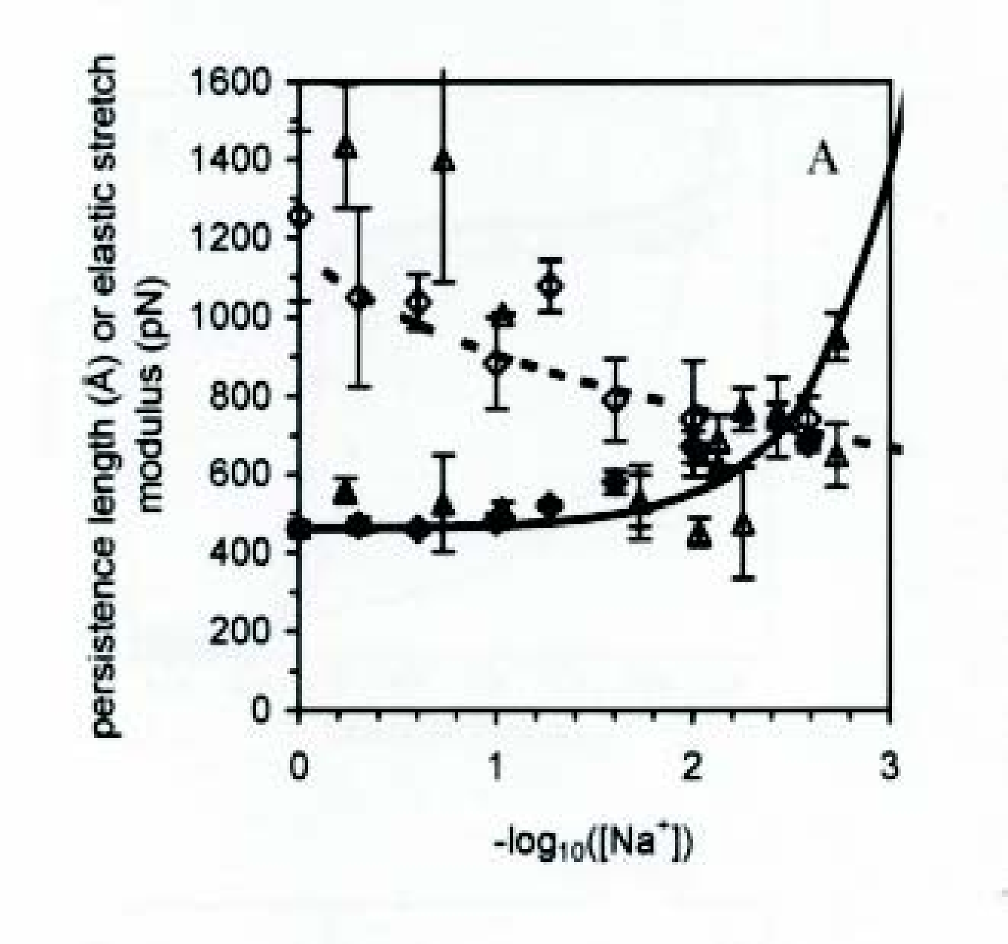
Entropic elasticity

$$\zeta = \frac{\ell^{(0)}}{kT} f + \mathcal{O}(f^2)$$

The experiment gives us both moduli $l^{(0)}$ as well as $\lambda^{(0)}$. ds-DNA is not very stretchable, but it is not rigid either.

48 kb λ-DNA (~ 16 μm) in 2.5 - 1000 mM univalent NaCl. Baumann *et al*. 1997, Wenner *et al*. 2002)

Elasticity and interactions XV (DNA not an elastic rod)



In classical elasticity one should have

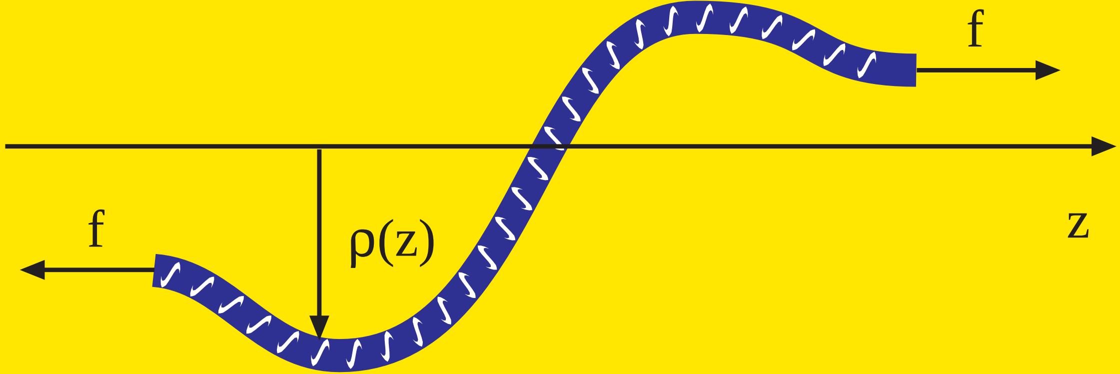
$$K_C = \frac{1}{4}\lambda R^2$$

Bending is just local stretching.
Landau and Lifshitz, 1995.

Since variations in ionic strength are involved, we assume that the foul play is due to electrostatics.

Lowering the ionic strength increases the measured persistence length, but seems to reduce DNA's elastic stretch modulus, contradicting the elastic rod model. Bustamante *et al*. (2000).

Elasticity and interactions XVI
(minimal model at large stretching)



$$u_{zz} = \frac{\partial u_z(z)}{\partial z} + \frac{1}{2}\left(\frac{\partial \boldsymbol{\rho}(z)}{\partial z}\right)^2$$

$$\begin{aligned}\mathcal{H}[u_z(z), \boldsymbol{\rho}(z)] \quad = \quad & \frac{1}{2}\lambda^{(0)} \int_0^L u_{zz}^2 ds(z) + \\ & + \frac{1}{2} K_C \int_0^L \left(\frac{\partial^2 \boldsymbol{\rho}(z)}{\partial z^2}\right)^2 ds(z) + \\ & + f\left(u_z(z) - u_z(0)\right) + \\ & + \frac{1}{2}\int_0^L \int_0^L V\left(|\mathbf{r}(z) - \mathbf{r}(z')|\right) ds(z) ds(z').\end{aligned}$$

stretching

bending

external force

interactions

A minimal model for a semiflexible, stretchable chain.

Elasticity and interactions XVI
(integrating out the interactions)

Just like in the OSF case here too the interactions renormalize elasticity

$$
\begin{aligned}
\mathcal{H}^{(R)}[u_z(z),\boldsymbol{\rho}(z)]-\mathcal{H}[\zeta] \quad = \quad & \frac{1}{2}\lambda^{(R)}\int_0^L\left(\delta\zeta+\frac{\partial u_z(z)}{\partial z}+\tfrac{1}{2}\left(\tfrac{\partial^2\boldsymbol{\rho}(z)}{\partial z^2}\right)^2\right)^2 ds(z)+\\
&+\frac{1}{2}K_C^{(R)}\int_0^L\left(\frac{\partial^2\boldsymbol{\rho}(z)}{\partial z^2}\right)^2 ds(z)+\\
&+f\int_0^L\delta\zeta\, ds(z).
\end{aligned}
$$

Renormalized elastic moduli, but different signs

$$K_C^{(R)} = K_C^{(0)} \boxed{+\delta} K_C[V(|\mathbf{r}(z)-\mathbf{r}(z')|)] \qquad \lambda^{(R)} = \lambda^{(0)} \boxed{-\delta}\lambda[V(|\mathbf{r}(z)-\mathbf{r}(z')|)$$

$$\delta K_C = \frac{1}{12}\int_0^L ds(z) z^4 \partial_{\mathcal{B}(z)} V(\mathcal{B}(z)) \qquad \delta\lambda = \int_0^L ds(z) z^2 \partial_{\mathcal{B}(z)} V(\mathcal{B}(z))$$

Interactions thus merely renormalize the elastic constants but leave the form of the Hamiltonian untouched. This is indeed the general philosophy of continuum mechanics.

Elasticity and interactions XVII

$$\zeta = 1 + \frac{f}{\lambda^{(0)}} + \frac{1}{2}\sqrt{\frac{(kT)^2}{K_C^{(0)} f}} \longrightarrow \zeta = 1 + \frac{f}{\lambda^{(R)}} + \frac{1}{2}\sqrt{\frac{(kT)^2}{K_C^{(R)} f}}$$

For screened (WC) electrostatics

$$V(\mathbf{r}(z),\mathbf{r}(z')) = \frac{kTl_B}{a^2}\frac{\exp(-\kappa|\mathbf{r}(z)-\mathbf{r}(z')|)}{|\mathbf{r}(z)-\mathbf{r}(z')|},$$

$$K_C^{(R)} = K_C^{(0)} + \frac{kT\,\ell_B}{4\Delta^3(\kappa a)^2} \qquad \lambda^{(R)} = \lambda^{(0)} - \frac{kT\,\ell_B}{4\Delta^2 a^2}(1 - \mathrm{Ei}(-\kappa b))$$

$$K_C^{(R)} = K_C^{(0)} + \frac{kT\,\ell_B}{4(\kappa a)^2}$$

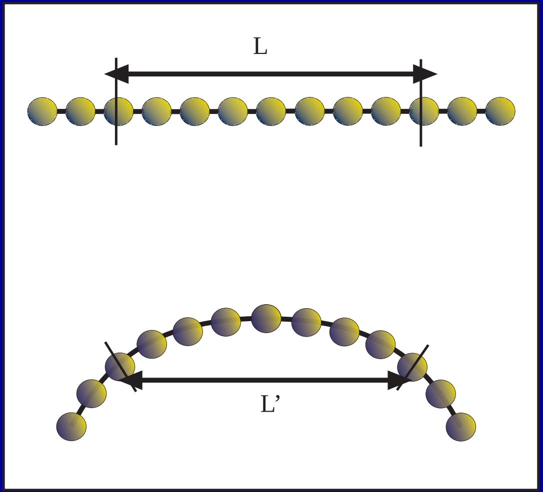
Standard OSF

$$\Delta^2 = \frac{\mathcal{B}(z)}{(z - z)^2} \approx \frac{\lambda^{(0)}}{\lambda^{(R)}}$$

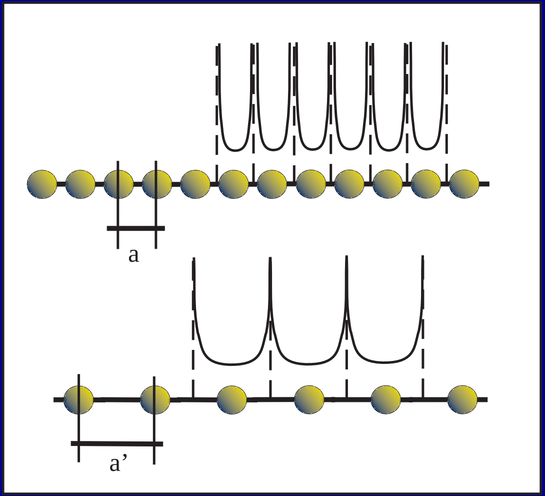
$$K_C^{(R)} \neq \tfrac{1}{4}\lambda^{(R)} R^2$$

In general one obtains Q dependend elastic moduli, Barrat and Joanny (1993).

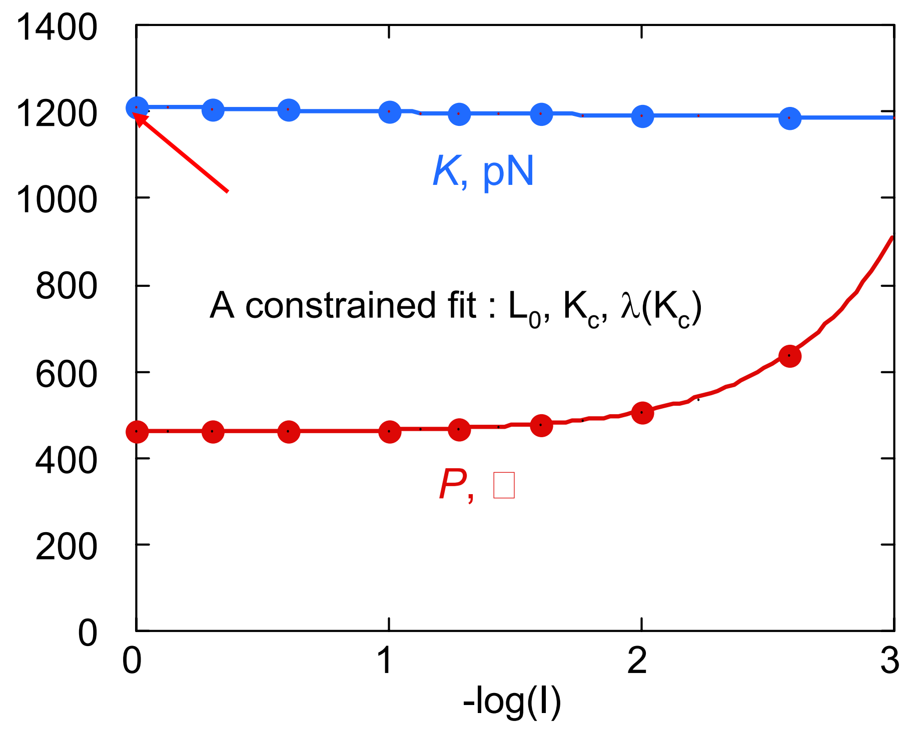
Elasticity and interactions XVIII
(comparison with experiment)



Bending rigidity



Stretching modulus

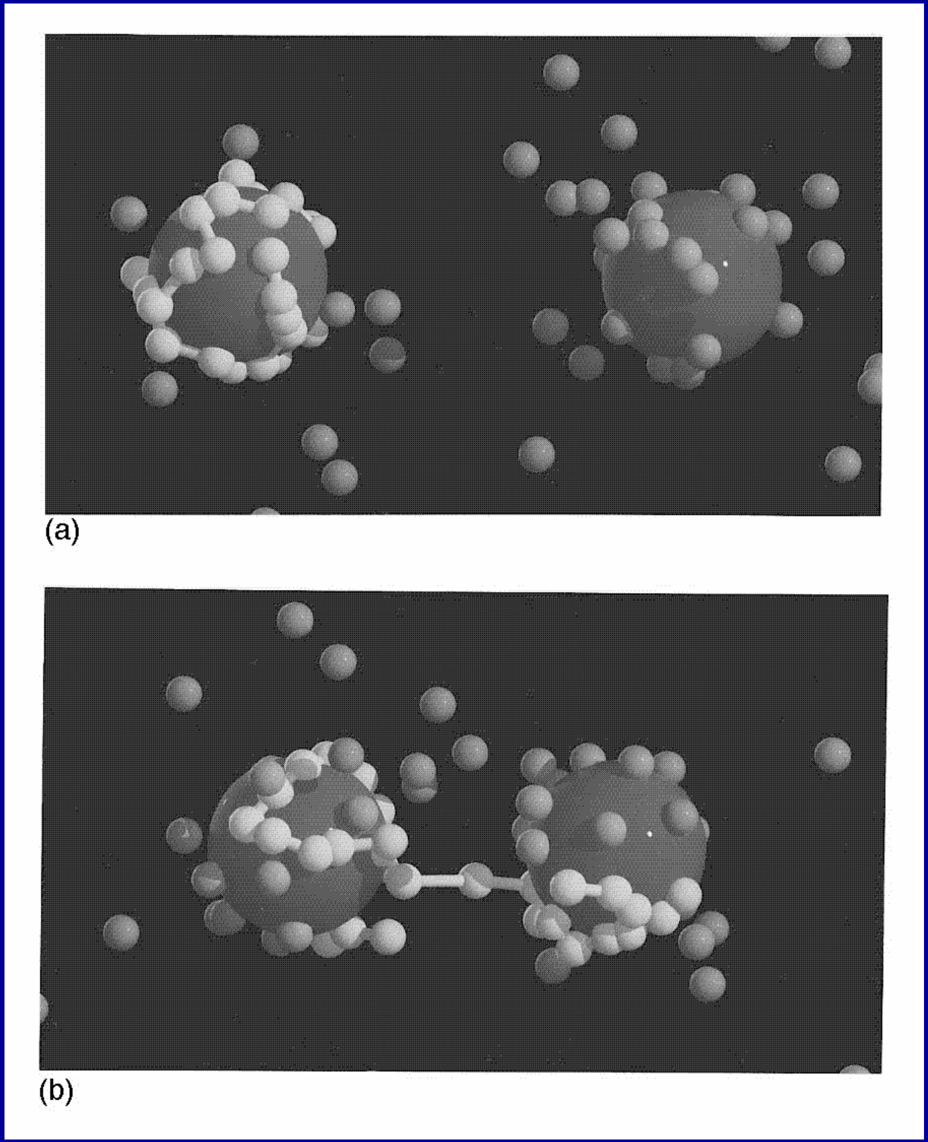


Rouzina (2002)

a = 6.7 ± 0.7 Å (Manning a = 7.2 Å)

Wenner, Williams, Rouzina and Bloomfield (2002). For ionic strengths: 1000, 500, 250, 100, 53.3, 25, 10, 2.6 mM.

Polyelectrolyte bridging I



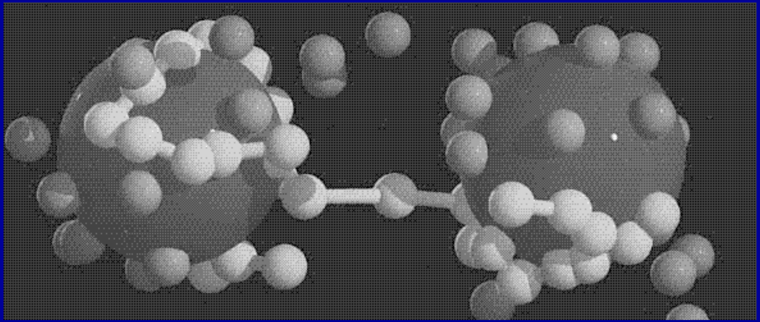
Electrostatic interactions effect polymer structural parameters (persistence length, stretching modulus) as well as conformations (DNA condensation).

Polyelectrolyte bridging: another case of coupling between conformations and interactions.
Podgornik (2004)

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

Polyelectrolyte bridging VIII
(two spherical macroions)

A flexible charged chain, with screened electrostatics in the field of two macroions.Self-interactions included (electrostatic stiffening)



$$\beta\mathcal{H}[\mathbf{r}_i(n)] = \frac{3}{2\ell^2}\sum_{i=1}^{2}\int_0^N \dot{\mathbf{r}}_i^2(n)dn + \frac{1}{2}\beta\sum_{i,j=1}^{2}\int_0^N\int_0^N u(\mathbf{r}_i'(n),\mathbf{r}_j(n))dndn' + \beta\sum_{i=1}^{2}\int_0^N \phi_{ext}(\mathbf{r}_i(n))$$

Chain flexibility

Inter and intra-chain interactions

External (macroions) fiel

Screened electrostatics - WC limit for small ions

$$u(\mathbf{r}',\mathbf{r}) = \frac{e^2}{4\pi\epsilon\epsilon_0}\frac{e^{-\kappa|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}$$

$$\phi_{ext}(\mathbf{r}) = \frac{e_1e_0}{4\pi\epsilon\epsilon_0}\frac{e^{-\kappa|\mathbf{r}-\mathbf{r}_1|}}{|\mathbf{r}-\mathbf{r}_1|} + \frac{e_2e_0}{4\pi\epsilon\epsilon_0}\frac{e^{-\kappa|\mathbf{r}-\mathbf{r}_2|}}{|\mathbf{r}-\mathbf{r}_2|}$$

Podgornik (2003)

Polyelectrolyte bridging IX
(variational ansatz)

Two chains in harmonic external potentials with variationally determined width and position.

$$\beta\mathcal{H}_0[\mathbf{r}_i(n)] = \frac{3}{2\ell^2}\sum_{i=1}^{2}\int_0^N \dot{\mathbf{r}}_i^2(n)dn + \frac{3}{2}\sum_{i=1}^{2}\zeta_i^2(\mathbf{r}_{0i})\int_0^N (\mathbf{r}_i(n)-\mathbf{r}_{0i})^2 dn + \beta N\mathcal{L}(\mathbf{r}_{01}, \mathbf{r}_0$$

Feynman - Kleinert ‘86, Bratko and Dawson, 1993 Podgornik, 1994.

Harmonic ansatz gives Gaussian distribution of monomers.

$$\rho(\mathbf{r}, \mathbf{r}_{01}, \mathbf{r}_{02}) = \rho_{a_1^2}(\mathbf{r}, \mathbf{r}_{01}) + \rho_{a_2^2}(\mathbf{r}, \mathbf{r}_{02})$$

$$\rho_{a_i^2}(\mathbf{r}, \mathbf{r}_{0i}) = \frac{N}{(2\pi a_i^2)^{3/2}} \exp -\frac{|\mathbf{r}-\mathbf{r}_{0i}|^2}{2a_i^2}$$

$$a_i^2(\mathbf{r}_{0i}) = \frac{1}{3N}\int_0^N \left\langle (\mathbf{r}_i(n)-\mathbf{r}_{0i})^2 \right\rangle dn = \frac{1}{3\zeta_i}\mathcal{L}\left(\frac{\zeta_i \ell^2 N}{2}\right)$$

The size of the chain is then determined variationally:

$$\mathcal{W}_{a_i,a_j}(\mathbf{r}, \mathbf{r}') = \int \frac{d^3\mathbf{k}}{(2\pi)^3}\; \rho_{a_i^2}(\mathbf{k})u(\mathbf{k})\rho_{a_j^2}(-\mathbf{k})\; e^{i\mathbf{k}(\mathbf{r}-\mathbf{r}')}.$$

$$\frac{3}{2}\zeta_i^2(\mathbf{r}_{0i})N = \beta\frac{\partial}{\partial a_i^2}W(\mathbf{r}_{01}, \mathbf{r}_{02})$$

Polyelectrolyte bridging X

The solution of the variational equations depends on whether the interaction with the macroions is stronger or weaker than the interchain and self-interactions:

- strong coupling limit - $\zeta^2 > 0$. Chain conformation determined by the macroions.
- weak coupling limit - $\zeta^2 < 0$. Chain conformation determined by inter and intra.

QuickTime™ and a TIFF (LZW) decompressor are needed to see this picture.

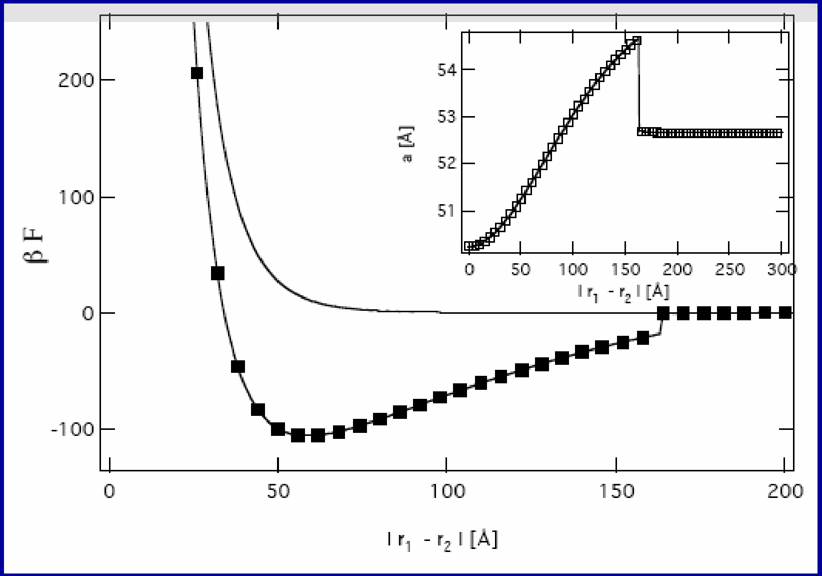
QuickTime™ and a TIFF (LZW) decompressor are needed to see this picture.

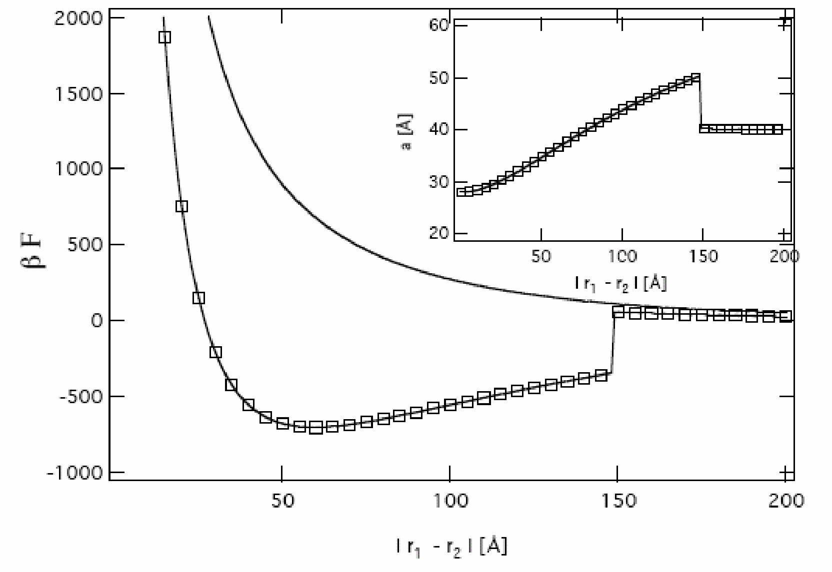
(Dzubiella, Moreira and Pincus, 2003)

Bridging attractions (strong coupling) vs. coronal repulsions (weak coupling).

Polyelectrolyte bridging XI
(strong coupling limit)

Charges on the chain and on the macroions: N = 100 and M = 30

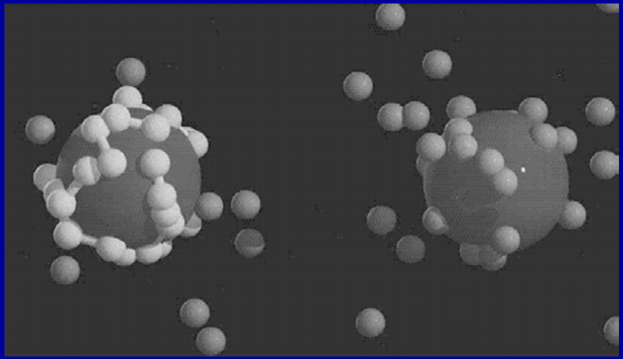




60 mM

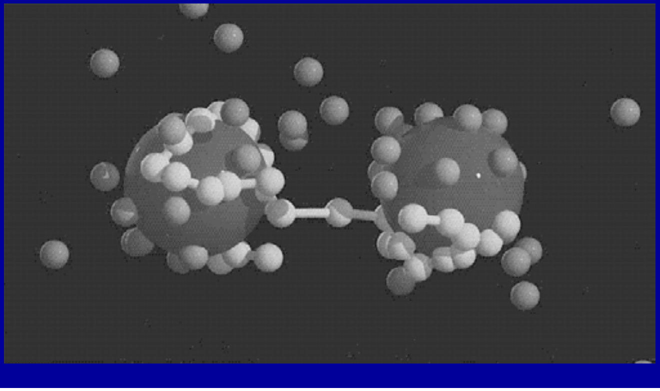
1 mM

Chain conformation determined by the macroions.



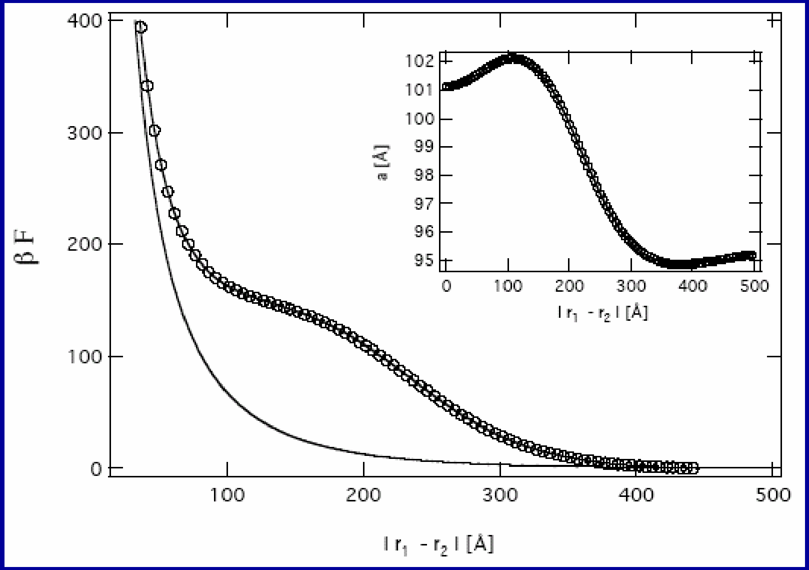
Bridging

Non-bridging

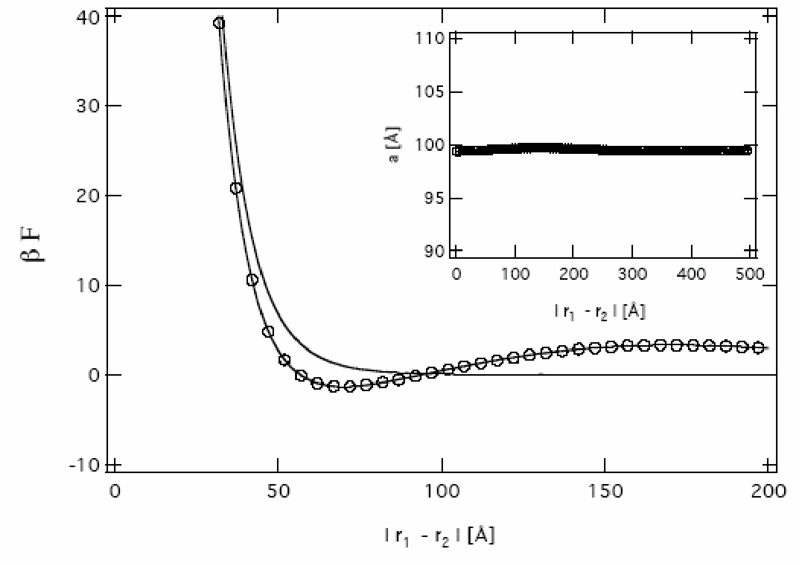


Polyelectrolyte bridging XII
(weak coupling limit)

Charges on the chain and on the macroions: N = 50 and M = 40



60 mM



1 mM

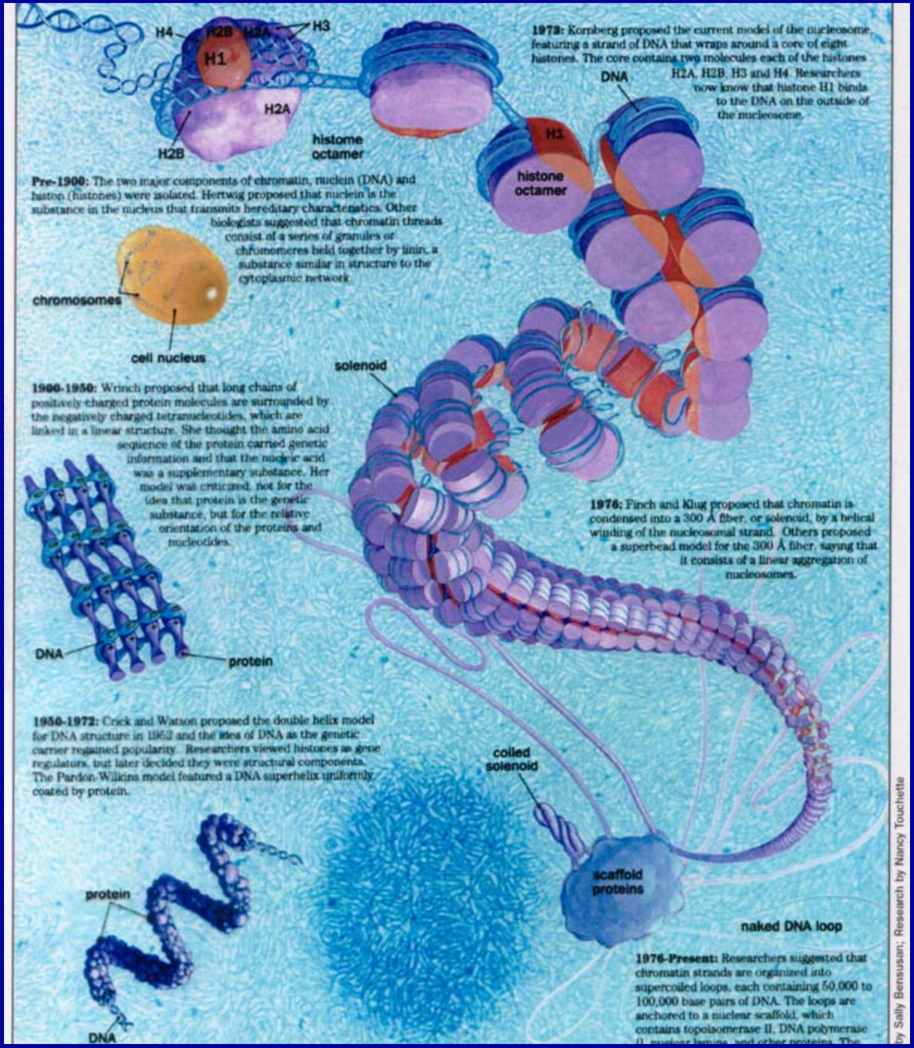
Chain conformation determined by inter and intra.

QuickTime™ and a TIFF (LZW) decompressor are needed to see this picture.

Formation of a polymer brush corona.

Dzubiella, Moreira and Pincus, 2003
Chodanowski and Stoll, 2001

Eucariotic Genome



1973: Kornberg proposed the current model of the nucleosome, featuring a strand of DNA that wraps around a core of eight histones. The core contains two molecules each of the histones H2A, H2B, H3 and H4. Researchers now know that histone H1 binds to the DNA on the outside of the nucleosome.

Pre-1900: The two major components of chromatin, nuclein (DNA) and histon (histones) were isolated. Hertwig proposed that nuclein is the substance in the nucleus that transmits hereditary characteristics. Other biologists suggested that chromatin threads consist of a series of granules or chromomeres held together by linin, a substance similar in structure to the cytoplasmic network.

1900-1950: Wrinch proposed that long chains of positively charged protein molecules are surrounded by the negatively charged tetranucleotides, which are linked in a linear structure. She thought the amino acid sequence of the protein carried genetic information and that the nucleic acid was a supplementary substance. Her model was criticized, not for the idea that protein is the genetic substance, but for the relative orientation of the proteins and nucleotides.

1976: Finch and Klug proposed that chromatin is condensed into a 300 Å fiber, or solenoid, by a helical winding of the nucleosomal strand. Others proposed a superbead model for the 300 Å fiber, saying that it consists of a linear aggregation of nucleosomes.

1950-1972: Crick and Watson proposed the double helix model for DNA structure in 1962 and the idea of DNA as the genetic carrier regained popularity. Researchers viewed histones as gene regulators, but later decided they were structural components. The Pardon-Wilkins model featured a DNA superhelix uniformly coated by protein.

1976-Present: Researchers suggested that chromatin strands are organized into supercoiled loops, each containing 50,000 to 100,000 base pairs of DNA. The loops are anchored to a nuclear scaffold, which contains topoisomerase II, DNA polymerase II, nuclear lamins, and other proteins. The

by Sally Bensusan; Research by Nancy Touchette

NCP

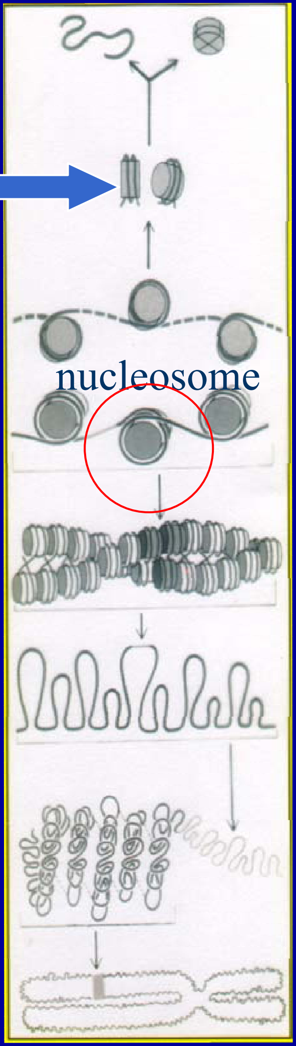
~ 10 nm

~ 30 nm

~ 300 nm

~ 700 nm

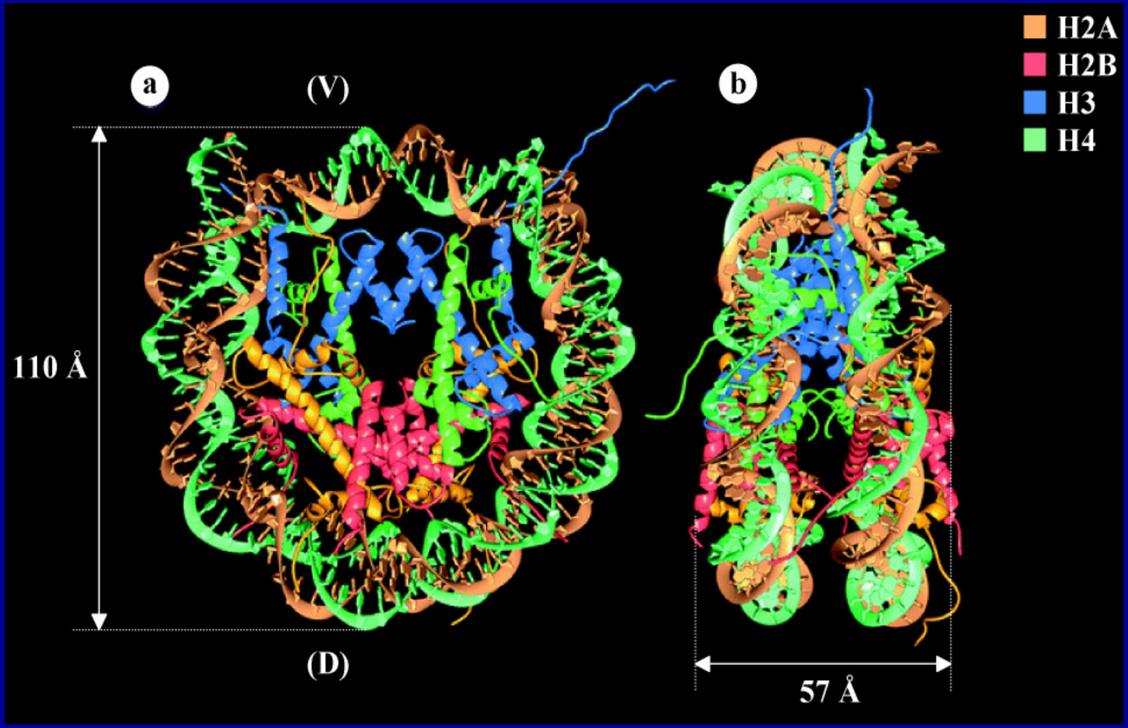
~ 1400 nm

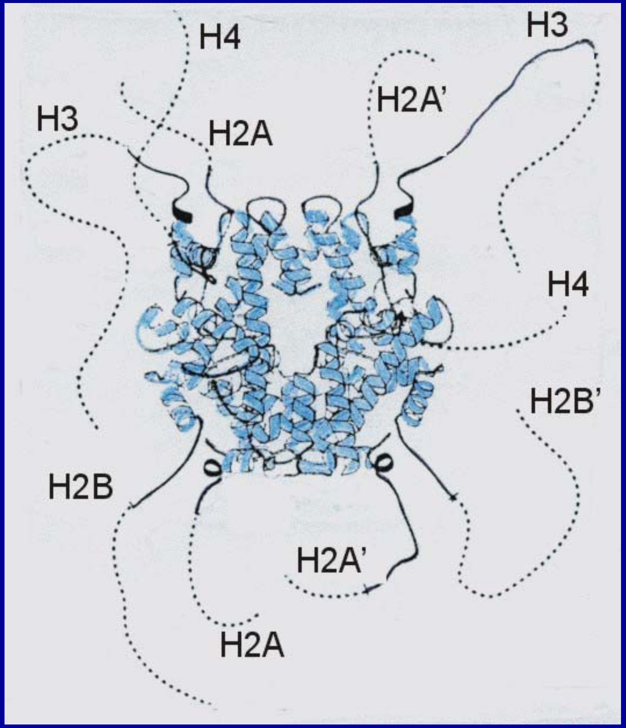

nucleosome

Viruses: toroidal packing just as in DNA collapse *in vitro*
Bacteria (prokariotes): nucleoid, a loose DNA - protein gel

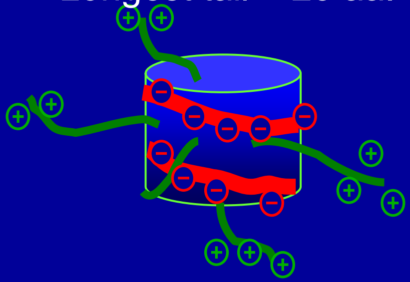
Nucleosome Core Particle (NCP)

A histone octamer (4 X 2) of 4 core histones: H2A, H2B, H3 and H4
147 bp DNA wrapped 1.75 times in a left-handed helix, stable up to 0.75 M salt





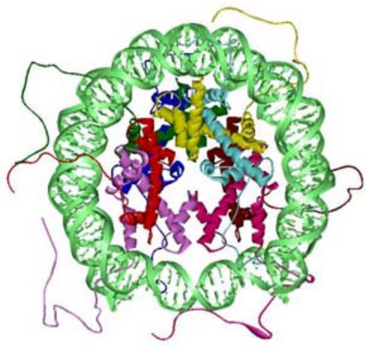
Longest tail ~ 25 aa.



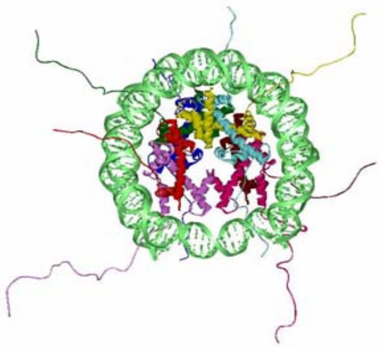
Lüger et al., *Nature*, 1997, 2002 at 1.9 Å resolution

A highly charged hairy particle
(- 2*147 + 134 (220) = - 165)
Excluding the histone buried charges
(Bertin *et al*., 2004)

Bridging of N-tails?

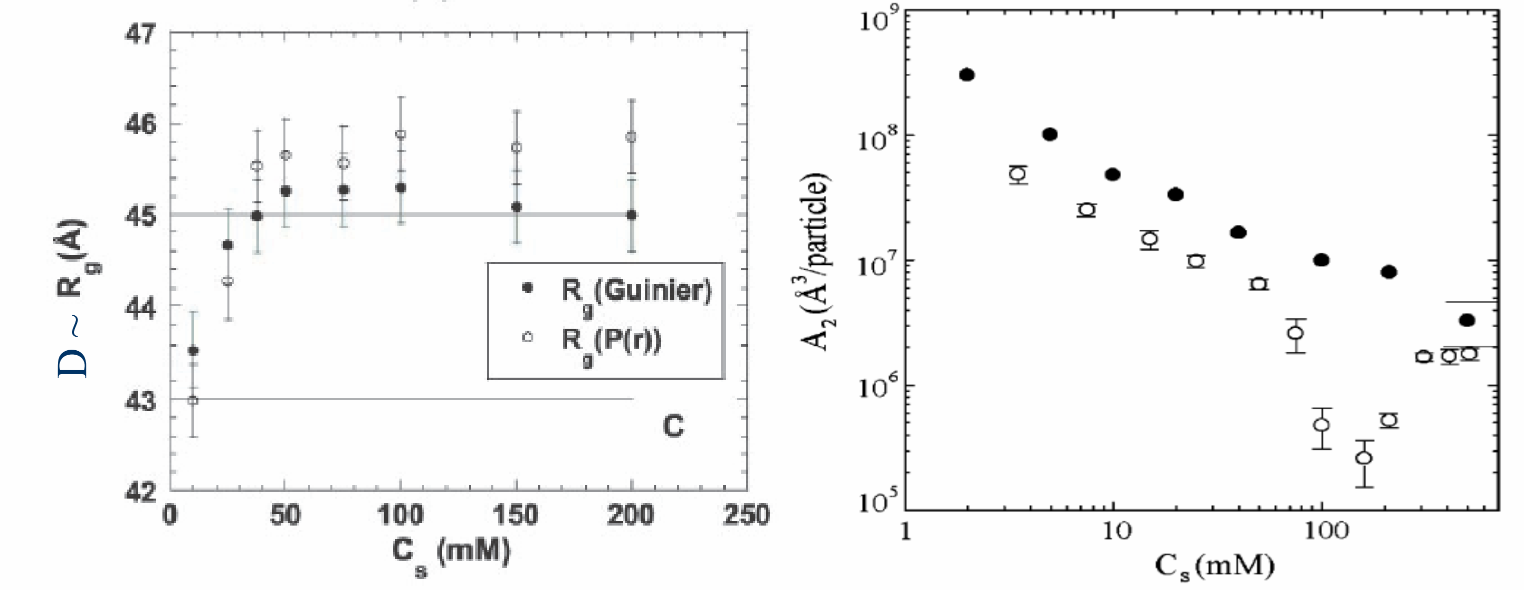


Folded N-tails



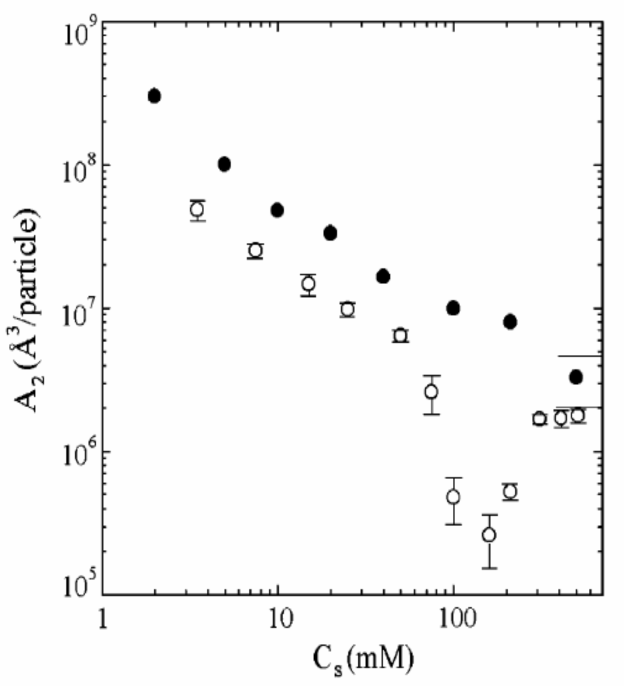
Expanded N-tails

Folded tails below 50 mM and expanded from 50 mM and above.



Mangenot et al. 2002

Bridging of N-tails? Not directly.



$\mathrm{Log}_{10}(A_2)$ [Å^3/particle]

Bald particles

QuickTime™ and a TIFF (LZW) decompressor are needed to see this picture.

Hairy particles

$0.02/\lambda_D$ [Å^{-1}]

R = 60 Å, M = 143, N = 50, l = 6 Å, salt between 0.004 and 1.8 M.

The news is thus not altogether good. N-tail charged “hair” by itself is not going to make the second virial coefficient non-monotonic as a function of salt. It will however make it smaller.

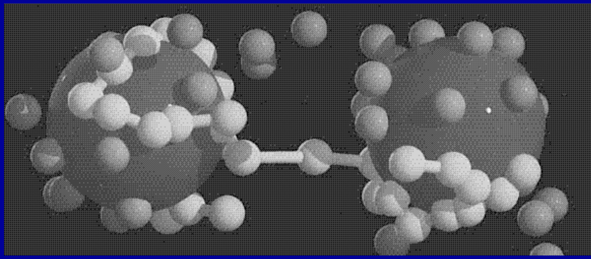
Again molecular electrostatics

Are there any similar cases in other systems? YES, A2 of proteins in solution:

- lysozyme (Tessier *et al*. 2002)
- b-lactoglobulin (Piazza *et al*. 2002)
- apoferritin (Petsev *et al*. 2000) …

Allahyarov et al. (2003):

Polyelectrolyte bridging II (mesoscopic model)



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

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

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).

$$-\epsilon\epsilon_0\nabla^2\phi = e_0 n_0\ e^{-\frac{e_0\phi}{kT}}. \quad \epsilon\epsilon_0\frac{\partial\phi}{\partial\mathbf{n}} + \sigma = 0.$$

The standard PB equation for mobile counterions.

Polyelectrolyte bridging III
(PEPB)

The Poisson - Boltzmann equation for PE.

$$-\epsilon\epsilon_0\nabla^2\phi = \rho_\phi = <\exp\left(-\beta e_\tau\phi\right)>$$

$$\rho_\phi = \frac{\int\int d^3\mathbf{r}' d^3\mathbf{r}"\ \int_0^L ds\ \mathcal{G}_\phi(\mathbf{r}',\mathbf{r};L-s)\mathcal{G}_\phi(\mathbf{r},\mathbf{r}";s)}{\int\int d^3\mathbf{r}' d^3\mathbf{r}"\mathcal{G}_\phi(\mathbf{r}',\mathbf{r}";L)}$$

Monomer density.

$$\left[\frac{\partial}{\partial n} - \frac{\ell^2}{6}\nabla^2 + \beta e_\tau\phi\right]\mathcal{G}_\phi(\mathbf{r},\mathbf{r}";n) = \delta^3(\mathbf{r}-\mathbf{r}')\delta(N)$$

Edwards equation.

Ground state dominance ansatz N >>1.

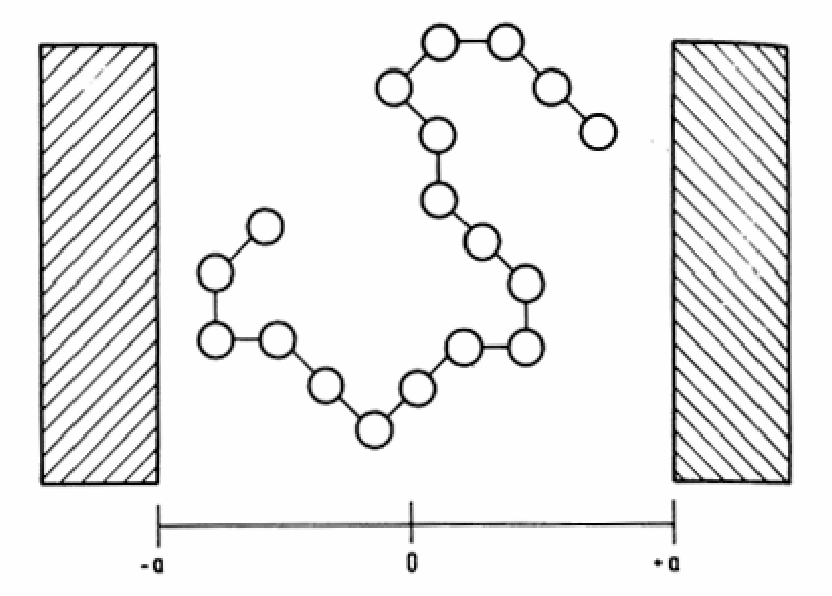
$$\mathcal{G}_\phi(\mathbf{r},\mathbf{r}';N) = \psi(\mathbf{r})\psi(\mathbf{r}')e^{-E_N N}$$

Only the first term in eigenfunction expansion.

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

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

Polyelectrolyte bridging IV
(PEPB)



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

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

A coupled set of two equations.

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

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

Polyelectrolyte Poisson - Boltzmann equation.

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

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

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

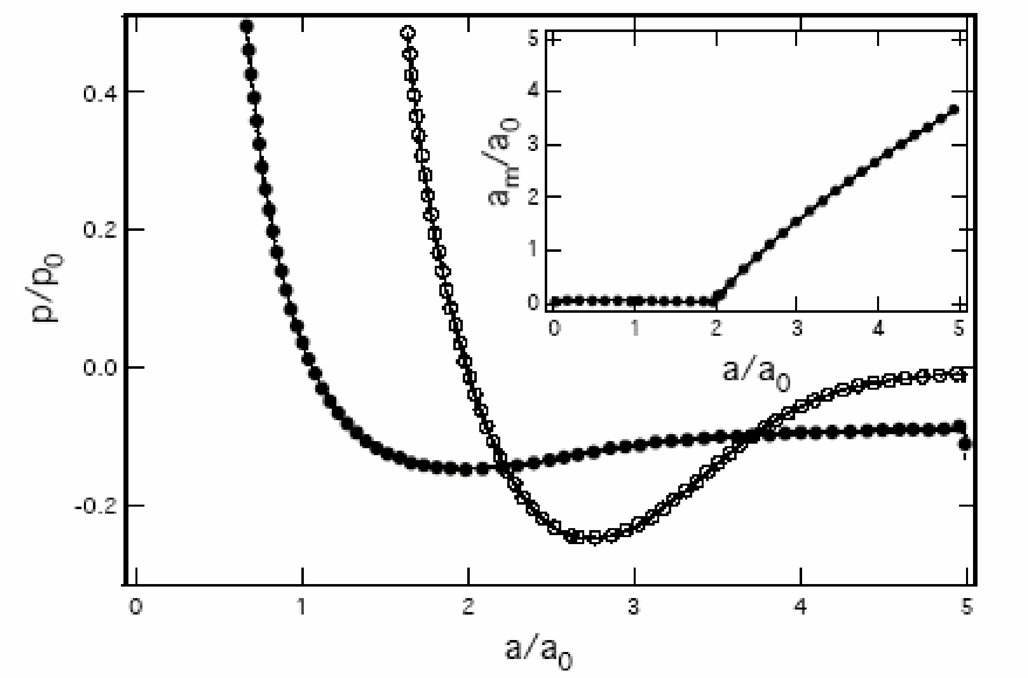
Polyelectrolyte bridging V
(single chain - numerics)

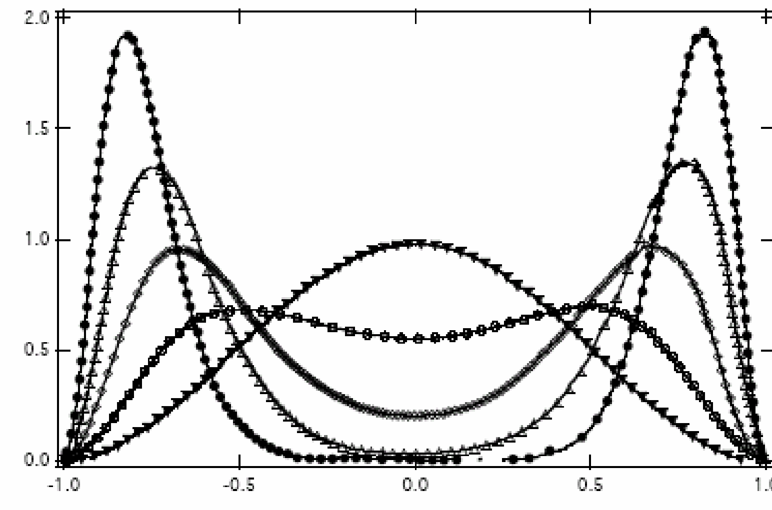
Small separation limit:

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

Large separation limit:

$$E_N = \frac{\ell^2}{6}\left(-\lambda_B^{1/3} a + a i_0 - \frac{1}{2} C(a i_0) \exp\left(-\frac{4}{3}\sqrt{\lambda_B a^3}\right)\right)$$





Monomodal-bimodal transition

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

Polyelectrolyte bridging VI (PE chain plus mobile ions)

QuickTime™ and a TIFF (LZW) decompressor are needed to see this picture.

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:

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

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

Dimensionless formulation $\kappa\ell.$

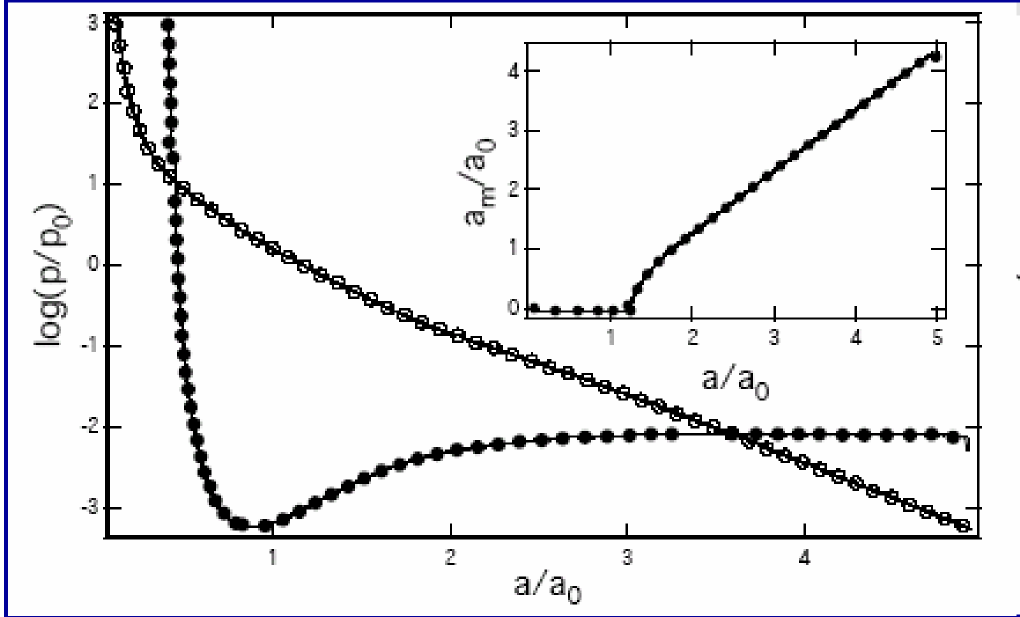
Large parameter space

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

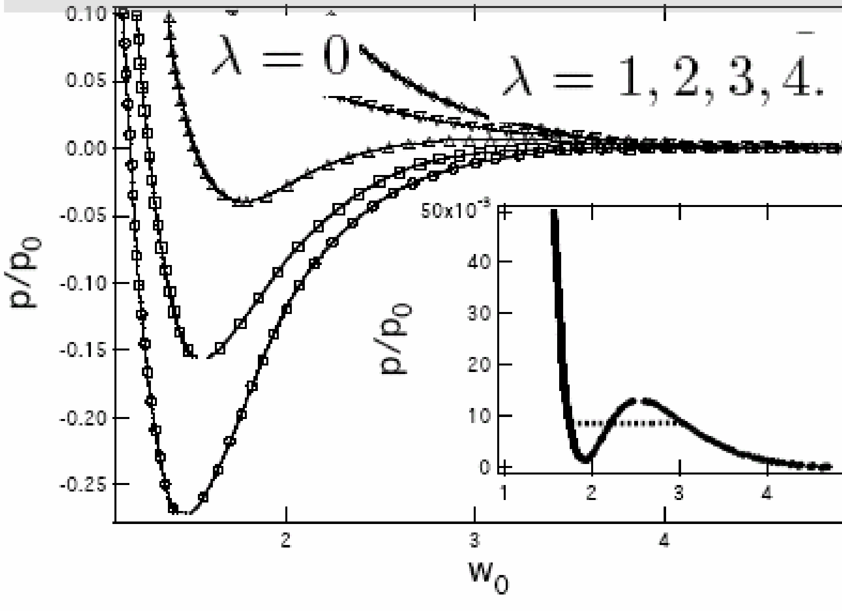
$\lambda = \frac{\beta e_0^2}{\epsilon\epsilon_0 \kappa}\frac{N}{S}$ Monomer density

$w_0 = \kappa a$ Separation

Polyelectrolyte bridging VII



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



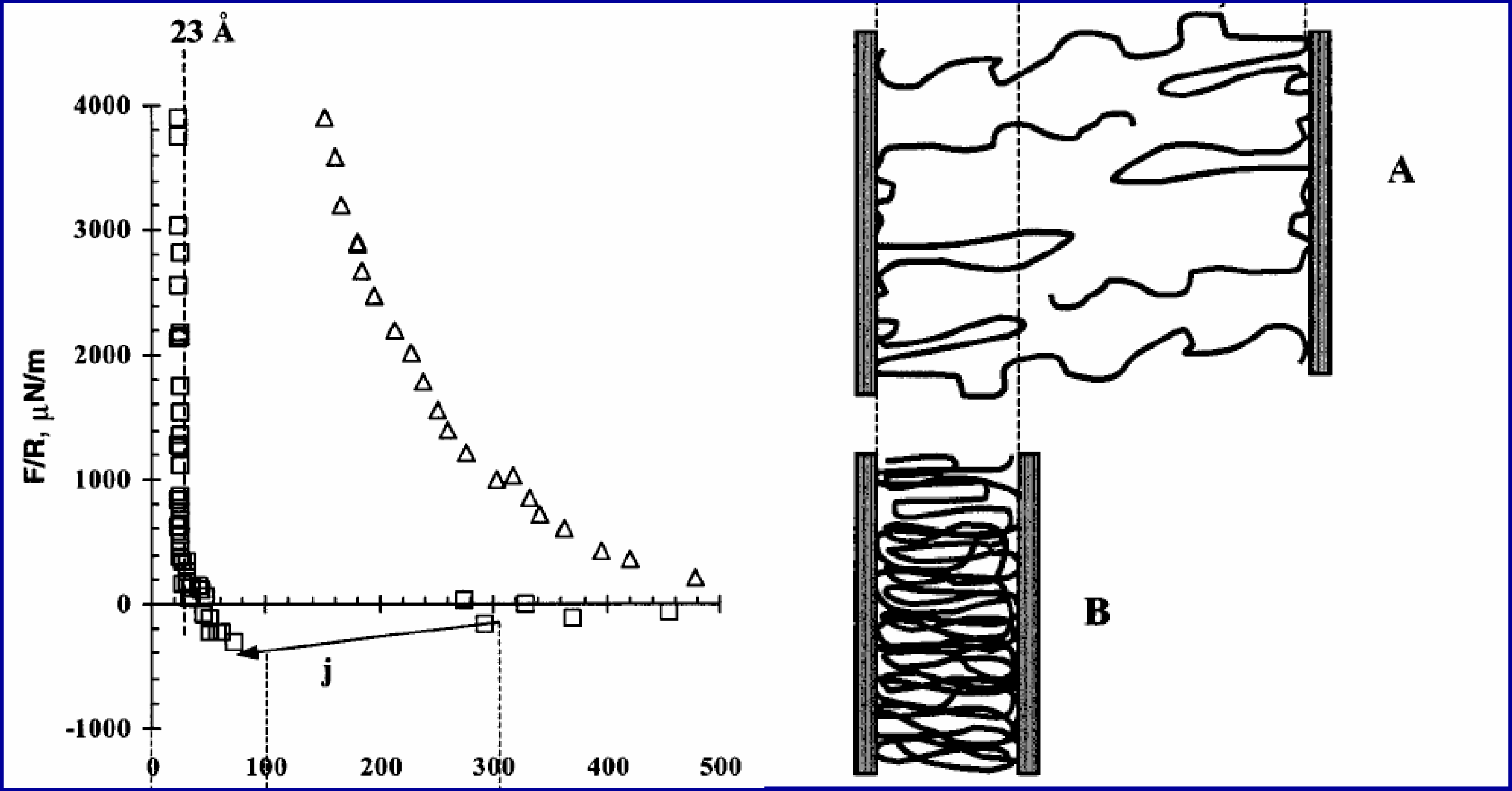
$\lambda = 2.5$ and $\Gamma = 5.45$

Γ= 5.45, l = 2.5 (corresponding to 1 charge per 2 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)

Polyelectrolyte bridging (experiment)



Abraham *et al.* (2001)
3 mM $MgCl_2$ 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.