

# Molecular attractions:

- a.) van der Waals interactions
- b.) electrostatic correlation interactions
- c.) polyelectrolyte bridging interactions

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**2007 Taiwan International Workshop on Biological Physics and Complex Systems  
(BioComplex Taiwan 2007)**

# Plan of lectures:

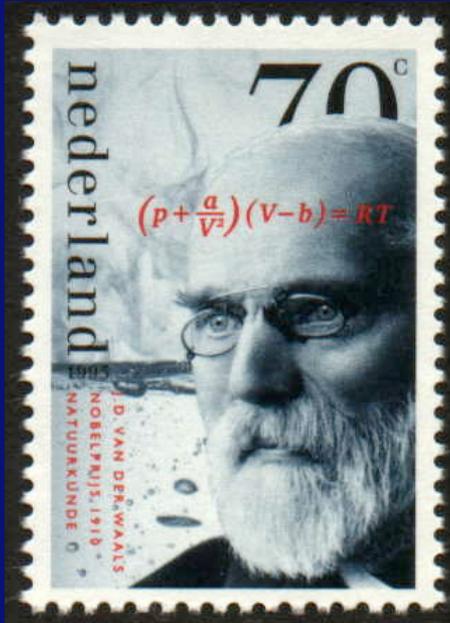
Three important sources of attractive interactions in soft matter systems. I will take time to introduce the general principles as well as introduce the audience to specific model systems:

1. **van der Waals interactions**, which are due to correlated electromagnetic field fluctuations in dielectrically inhomogeneous media, their role in osmotic pressure equilibria of multilamellar lipid systems
2. **the electrostatic correlation interactions** which are due to electrostatically strongly coupled mobile counterions between charged macromolecules, their role in DNA collapse in multivalent salts
3. **polyelectrolyte bridging interactions** that are due to elastic deformation of stretched polyelectrolyte chains between charged macromolecular interfaces, their role in organization of eucaryotic genome, specifically in the interactions between nucleosomal core particles.

# 1.

van der Waals interactions, which are due to correlated electromagnetic field fluctuations in dielectrically inhomogeneous media and their role in some biomaterials examples

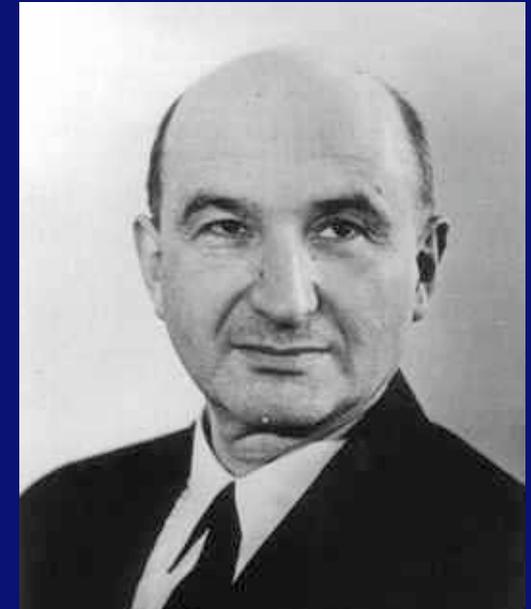
# Dramatis personae



Johannes Diderik van der Waals  
(1837–1923)



Hendrik Brugt Gerhard Casimir  
(1909–2000)



Evgeny Mikhailovich Lifshitz  
(1915 – 1985)

His equation of state was so successful that it stopped the development of liquid state theory for a hundred years.  
(Lebowitz, 1985)

I mentioned my results to Niels Bohr, during a walk. That is nice, he said, that is something new... and he mumbled something about zero-point energy.  
(Casimir, 1992)

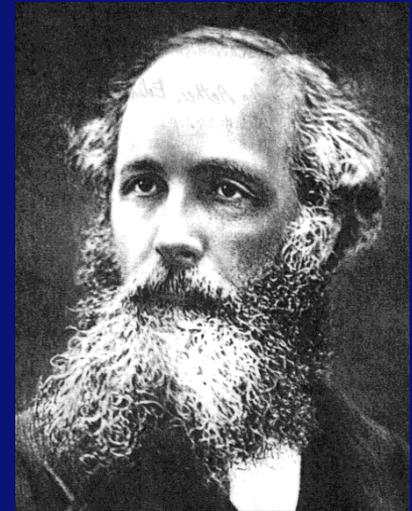
His calculations were so cumbersome that they were not even reproduced in the relevant Landau and Lifshitz volume, where, as a rule, all important calculations are given.  
(Ginzburg, 1979)

# Maxwell, Hertz and Lebedev



1864 and 1873 J. C. Maxwell

1888 H. Hertz



PhD thesis of P.N. Lebedev (1894):

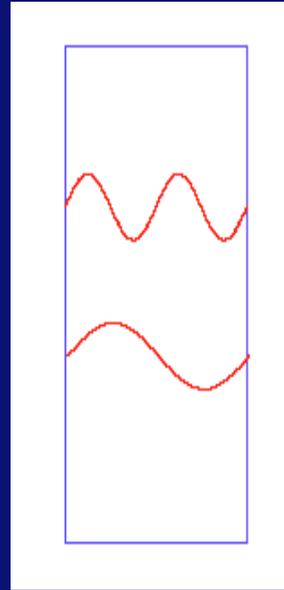
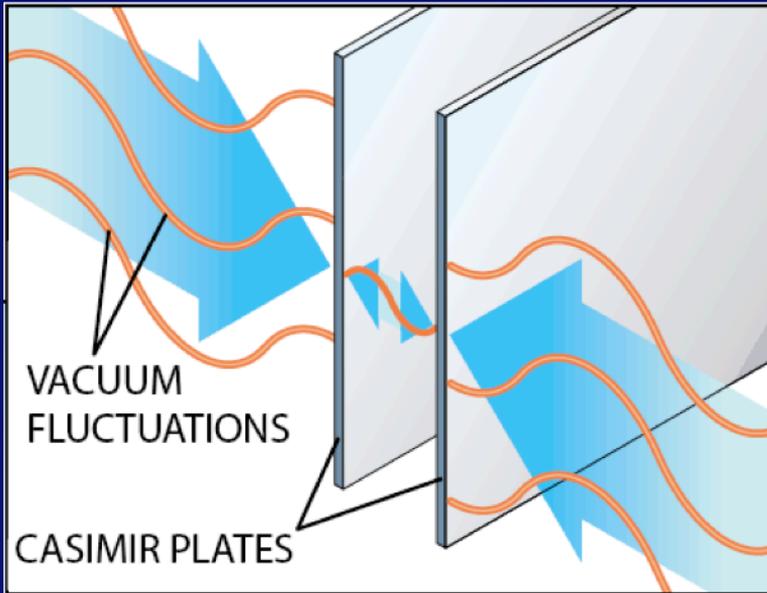
Hidden in Hertz's research, in the interpretation of light oscillations as electromagnetic processes, is still another as yet undealt with question, that of the source of light emission of the processes which take place in the molecular vibrator at the time when it give up light energy to the surrounding space; **such a problem leads us [...] to one of the most complicated problems of modern physics -- the study of molecular forces.**

[...] Adopting the point of view of the electromagnetic theory of light, we must state that between two radiating molecules, just as between two vibrators in which electromagnetic oscillations are excited, there exist ponderomotive forces: They are due to the electromagnetic interaction between the alternating electric current in the molecules [...] ; we must therefore state that **there exist between the molecules in such a case molecular forces whose cause is inseparably linked with the radiation processes.**

**Of greatest interest and of greatest difficulty is the case of a physical body in which many molecules act simultaneously on one another, the vibrations of the latter not being independent owing to their close proximity.**



# H. B. G. Casimir (1948).



Schematic representation of the geometry of the problem. We are solving the Maxwell's equations between the two bounding surfaces.

In empty space they are reduced to wave equations. Ideally polarizable (metal) interfaces.

EM field wave equation in empty space between the two conducting plates:

$$\nabla^2 \mathbf{E}(\mathbf{r}) + \frac{\epsilon\mu\omega^2}{c^2} \mathbf{E}(\mathbf{r}) = 0, \quad \nabla \cdot \mathbf{E}(\mathbf{r}) = 0, \quad \nabla^2 \mathbf{H}(\mathbf{r}) + \frac{\epsilon\mu\omega^2}{c^2} \mathbf{H}(\mathbf{r}) = 0, \quad \nabla \cdot \mathbf{H}(\mathbf{r}) = 0,$$

Eigenfrequencies of the EM field :

$$\omega_{\ell km}(D) = \pi c \sqrt{\left(\frac{\ell^2}{L^2} + \frac{k^2}{L^2} + \frac{m^2}{D^2}\right)} \longrightarrow \pi c \sqrt{\left(Q^2 + \frac{m^2}{D^2}\right)}$$

Quantum zero point energy :

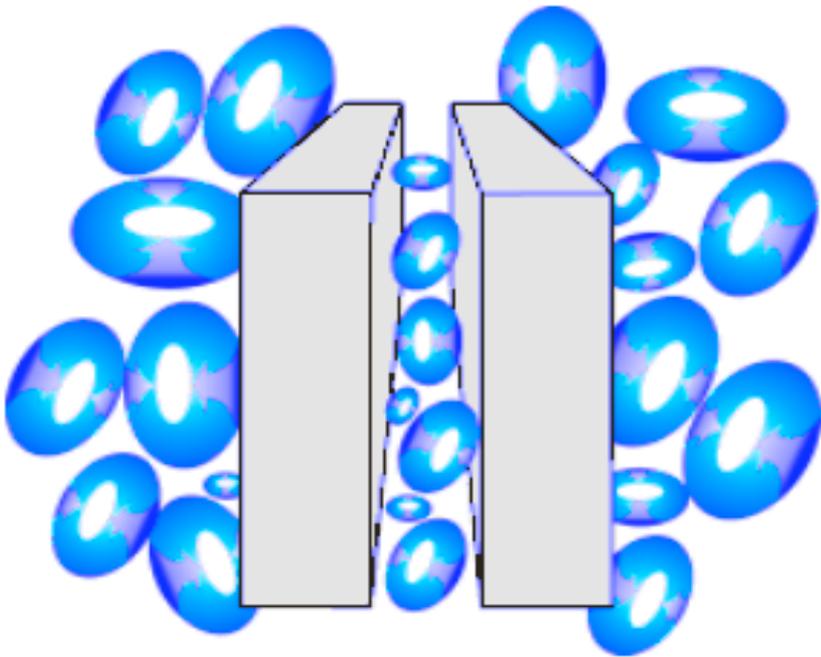
$$E(D) = 2 \sum'_{\ell, k, m} \frac{1}{2} \hbar \omega_{\ell km} \longrightarrow E(D) = -\frac{\pi^2 \hbar c}{720 D^3} L^2$$

# Casimir force as the EM depletion force

Evaluating the integrals and the sums via the Poisson summation formula (plus taking into account the physical considerations about the response of any body at large frequencies) one obtains Casimir's result:

$$U(d) = \left( \frac{\pi^2 \hbar c}{4d^3} \right) L^2 \left( \frac{-4}{720} \right) = - \left( \frac{\pi^2 \hbar c}{720d^3} \right) L^2$$

What is the physical meaning of this result? The Casimir force is the EM field depletion force!



Not all EM modes fit between the two ideally polarizable interfaces! Only those fit, with the appropriate wavelength.

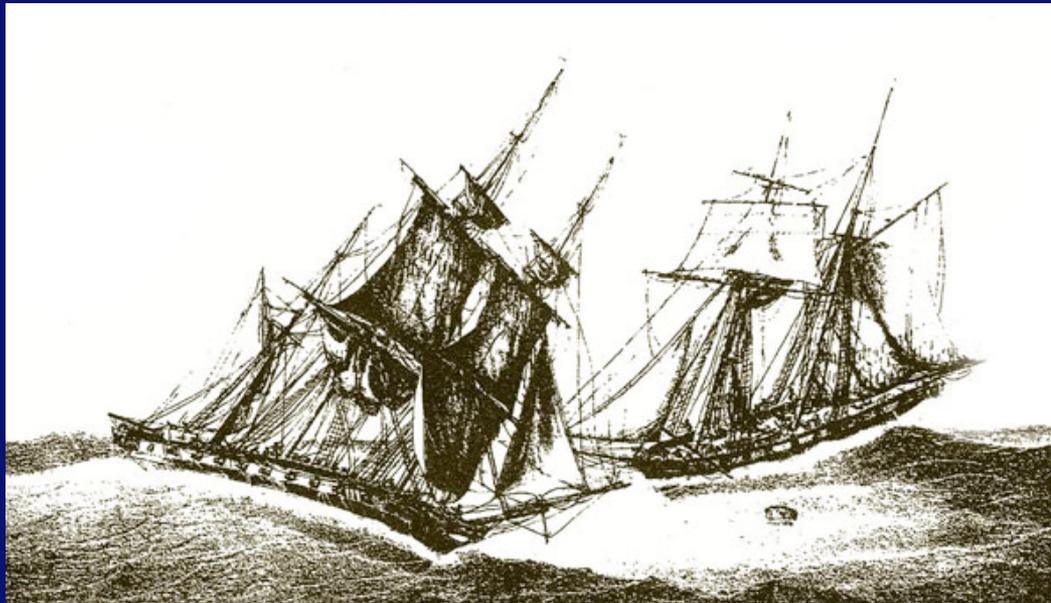
There are more modes outside than inside and each mode exerts Maxwell's pressure on the boundary thus  
– presto –  
the Casimir effect is there!

1 cm<sup>2</sup> areas 1 μm apart attract with 10<sup>-7</sup> N – weight of water droplet 0.5 mm in diameter. At 10 nm the Casimir force is equivalent to 1 atm pressure.

# “Une force certaine d’attraction“

In 1996 by Dutch scientist Sipko Boersma (A maritime analogy of the Casimir effect Am.J.Phys. 64. 539–541 (1996)) dug up the French nautical writer P. C. Caussée and his 1836 book **The Album of the Mariner** that two ships should not be moored too close together because they are attracted one towards the other by a **certain force of attraction**. Boersma suggested that this early observation could be described by a phenomenon analogous to the Casimir effect.

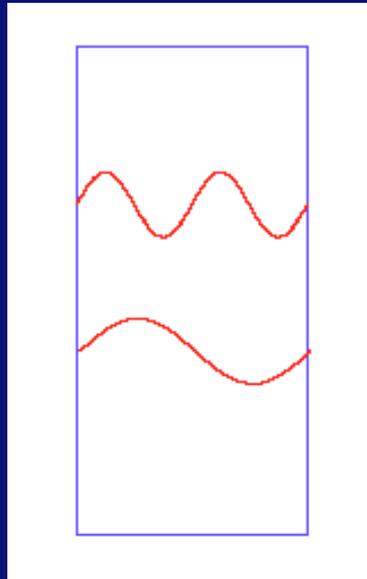
P.C. Causee: L'Album du Marin, (Mantes, Charpentier, 1836)



In the age of great sailboats it was noted that at certain conditions of the sea the ships attract misteriously, leading often to major damage.

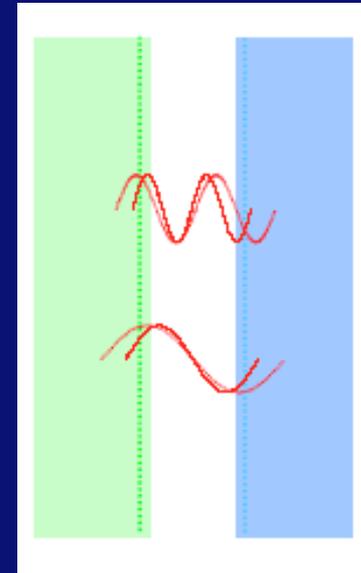
G. Nolan: I had first hand experience of this in 1998, while waiting for our start in the sailing regatta for the New South Wales Hood championships on Sydney Harbour. We had ... a lot of waves caused by everything from power boat and ferry wakes to waves made by arriving and departing float planes. I made the prediction that, because of the conditions and the Casimir effect, the waiting boats would drift together. Within minutes that's exactly what had happened ...r

# Enter Lifshitz (1954).

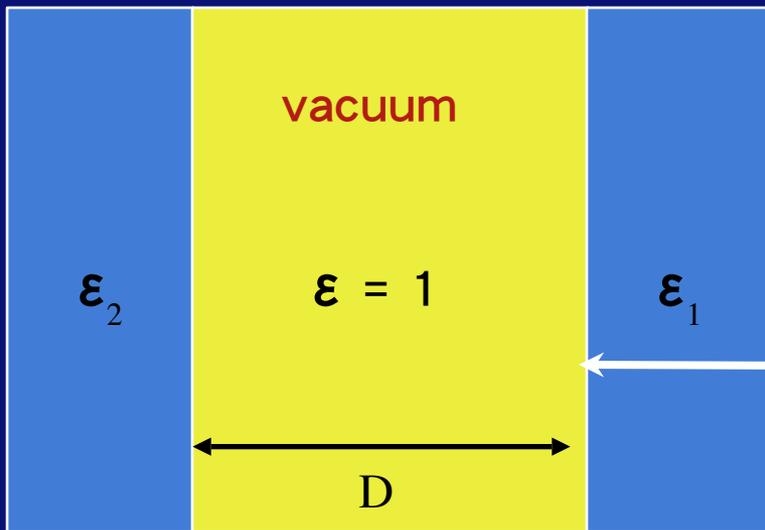


Real dielectric as opposed to Casimir's idealized interfaces.  
Casimir vs. Lifshitz  
Hard boundary vs. soft boundary

$$\begin{aligned}
 B_{1n} &= B_{2n} & D_{1n} &= D_{2n} \\
 E_{1t} &= E_{2t} & H_{1t} &= H_{2t}
 \end{aligned}$$



$$\epsilon = \epsilon(\omega)$$



Maxwell stress tensor **in vacuo**:

$$p_{ik} = \epsilon_0 E_i E_k - \frac{1}{2} \epsilon_0 E^2 \delta_{ik} + \frac{1}{\mu_0} B_i B_k - \frac{1}{2\mu_0} B^2 \delta_{ik},$$

$$\langle p_{zz}(D) \rangle$$

Thermodynamic average of the stress tensor at the boundary.

Lifshitz in 1954 got the most prestigious soviet science prize for this theory.

# Main ingredients of the Lifshitz calculation ...

His calculations were so cumbersome that they were not even reproduced in the relevant Landau and Lifshitz volume, where, as a rule, all important calculations are given.  
(Ginzburg, 1979)

Theoretical constituents for a **finite temperature, real dielectric interfaces in planar geometry.**

FD theorem:

$$\langle A_i(\omega, \mathbf{r}) A_k(\omega, \mathbf{r}') \rangle = \text{ctanh} \frac{\hbar\omega}{2k_B T} \text{im} \mathcal{D}_{ik}(\omega, \mathbf{r}, \mathbf{r}')$$

Maxwell equations:

$$\begin{aligned} \nabla \cdot \mathbf{D} &= 0 & \nabla \cdot \mathbf{B} &= 0 \\ \nabla \times \mathbf{H} &= \frac{\partial \mathbf{D}}{\partial t} & \nabla \times \mathbf{E} &= -\frac{\partial \mathbf{B}}{\partial t} \end{aligned}$$

$$\begin{aligned} B_{1n} &= B_{2n} & D_{1n} &= D_{2n} \\ E_{1t} &= E_{2t} & H_{1t} &= H_{2t} \end{aligned}$$

Constitutive relations  
and BC:

$$\begin{aligned} \mathbf{D} &= \epsilon \epsilon_0 \mathbf{E} & \epsilon &= \epsilon(\omega) \\ \mathbf{B} &= \mu \mu_0 \mathbf{H} & \mu &= \mu(\omega) \end{aligned}$$

The average of the stress tensor again on the vacuum side:

$$\langle p_{zz} \rangle = \epsilon_0 \langle E_z^2 \rangle - \frac{1}{2} \epsilon_0 \langle E^2 \rangle + \frac{1}{\mu_0} \langle B_z^2 \rangle - \frac{1}{2\mu_0} \langle B^2 \rangle$$

# Lifshitz result:

$$\langle p_{zz}(D) \rangle = \frac{k_B T}{\pi c^3} \sum_{n=0}^{\infty} \omega_n^3 \int_1^{\infty} p^2 \left( \left[ \frac{(s_1 + p)(s_2 + p)}{(s_1 - p)(s_2 - p)} e^{-\frac{2p\omega_n D}{c}} - 1 \right]^{-1} + \left[ \frac{(s_1 + p\epsilon_1)(s_2 + p\epsilon_2)}{(s_1 - p\epsilon_1)(s_2 - p\epsilon_2)} e^{-\frac{2p\omega_n D}{c}} - 1 \right]^{-1} \right) dp$$

$$s_i = \sqrt{\epsilon_i - 1 + p^2} \quad \omega_n = \frac{2\pi n k_B T}{\hbar}$$

$10^{15}$  n Hz

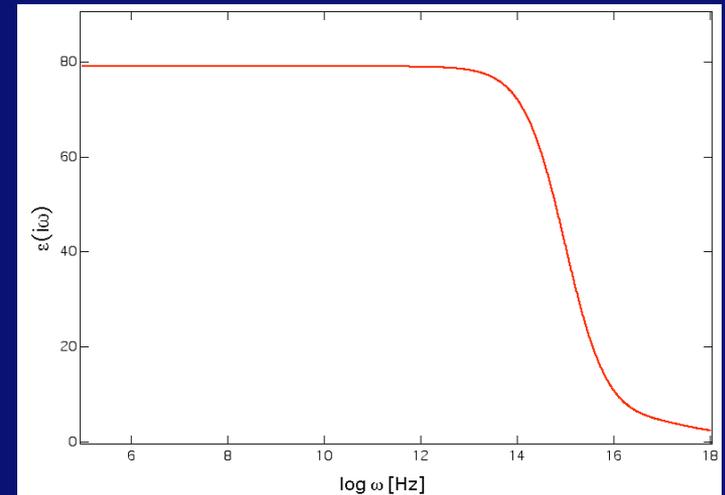
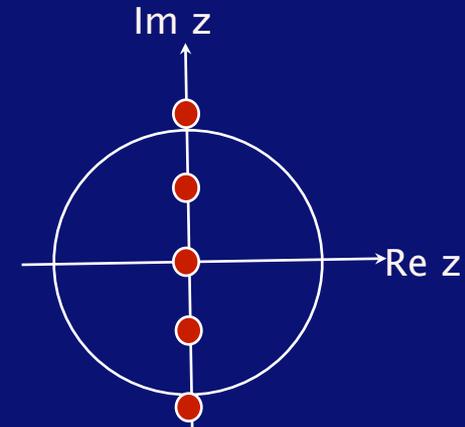
All the frequency dependence is reduced to discrete sum over Matsubara frequencies:

$$\epsilon_i = \epsilon_i(i\omega_n)$$

Discrete frequencies are due to the poles of the coth function in the FT theorem in the complex plane.

$$\epsilon_i(i\omega) = 1 + \frac{2}{\pi} \int_0^{\infty} \frac{\zeta \operatorname{Im} \epsilon(\zeta) d\zeta}{\omega^2 + \zeta^2}$$

Kramers-Kronig relations for the epsilons of imaginary frequencies – real and decaying!



# Limiting forms:

The influence of temperature usually (but not always!!!) not very important.  
Summation over  $n$  turned into an integral.

## Small separations

$$\langle p_{zz}(D \rightarrow 0) \rangle = \frac{\hbar}{16\pi^2 D^3} \int_0^\infty \int_0^\infty x^2 \left[ \frac{(\epsilon_1(i\zeta) + 1)(\epsilon_2(i\zeta) + 1)}{(\epsilon_1(i\zeta) - 1)(\epsilon_2(i\zeta) - 1)} e^x - 1 \right]^{-1} dx d\zeta$$

At small separations corresponds to the Hamaker formula:

$$\langle p_{zz}(D \rightarrow 0) \rangle = \frac{A}{6\pi D^3}$$

## Large separations

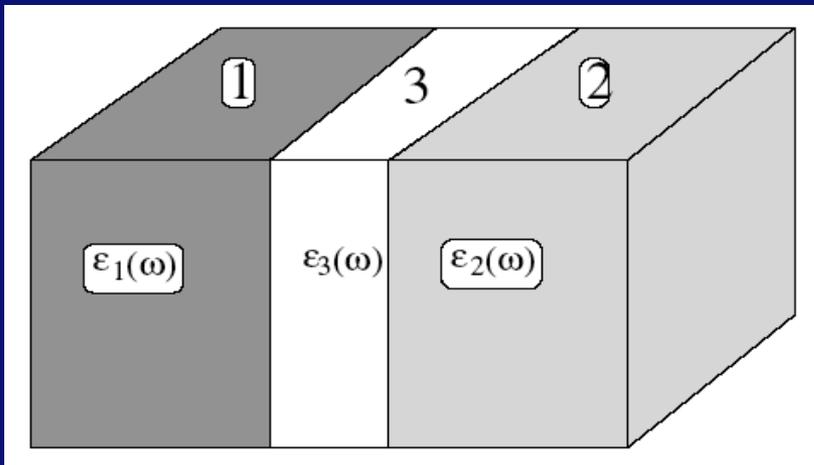
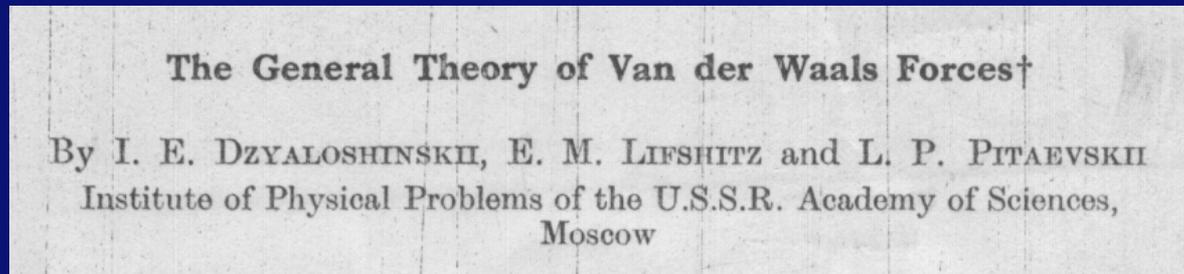
$$\langle p_{zz}(D \rightarrow \infty) \rangle = \frac{\hbar c}{16\pi^2 D^3} \int_0^\infty \int_1^\infty \frac{x^3 dx d\zeta}{\zeta^2 \left( \frac{(\epsilon_1(0)+1)(\epsilon_2(0)+1)}{(\epsilon_1(0)-1)(\epsilon_2(0)-1)} e^x - 1 \right)} \rightarrow -\frac{\pi^2 \hbar c}{240 D^4}$$

For ideal metals  $\epsilon(0) \rightarrow \infty$ , obviously reduces to the Casimir result!

$$E(D) = 2 \sum'_{\ell, k, m} \frac{1}{2} \hbar \omega_{\ell k m} \rightarrow E(D) = -\frac{\pi^2 \hbar c}{720 D^3} L^2$$

Lifshitz result is a straightforward generalization of the Casimir result and **contains it as a limit**.  
An incredible tour de force!

# Dzyaloshinskii, Lifshitz, Pitaevskii (1961).



$$\epsilon_2 > \epsilon_3 > \epsilon_1$$
$$\epsilon_2 > \epsilon_3 < \epsilon_1$$

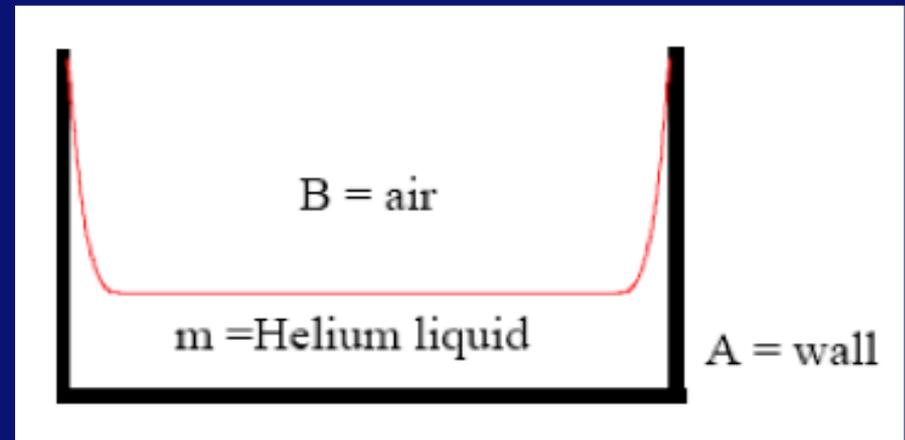
Complicated separation dependence because  $\epsilon = \epsilon(\omega)$

QED calculation.

Pressure is not necessarily monotonic!

$$\langle p_{zz}(D) \rangle \lesssim 0.$$

Thickness from 10 Å to 250 Å.  $\epsilon \sim 1.057$   
Sabisky and Anderson, 1970.



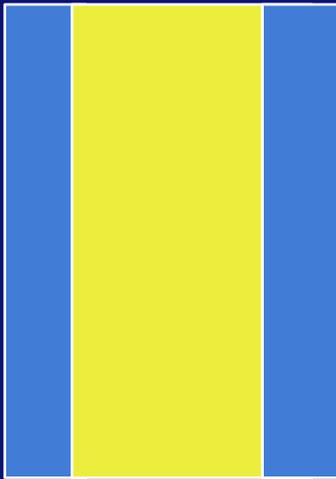
# The heuristic theory of vdW interactions

Nice, but too difficult to use for anything!

The theory just too complex to apply to any new problems, thus:

Van Kampen, Nijboer, Schramm (1968) – Parsegian, Ninham, Weiss (1972) – Barash, Ginzburg (1975).  
Based on the concept of EM mode eigenfrequencies and secular determinants.

In some respects a return to the original Casimir formulation! Take the eigenfrequencies of the EM field and get the corresponding free energy from quantum harmonic oscillators (which are not really harmonic oscillators):



Eigenmodes for a particular geometry

van Kampen et al.  $T = 0$

$$E(T = 0) = \frac{1}{2} \sum_i \hbar \omega_i$$

.... and Parsegian et al.  $T \neq 0$ .

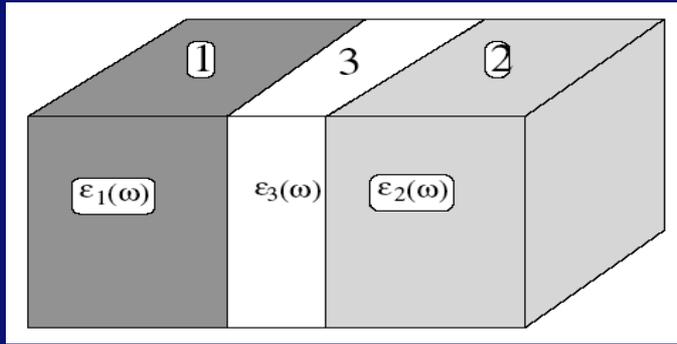
$$\mathcal{F}(T \neq 0) = k_B T \sum_i \ln 2 \sinh \frac{\hbar \omega_i}{2k_B T}$$

Use the argument principle to do the summation over the modes:

$$\frac{1}{2\pi i} \oint_C g(z) \frac{d}{dz} f(z) dz = \sum_i g(z_i) |_{f(z_i)=0} - \sum_i g(z_i) |_{f(z_i)=\infty}$$

# EM modes and vdW interactions

The brilliant idea of Niko van Kampen. Modes and energies.



$$\rho_{A,B}^2 = Q^2 - \frac{\epsilon_{A,B}\omega^2}{c^2}$$

$$D_{TM}^R(\omega) = 1 + \bar{\Delta}_{12}^R(\omega)\bar{\Delta}_{23}^R(\omega)e^{-2\rho_2(\omega)d} = 0,$$

$$D_{TE}^R(\omega) = 1 + \Delta_{12}^R(\omega)\Delta_{23}^R(\omega)e^{-2\rho_2(\omega)d} = 0,$$

$$\bar{\Delta}_{ij}^R(\omega) = \frac{\epsilon_i(\omega)\bar{\rho}_j(\omega) - \epsilon_j(\omega)\bar{\rho}_i(\omega)}{\epsilon_i(\omega)\bar{\rho}_j(\omega) + \epsilon_j(\omega)\bar{\rho}_i(\omega)},$$

$$\Delta_{ij}^R(\omega) = \frac{\rho_i(\omega) - \rho_j(\omega)}{\rho_i(\omega) + \rho_j(\omega)}.$$

Secular determinant of the modes. It gives eigenfrequencies as a function of the separation.  
Much easier to calculate than Green functions!

$$\mathcal{D}(i\xi_N, Q) = \mathcal{D}_E(i\xi_N, Q)\mathcal{D}_H(i\xi_N, Q) = 0.$$

$$\xi_N = N\frac{kT}{\hbar}$$

And then the interaction free energy comes from the application of the argument principle:

$$\mathcal{F} = kT \sum_{\mathbf{Q}} \sum_{N=0}^{\infty'} \log \mathcal{D}(i\xi_N, Q) = kT \sum_{\mathbf{Q}} \sum_{N=0}^{\infty'} \log \mathcal{D}_E(i\xi_N, Q) + kT \sum_{\mathbf{Q}} \sum_{N=0}^{\infty'} \log \mathcal{D}_H(i\xi_N, Q).$$

# Final result for the T-dependent vdW interactions

$$G_{LmR}(l) = \frac{kT}{(2\pi)} \sum_{n=0}^{\infty} \int_{\frac{\xi_n}{c}}^{\infty} \rho_m \ln \left[ \left(1 - \bar{\Delta}_{Lm} \bar{\Delta}_{Rm} e^{-2\rho_m l}\right) \left(1 - \Delta_{Lm} \Delta_{Rm} e^{-2\rho_m l}\right) \right] d\rho_m$$

This is the interaction free energy between two planar dielectric interfaces. The following definitions have been used:

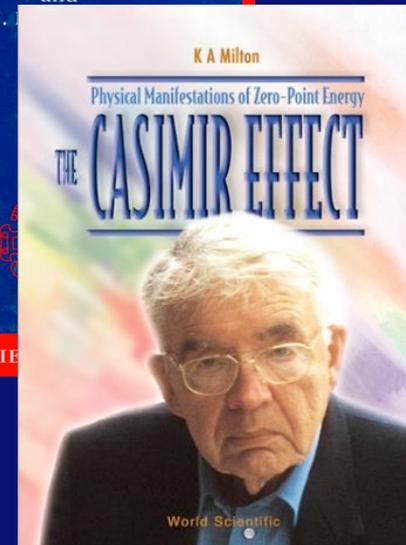
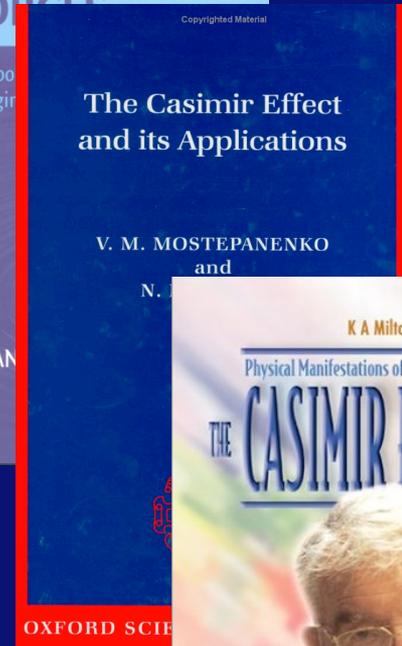
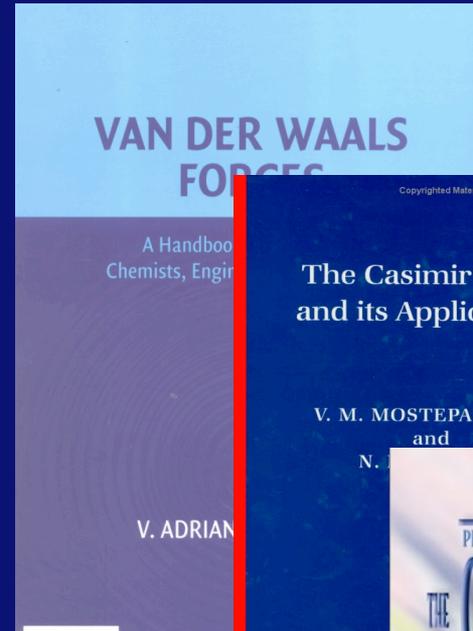
$$\bar{\Delta}_{ji} = \frac{\rho_i \epsilon_j - \rho_j \epsilon_i}{\rho_i \epsilon_j + \rho_j \epsilon_i}, \quad \Delta_{ji} = \frac{\rho_i \mu_j - \rho_j \mu_i}{\rho_i \mu_j + \rho_j \mu_i}, \quad \rho_i^2 = \rho_m^2 + \frac{\xi_n^2}{c^2} (\epsilon_i \mu_i - \epsilon_m \mu_m).$$

$$\rho_L^2 = \rho^2 + \frac{\epsilon_L \mu_L \xi_n^2}{c^2}, \quad \rho_m^2 = \rho^2 + \frac{\epsilon_m \mu_m \xi_n^2}{c^2}, \quad \rho_R^2 = \rho^2 + \frac{\epsilon_R \mu_R \xi_n^2}{c^2}.$$

$$\xi_N = N \frac{kT}{\hbar}$$

Still looks complicated but can be cast into a variety of simplified forms and can be easily generalized.

A lively subject to this day!



# Experimental confirmation of the Lifshitz theory?

Deryagin and Abrikosova (1953), Spaarnay, 1958. 100% error!  
 "did not contradict Casimir's theoretical prediction"

Shih and Parsegian, 1975.

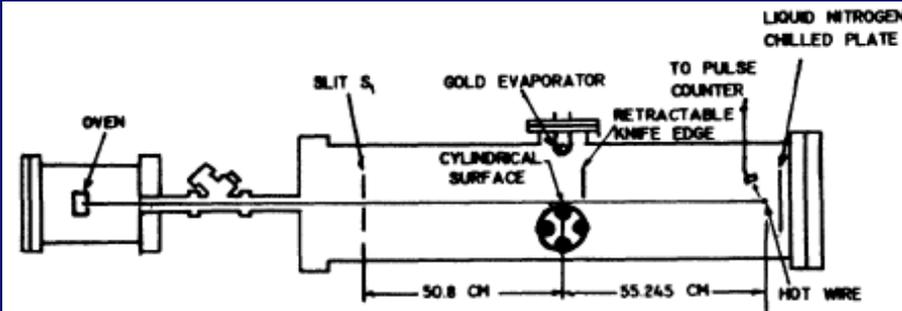


FIG. 1. Atomic beam apparatus.

Atomic beam of alkali metals above gold.

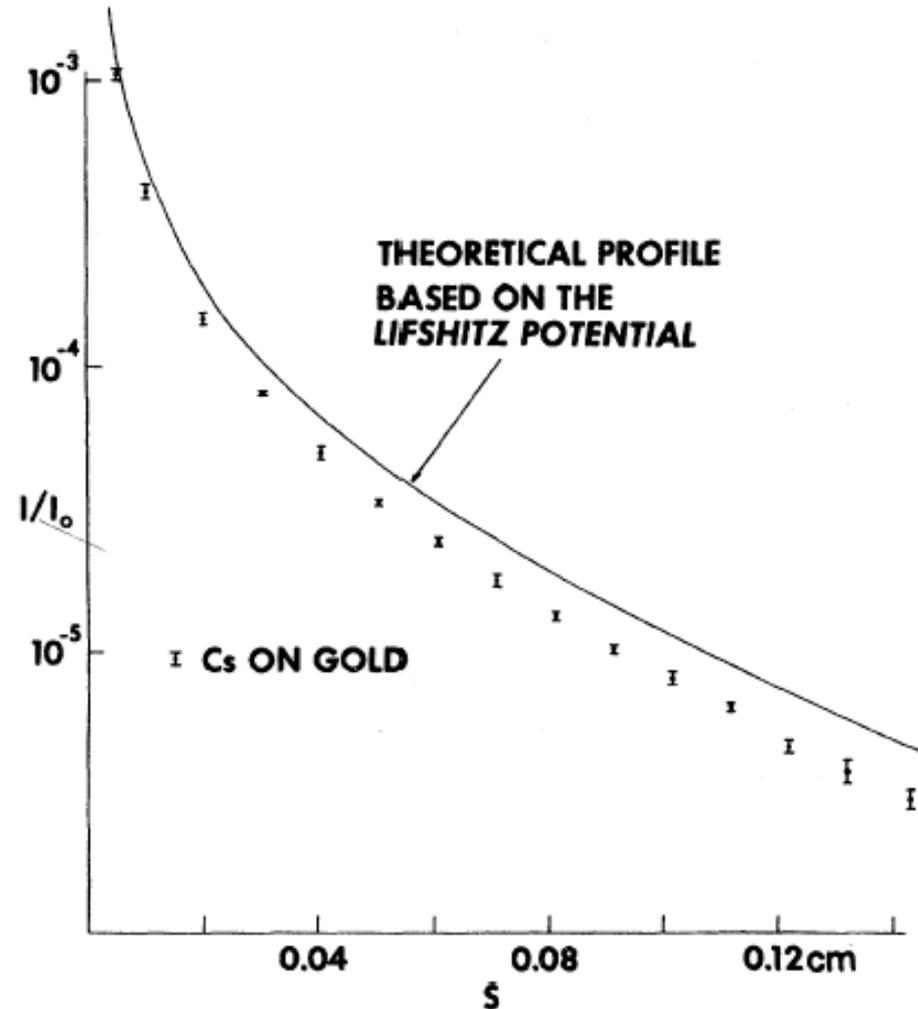
$$V(R) = -k_L/R^3,$$

where

$$k_L = \frac{\kappa T}{2} \sum_{n=0}^{\infty} \alpha(i\xi_n) \frac{\epsilon(i\xi_n) - 1}{\epsilon(i\xi_n) + 1} \left(1 + r_n + \frac{1}{4} r_n^2\right) e^{-r_n}$$

$$r(n) = 2 \xi(n) R/c$$

Computation based upon Lifshitz theory.

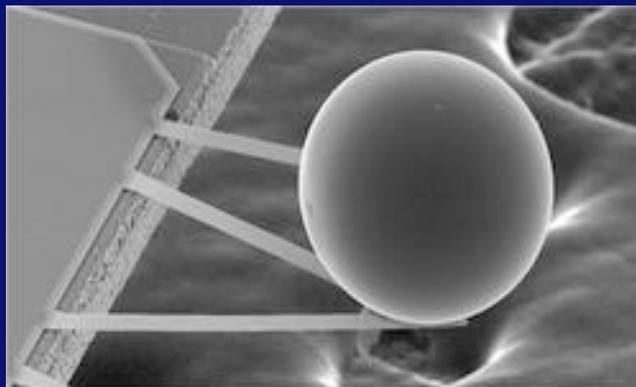
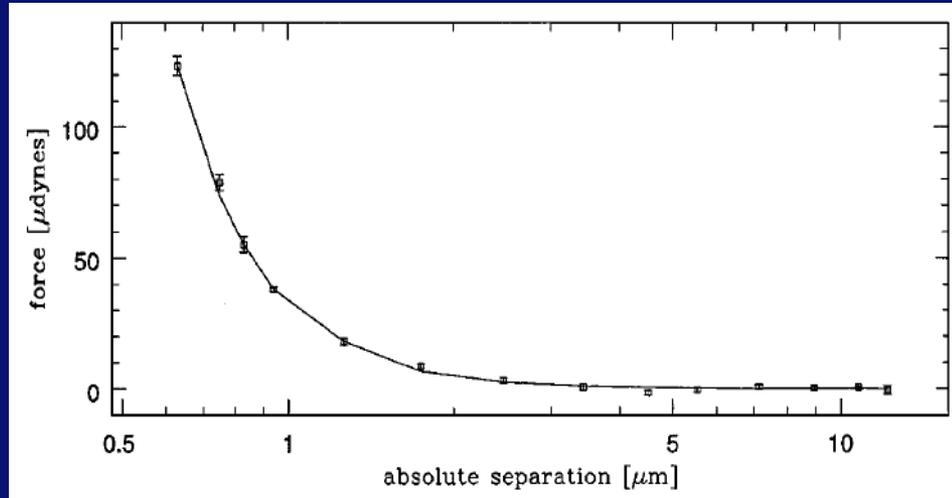


Almost quantitative correspondence ...

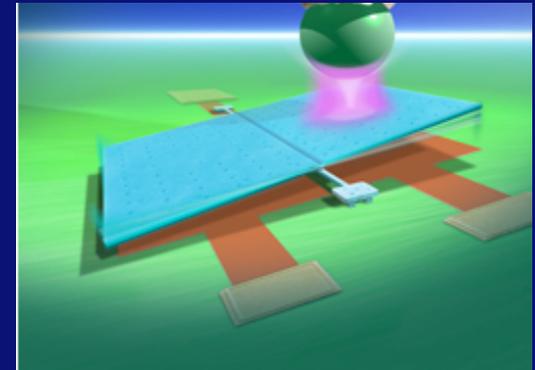
# Experimental confirmation of the Casimir theory!

Modern developments show that also the Casimir effect proper can be exactly measured even though it is small.

Lamoreaux, 1997.

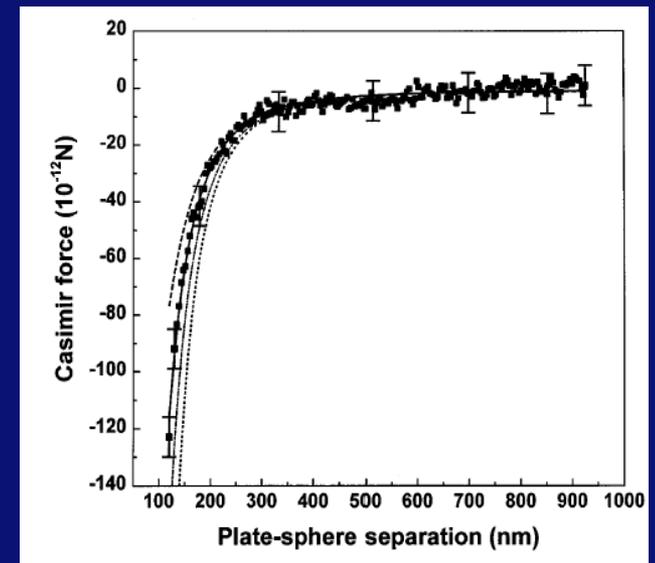


Sensitive sphere. This 200- $\mu\text{m}$ -diameter sphere mounted on a cantilever was brought to within 100 nm of a flat surface (not shown) to detect the elusive Casimir force.



Bell Labs

Chan, Aksyuk, Kleiman, Bishop, Capasso, 2001.



Mohideen and Roy, 1998.

# Science Times

The New York Times

TUESDAY, JANUARY 21, 1997

## Physicists Confirm Power of Nothing, Measuring Force of Quantum 'Foam'

Fluctuations in the vacuum are  
the universal pulse of existence.

By MALCOLM W. BROWNE

**F**OR a half century, physicists have known that there is no such thing as absolute nothingness, and that the vacuum of empty space, devoid of even a single atom of matter, seethes with subtle activity. Now, with the help of a pair of metal plates and a fine wire, a scientist has directly measured the force exerted by fleeting fluctuations in the vacuum that pace the universal pulse of existence.

The sensitive experiment performed at the University of Washington in Seattle by Dr. Steve K. Lamoreaux, an atomic physicist who is now at Los Alamos National

Laboratory, was described in a recent issue of the journal *Physical Review Letters*. Dr. Lamoreaux's results almost perfectly matched theoretical predictions based on quantum electrodynamics, a theory that touches on many of the riddles of existence and on the origin and fate of the universe.

The theory has been wonderfully accurate in predicting the results of subatomic particle experiments, and it has also been the basis of speculations verging on science fiction. One of the wilder ones is the possibility that the universal vacuum — the ubiquitous empty space of the universe — might actually be a false vacuum.

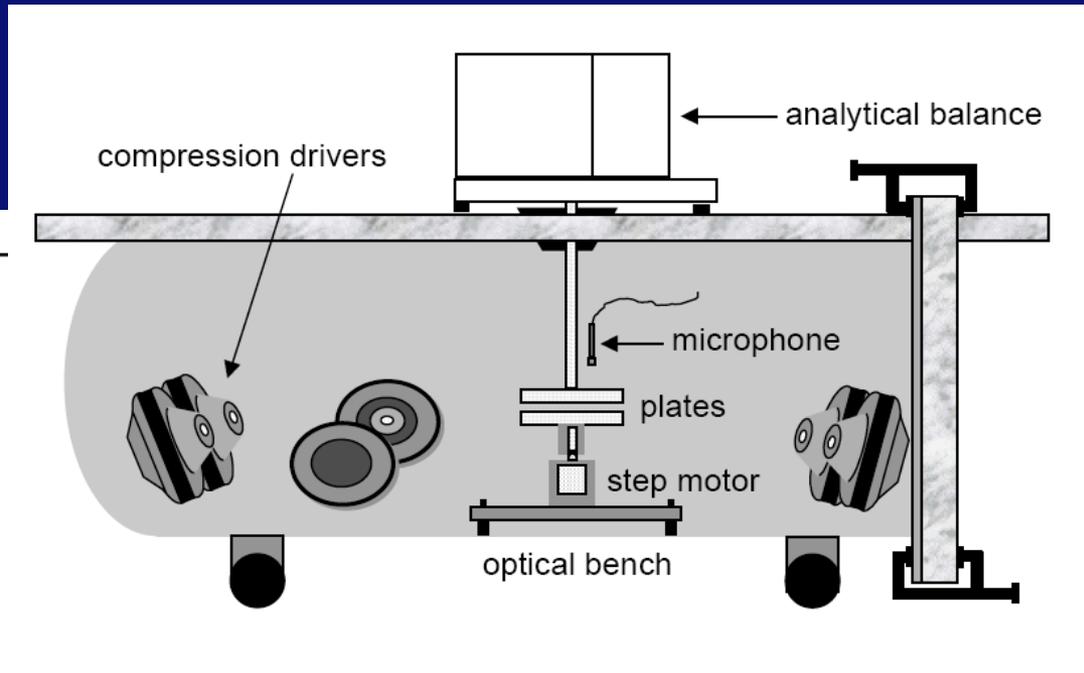
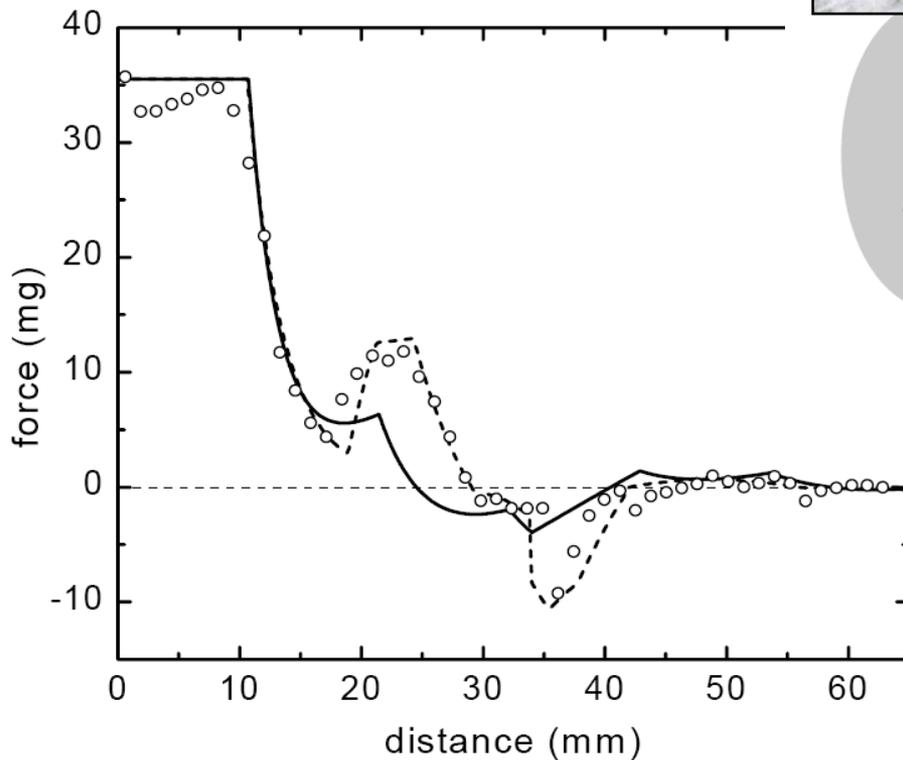
If that were so, something might cause the present-day universal vacuum to collapse to a different vacuum of a lower energy. The effect, propagating at the speed of light, would be the annihilation of all matter in the universe. There would be no warning for humankind; the earth and its inhabitants would simply cease to exist at

*Continued on Page C6*

# Interesting variations: acoustic Casimir effect

This variant of the “Casimir effect” is not driven by thermal fluctuations!  
It is driven by the **artificially generated acoustic noise**.

Not a thermal acoustic noise.  
Results depend on the nature of  
the noise spectrum.



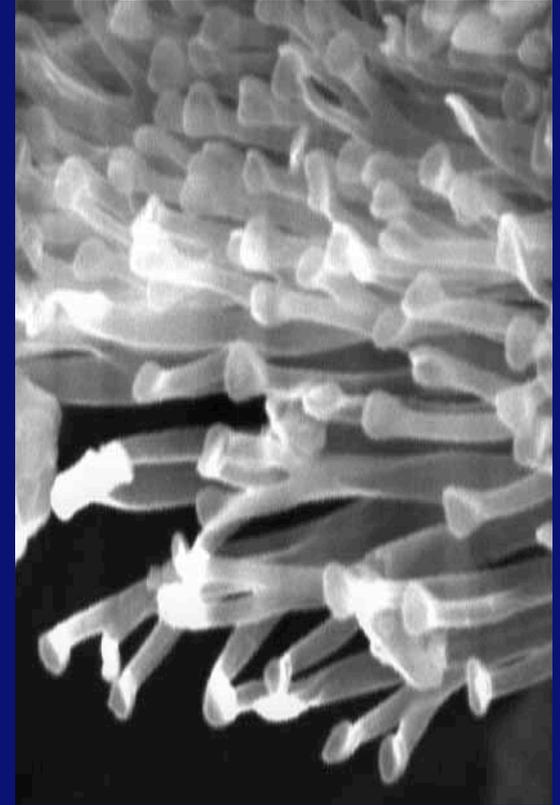
Flat white-noise spectrum vs.  
frequency dependent spectrum.

Non-monotonic interactions!

A. Larraza and B. Denardo 1998.

Hydrodynamic Casimir effect invoked in a **cryptic remark** at the end of the Dzyaloshinskii et al. 1961.

# Casimir effect *in vivo*

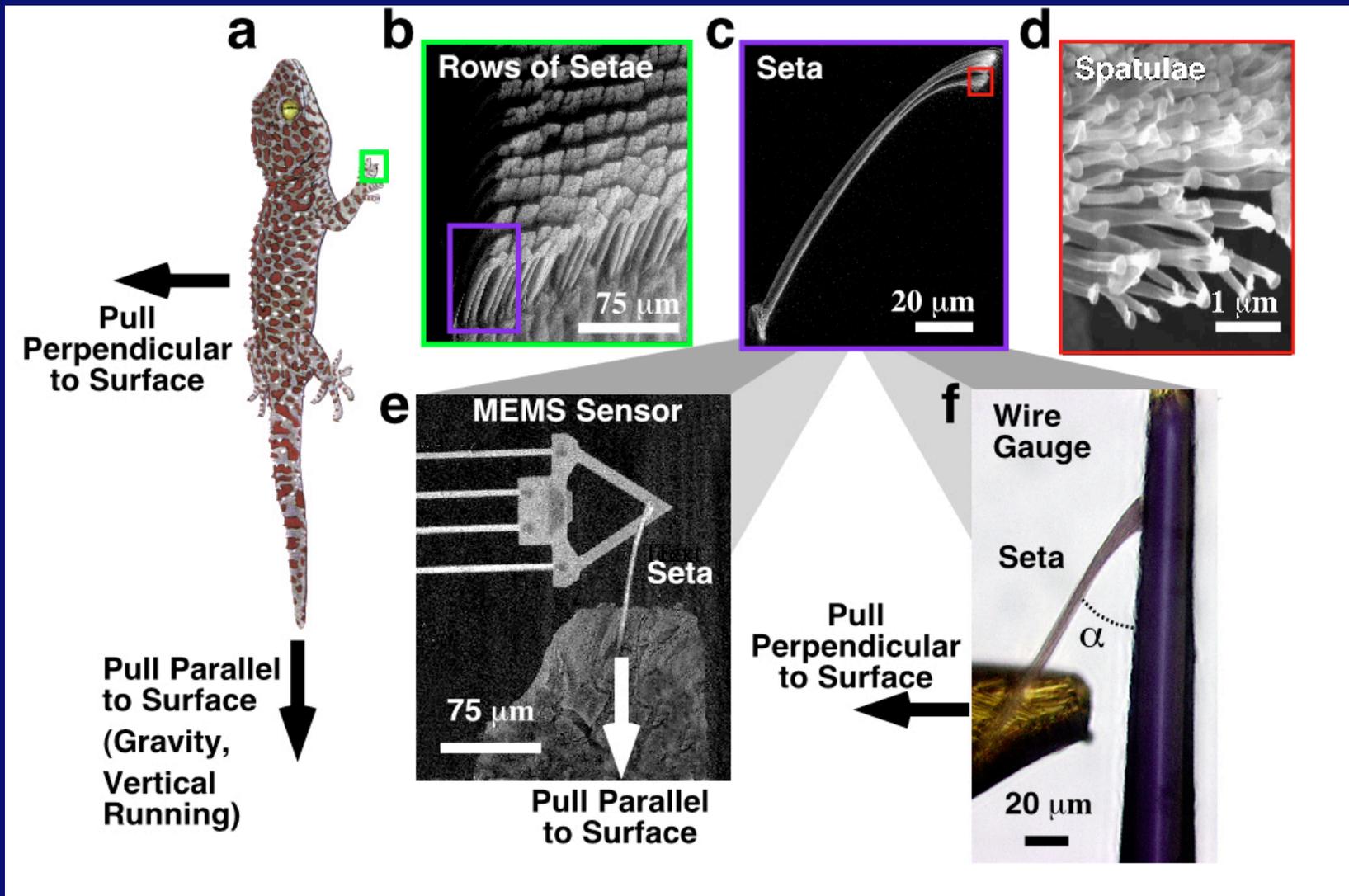


K. Autumn, W.-P. Chang, R. Fearing, T. Hsieh, T. Kenny, L. Liang, W. Zesch, R.J. Full. Nature 2000.  
Adhesive force of a single gecko foot-hair.

How does Gecko manage to walk on vertical smooth walls?

Suction? (Salamander). Capillary adhesion? (Small frogs). Interlocking? (Cockroach)

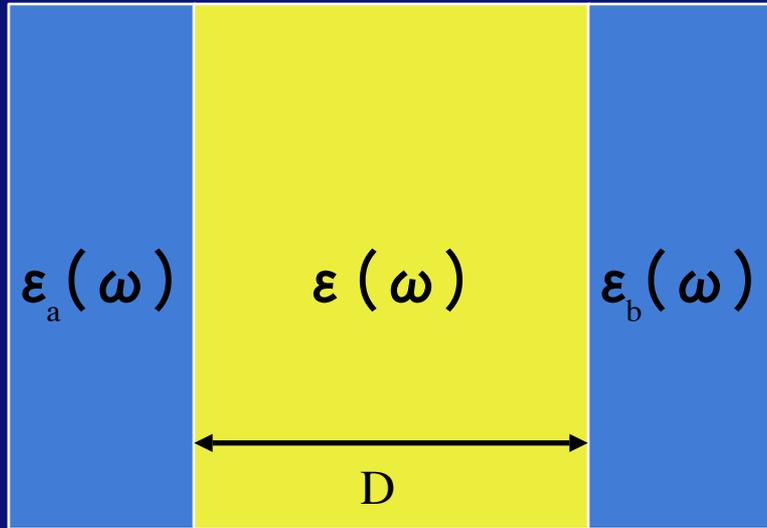
It's van der Waals interactions!



A single seta can lift the weight of an ant  $200 \mu\text{N} = 20 \text{ mg}$ . A million setae (1 square cm) could lift the weight of a child (20kg, 45lbs). Maximum potential force of 2,000,000 setae on 4 feet of a gecko =  $2,000,000 \times 200 \text{ micronewton} = 400 \text{ newton} = 40788 \text{ grams force}$ , or about 90 lbs! Weight of a Tokay gecko is approx. 50 to 150 grams.

# Pair interactions and the Pitaevskii *ansatz*

How does one derive the interactions between isolated atoms (molecules)?  
L.P. Pitaevskii, 1959.



$$\epsilon_{a,b}(\omega) \simeq \epsilon(\omega) + n_{a,b}\alpha_{a,b}(\omega)$$

The Pitaevskii equation (1959):

$$\frac{\partial^3 \mathcal{F}_{a,b}(D)}{\partial D^3} = -2\pi D n_a n_b f_{a,b}(D)$$

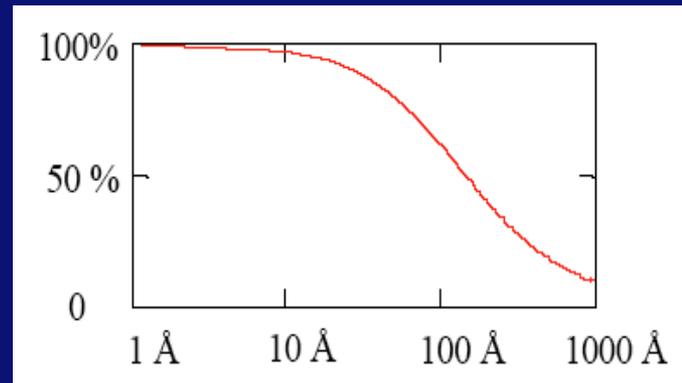
For rarefied dispersive media.

$$f_{a,b}(D) = -\frac{3k_B T}{8\pi^2 D^6} \sum_{n=0}^{\infty} \frac{\alpha_a(i\omega_n)\alpha_b(i\omega_n)}{\epsilon^2(i\omega_n)} \mathcal{R}(r_n)$$

$$r_n = \frac{2\sqrt{\epsilon(i\omega_n)\mu(i\omega_n)} \omega_n}{c} D$$

Retardation effects. Finite velocity of light!

$n=0$  terms is classical!



# London-van der Waals dispersion interaction

Back to the beginning of the story.

$$f_{a,b}(D \rightarrow 0) \cong -\frac{3\hbar}{16\pi^3 D^6} \int_0^\infty d\omega \frac{\alpha_a(i\omega)\alpha_b(i\omega)}{\epsilon^2(i\omega)}$$

London interaction, 1930.  
Debye-Keesom-London interaction

$$f_{a,b}(D \rightarrow \infty) \cong -\frac{23\hbar c}{64\pi^3 D^7} \frac{\alpha_a(0)\alpha_b(0)}{\epsilon^{5/2}(0)}$$

Casimir - Polder interaction, 1948.

**Non-pairwise additive:** Axilrod-Teller potential

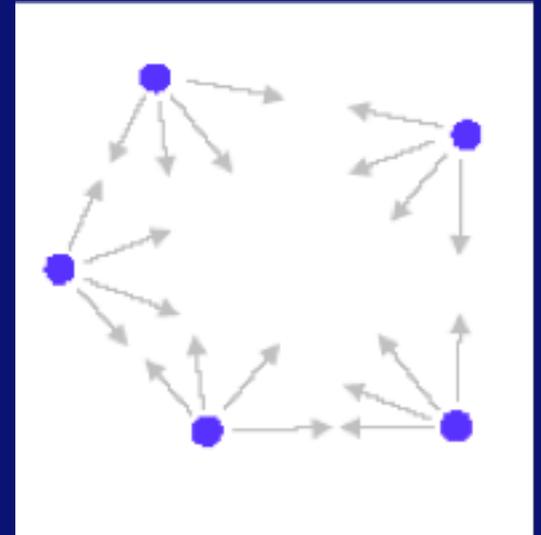
$$E_{AT}(i, j, k) = \frac{\gamma(1 + 3\cos\theta_{ij}\cos\theta_{jk}\cos\theta_{ki})}{R_{ij}^3 R_{jk}^3 R_{ki}^3}$$

Historically a reversed course via **Hamaker - de Boer summation**, 1937.

$$\mathcal{F}(D) = n_1 n_2 \int_{V_1} \int_{V_2} f(|\mathbf{r}_1 - \mathbf{r}_2|) dV_1 dV_2$$

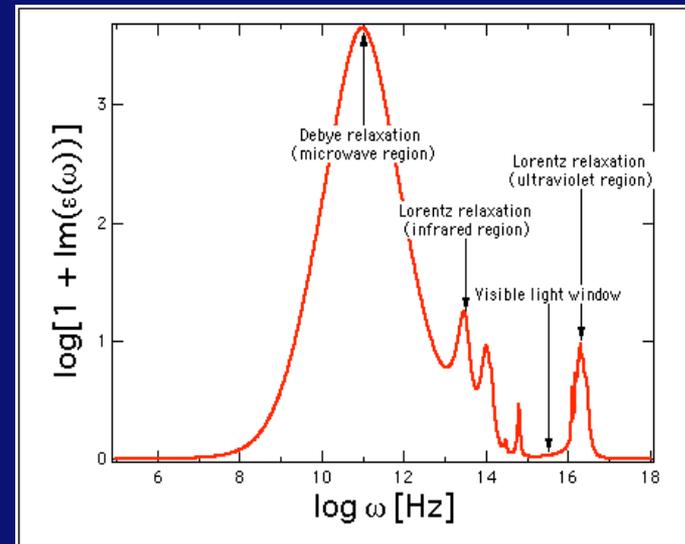
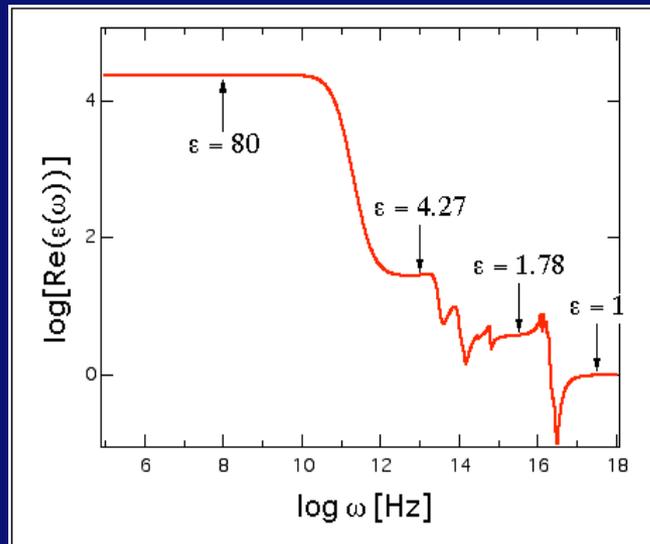
van der Waals equation of state, 1873.

$$(p + (a/V^2))(V - b) = NkT .$$



# Calculating vdW interactions - Lebedev's dream fulfilled

Connecting the strength of van der Waals interaction with spectra. Lebedev's dream fulfilled.  
Parsegian - Ninham calculations, 1970-80.



The dielectric spectrum of water.

Let us investigate the limit of small separations:

$$\langle p_{zz}(D \rightarrow 0) \rangle = \frac{\hbar}{16\pi^2 D^3} \int_0^\infty \int_0^\infty x^2 \left[ \frac{(\epsilon_1(i\zeta) + 1)(\epsilon_2(i\zeta) + 1)}{(\epsilon_1(i\zeta) - 1)(\epsilon_2(i\zeta) - 1)} e^x - 1 \right]^{-1} dx d\zeta$$

At small separations corresponds to the Hamaker (pairwise summation) formula:

$$\langle p_{zz}(D \rightarrow 0) \rangle = \frac{A}{6\pi D^3}$$

# The Hamaker coefficient

The Hamaker coefficient quantifies the magnitude of the vdW interaction.  
Different cultures within the physics community.

$A_{Am/Am} (l = 0)$ , Symmetric systems, retardation screening neglected	
Interaction	Hamaker coefficient ( $kT_{\text{room}}$ units)
hydrocarbon across water	0.95 $kT_{\text{room}}$
mica across hydrocarbon	2.1 $kT_{\text{room}}$
mica across water	3.9 $kT_{\text{room}}$
gold across water	28.9 $kT_{\text{room}}$
water across vacuum	9.4 $kT_{\text{room}}$
hydrocarbon across vacuum	11.6 $kT_{\text{room}}$
mica across vacuum	21.8 $kT_{\text{room}}$
gold across vacuum	48.6 $kT_{\text{room}}$

SOFT

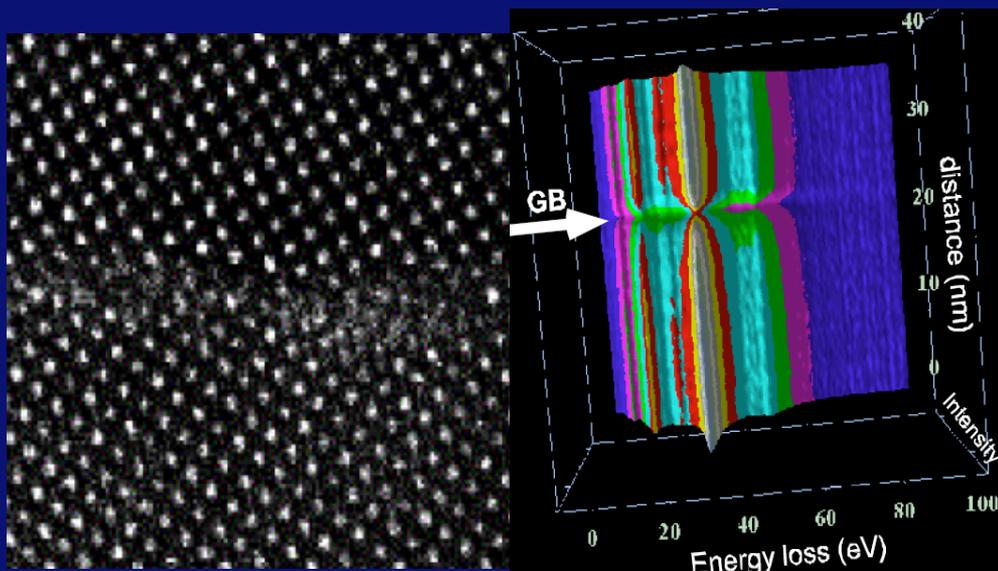
In order to evaluate the Hamaker coefficient one needs the dielectric spectrum  $\epsilon(i\omega)$ .  
This spectrum can be sometimes measured directly or can be calculated from models.

$A_{\text{AlN}/\text{water}/\text{AlN}} = 102.2\text{zJ}$	$A_{\text{AlN}/\text{vac}/\text{AlN}} = 228.5\text{zJ}$
$A_{\text{Al}_2\text{O}_3/\text{water}/\text{Al}_2\text{O}_3} = 58.9\text{zJ} (27.5\text{zJ}^{108})$	$A_{\text{Al}_2\text{O}_3/\text{vac}/\text{Al}_2\text{O}_3} = 168.7\text{zJ} (145\text{zJ}^{108})$
$A_{\text{MgO}/\text{water}/\text{MgO}} = 26.9\text{zJ}$	$A_{\text{MgO}/\text{vac}/\text{MgO}} = 114.5\text{zJ}$
$A_{\text{SiO}_2/\text{water}/\text{SiO}_2} = 6.0\text{zJ} (1.6\text{zJ}^{108})$	$A_{\text{SiO}_2/\text{vac}/\text{SiO}_2} = 66.6\text{zJ} (66\text{zJ}^{108})$
$A_{\text{Si}/\text{water}/\text{Si}} = 112.5\text{zJ}$	$A_{\text{Si}/\text{vac}/\text{Si}} = 212.6\text{zJ}$

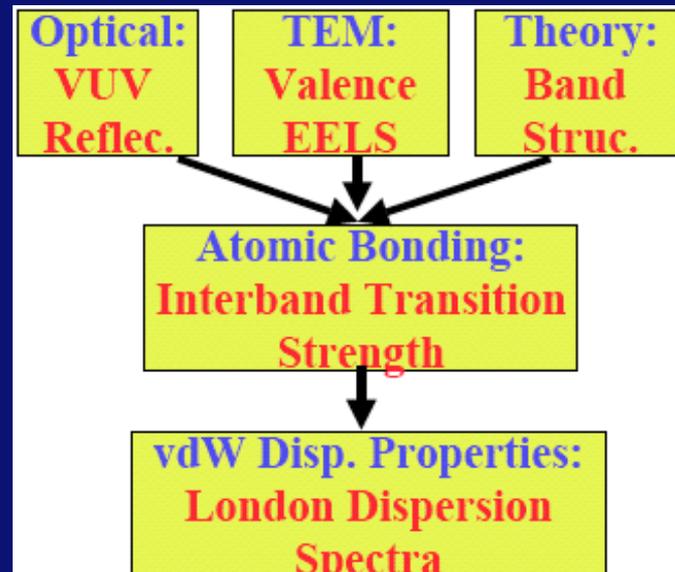
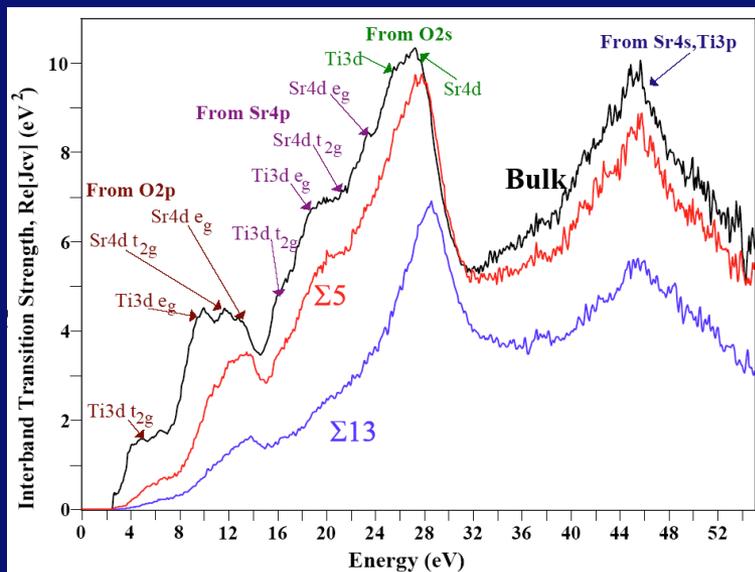
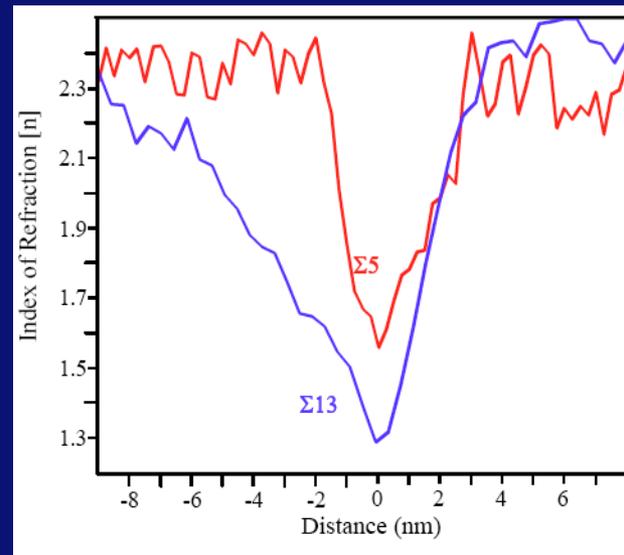
HARD

# Current approach

SrTiO<sub>3</sub> vdW interaction across grain boundaries. R. French, 2003.



Kienzle, 1999.



# The Hamaker coefficient - directly from experiment

Calculated Hamaker coefficients from measured dielectric spectra:

- ◆ Using Lifshitz Theory, QED

- ◆ Acquire Exp. Spectra
- ◆ Calc. London Disp. Spectrum
  - Kramers Kronig Transform

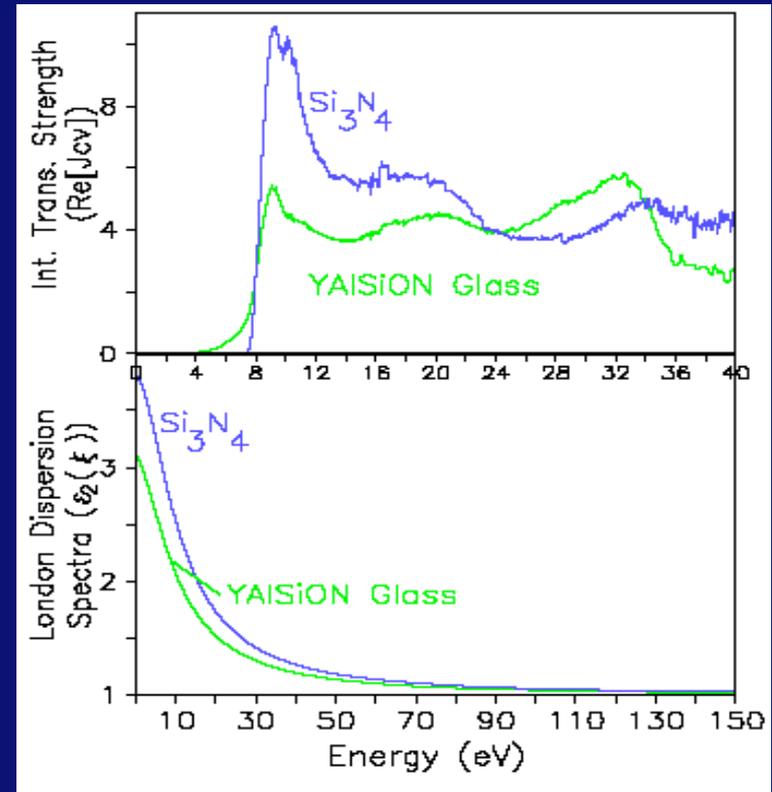
$$\epsilon_2(\xi) = 1 + \frac{2}{\pi} \int_0^{\infty} \frac{\omega \epsilon_2(\omega)}{\omega^2 + \xi^2} d\omega$$

- ◆ Then Hamaker Constant
  - Calc'd by Spectral Differences
  - of London Disp. Spectra

$$A = \frac{-3\hbar L^2}{\pi} \int_0^{\infty} \rho d\rho \int_0^{\infty} \ln G(\xi) d\xi$$

$$G_{121}^{NR}(\xi) = 1 - \Delta_{12}^2 e^{-2a\rho}$$

$$\Delta_{kj} = \frac{\epsilon_{2,k}(\xi) - \epsilon_{2,j}(\xi)}{\epsilon_{2,k}(\xi) + \epsilon_{2,j}(\xi)}$$



R. French, 2003.

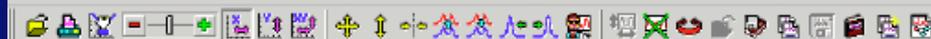
## Hamaker Constant $A_{121}^{NR}$ (zJ)

SrTiO <sub>3</sub>   Vacuum   SrTiO <sub>3</sub>	<b>245 zJ</b>
SrTiO <sub>3</sub>   <b>Σ13 Boundary</b>   SrTiO <sub>3</sub>	<b>78.6 zJ</b>
SrTiO <sub>3</sub>   <b>Σ5 Boundary</b>   SrTiO <sub>3</sub>	<b>34.5 zJ</b>

Project acronym: INCEMS

Project full title: Interfacial Materials – Computations and Experimental Multi-Scale Studies

Proposal/Contract no.: Proposal 013862 /



Sort Up Dn Database contains 120 rows

Layer	SpectrumName	SpectrumData	nVis	DSpectrumData	Comment
1	PBRUOT		n=3.56,Ln250,Lv3,Hv3		552 Pb2Ru207 L SILVERMAN 300 HP-KKn30 @1240,Hew6.55.
2	TIO2RUTT		n=2.41,Ln250,Lv3,Hv3		527 TiO2 YET 300 RUTILE-1M/OSN-ANN4KKn2.55
3	KH9GLT		n=1.62,Ln250,Lv3,Hv3		432 KH9GLASS 65SiO2 34PbO 1 Al2O3 Lee KKn1.8 @633,Hew6.83.
4	TIO2RUTT		n=2.41,Ln250,Lv3,Hv3		527 TiO2 YET 300 RUTILE-1M/OSN-ANN4KKn2.55
5	PBRUOT		n=3.56,Ln250,Lv3,Hv3		552 Pb2Ru207 L SILVERMAN 300 HP-KKn30 @1240,Hew6.55.
999	PDN7ST		n=1.55,Ln250,Lv1,Hv3		#360-323.PDN7S heptM_meth.tl.300.1890391 compKKn1.54
999	CDST		n=2.27,Ln250,Lv3,Hv3		#272.CdS,YWong.Single.,300,KKn2.4 @633,Hew6.33.
999	CDMOO4T		n=1.95,Ln250,Lv3,Hv3		#367B.cDmOo4.Brics.txtLC avs.300KcpKKn1.85 @600_Hew7.33.
999	CAF2T		n=1.44,Ln250,Lv3,Hv3		549 CAF HARRICK WINDOW 0 KKn1.46 @633,Hew6.33.
999	CAW04T		n=1.74,Ln250,Lv3,Hv3		#332.CaWO4.briener.Sxtol.300.1uKKn1.71 @600_Hew6
999	CAM004T		n=1.88,Ln250,Lv3,Hv3		#333.CaMoO4.Brics_sxtal.300.1UKKn1.95 @633_Hew6.77.
999	icedT		n=2.15,Ln250,Lv1,Hv3		-LOs (01.08.00)(11.05.00)(40.02.00)(8.6.73) #404.cdiocytSilane.meth.tl.300.1
999	PDN8ST		n=1.53,Ln250,Lv1,Hv3		

HAMAKER DASHBOARD

Open DB Save As Close DB View Log

Add Spectrum Create Dispersion Spec Vers

Delete Row Clone Row Extract Spc Help

Add A Layer

Highlight Database Row, then push layer button.

Layer 1 PBRUOT nVis=n=3.56,Ln250,Lv3 X

Layer 2 TIO2RUTT nVis=n=2.41,Ln250,L X

Layer 3 KH9GLT nVis=n=1.62,Ln250,Lv3 X

Layer 4 TIO2RUTT nVis=n=2.41,Ln250,L X

Layer 5 PBRUOT nVis=n=3.56,Ln250,Lv3 X

Layer 6 SpectrumName nVis X

Layer n SpectrumName nVis X

Hamaker Coefficients

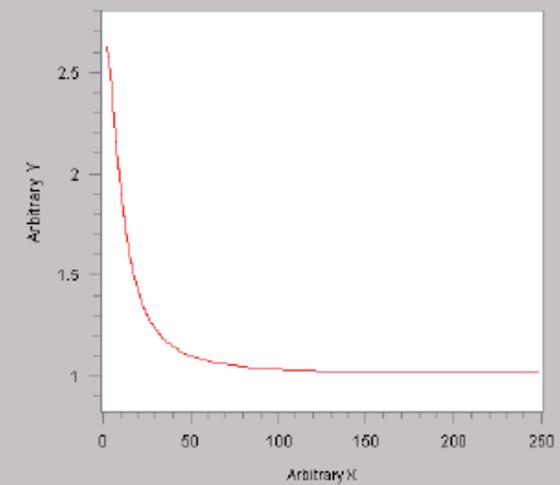
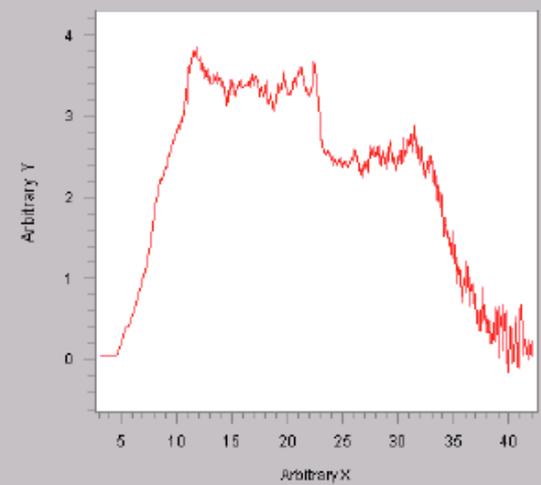
NonRetarded Retarded Add A Layer

N-121 R-121 Calculate

N-123 R-123

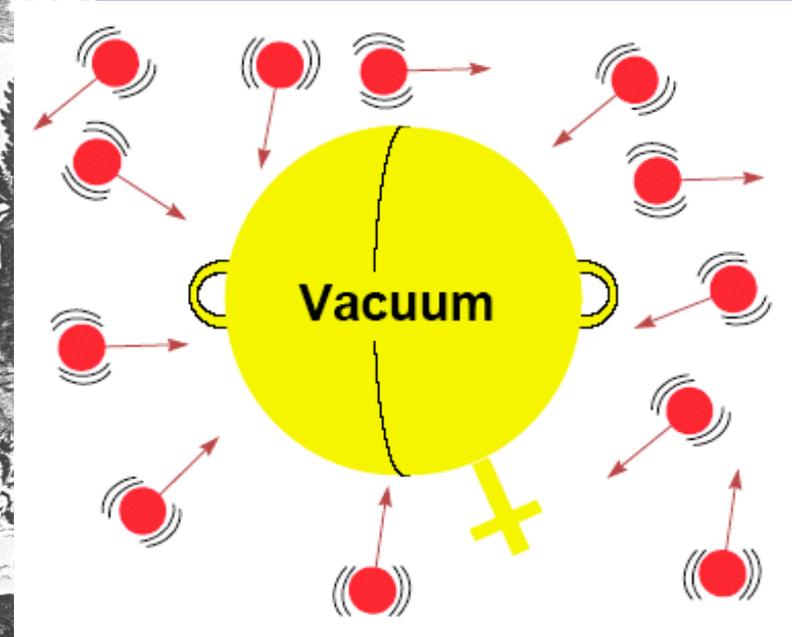
N-12321

Contact Angle 1-on-2



# Non-trivial effects of geomtrey

Von Guericke (1602–1686) and the Magdeburg sphere.



Scattering of EM waves!

Casimir model (1956) of the electron.  
Electrostatic repulsion and Casimir attraction  
have to balance!

Sometimes even the sign is difficult to guess.  
Spherical geometry.

$$E = \frac{e_0^2}{4\pi\epsilon_0 a} - Z \frac{\hbar c}{a}$$

Boyer, Davies, Balian and Duplantier,  
Milton, DeRaad and Schwinger (1978)  
 $Z < 0!$

# Some “modern” developments

The pseudo-Casimir effect.  $n=0$  (classical) term.

Casimir effect exists also for non-EM fields described with similar equations.

Critical Hamiltonian

$$\delta\mathcal{F}(H) = -k_B T \times \frac{A}{H^2} \times \Delta.$$

$$\mathcal{H}[\phi] = \frac{K}{2} \int d^3\mathbf{x} (\nabla\phi)^2,$$

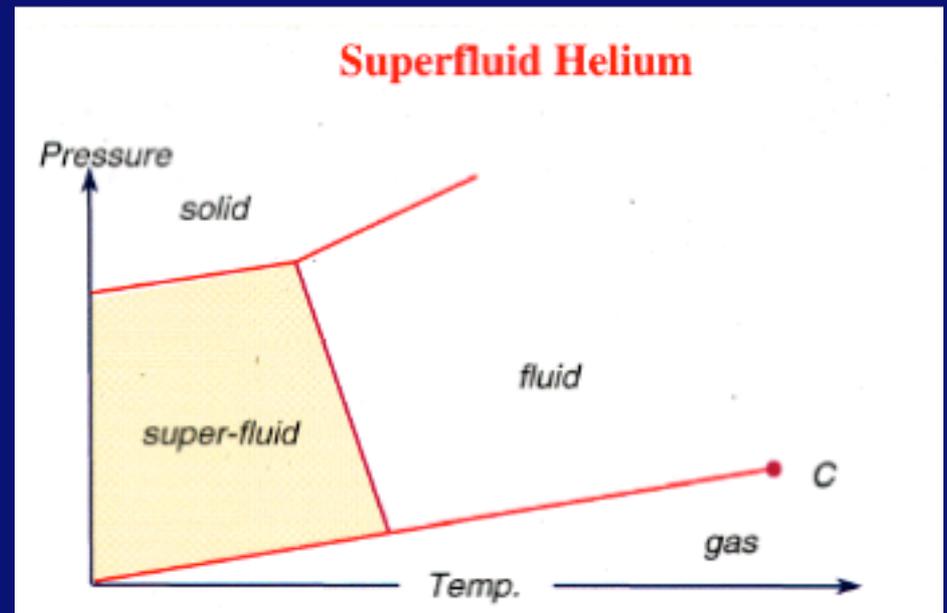
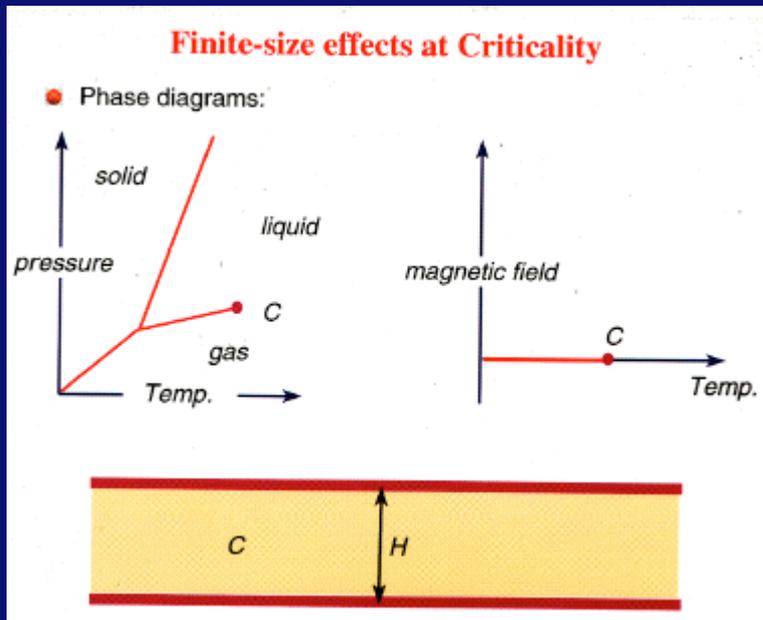
$$\delta\mathcal{F}(H) = -k_B T \times \frac{A}{H^2} \times \frac{\zeta(3)}{16\pi}.$$

Critical fluids (Fisher and de Gennes, 1978).

Critical density fluctuations.

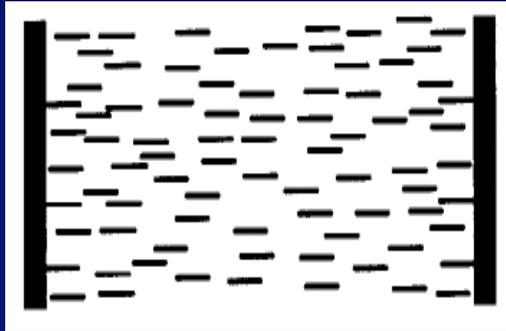
Superfluid films (Li and Kardar, 1991).

Superfluid He Goldstone (massless) bosons associated with the phase of the condensate.

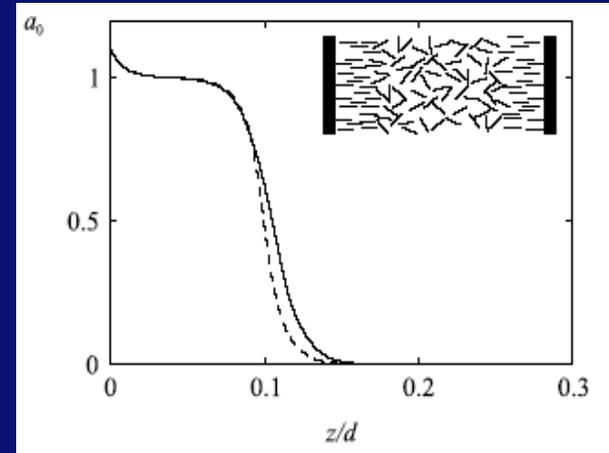


# Nematic and smectic pseudo-Casimir interactions

Nematic liquid crystals.



Critical fluctuations  
in the director field.



$$\mathcal{H}_N = \frac{1}{2} \int d^3 \mathbf{r} [\kappa_1 (\nabla \cdot \mathbf{n})^2 + \kappa_2 (\mathbf{n} \cdot \nabla \times \mathbf{n})^2 + \kappa_3 (\mathbf{n} \times \nabla \times \mathbf{n})^2].$$

$$\delta \mathcal{E}_N = -k_B T \times \frac{A}{H^2} \times \frac{\zeta(3)}{16\pi} \left( \frac{\kappa_3}{\kappa_1} + \frac{\kappa_3}{\kappa_2} \right).$$

Nematic film with stiff boundaries (Mikheev, 1989).

$$\mathcal{F} = -\frac{kTS}{8\pi d^3} \zeta(3) - \frac{kTS}{4\pi \xi^2 d} \exp(-2d/\xi)$$

Nematic wetting (Ziherl, Podgornik and Zumer, 1998).

Smectic LC

$$\mathcal{H}_S = \frac{1}{2} \int d^3 \mathbf{r} \left[ B \left( \frac{\partial u}{\partial z} \right)^2 + \kappa (\nabla^2 u)^2 \right].$$

$$\delta \mathcal{E}_S = -k_B T \times \frac{A}{H\lambda} \times \frac{\zeta(2)}{16\pi}, \quad \text{with } \lambda \equiv \sqrt{\frac{\kappa}{B}}$$

Smectic films (Li and Kardar, 1992).

# Ionic pseudo-Casimir interactions

Charged fluids

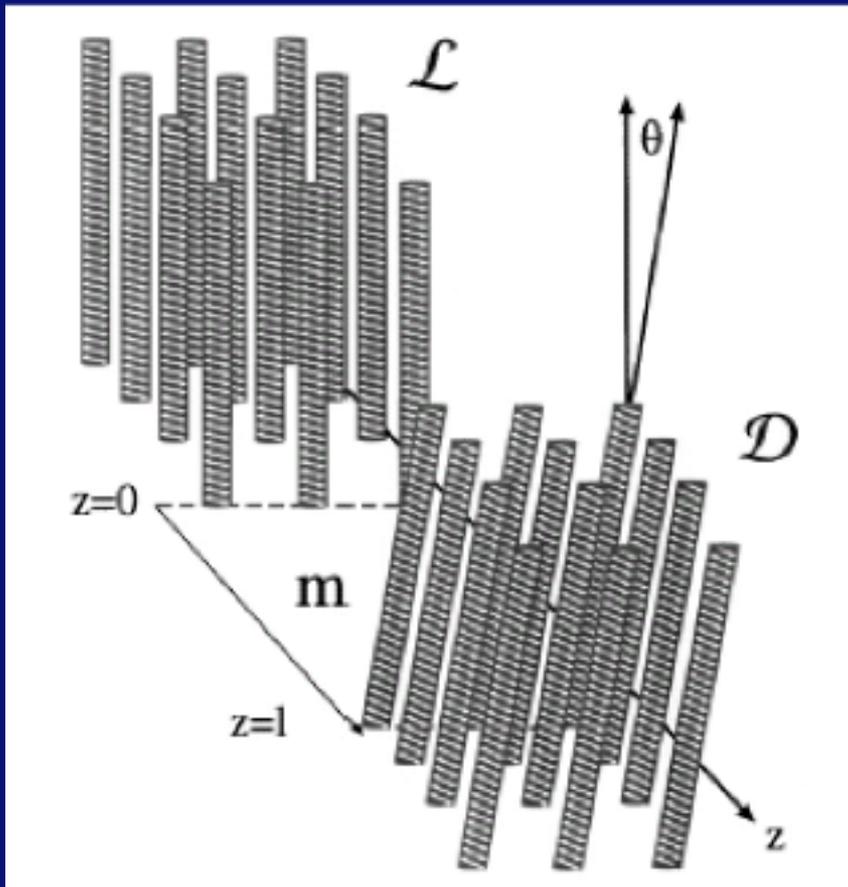
$$\mathcal{F}[n_0, \phi, \nabla\phi] = \int_V \left( \frac{1}{2} \epsilon \epsilon_0 \int_V \nabla\phi^2 - kT n_0 (e^{-\frac{e_0\phi}{kT}} - 1) \right) d^3\mathbf{r}$$

$$F_{\text{FI}} = -k_B T \times \frac{A}{H^2} \times \frac{\zeta(3)}{16\pi}$$

(Podgornik and Zeks, 1989).

$$F_{\text{FI}} = k_B T \times \frac{A}{\lambda_{\text{GC}}^2} \times \Delta_c \times \ln\left(\frac{H}{\lambda_{\text{GC}}}\right),$$

(Golestanian and Kardar, 1998).



This is part of the weak coupling approximation in the theory of coulomb fluids (Netz and Moreira, 2000)

Pseudo-Casimir interaction coincides with the  $n=0$  Lifshitz result exactly.

Fluctuation (pseudo-Casimir) interactions are non-pairwise additive. The total energy of an assembly is difficult to calculate.

(Podgornik and Parsegian, 2001)

Non-pairwise additive effects are essential in all fluctuation driven interactions.

# Elastic pseudo-Casimir interactions

Membrane inclusions (Goulian et al. 1993).

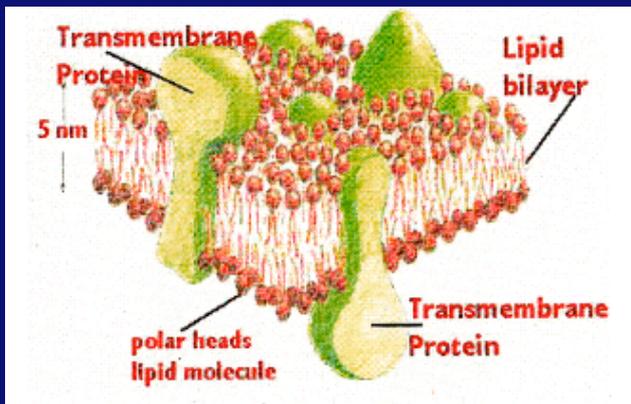
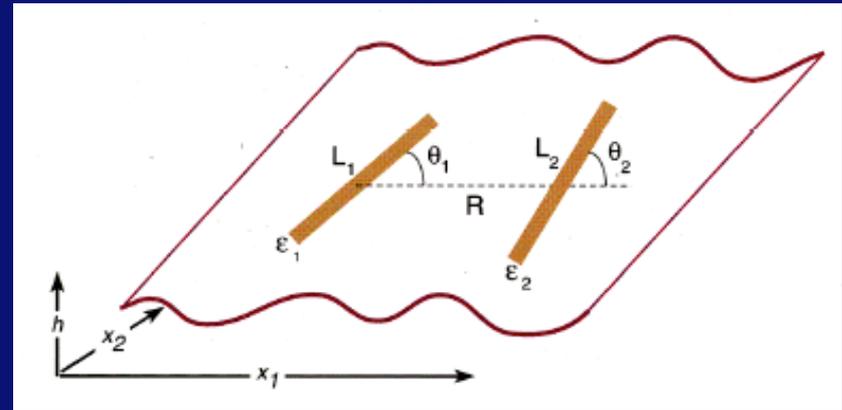
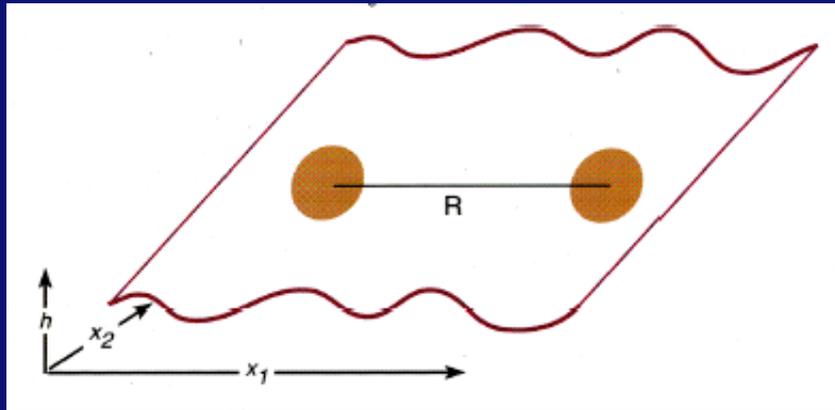
$$\mathcal{H} = \frac{\kappa}{2} \int d^2\mathbf{x} (\nabla^2 h(\mathbf{x}))^2,$$

$$\mathcal{V}(R) = -k_B T \times \frac{A^2}{R^4} \times \frac{6}{\pi^2},$$

(Goulian, Bruinsma, Pincus . 1993).

$$V^T(R, \theta_1, \theta_2) = -\frac{k_B T}{128} \times \frac{L_1^2 L_2^2}{R^4} \times \cos^2[2(\theta_1 + \theta_2)],$$

(Golestanian, Goulian and Kardar, 1996).



Interaction between (lipid) membrane inclusions such as proteins.

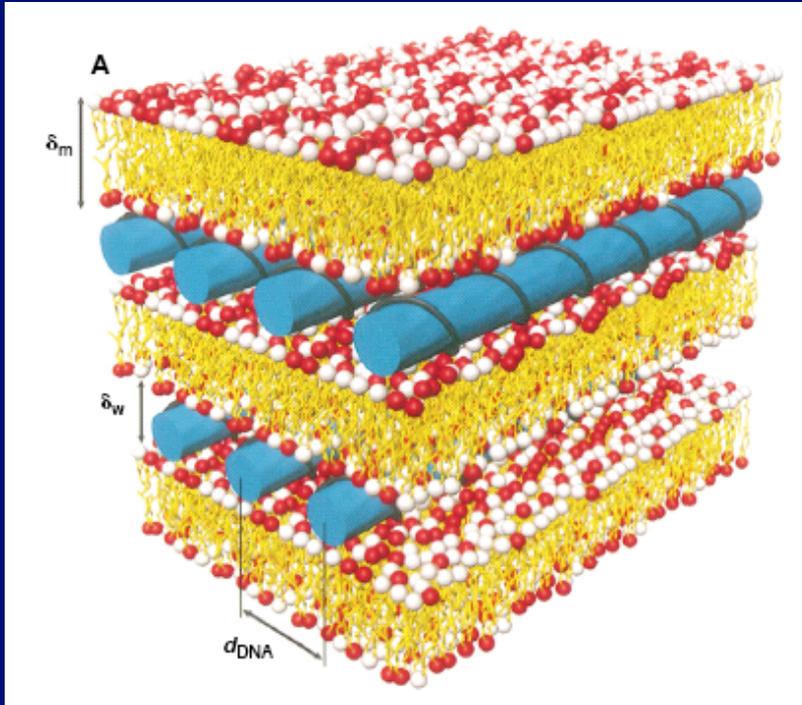
Important in understanding aggregation of membrane proteins.

# Van der Waals interactions in lipid bilayers

Multilamellar arrays are ubiquitous in biophysics.

Are interactions between a pair of bilayers different from interactions in a stack?

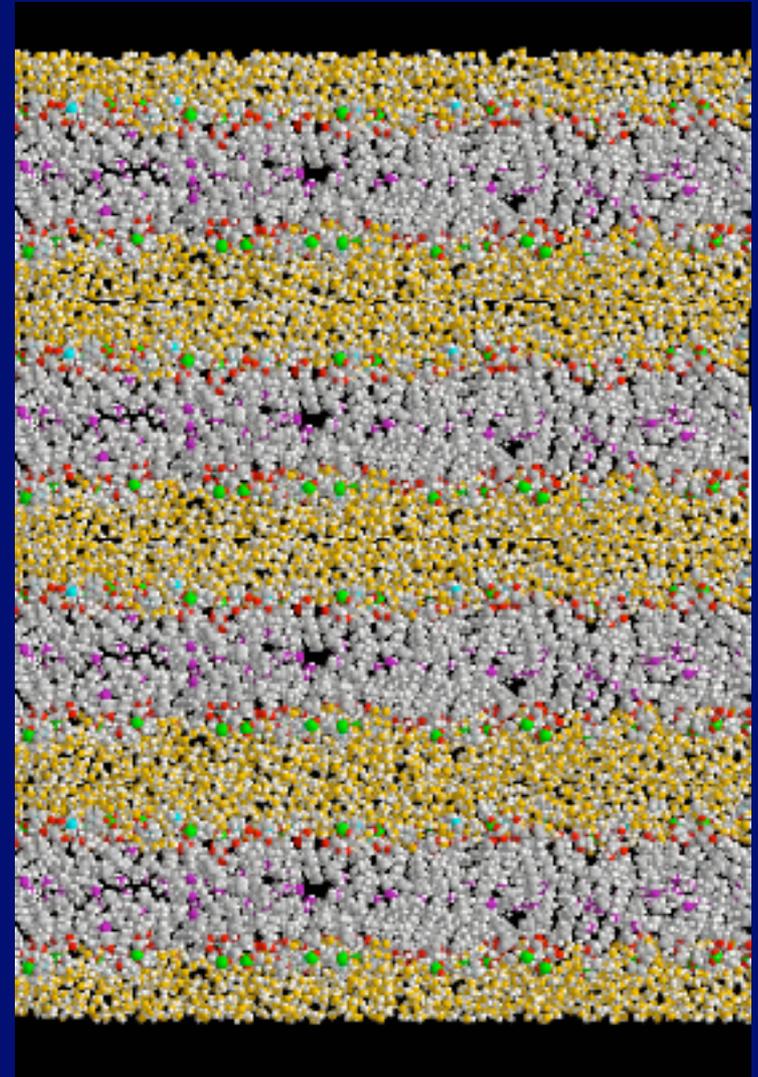
Interactions between neutral molecules.



Complexes of DNA and cationic lipids  
but also neutral lipids!

DOTAP + helper lipid. Raedler et al. 1997.  
Dan Lasic et al. 1996.

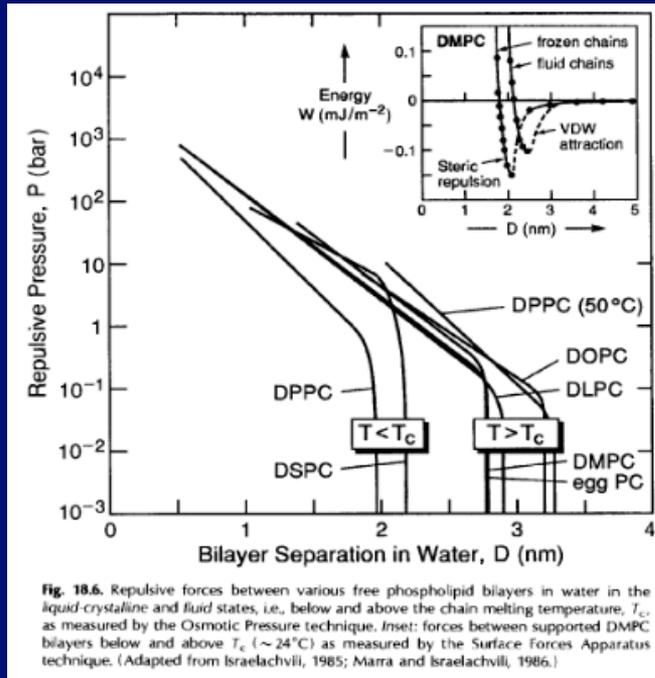
Multilamellar lipid arrays.



B. Brooks

# Van der Waals interactions in lipid bilayer stems

Force equilibria in arrays of lipid bilayers.



Undulation:

$$F \approx \frac{(kT)^2}{2k_b D^3}$$

Peristaltic:

$$F \approx \frac{(kT)^2}{5k_a D^3}$$

Protrusion:

$$F \approx \frac{2.7\Gamma kT e^{-D/\lambda}}{\lambda}, \quad \text{where } \lambda \approx kT/\alpha_p$$

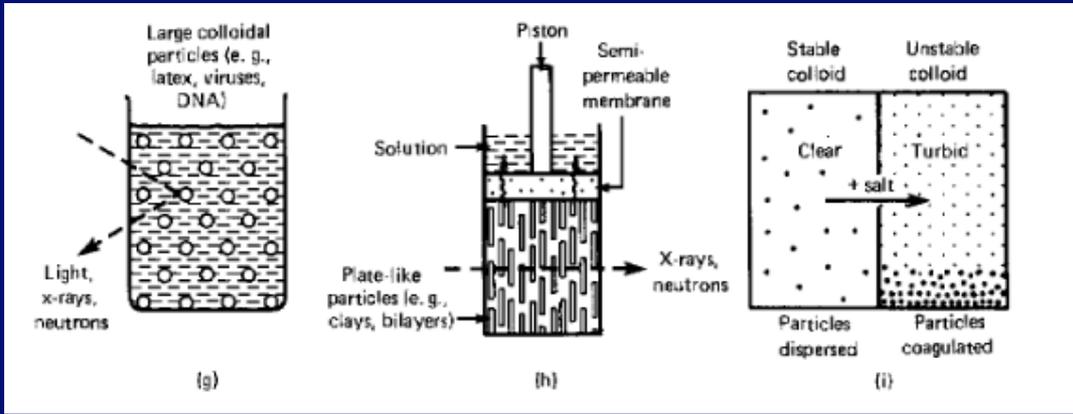
Headgroup overlap:

$$F \approx 100\Gamma^{3/2} kT e^{-D/\lambda}, \quad \text{where } \lambda \approx L/\pi$$

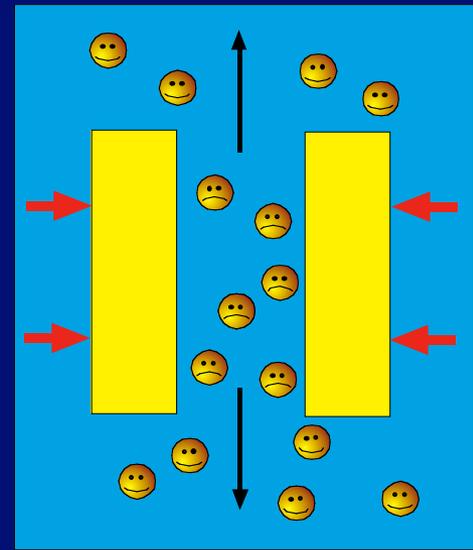
The repulsive component can have various origins.

Hydration repulsion balanced by a vdW force.

Osmotic stress method.



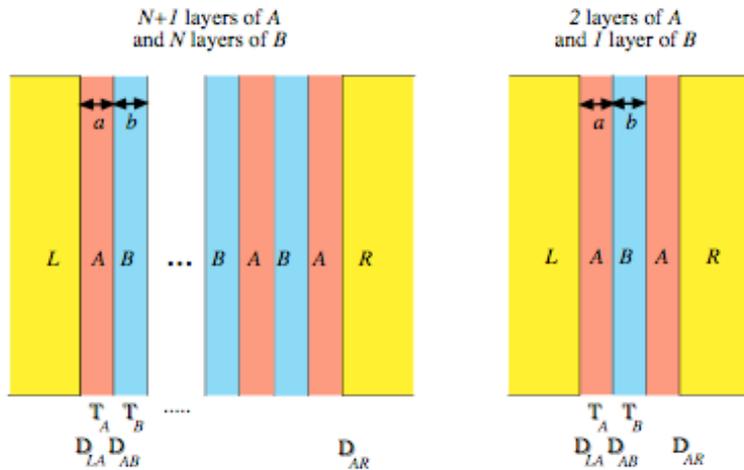
Various methods of measurements (Israelachvili, 2000).



$$\Pi dV$$

$$-\mu dN$$

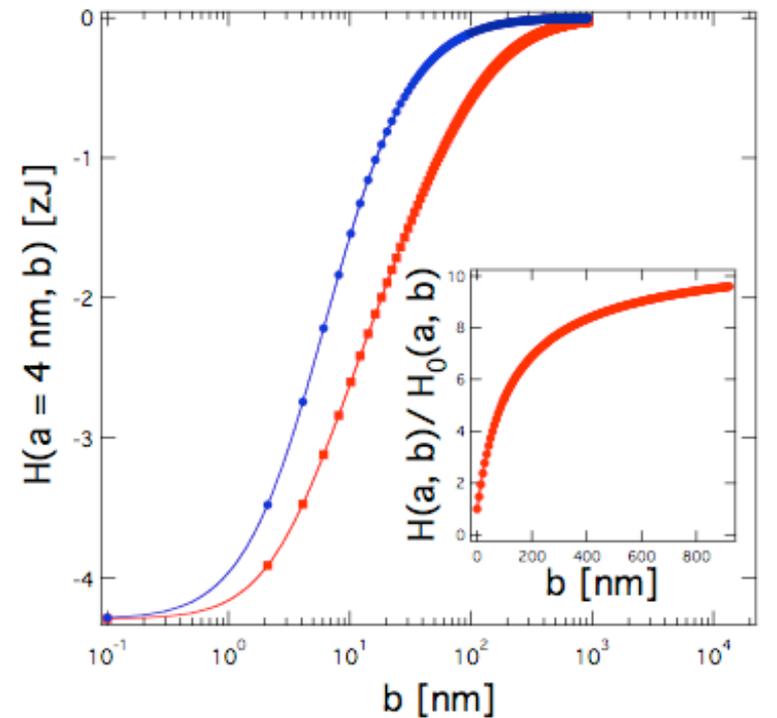
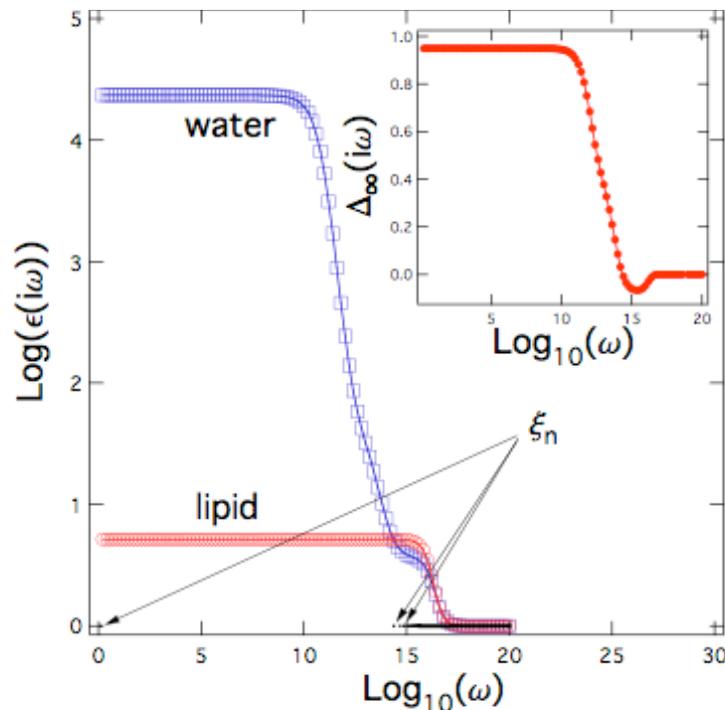
# Strength of Van der Waals interactions



Strong non-pairwise additive effects and also retardation effects (?).

The effective Hamaker coefficient is 4.3 zJ.

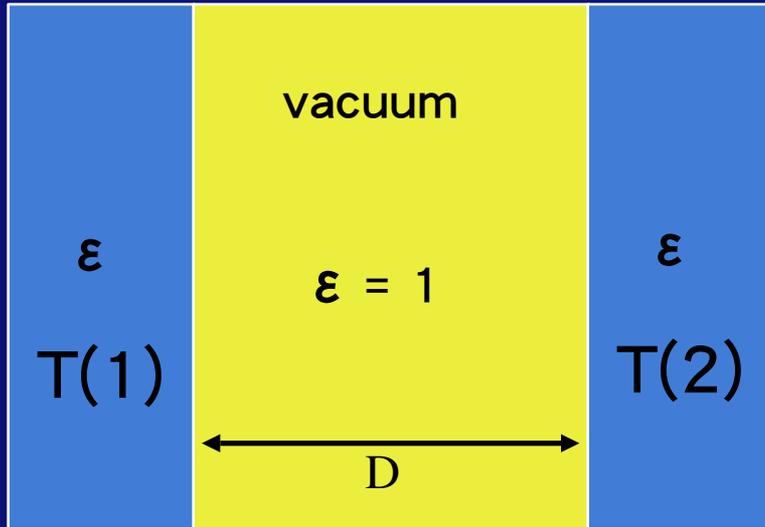
The best value currently available in the literature. R.Podgornik, R.H. French and V.A. Parsegian., J. Chem. Phys. Vol. 124, 044709 (2006).



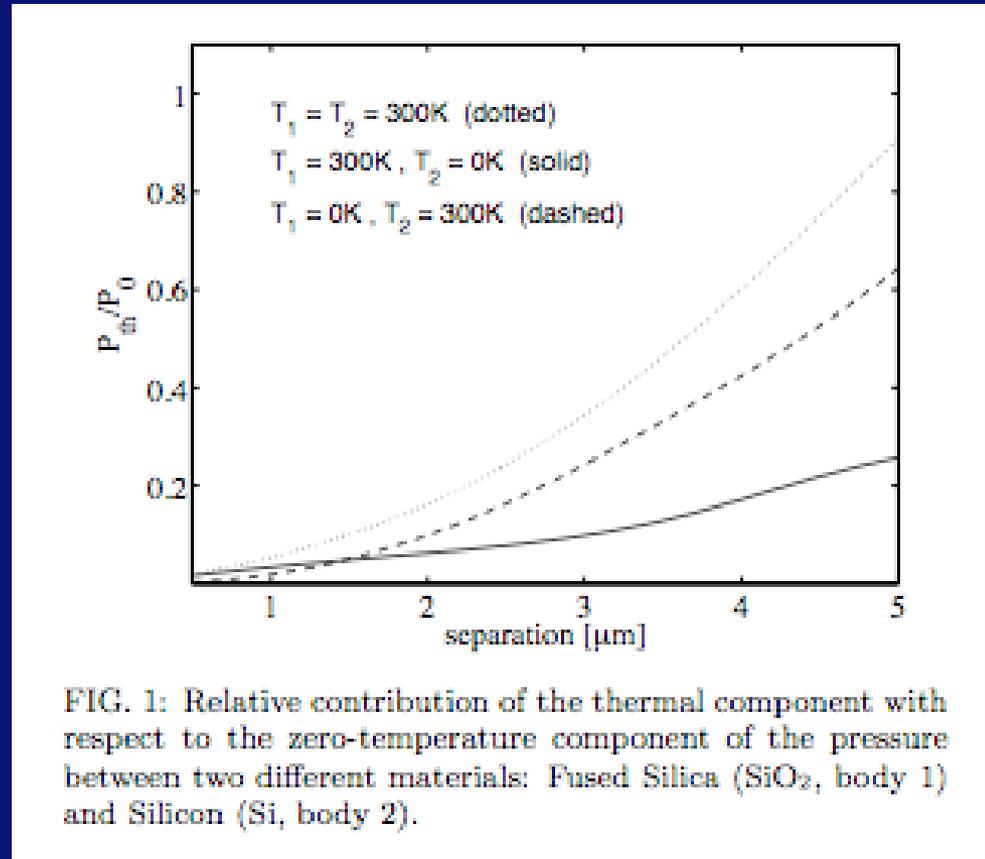
Experiments: Pabst, Podgornik et al. (2007) in print.

# Van der Waals interactions in non-equilibrium systems

Recent work of Pitaevskii and the Trento group (2006).



The two semi-infinite slabs are not at the same temperature and thus the system is not at a thermodynamic equilibrium.

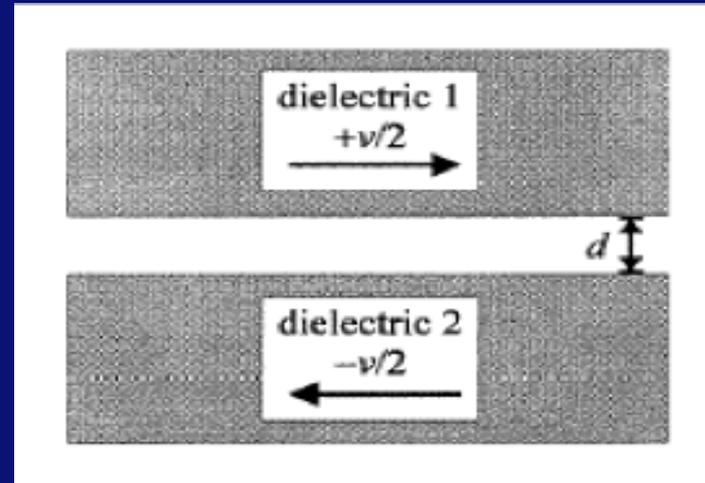
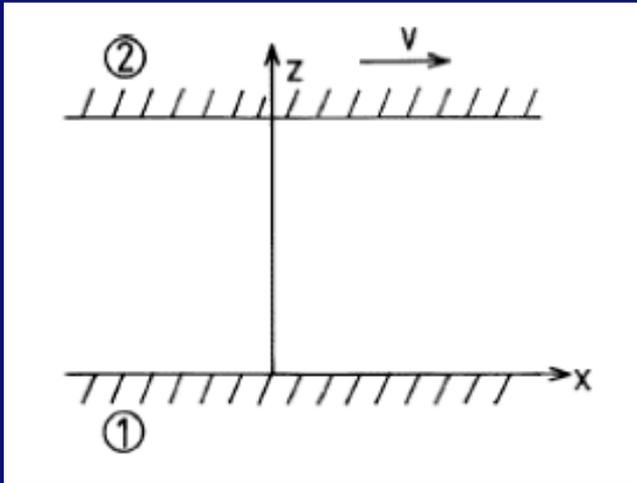


In this case there is a big difference between the propagating modes and the evanescent modes that cancel in the equilibrium case since they have different signs.

The non-equilibrium case leads usually to smaller interactions, except if one of the components is a rarefied gas...

# The dissipative Lifshitz interactions

The dissipative component of the Casimir effect in general.  
Velocity dependent Casimir effect.



Not to forget:  $\epsilon(\omega)$  is defined in a rest-frame!

$$\mathbf{E}'_{\parallel} = \mathbf{E}_{\parallel}$$

$$\mathbf{E}'_{\perp} = \gamma (\mathbf{E}_{\perp} + (\mathbf{v} \times \mathbf{B}))$$

Lorentz boost  
for boundary conditions

$$\mathbf{B}'_{\parallel} = \mathbf{B}_{\parallel}$$

$$\mathbf{B}'_{\perp} = \gamma \left( \mathbf{B}_{\perp} - \frac{1}{c^2} (\mathbf{v} \times \mathbf{E}) \right)$$

Again consider the (averaged) Maxwell stress tensor

$$T_{ij} = \frac{1}{2} \left\{ +\epsilon_0 E_i E_j^* + \epsilon_0 E_i^* E_j - \epsilon_0 \delta_{ij} \mathbf{E} \cdot \mathbf{E}^* + \mu_0 H_i H_j^* + \mu_0 H_i^* H_j - \mu_0 \mathbf{H} \cdot \mathbf{H}^* \right\}.$$

# Transverse and longitudinal Lifshitz interactions

Transverse and longitudinal component of the force:  
Intervening vacuum. Pendry, 1997.

$$F_x = \frac{\hbar}{\pi} \sum_{k_x k_y} \int_{-\infty}^{+\infty} \exp(-2kd) k_x \Im \left[ \frac{\varepsilon(k_x v - \omega) - 1}{\varepsilon(k_x v - \omega) + 1} \right] \Im \left[ \frac{\varepsilon(\omega) - 1}{\varepsilon(\omega) + 1} \right] d\omega.$$

In the limit of frequency independent dielectric function:

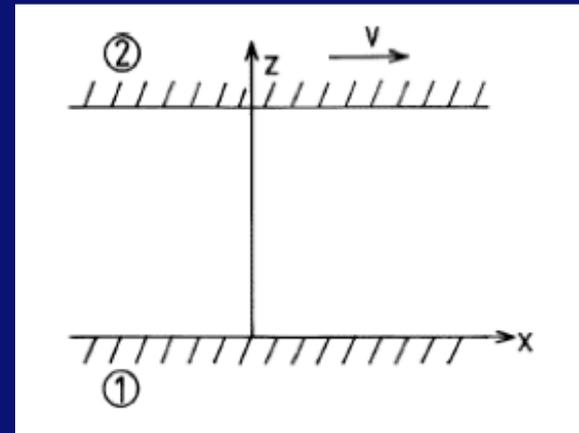
$$F = \left[ \Im \frac{\varepsilon - 1}{\varepsilon + 1} \right]^2 \frac{3\hbar v}{2^6 \pi^2 d^4}.$$

Compare this with Stokes formula and one has viscosity.

The “viscosity” of vacuum is in general small. Mkrтчian, 1995.

$$\eta = \frac{a}{c} \left( \bar{T}_{xz} \right) \Big|_{z = -a/2}.$$

“Viscosity” of vacuum.



$$\frac{f_{\max}}{f_{\text{Casimir}}} \sim \frac{v}{c}.$$

Large planar bodies.

“Viscosity” depends on the separation between the bodies.  
Of course it is a missnomer. Vacuum has no viscosity!

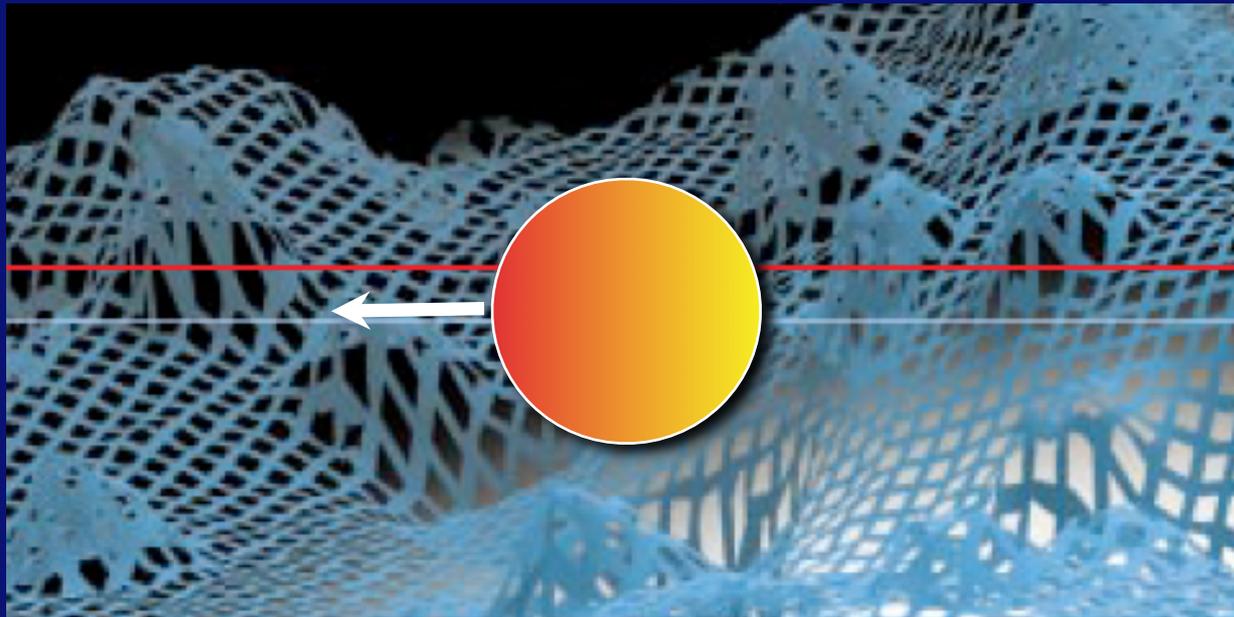
# The “viscosity” of vacuum

Increase the separation between the bodies.  
What happens to “viscosity” quantified as the relaxation time.  
(remember it is a missnomer)

$$\langle \vec{F} \rangle = V \vec{v} \left( \frac{\beta \hbar^2}{3 \pi c^5} \right) \int_0^\infty d\omega \frac{\omega^5 \chi_e''(\omega)}{\sinh^2(\frac{1}{2} \beta \hbar \omega)}.$$

$$\frac{1}{\tau} = \left( \frac{\beta \hbar^2}{3 \pi \rho_M c^5} \right) \int_0^\infty d\omega \frac{\omega^5 \chi_e''(\omega)}{\sinh^2(\frac{1}{2} \beta \hbar \omega)}.$$

It reaches a finite limit! Mkrтчian et al. 2003.



$$\varepsilon(\omega) = 1 + \chi(\omega)$$

The object moves with respect to the coordinate frame in which the Planck spectrum is stationary.

For a non-dissipative particle, there is no viscosity of the vacuum!

The effect persists only at finite temperatures.

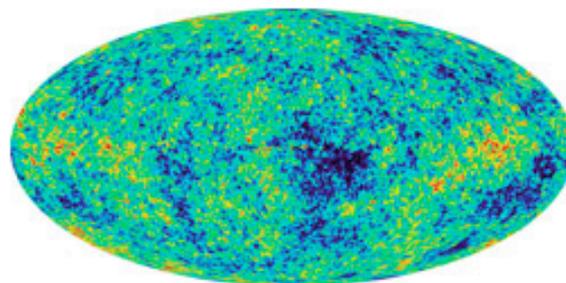
[Phys. Rev. Lett. 91, 220801](#)  
(issue of 28 November 2003)  
[Title and Authors](#)

5 December 2003

## Photons Are a Drag

There's no escape from friction. Objects moving through a vacuum or even interstellar space feel a universal drag from the photons that are everywhere, according to the 28 November *PRL*. Although the drag is tiny, the researchers believe it may alter cosmologists' estimates of the time it took for atoms to coalesce after the big bang. But some cosmologists say the effect, although real, is not relevant to cosmology.

Bring two pieces of metal close enough together, and they will almost always attract or repel one another, even in a vacuum, thanks to the Casimir effect. This minute force comes from virtual photons--particles of light--that continually flit in and out of existence. The effect leads to friction as one chunk of metal moves past another. Rudi Podgornik, of the University of Ljubljana, Slovenia, and his colleagues imagined taking away the second chunk, and wondered what the remaining piece of metal would experience simply moving through space.



NASA/WMAP Science Team

**Glowing cosmos.** Any object in motion should feel a tiny slowing force from the sea of light emitted by its surroundings. The glow from the big bang (full-sky image above) might have slowed hot debris and affected the early evolution of the Universe. (Click picture for larger image.)



## 2.

the electrostatic correlation interactions which  
are due to electrostatically strongly coupled  
mobile counterions between charged  
macromolecules and their role in DNA collapse  
in multivalent salts

# 1948 - annus mirabilis for colloid science

## THEORY OF THE STABILITY OF LYOPHOBIC COLLOIDS

THE INTERACTION OF SOL PARTICLES HAVING AN ELECTRIC DOUBLE LAYER

BY

E. J. W. VERWEY AND J. TH. G. OVERBEEK

*Natuurkundig Laboratorium N.V. Philips' Gloeilampenfabrieken, Eindhoven (Netherlands)*

With the collaboration of  
K. VAN NES

Gouy (1910)

Chapman (1913)

Debye & Huckel (1913)

Verwey & Overbeek  
(1948)

Deryaguin & Landau  
(1941)  
"disjoining pressure"

Hence we now have an expression for the charge density which may be inserted into eq. (1), when we obtain the *fundamental differential equation*:

$$\Delta\psi = \frac{8\pi nve}{\epsilon} \sinh(v\psi/kT) \quad (3)$$

For small values of  $\psi$  this equation simplifies to

$$\Delta\psi = \frac{8\pi ne^2 v^2 \psi}{\epsilon kT} = x^2 \psi \quad (4)$$

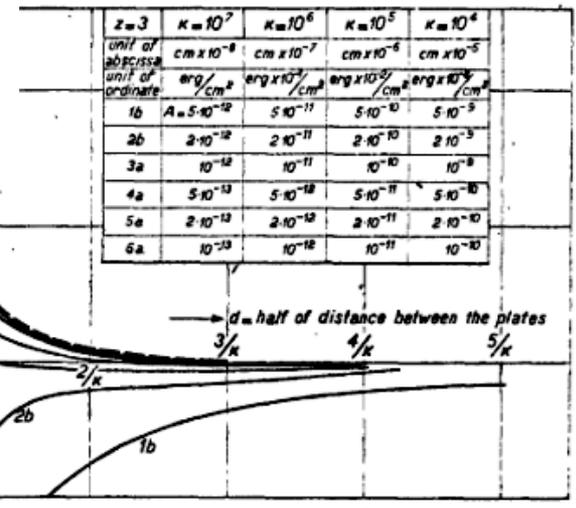
with:  $x^2 = \frac{8\pi ne^2 v^2}{\epsilon kT}$

Equation (4) is the well known starting point in the theory of Debye and Hückel for strong electrolytes (calculation of the electric potential in the ionic atmosphere around an ion).

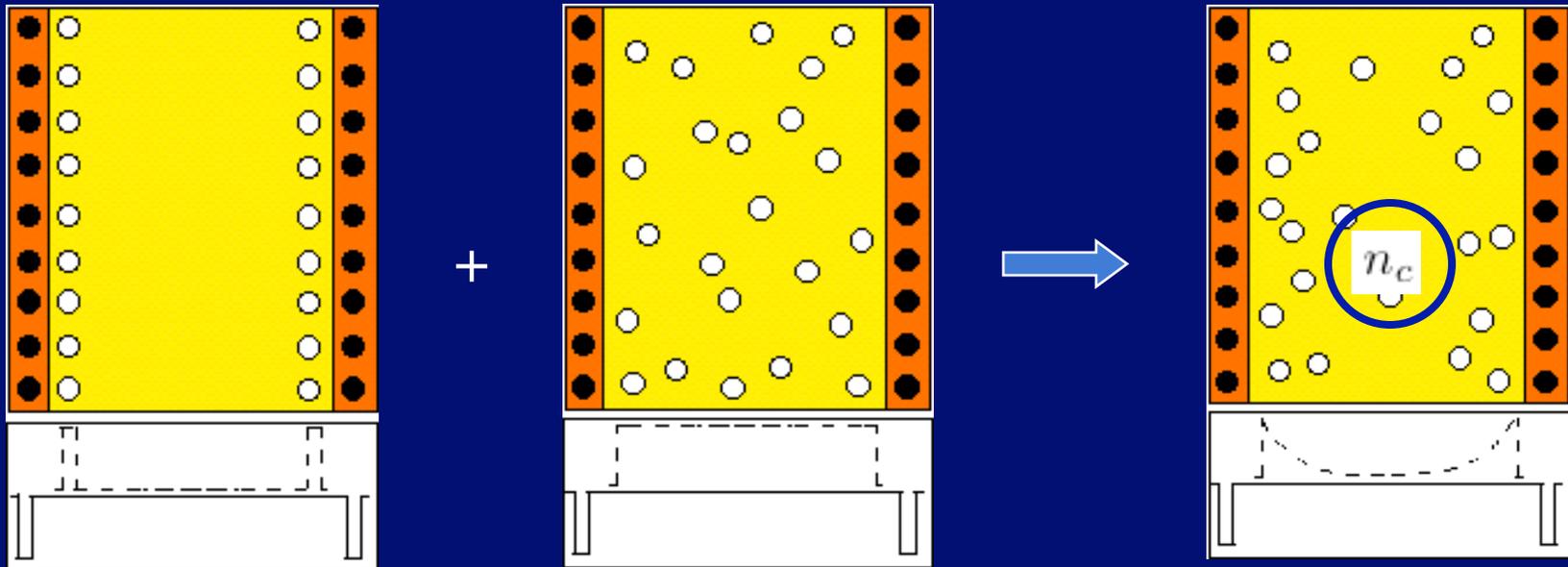
DLVO theory of colloid stability:

$$V_R + V_A$$

Electrostatics plus van der Waals.



# The Poisson - Boltzmann equation - 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)

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

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

plus electroneutrality

$$\int_V \rho d^3\mathbf{r} = \int_{\partial V} \sigma d^2\mathbf{r},$$

$$\epsilon\epsilon_0 E_n = \sigma.$$

# 1984 - annus horribilis for colloid science

Developments in the 80's colloid science:

- Oosawa derives attractive interactions between DNAs (late 60's early '70)
- Simulation of DLVO interactions (early 80's - electric bilayer simulation Torrie and Valleau)
- 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 stems from a correlation term in the stress tensor.

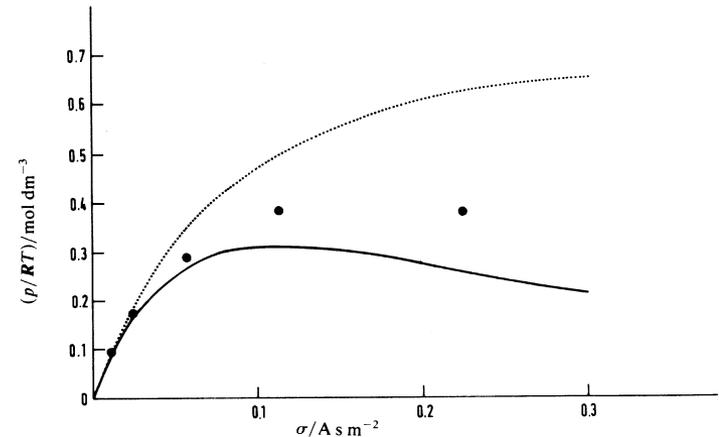


Fig. 4. The pressure in the counterion-only system at the intersurface separation  $2a = 2.1$  nm as a function of the surface charge density. The counterions are monovalent. The PB approximation ( $\cdots$ ) and the simulation results<sup>4</sup> ( $\bullet$ ) are also presented for comparison.

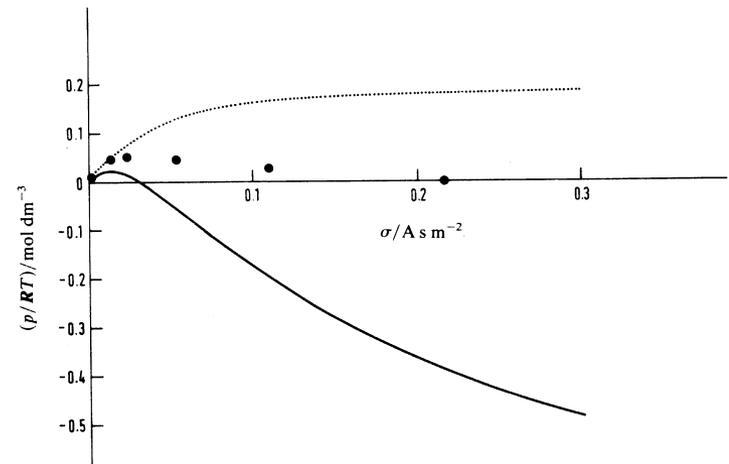


Fig. 5. As fig. 4 except that here the counterions are divalent.

Probably the biggest advance in colloid science since DLVO.

# A historical guide to the correlation effect

Oosawa (1971)  
(counterion fluctuations)

Gulbrand, Jonsson, Wennerstrom and Linse  
(1984)

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

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

Rouzina and Bloomfield (1996)  
(checkerboard model)

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

Kjellander and Marcelja  
(1984-1986)  
(inhomogeneous integral  
equations closure)

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

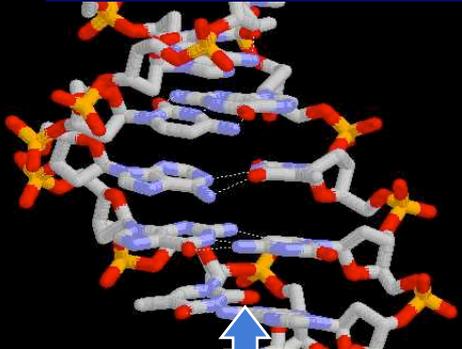
Netz and Moreira (2000-2001)  
Naji and Netz (2003-2004)  
(General analysis of Coulomb fluids)

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

# DNA

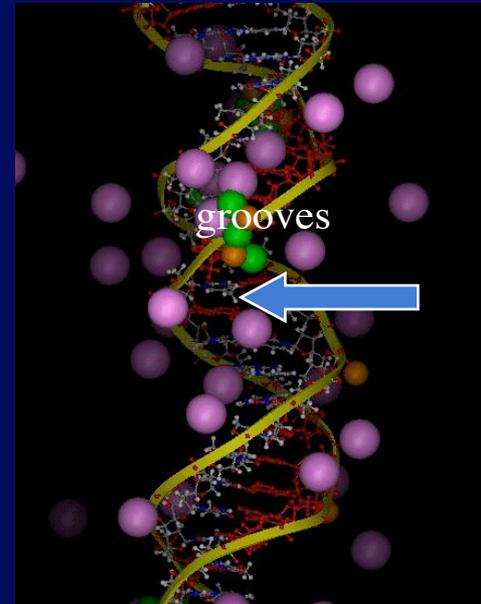
Structure  
(B-form double-helix)

← helix

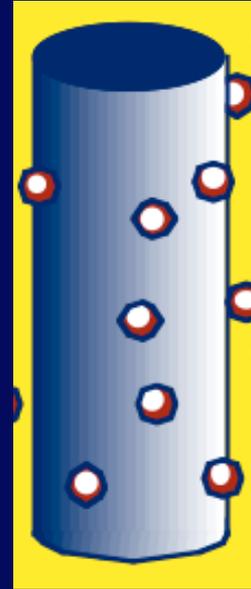


↑ discrete charges

Charge:  
 $2 e_0 / 3.4 \text{ \AA}$   
 $\sim e_0 / \text{nm}^2$



← grooves



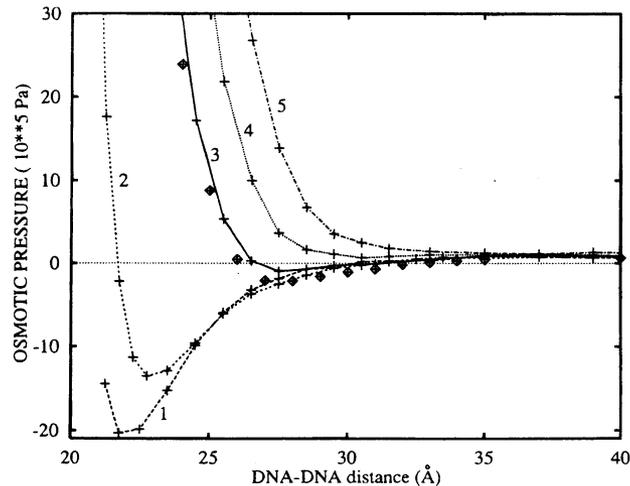
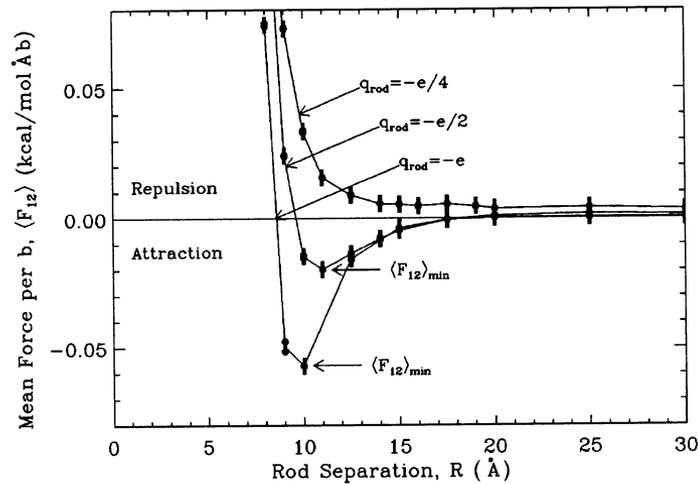
Polipeptides:  $0.6 e_0 / \text{nm}$

Membranes:  $0.1 - 1 e_0 / \text{nm}^2$

- $a \sim 1 \text{ nm}$
- $h \sim 0.17 \text{ nm}$
- DNA pitch  $p \sim 3.4 \text{ nm}$
- DNA length  $L \sim 50 \text{ nm}$  to  $\sim \mu\text{m}$
- DNA persistence length  $L_p \sim 50 \text{ nm}$

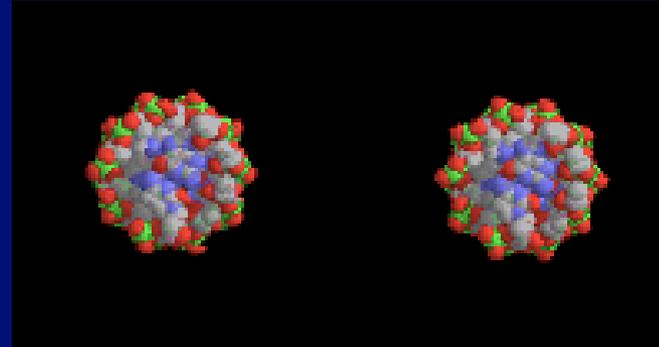
- it is a RH double helix
- it has lots of discrete structural (phosphate) charges ( $\text{pH} > 1$ )
- it has lots of room to accommodate small counterions

# Getting worse and worse...



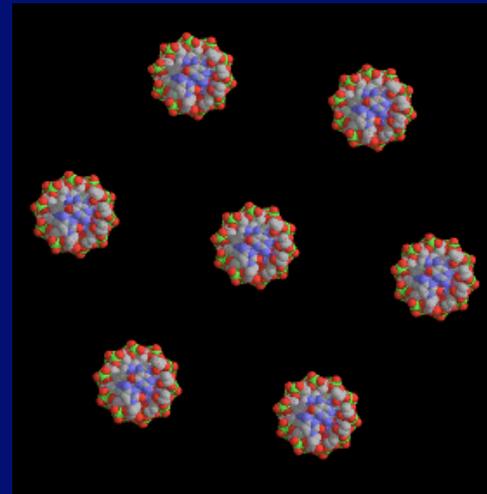
**Figure 7.** Osmotic pressure in the ordered DNA system with +2 counterions. Lines: one DNA in the cell and ion diameter  $\sigma = 0$  (1),  $\sigma = 1 \text{ \AA}$  (2),  $\sigma = 4 \text{ \AA}$  (3),  $\sigma = 5 \text{ \AA}$  (4),  $\sigma = 6 \text{ \AA}$  (5). Points: seven DNA's in the cell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

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



Screening. Debye length  $\sim 3.05 \text{ \AA} / \sqrt{M}$

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



Attractions seem to be everywhere!

# 2000 - annus reconciliationis for colloid science

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

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

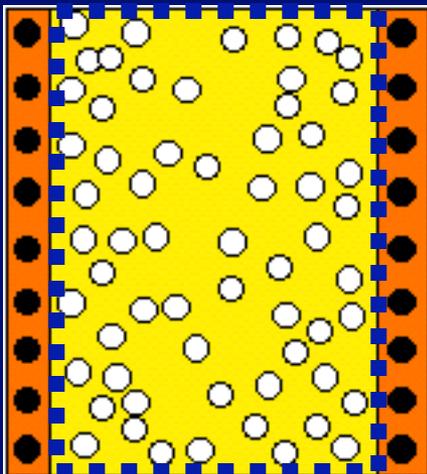
Ratio between the Bjerrum and the Gouy - Chapman lengths. Bulk versus surface interactions.

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

Coupling parameter

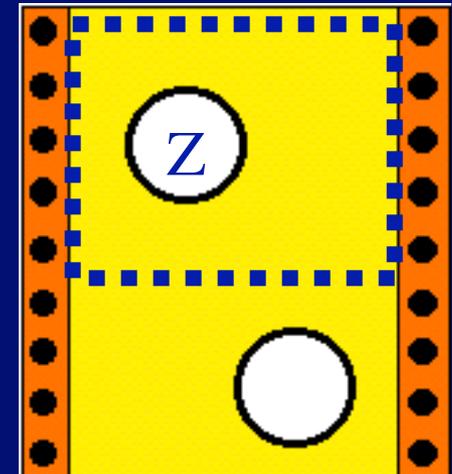
$$\Xi = 2\pi Z^3 \ell_B^2 \sigma$$

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)



How was that accomplished?

# Statmech of Coulomb fluids

JOURNAL OF MATHEMATICAL PHYSICS VOLUME 3, NUMBER 4 JULY-AUGUST 1962

## Exact Statistical Mechanics of a One-Dimensional System with Coulomb Forces. II. The Method of Functional Integration

S. F. EDWARDS

*Department of Theoretical Physics, Manchester University, Manchester, England*

AND

A. LENARD\*

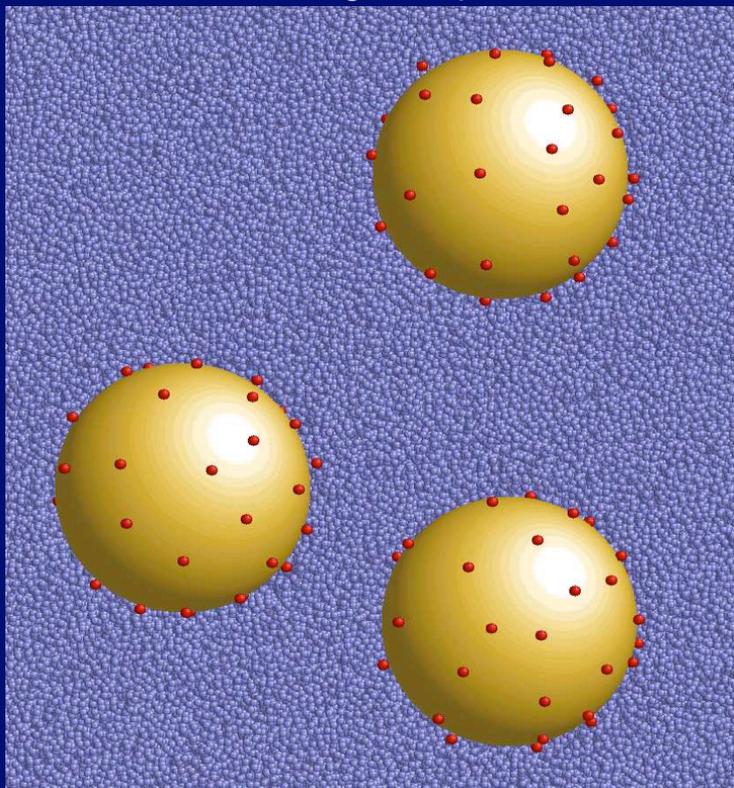
*Plasma Physics Laboratory, Princeton University, Princeton, New Jersey*

(Received January 11, 1962)

$$\mathcal{H} = \sum_{j=1}^{N-1} \sum_{k=j+1}^N \frac{q^2 \ell_B}{|\mathbf{r}_j - \mathbf{r}_k|} + 2\pi q \ell_B \sigma_s \sum_{j=1}^N z_j,$$

Coulomb fluid = an ensemble of interacting Coulomb charges.

Functional integral representation of the Coulomb fluid grand canonical partition function.



Barbosa (2005).

$$\mathcal{Z}_\lambda = \sum_{N=0}^{\infty} \lambda_0^N \mathcal{Z}_N,$$

Grand canonical partition function can be written as

$$\mathcal{Z}_\lambda = \int \frac{\mathcal{D}\phi}{\mathcal{Z}_v} \exp \{-H[\phi]\}$$

$$H[\phi] = \int d\mathbf{r} \left[ \frac{1}{8\pi \ell_B q^2} (\nabla \phi(\mathbf{r}))^2 - \frac{z}{q} \phi(\mathbf{r}) \sigma(\mathbf{r}) - \lambda \Omega(\mathbf{r}) e^{h(\mathbf{r}) - i\phi(\mathbf{r})} \right].$$

Exactly solvable for 1D Coulomb gas.  
"Schroedinger equation".

# PB equation and saddle point

Faraday Trans. 2, 1988, 84(6), 611-631

## Inhomogeneous Coulomb Fluid A Functional Integral Approach

Rudi Podgornik\*

Jefan Institute, Jamova 39, p.p. 100, 61111 Ljubljana,

Boštjan Žekš

Department of Biophysics, Lipičeva 2, Medical Faculty, University of Ljubljana

(Podgornik & Zeks, 1988)

$$S = -\frac{1}{2}\beta\epsilon\epsilon_0 \int [\nabla\varphi(\mathbf{r})]^2 d^3\mathbf{r} + \int \rho[\varphi(\mathbf{r})] d^3\mathbf{r} - \beta \oint f[\varphi(s)] d^2s.$$

Functional integral “action”.

Functional integral representation of the grand canonical partition function paves the way to a derivation of the PB equation **plus the fluctuational corrections** to it!

$$\left[ \frac{\delta S}{\delta\varphi(\mathbf{r})} \right]_0 = 0.$$

= the Poisson - Boltzmann equation

Saddle point = mean-field (MF)

$$\epsilon\epsilon_0 \nabla^2 \phi_{\text{MF}}(\mathbf{r}) + \bar{\lambda} Z e_0 \Omega(\mathbf{r}) e^{-\beta Z e_0 \phi_{\text{MF}}(\mathbf{r})} = -\rho_0(\mathbf{r}).$$

$$S = S_0 + \frac{1}{2} \iiint \left[ \frac{\delta^2 S}{\delta\varphi(\mathbf{r})\delta\varphi(\mathbf{r}')} \right]_0 \times \delta\varphi(\mathbf{r})\delta\varphi(\mathbf{r}') d^3\mathbf{r} d^3\mathbf{r}',$$

= Poisson - Boltzmann equation plus second order fluctuational (Gaussian) corrections. Hessian of the Coulomb action.

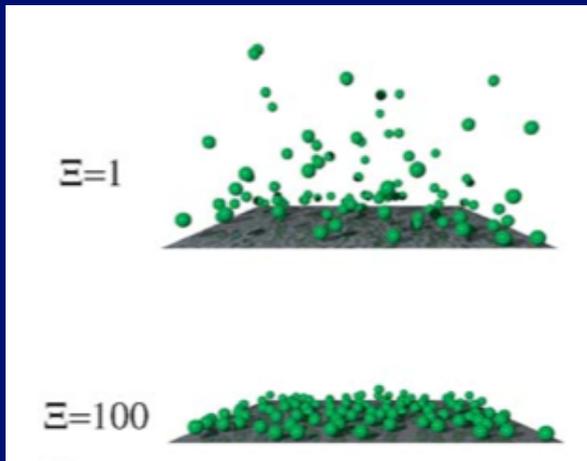
**Second order fluctuational (Gaussian) corrections = zero frequency Lifshitz-van der Waals term!**

# Weak and strong coupling - Netz (2000)

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

Weak coupling = Poisson - Boltzmann (MF) + fluctuations

Weak and strong coupling refer to the value of the Netz coupling constant.

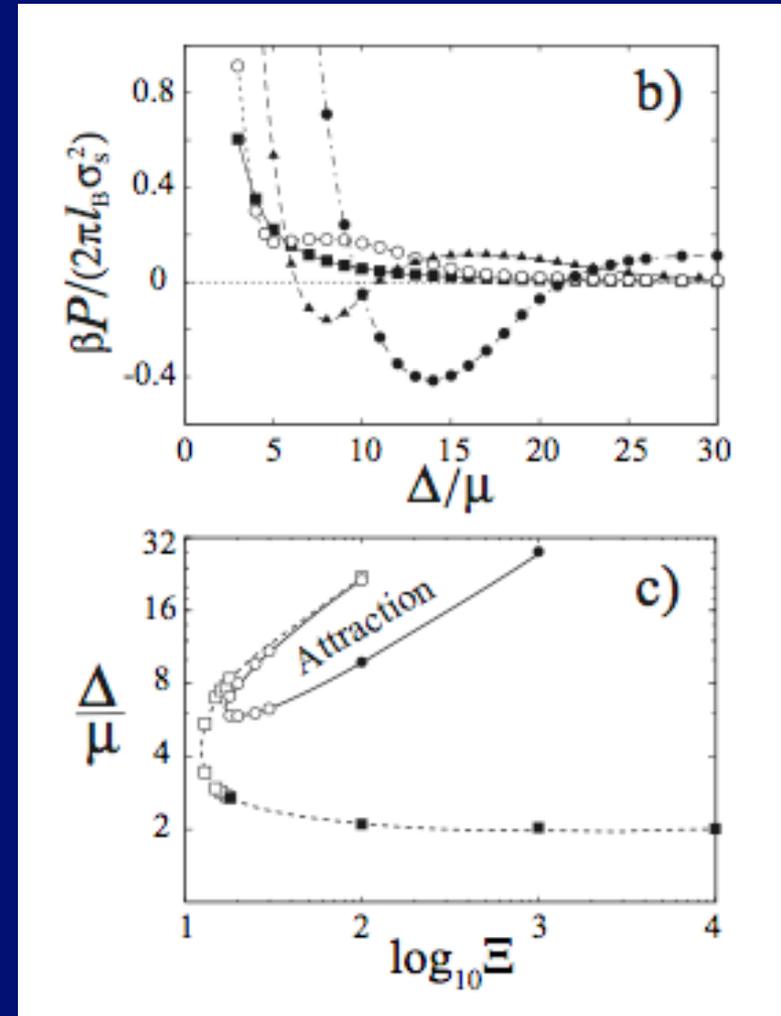


Weak coupling

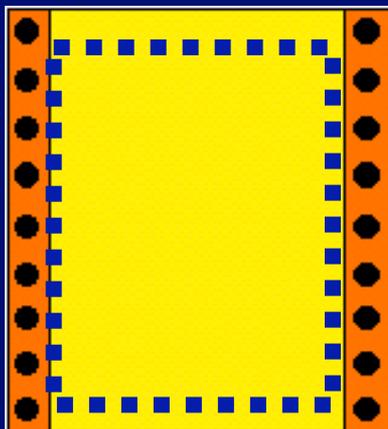
- interactions in the symmetric case strictly **repulsive** and large (Confusion: Bowen & Sharif (1998).
- fluctuation contribution in the symmetric case strictly attractive and small

Strong coupling

- interactions in the symmetric case mostly **attractive** and large
  - repulsive only at small separations
- Wigner crystal heuristic model (Shklovskii 1999)

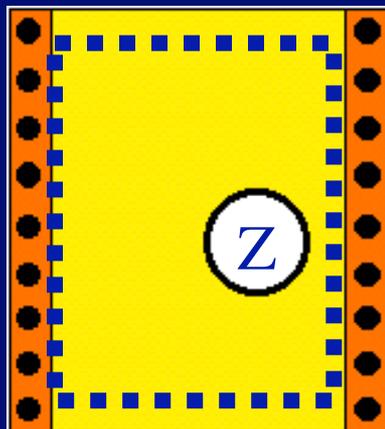


# What is the strong coupling limit?



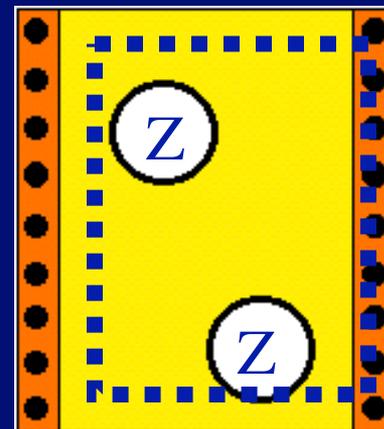
Electrostatic energy without mobile counterions

+



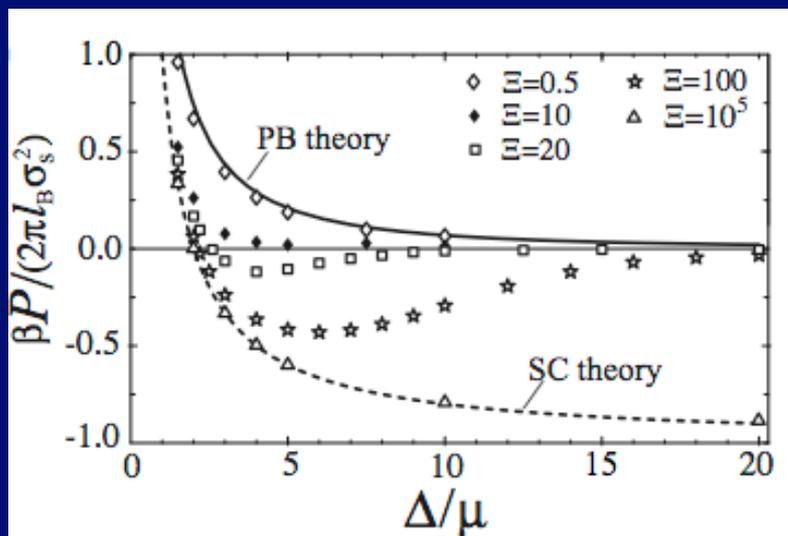
Electrostatic energy of a single counterion

+



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)

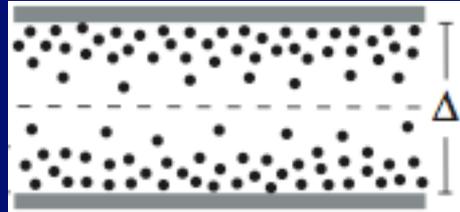
Fixed constant surface charge!

Strong coupling limit = virial expansion to first order.

# Interaction between planar charged surfaces

A.) Weak coupling (= Poisson - Boltzmann + Gaussian fluctuations)

$$P = \rho_{\text{mid}} k_B T$$



$$\nabla^2 \psi(\mathbf{x}) = -\frac{qe\rho_0}{\epsilon\epsilon_0} \exp(-qe\psi/k_B T),$$

$$P(\Delta) = P_{\text{PB}}(\Delta) + \Xi P_{\text{PB}}^{(1)}(\Delta) + \mathcal{O}(\Xi^2),$$

Total pressure (PB+ fluctuations)

$$\frac{\beta P_{\text{PB}}(\Delta)}{2\pi\ell_B\sigma_s^2} = \Lambda$$

$$\Lambda^{1/2} \tan[\Lambda^{1/2}(\Delta/2\mu)] = 1.$$

Poisson - Boltzmann (analytic)

$$\frac{\beta P_{\text{PB}}^{(1)}}{2\pi\ell_B\sigma_s^2} \approx -\left(\frac{\mu}{\Delta}\right)^3 \left[ \frac{\zeta(3)}{4} + \frac{\pi^3}{4} + \pi^2 \ln(\Delta/\pi\mu) \right].$$

Fluctuational (analytic)

B.) Strong coupling

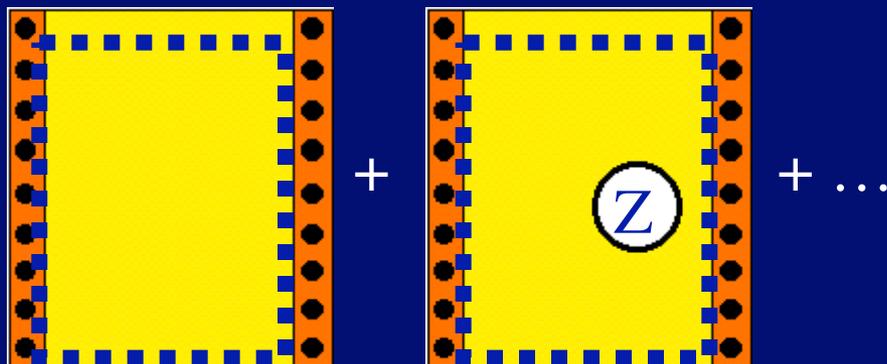


$$\frac{\beta P_{\text{SC}}(\Delta)}{2\pi\ell_B\sigma_s^2} = -1 + \frac{2\mu}{\Delta}.$$

$$\Delta_* = 2\mu.$$

(a lot easier to evaluate)

# Interaction between cylinders



Electrostatic energy  
of a single counterion

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

Electrostatic energy  
without mobile counterions

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

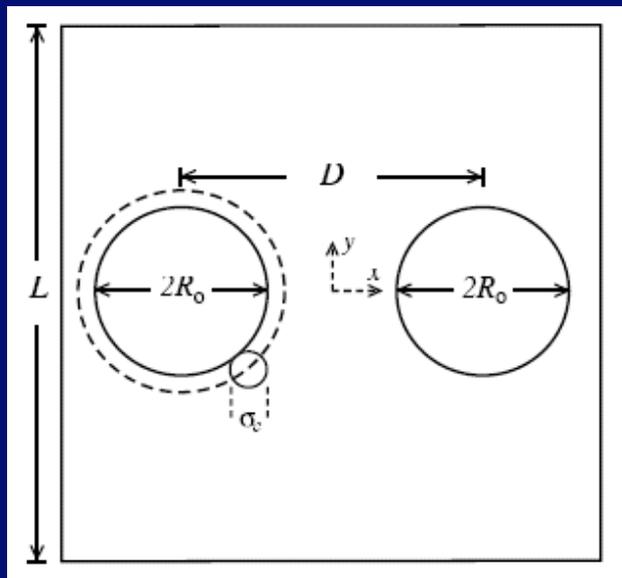
$$Q_c = \frac{2}{3}.$$

Critical Manning parameter.

Asymptotic forms of the free energy:

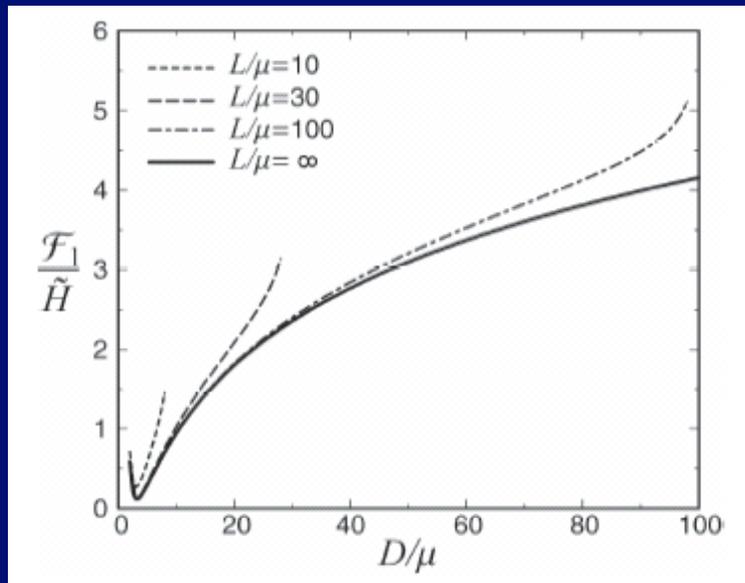
$$\mathcal{F}(Q < 1) \frac{\lambda_{GC}}{h} \sim -6Q(Q_c - Q) \log \frac{D}{\lambda_{GC}}$$

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

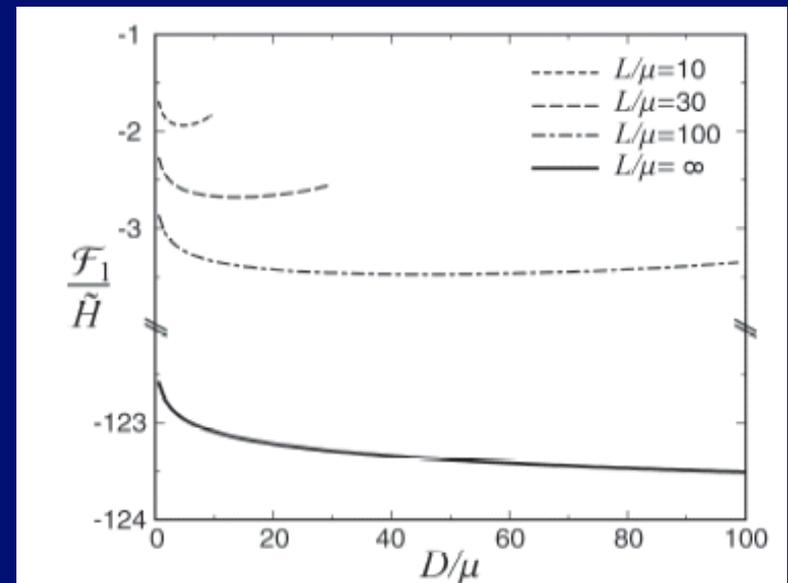


Naji and Netz, 2004.

# Interaction between cylinders (continue)



$Q = 1.$



$Q = 0.3$

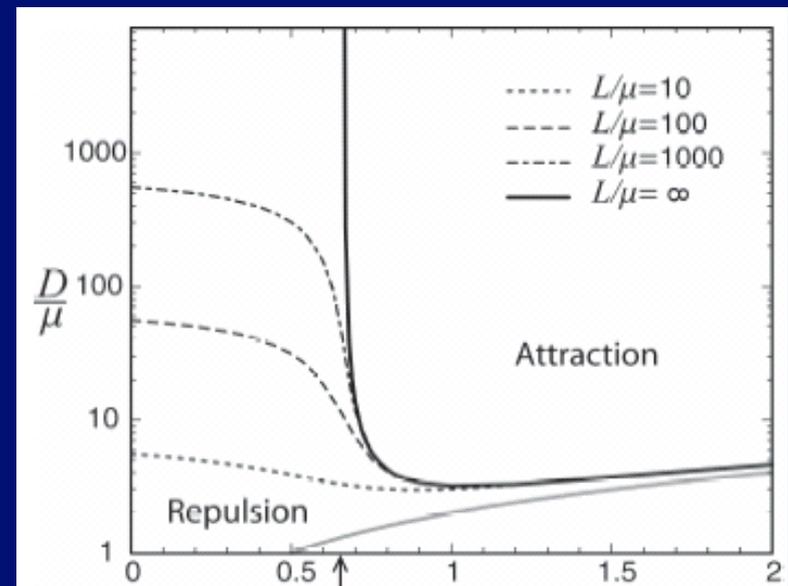
Equilibrium spacing.

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

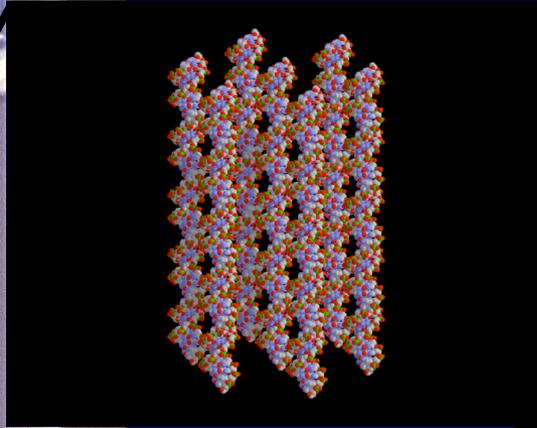
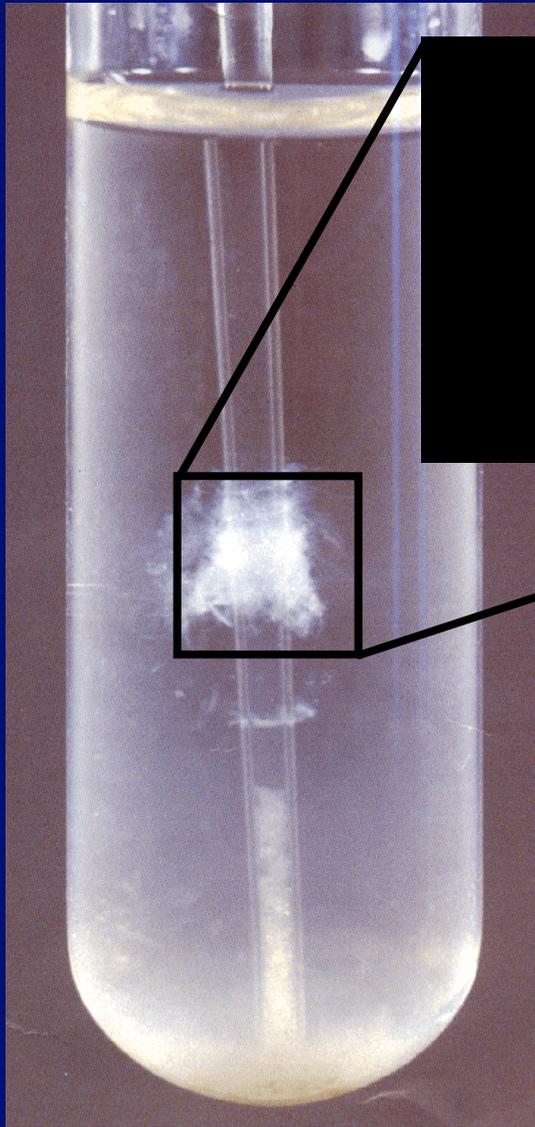
Close to the critical value of  $Q$

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

Naji and Netz, 2004.



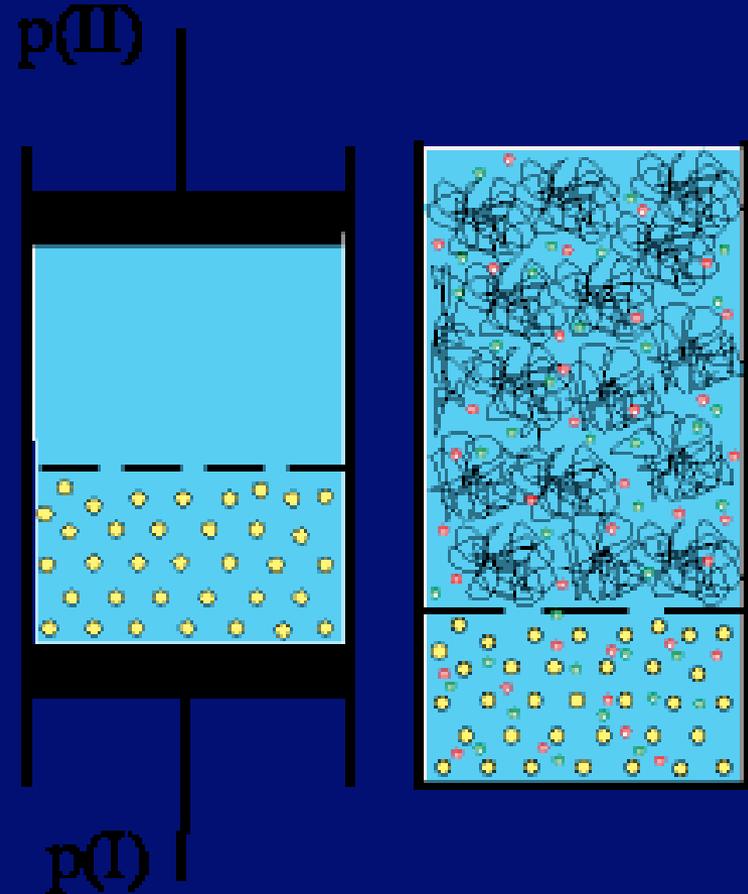
# Interactions can be measured



Setting the osmotic pressure and measuring the density of DNA.

DNA equation of state!

Different ionic conditions, different DNA length, type of ions.....

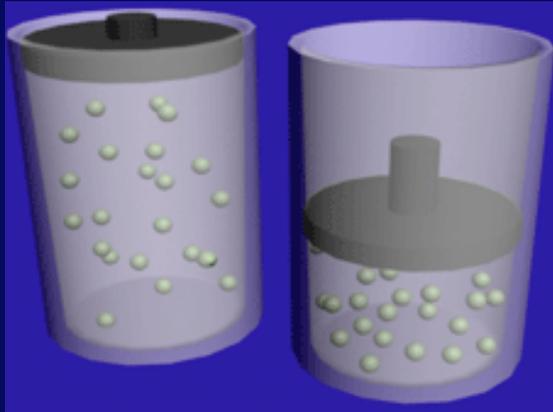


The Boyle experiment

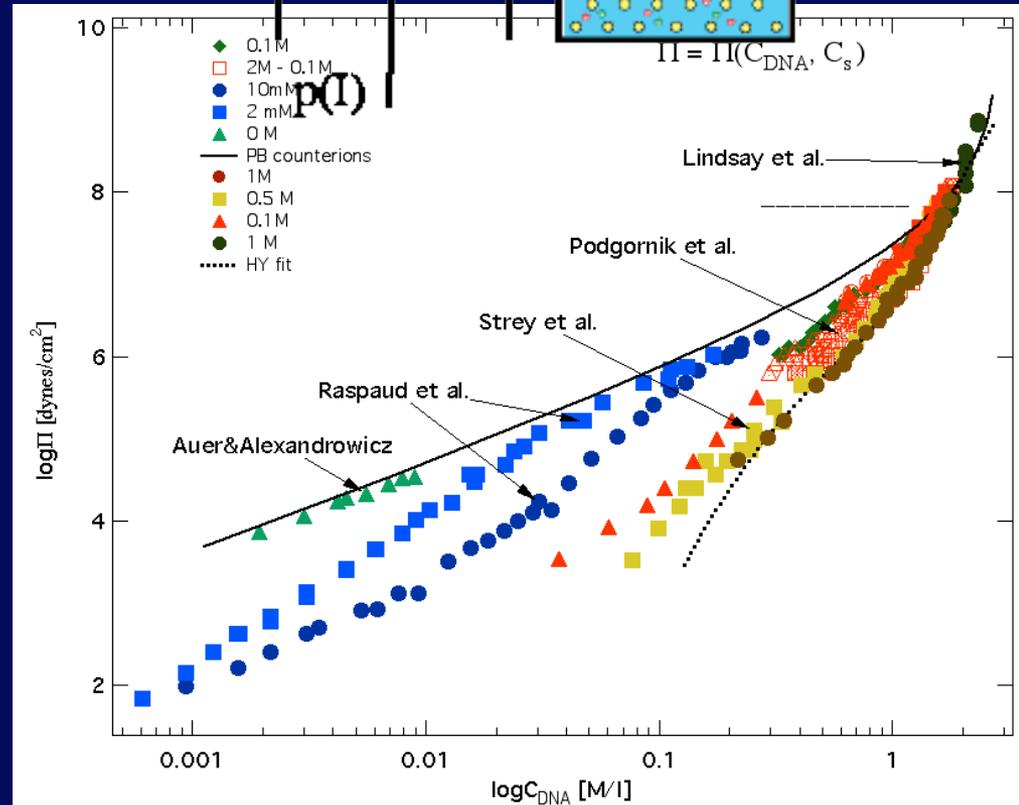
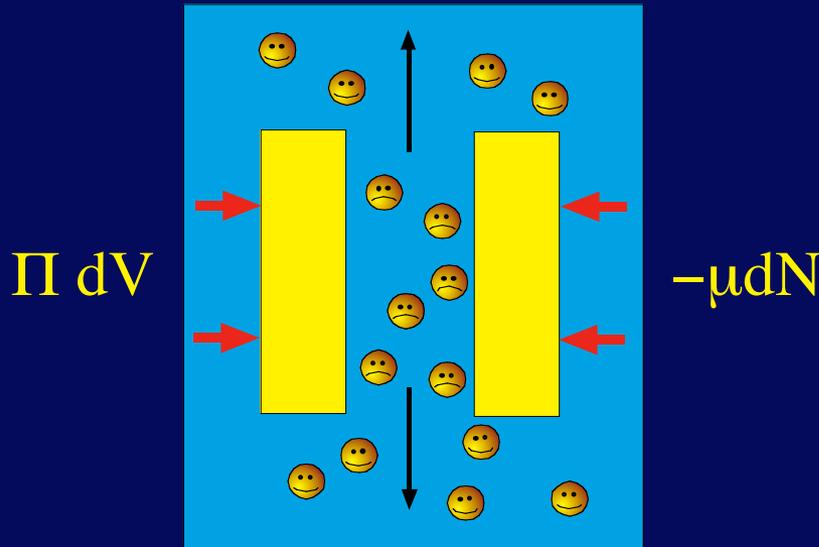
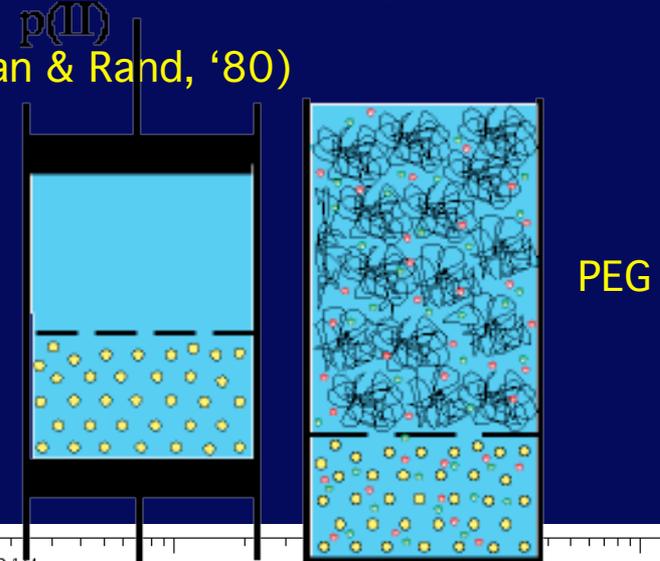
Osmotic stress method (Parsegian & Rand)

# The Boyle experiment - osmotic stress method

Osmotic stress method (Parsegian & Rand, '80)

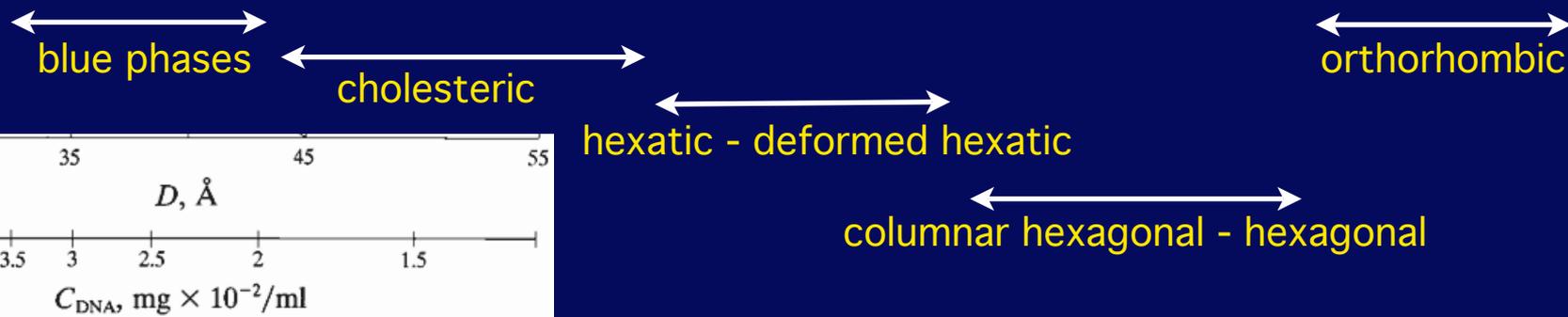
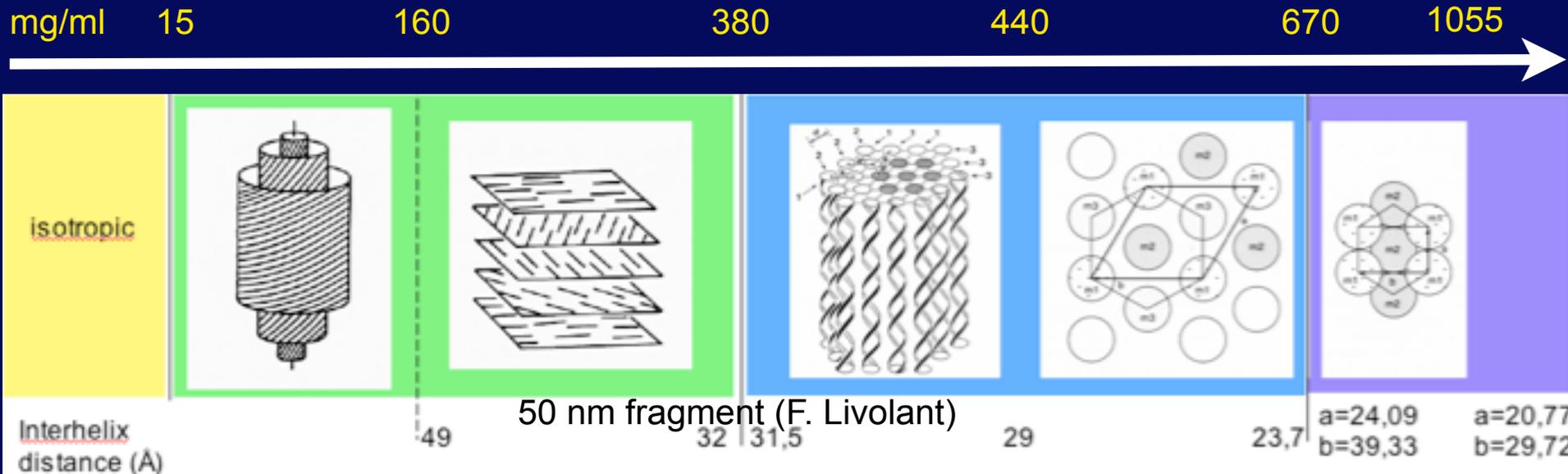


pressure  
 osmotic pressure



# DNA mesophase zoo

Mesophases at different DNA density.

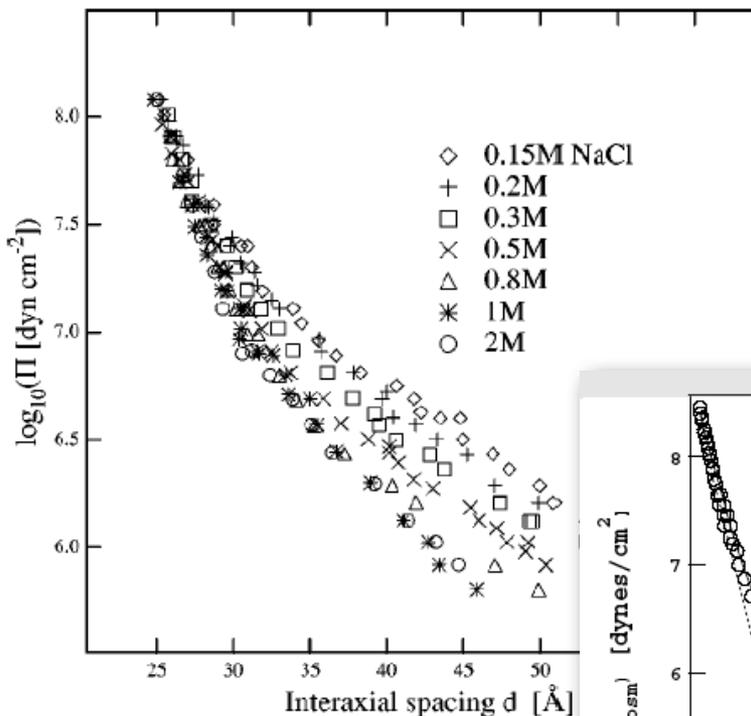


The exact positions of the phase boundaries do depend on the method of preparation (osmotic stress, controlled drying, condensation ) and the length of the DNA.

Durand, Doucet, Livolant (1992) J. Physique 2, 1769.  
 Pelta, Durand, Doucet, Livolant (1996) Biophys. J., 71, 48  
 RP et al. COSB. 8 (1998) 309. COCIS. 3 (1998) 534.

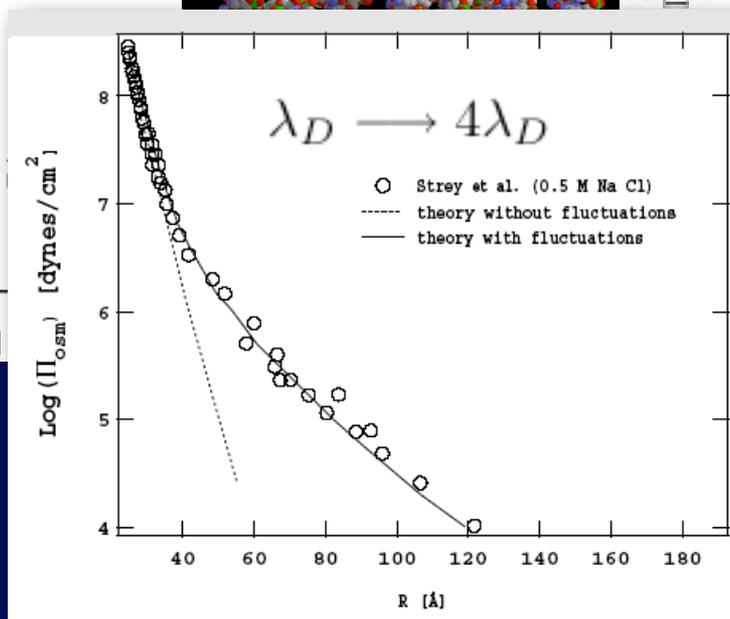
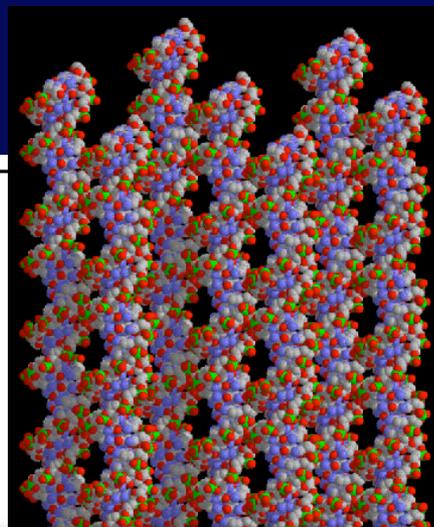
# Experimental evidence for the great electrostatic divide

Electrostatic repulsion:  
not exactly PB but  
a lot stronger.

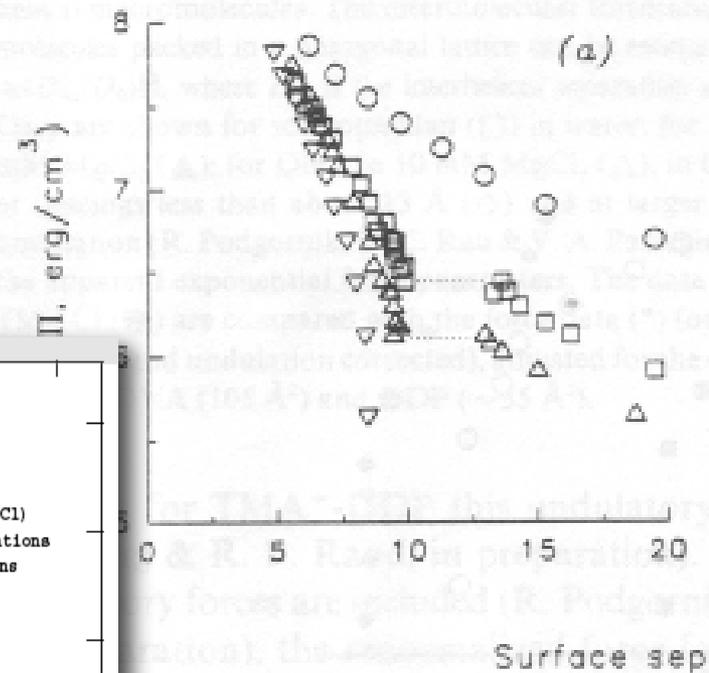


Podgornik et al. 2000

Monovalent counterions



Correlation attractions.  
Hydration attractions.  
~ 0.1 kT/ base pair.



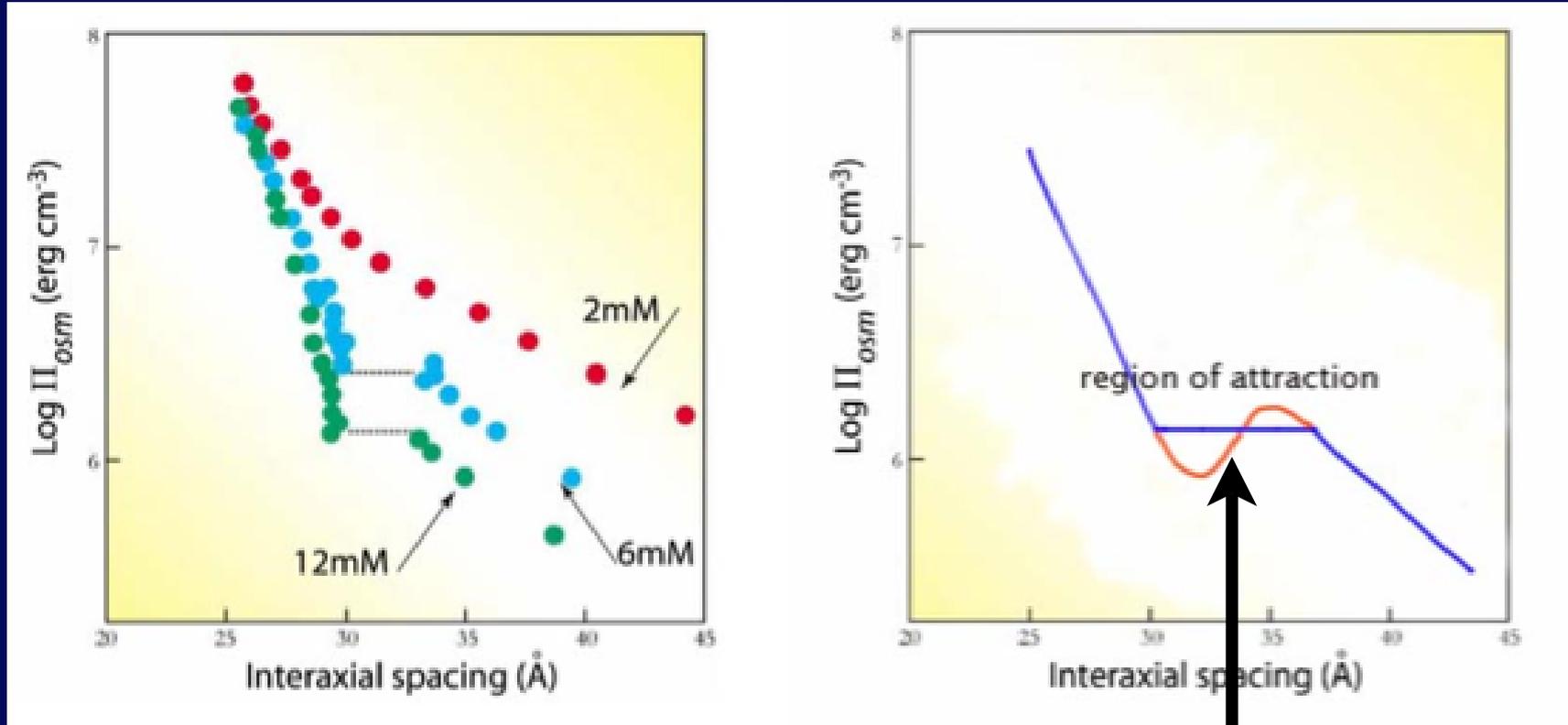
Rau et al., 1997.

Polyvalent counterions

Electrostatics can only be seen indirectly, as modified by the presence of conformational fluctuations. Renormalized value of  $\lambda$ .

# How does one understand this?

Compare with the van der Waals isotherm!



It is not an isotherm it is an iso-ionic strength line.  
van der Waals equation of state, 1873.

isotherm

$$\left(p + \left(\frac{a}{V^2}\right)\right)(V - b) = NkT.$$

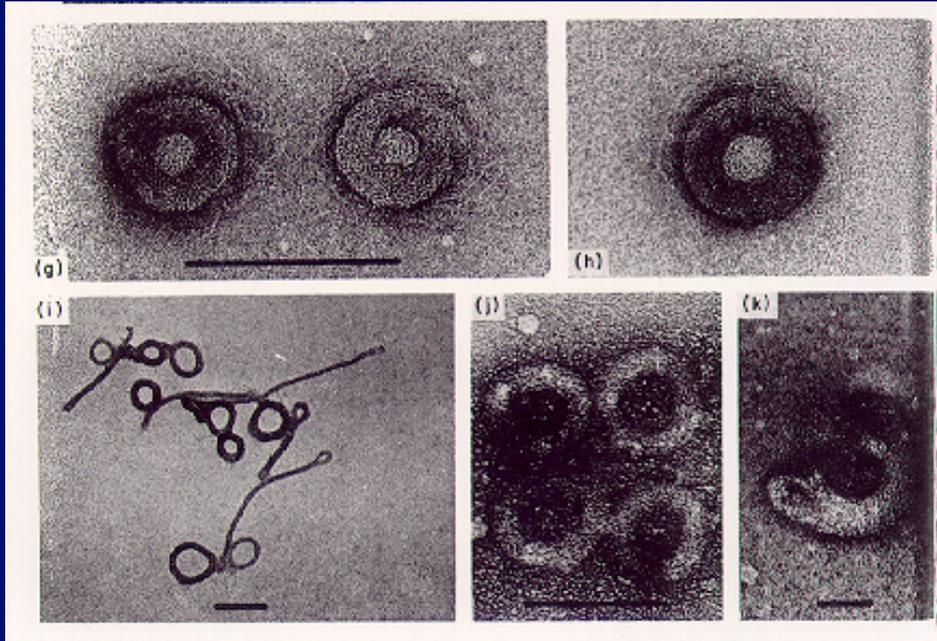
attractions-repulsions

For polyvalent counterions one obtains discontinuous jumps in the force curve - an indication of the underlying SC attractions.

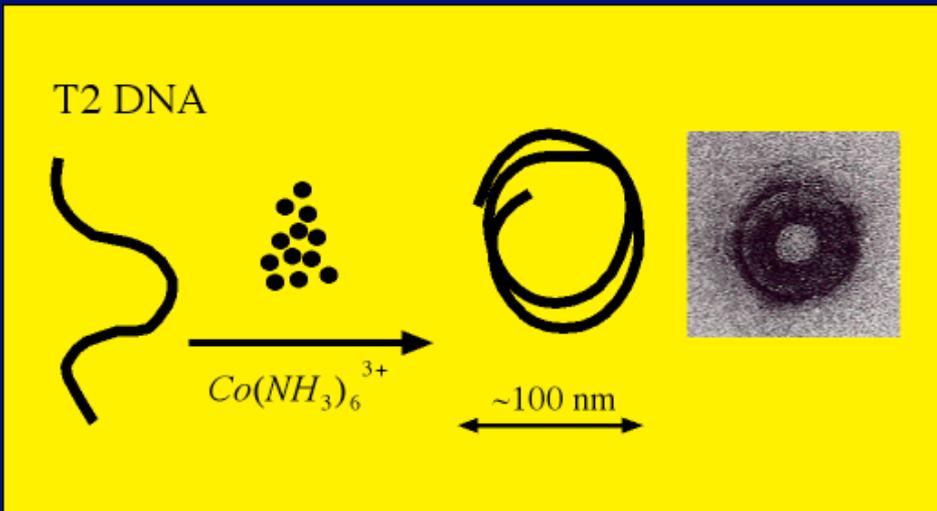
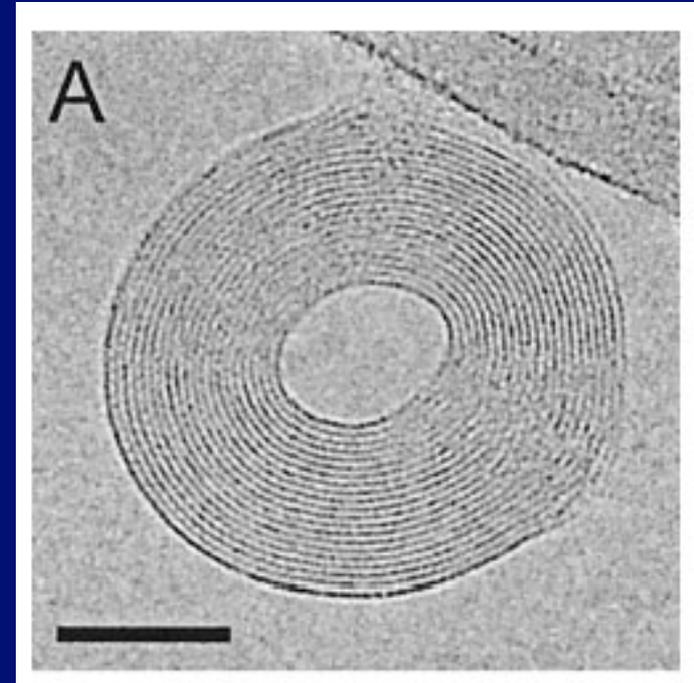
But also a repulsive part dependent on the ionic strength and the amount of polyvalents.

# DNA condensation

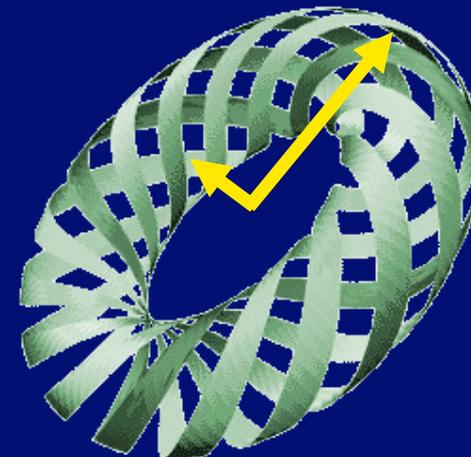
Effect of SC attractions on the level of a single molecule.



Hud & Downing (2001)



Chattoraj et al. (1978).

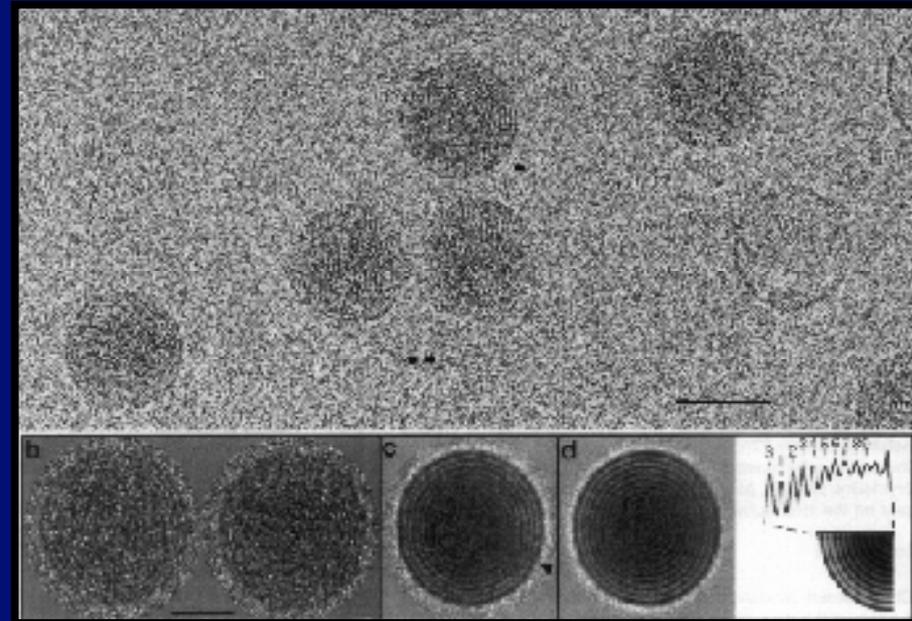


95-185 nm  
35-85 nm  
2.4 nm

## DNA condensation (continue)

In most vertebrate sperm cells DNA is condensed by arginine-rich proteins into thousands of toroidal structures, each measuring  $\sim 100$  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 than spermidine!).



Cerritelli et al.(1997). T7 DNA.

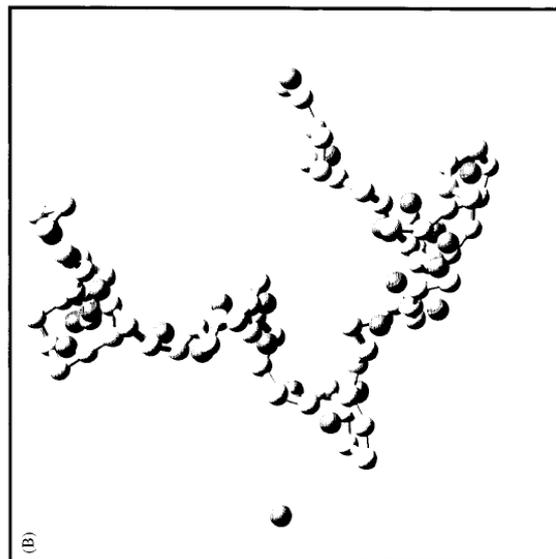
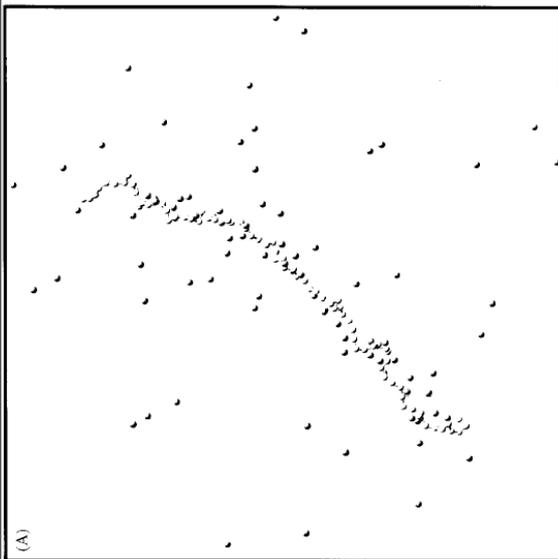
# Flexible polyelectrolyte condensation simulations

Existence of correlation attractions has important consequences  
For polyelectrolyte conformations.  
For polyvalent counterions the chain collapses into a tight coil.

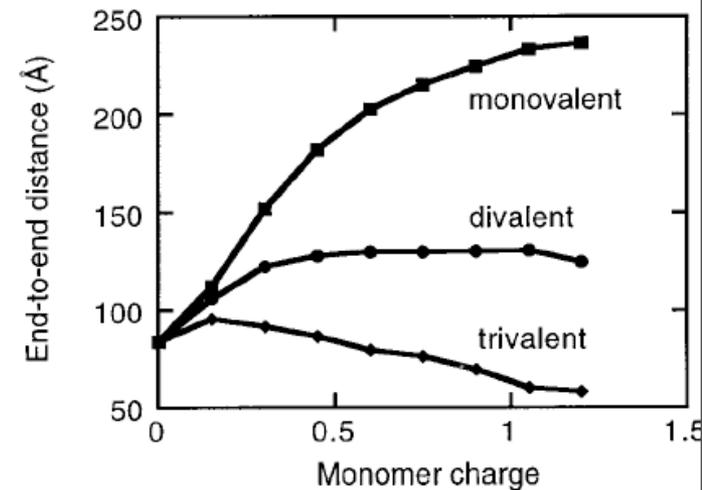
Swedish polyelectrolyte (no hard cores etc).

Extended

Collapsed



ing  
not  
the



**FIGURE 1** The end-to-end distance is shown as a function of monomer charge, for different valency of the counterions. No salt was added ( $N = 80$ ,  $c_m = 5.4$  mM, and  $\sigma = 6$  Å).

FIG  
the  
of  
end

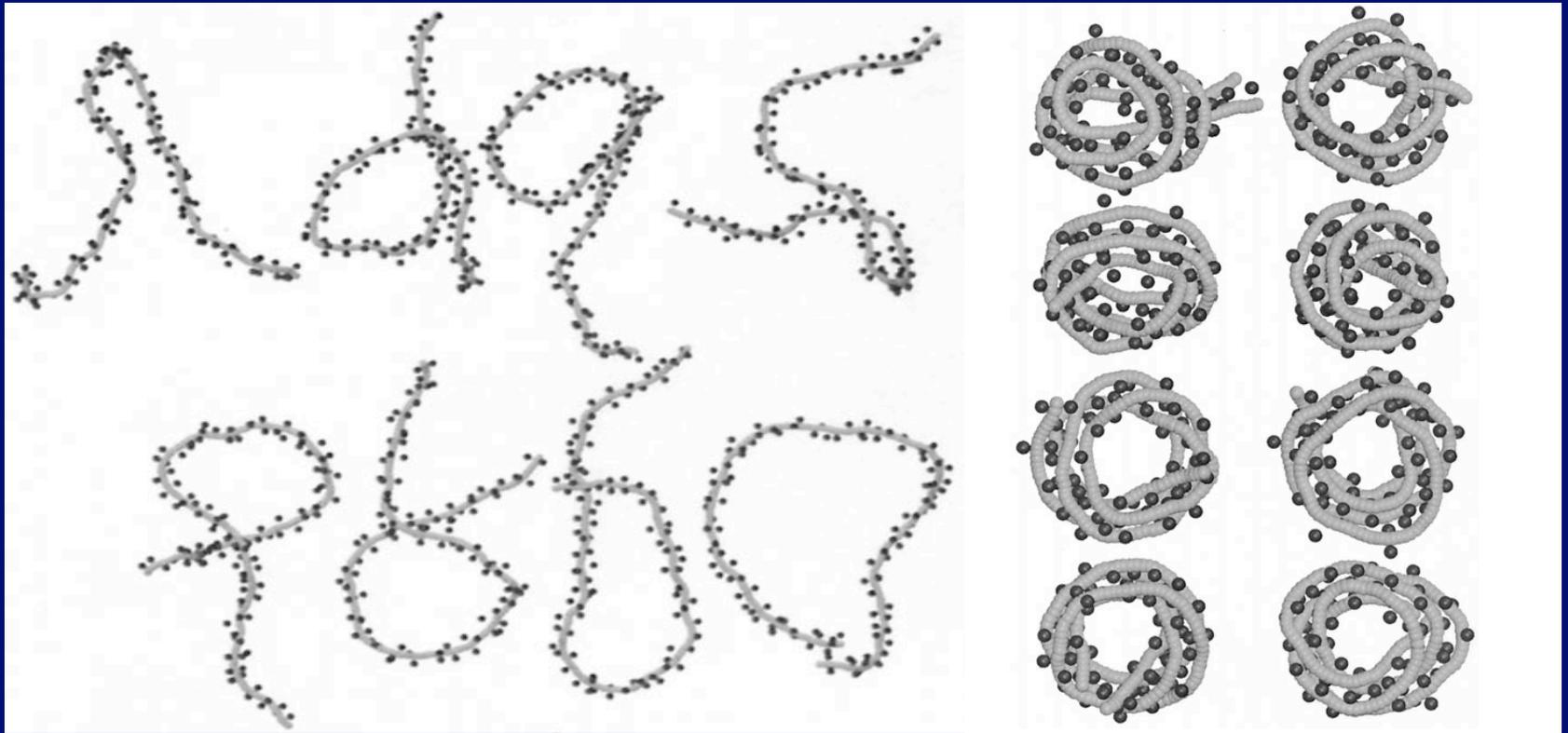
Khan and Jonsson, (1999): polyvalent counterions can collapse a flexible chain.  
A new problem: interactions and polyelectrolyte flexibility.

Confirmed experimentally by Yamakawa ('90)

## DNA condensation simulations

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

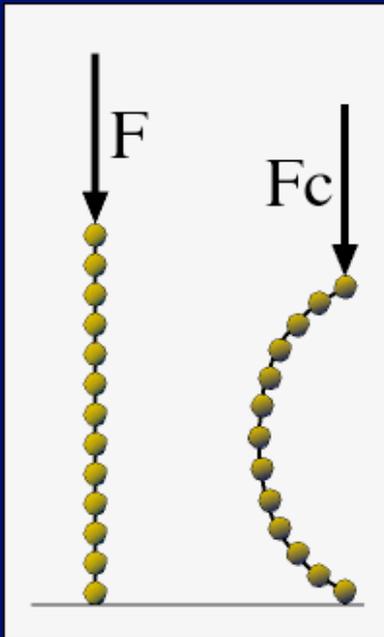
There might be a whole slew of Euler-like intermediate states that lead to DNA collapse. Much more ordered collapsed state than in Khan and Jonsson.



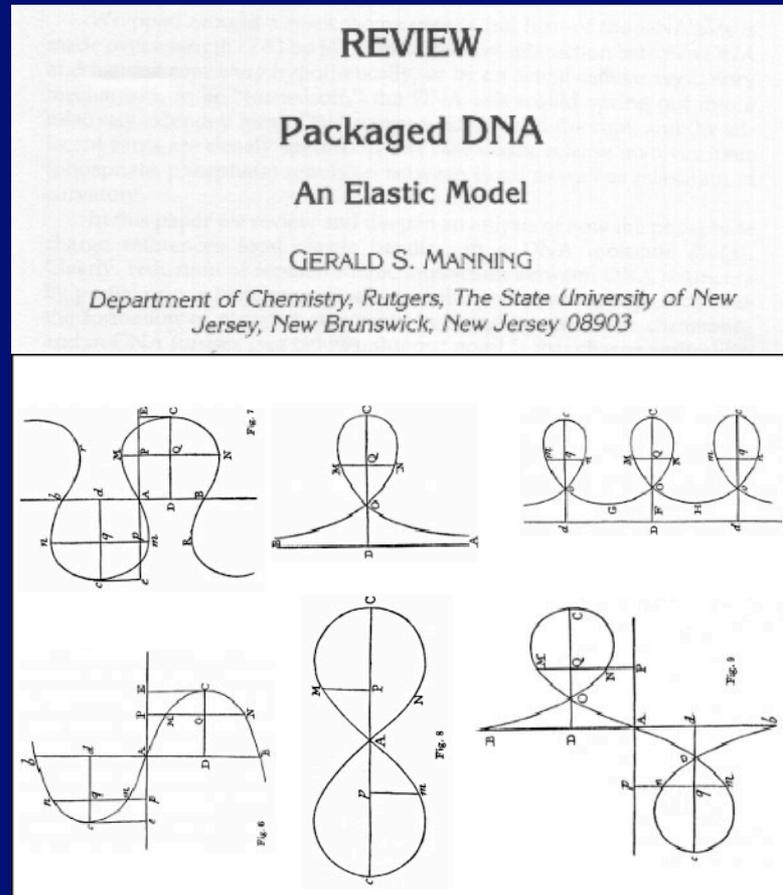
Stevens BJ (2001). This collapse is very different from a flexible chain.

# Manning buckling

Euler buckling instability: Press on an elastic filament hard enough and it buckles



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



Original Euler drawing.

The role of compressional force is played by **diminished** (on addition of polyvalent counterions) electrostatic interactions. No correlation effect at that time!

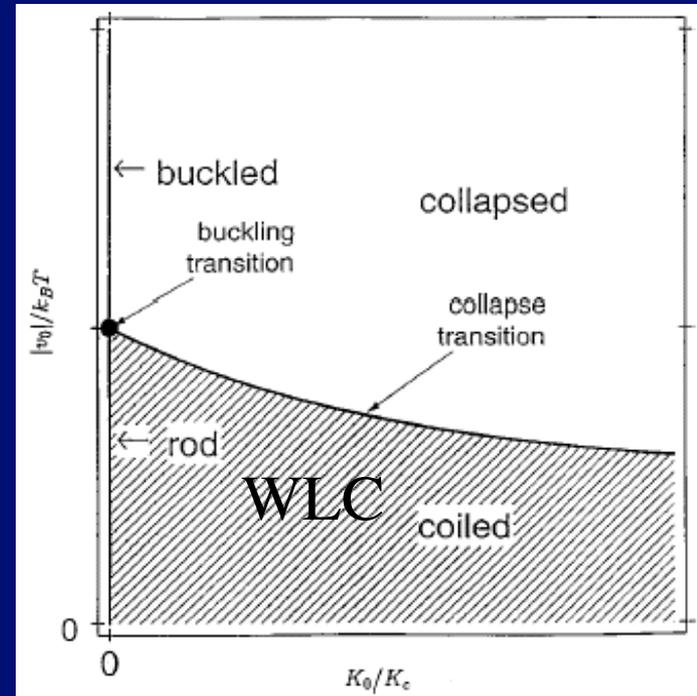
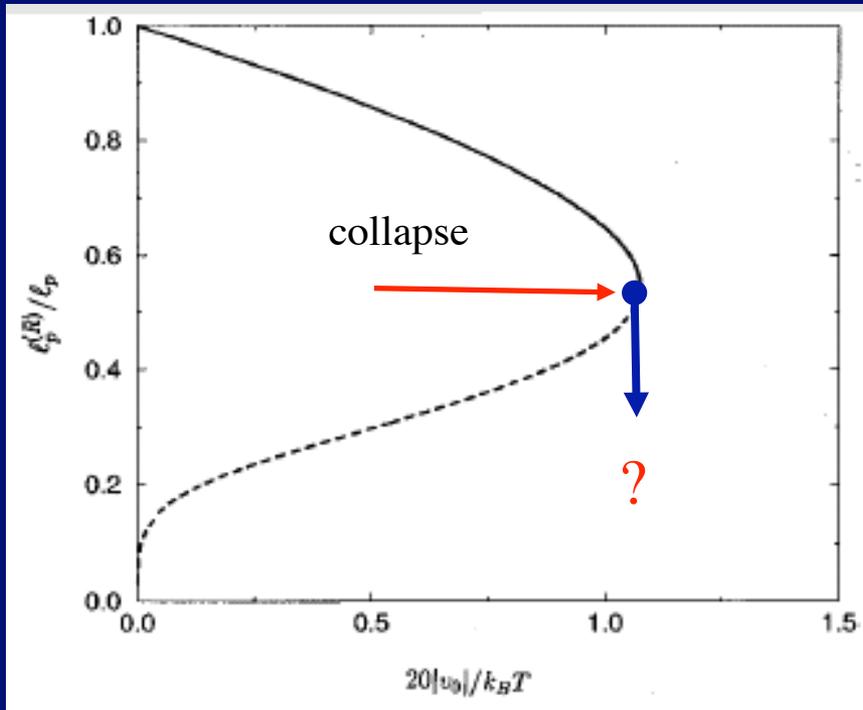
# Buckling and thermal fluctuations

Renormalization of the bending rigidity. A full non-linear theory (Hansen, Podgornik, Parsegian 1999) takes us to:

$$V(\mathbf{r}(s), \mathbf{r}(s')) = V(\mathbf{r}(s), \mathbf{r}(s'))_R + V(\mathbf{r}(s), \mathbf{r}(s'))_A$$

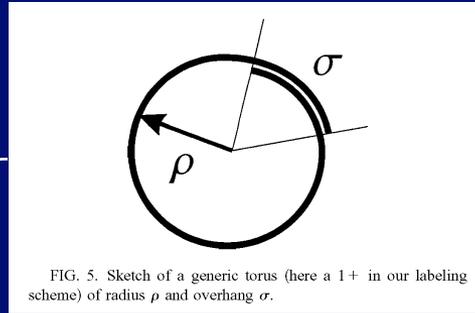
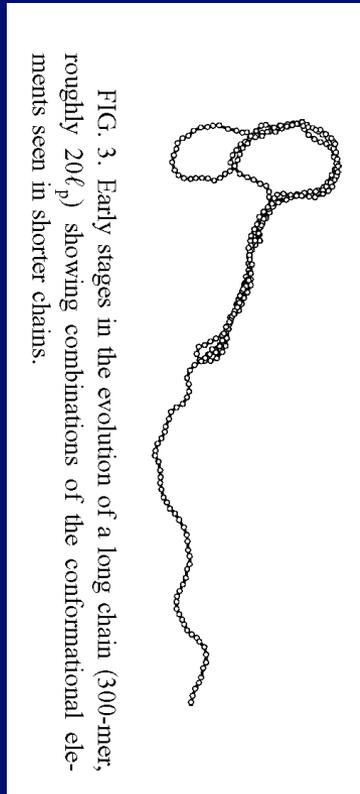
Interaction has a repulsive (WC) and an attractive part (SC).

$$K_C^{(R)} = K_C^{(0)} + K_C^{(R)} [V(\mathbf{r}(s), \mathbf{r}(s'))_R] - K_C^{(R)} [V(\mathbf{r}(s), \mathbf{r}(s'))_A]$$

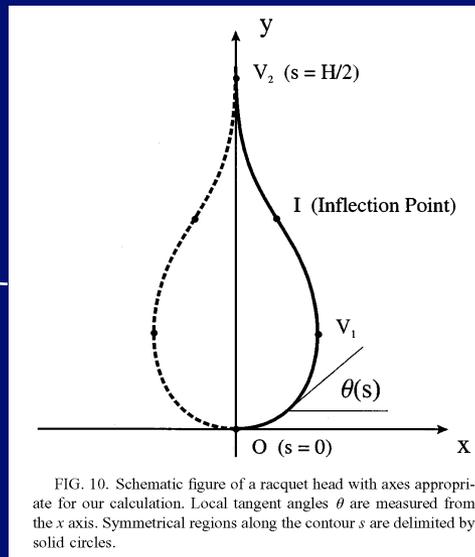


# DNA condensation simulations

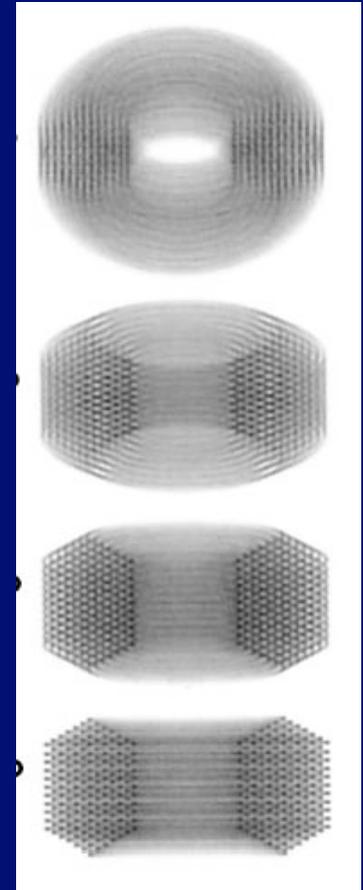
Simulations point to various eulerian precursors of the collapsed phase.



toroidal



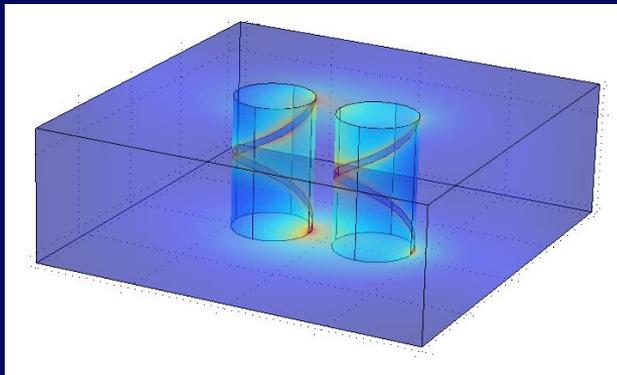
racquet-like



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.

# WC and SC for helical charge distributions

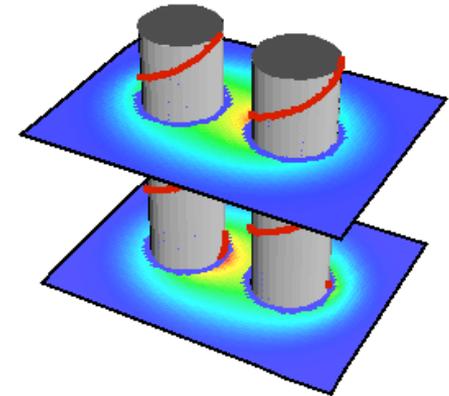


An “ab initio” calculation.

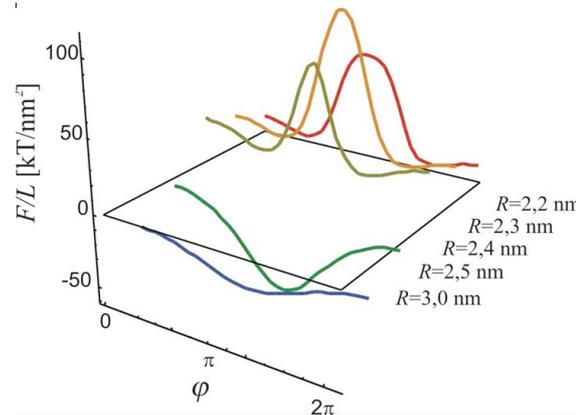
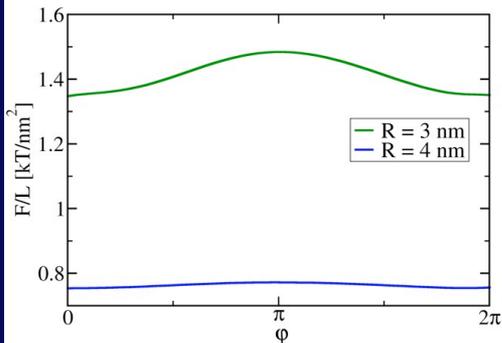
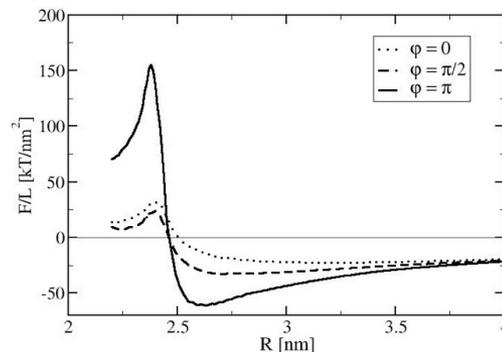
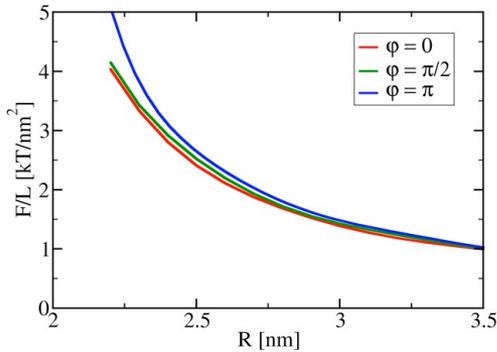
Poisson-Boltzmann  
(Kornyshev-Leikin approx.)

vs.

strong coupling limit



Strongly coupled  
counterion spatial  
distribution.



Whereas in the KL theory the strongly coupled counterions are put in “by hand”, here all interactions are electrostatic.

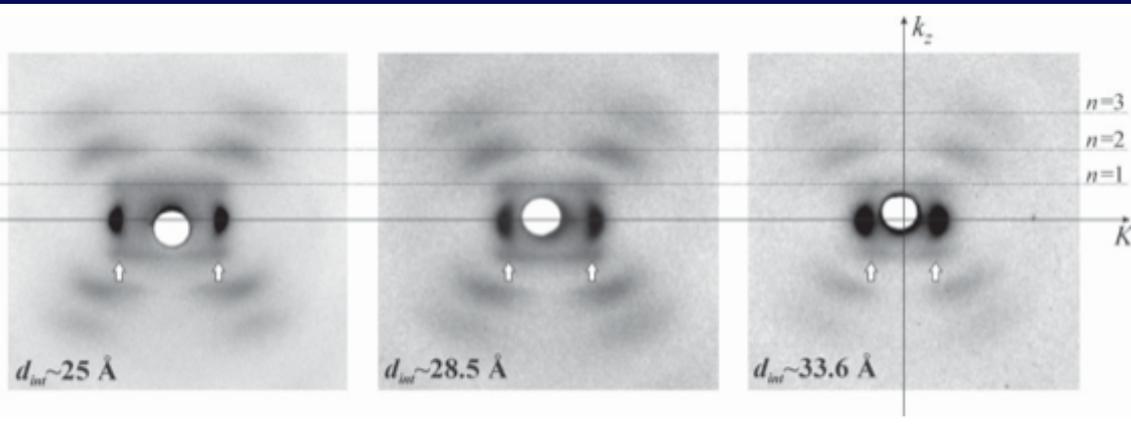
Qualitatively the results are the same.

Kanduč & Podgornik (2007)

# Is this real?

Can one observe azimuthal correlations predicted in the theory of helical charge distribution interactions?

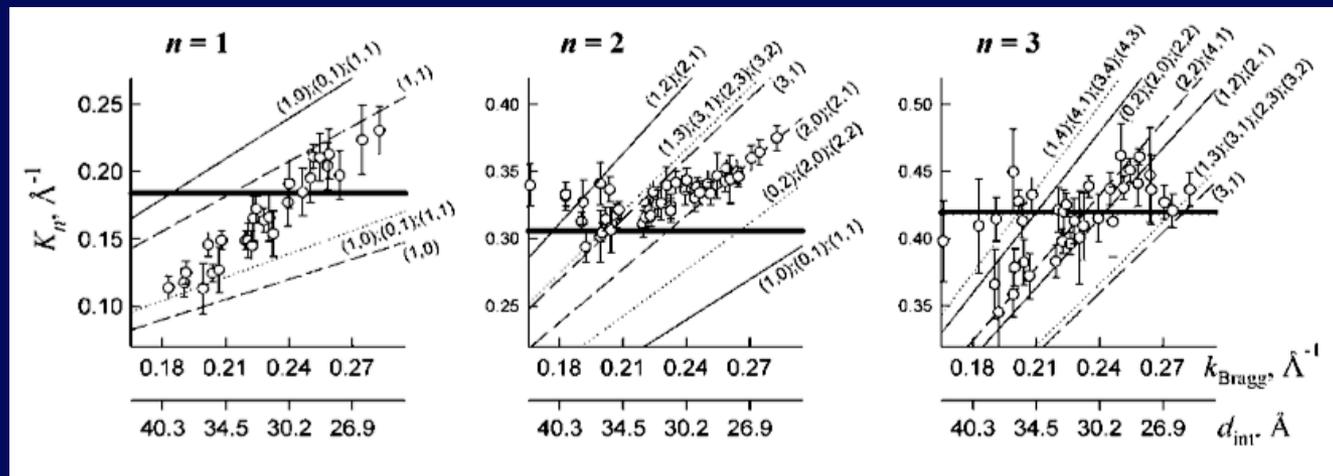
Kornyshev and Leikin (PRL, 2005) reanalyzed the old diffraction data by S.B. Zimmerman. From almost contact to 40 Å separation.



- equatorial  $n=0$  peaks change with DNA density, positional order
- for small inter-chain correlations  $n \neq 0$  peaks should show no density variation

Equatorial lines remain the same - B-DNA for all densities.

Strong azimuthal correlations of the type A, 2a or 2c.



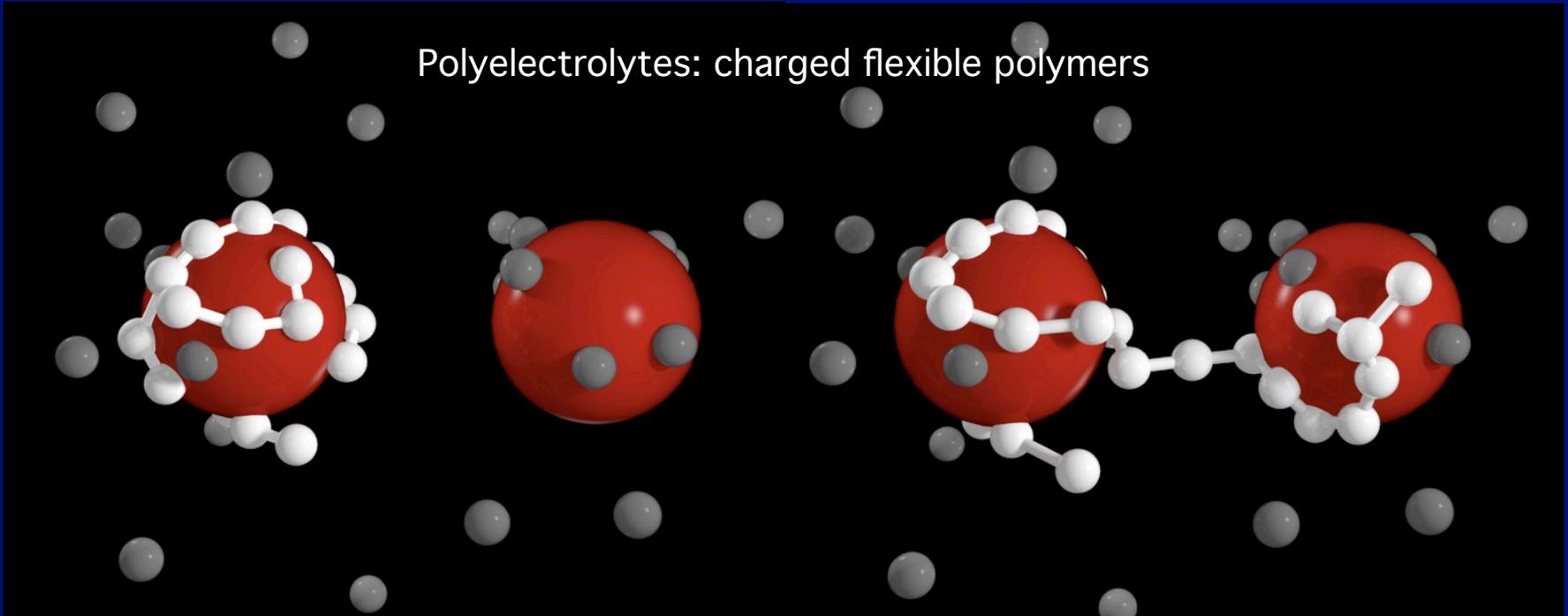


# 3.

polyelectrolyte bridging interactions that are due to elastic deformation of stretched polyelectrolyte chains between charged macromolecular interfaces, their role in organization of eucaryotic genome, specifically in the interactions between nucleosomal core particles.

# Polyelectrolyte bridging

Polyelectrolytes: charged flexible polymers



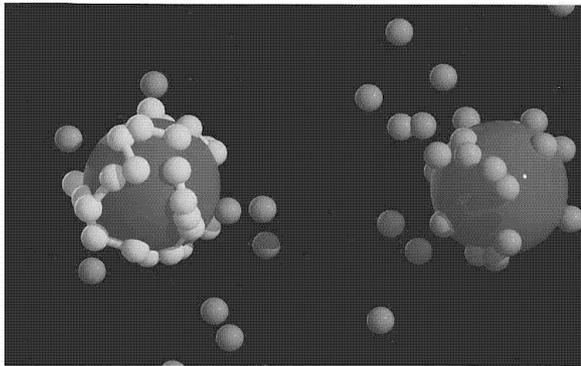
Electrostatic interactions effect  
polymer **structural parameters**  
(persistence length, stretching modulus)  
as well as **conformations**  
(DNA condensation).

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

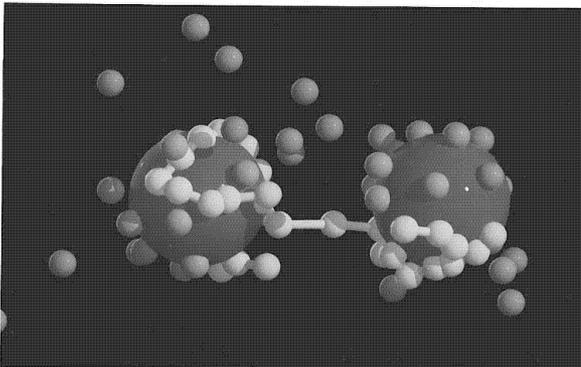
Podgornik and Jonsson (1993) Podgornik, Akesson and Jonsson,(1995)  
Podgornik and Licer (2006).

# Bridging between small macroions: simulations

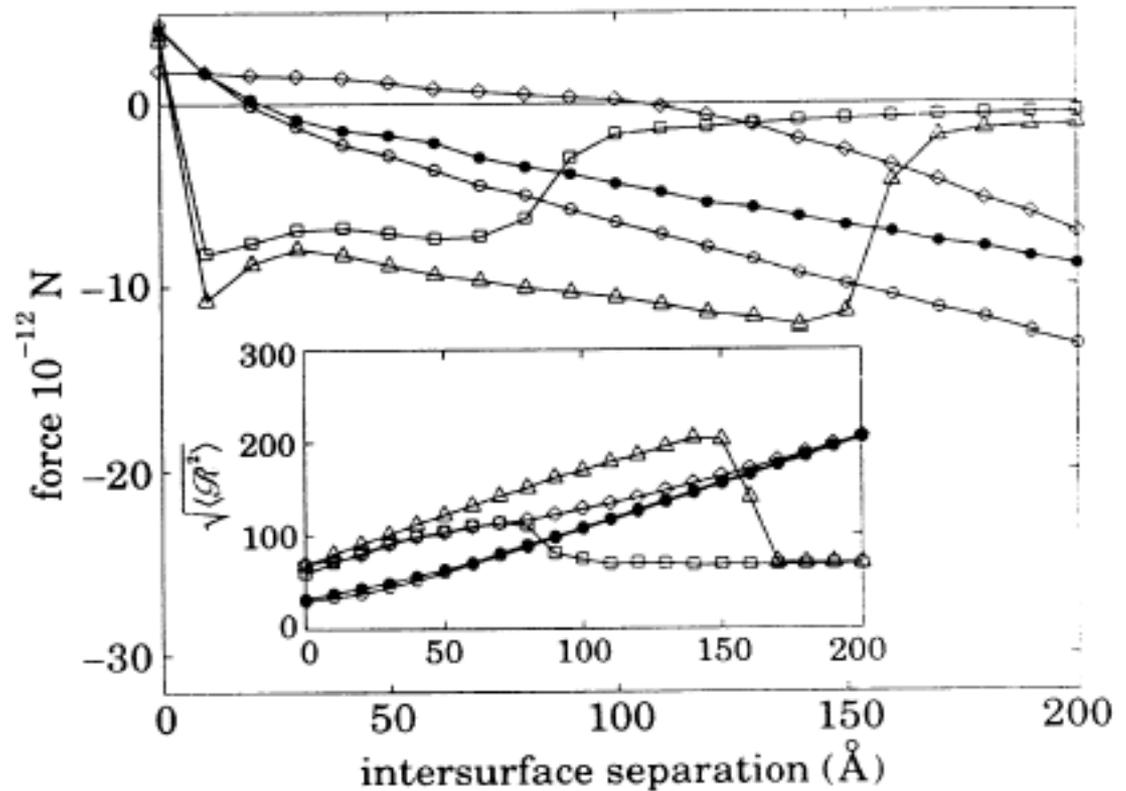
Two charged macroions with a compensating one, or many polyelectrolyte chains.  
N = 20, 30 monomers and size of the macroion ~ 40 Å.



(a) N = 20, 30. No salt ions.

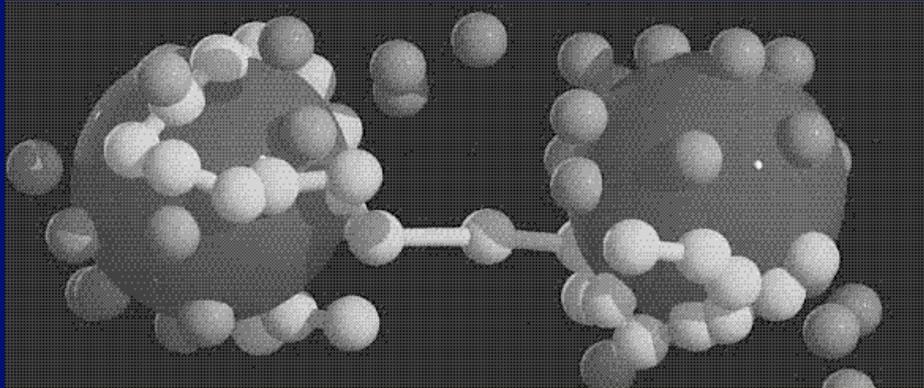


(b)



# Two spherical macroions with PE chains

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



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

Chain flexibility

Inter and intra-chain interactions

External (macroions) field

Screened electrostatics - WC limit for small ions

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

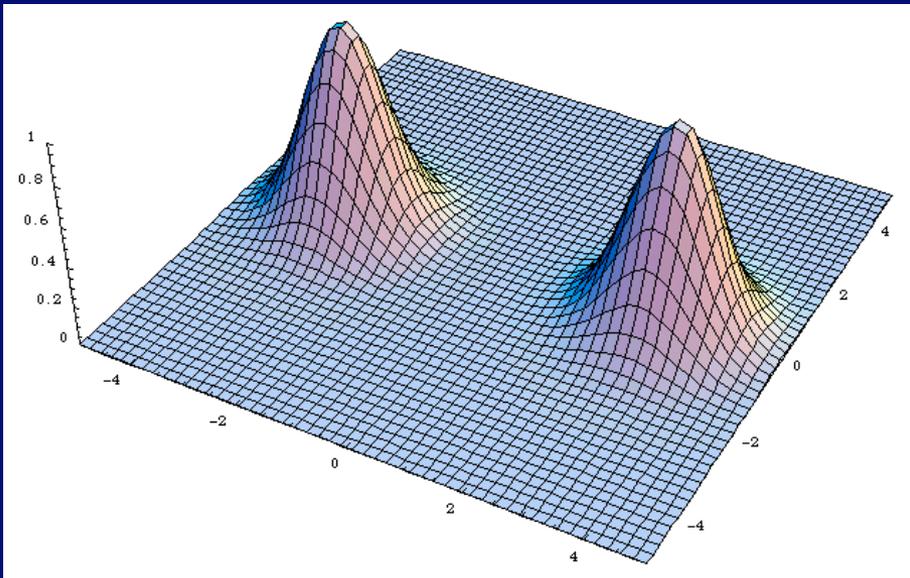
$$\phi_{ext}(\mathbf{r}) = \frac{e_1 e_0}{4\pi\epsilon\epsilon_0} \frac{e^{-\kappa|\mathbf{r}-\mathbf{r}_1|}}{|\mathbf{r}-\mathbf{r}_1|} + \frac{e_2 e_0}{4\pi\epsilon\epsilon_0} \frac{e^{-\kappa|\mathbf{r}-\mathbf{r}_2|}}{|\mathbf{r}-\mathbf{r}_2|}$$

## A variational ansatz

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

$$\beta\mathcal{H}_0[\mathbf{r}_i(n)] = \frac{3}{2\ell^2} \sum_{i=1}^2 \int_0^N \dot{\mathbf{r}}_i^2(n) dn + \frac{3}{2} \sum_{i=1}^2 \zeta_i^2(\mathbf{r}_{0i}) \int_0^N (\mathbf{r}_i(n) - \mathbf{r}_{0i})^2 dn + \beta N \mathcal{L}(\mathbf{r}_{01}, \mathbf{r}_{02})$$

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



Harmonic ansatz gives Gaussian distribution of monomers.

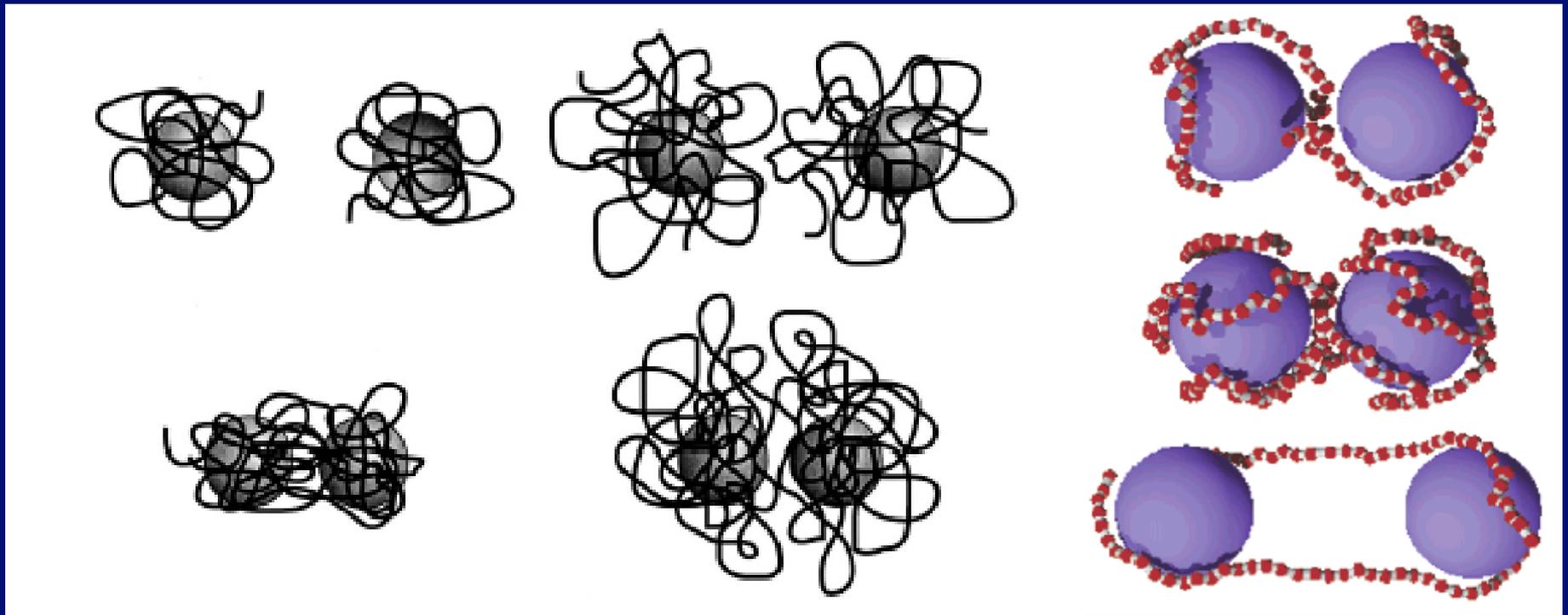
$$\rho_{a_i^2}(\mathbf{r}, \mathbf{r}_{0i}) = \frac{N}{(2\pi a_i^2)^{3/2}} \exp -\frac{|\mathbf{r} - \mathbf{r}_{0i}|^2}{2a_i^2}$$

The size of the chain is then determined variationally by calculating the value of  $\zeta^2$  that minimizes the difference between the original hamiltonian and the quadratic ansatz (Feynman-Kleinert)

## Two limits

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

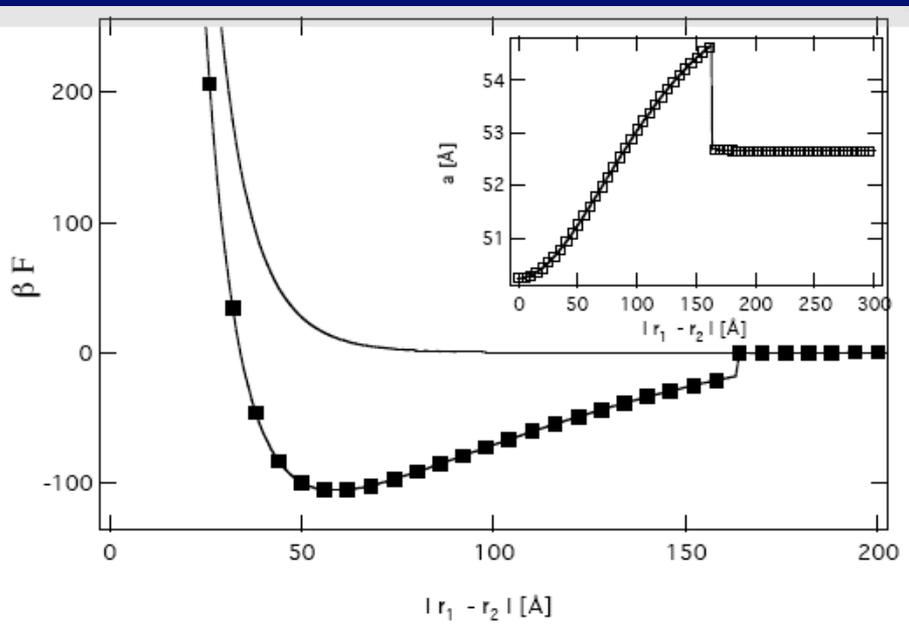


(Dzubiella, Moreira and Pincus, 2003)

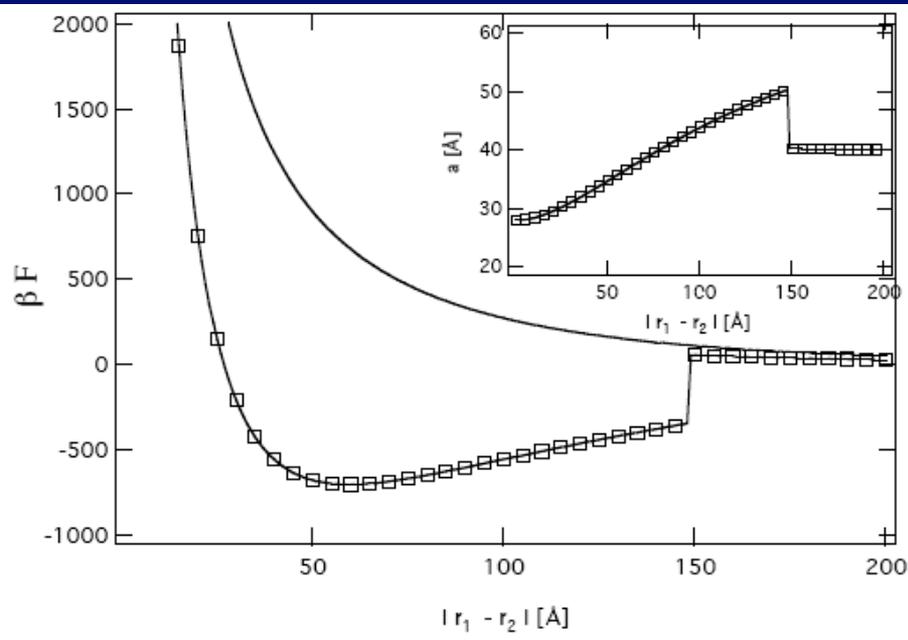
**Bridging attractions** (strong coupling) vs. **coronal repulsions** (weak coupling).

# Strong coupling limit

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

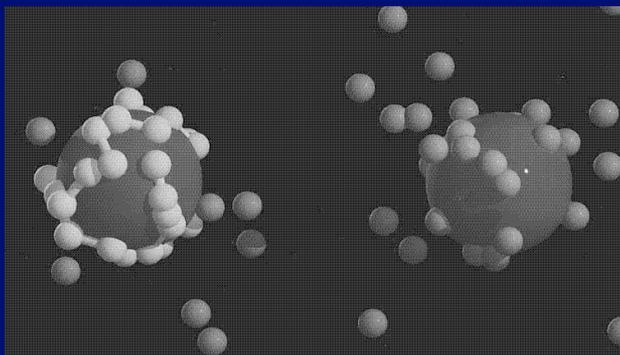


60 mM



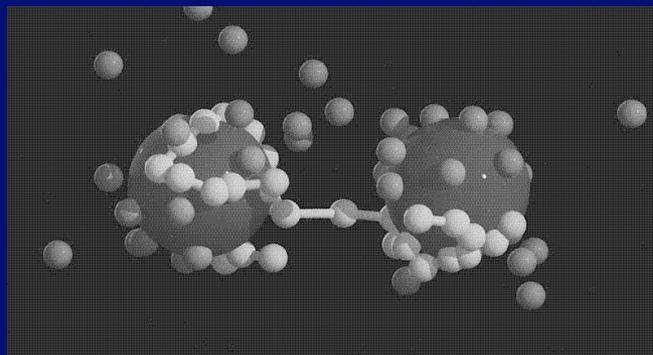
1 mM

Chain conformation determined by the macroions.



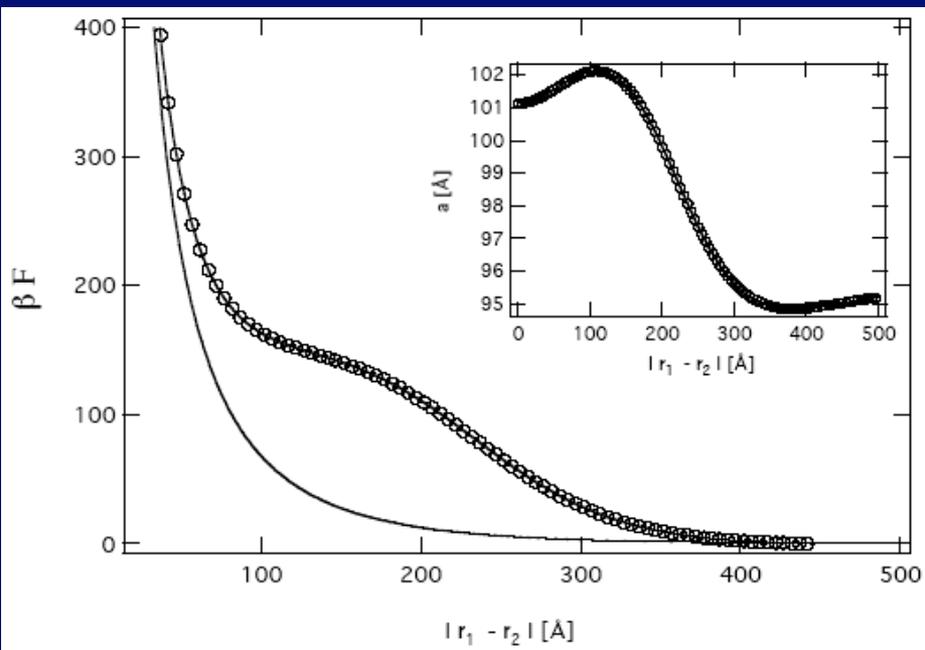
Bridging

Non-bridging

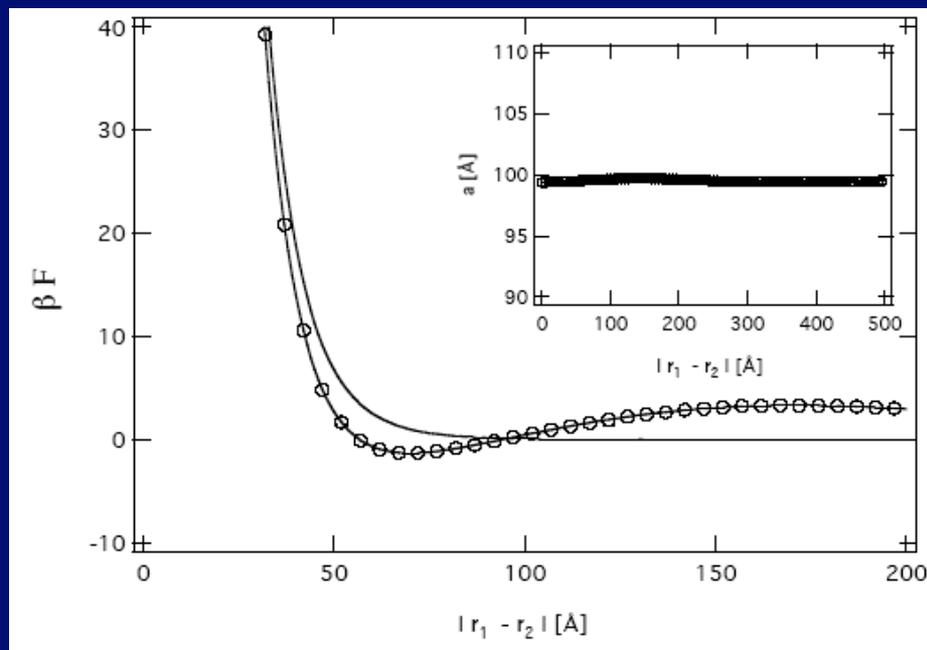


# Weak coupling limit

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

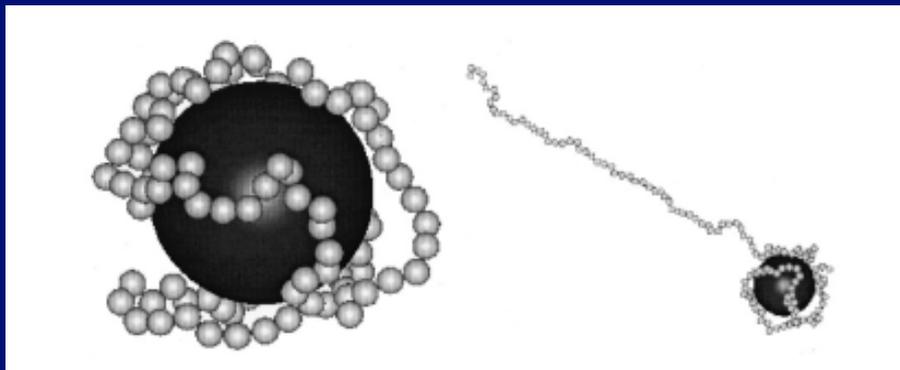


60 mM



1 mM

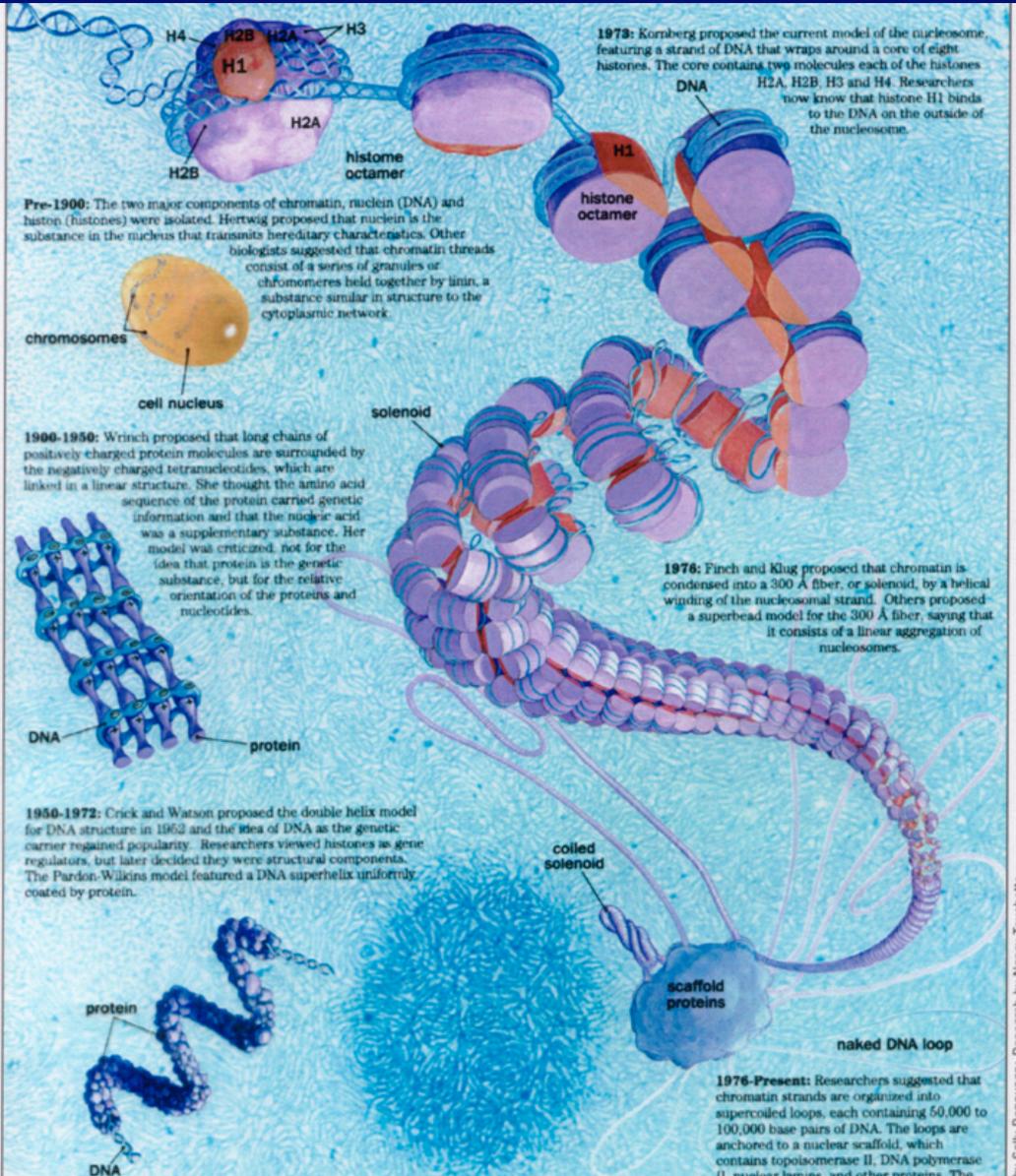
Chain conformation determined by inter and intra.



Formation of a polymer brush corona.

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

# Eucariotic Genome



NCP



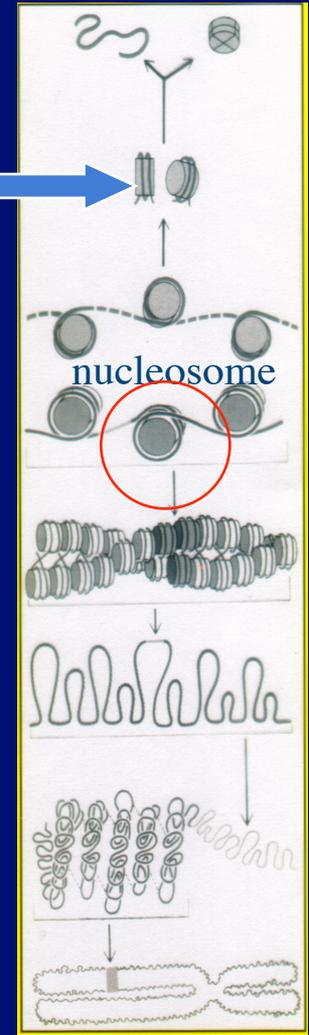
~ 10 nm

~ 30 nm

~ 300 nm

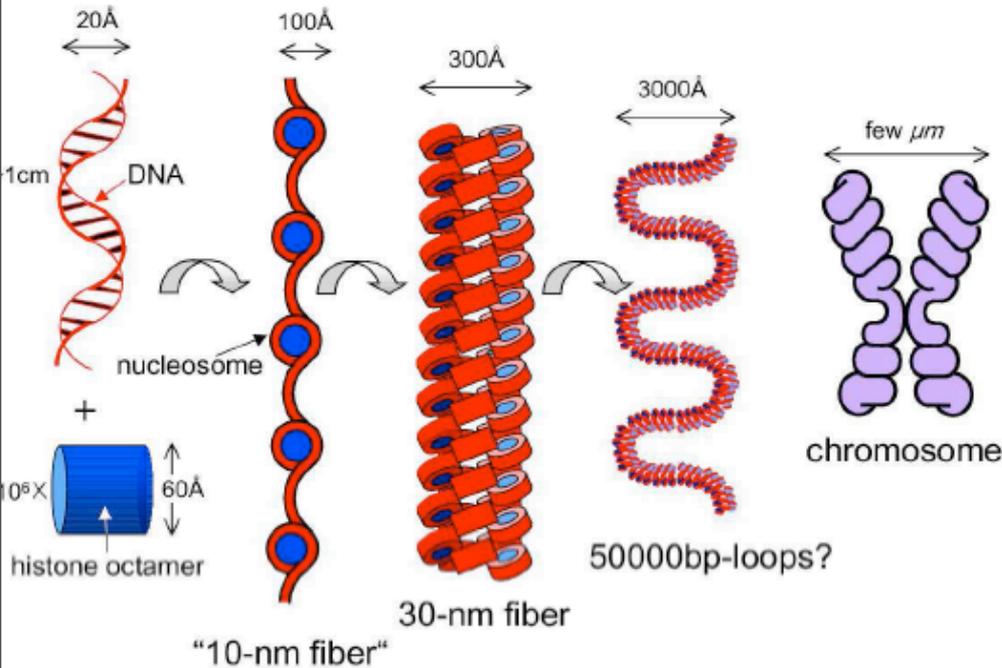
~ 700 nm

~ 1400 nm



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

# The chromosome size cascade



F. Muehlbacher, 2004.

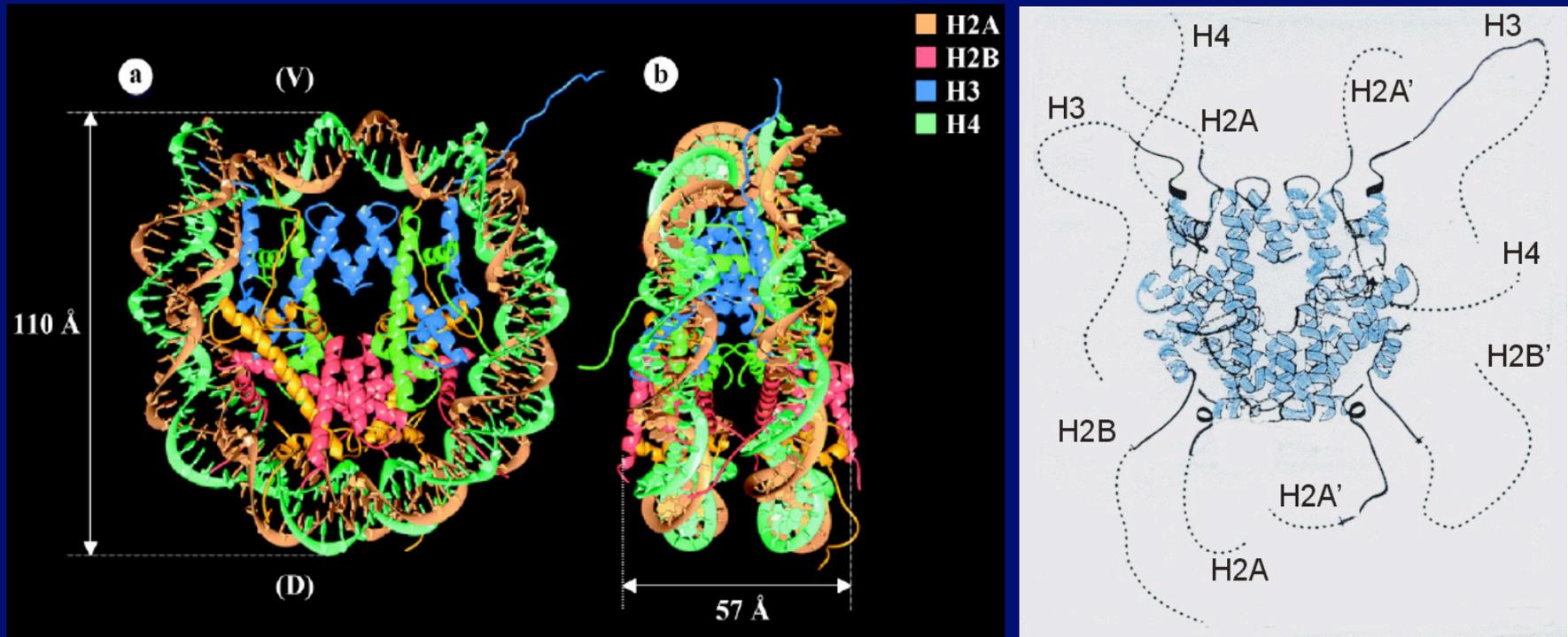
From DNA to chromosomes. Many levels of as yet poorly understood organization but with interesting physics (Schissel, 2002).

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



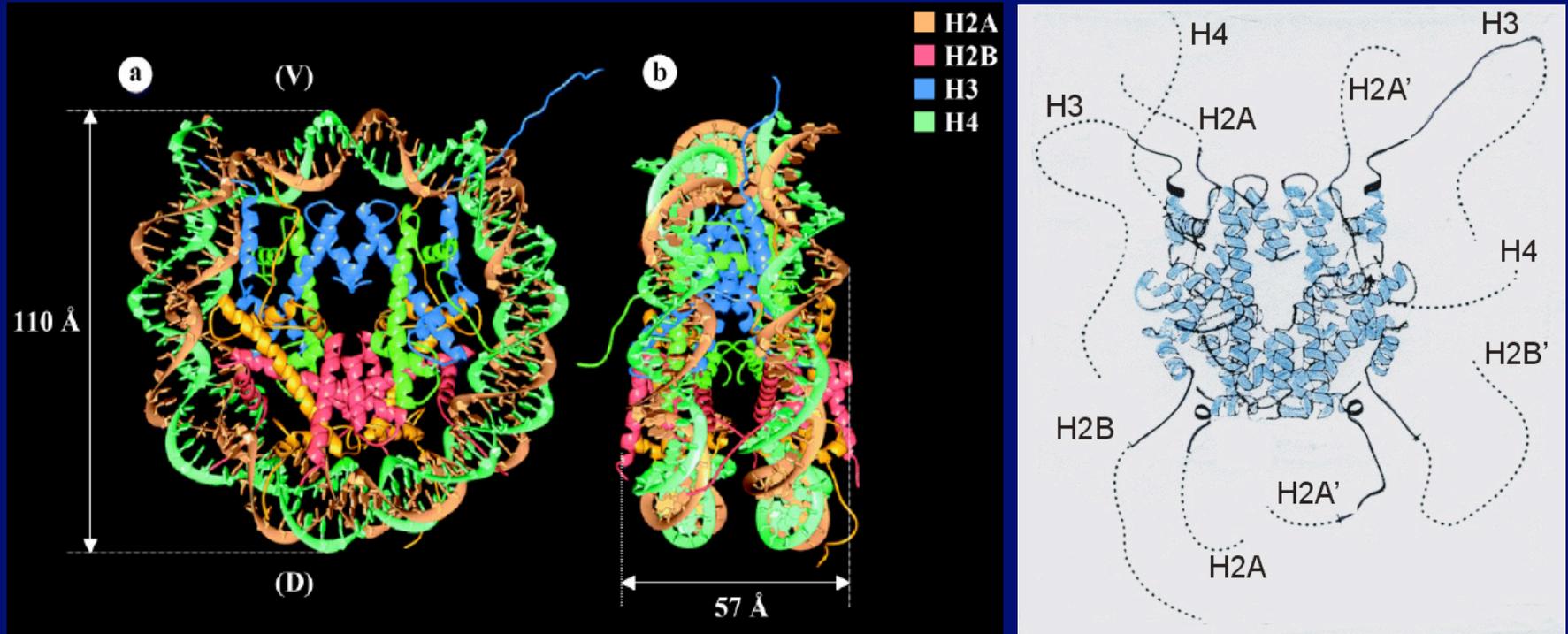
Longest tail ~ 25 aa.

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

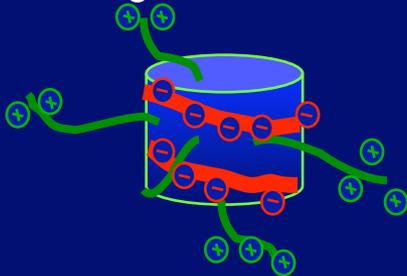
A highly charged hairy particle  
( $- 2 \cdot 147 + 134 (220) = - 165$ )  
Excluding the histone buried charges  
(Bertin et al., 2004)

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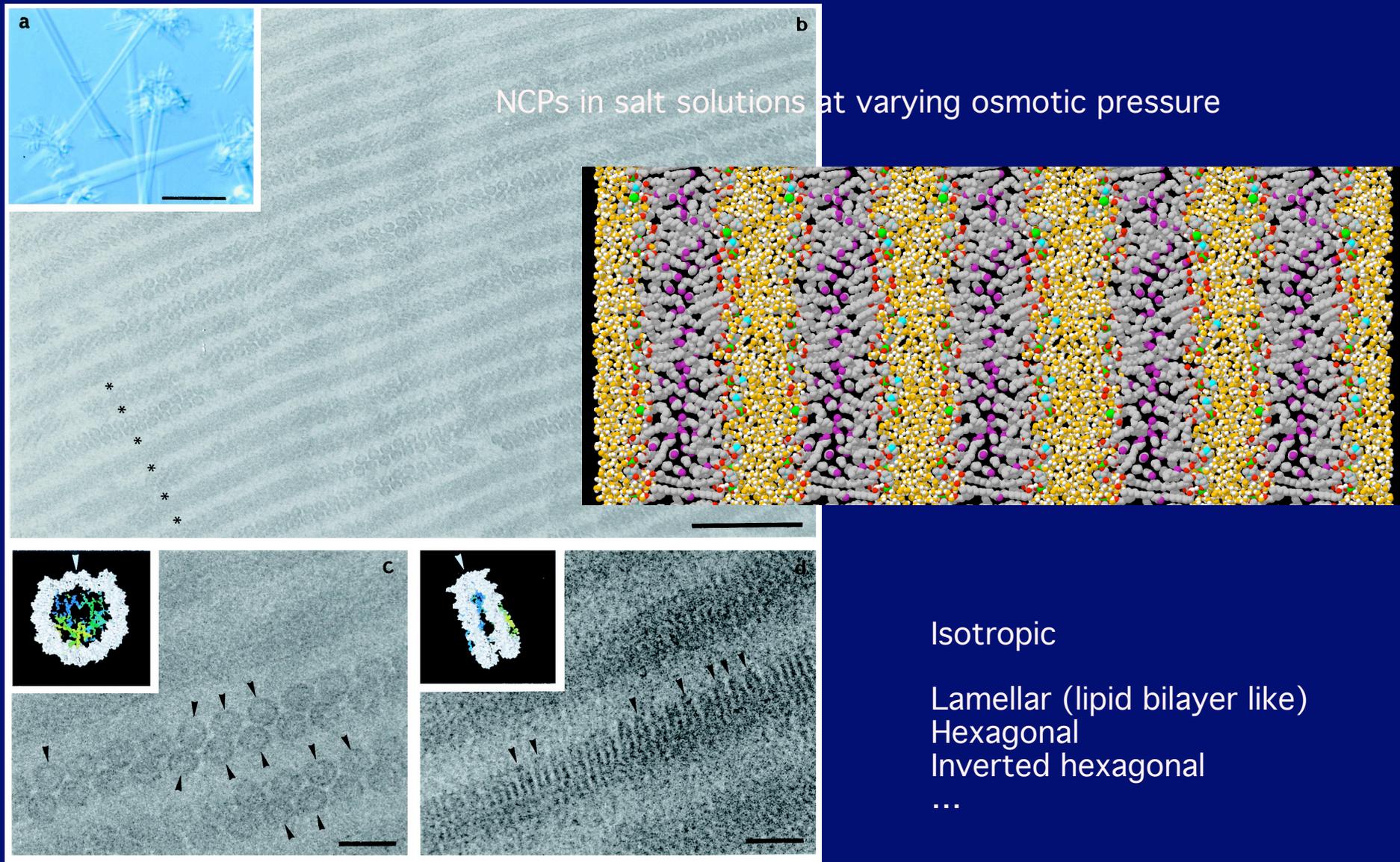
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Excluding the histone buried charges  
(Bertin et al., 2004)

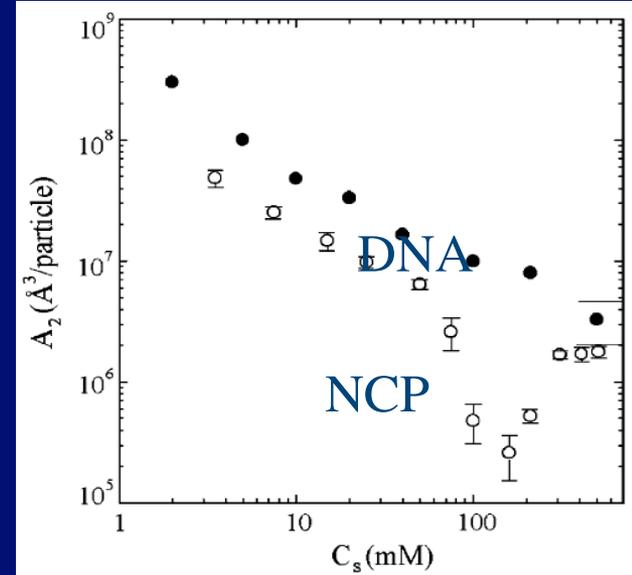
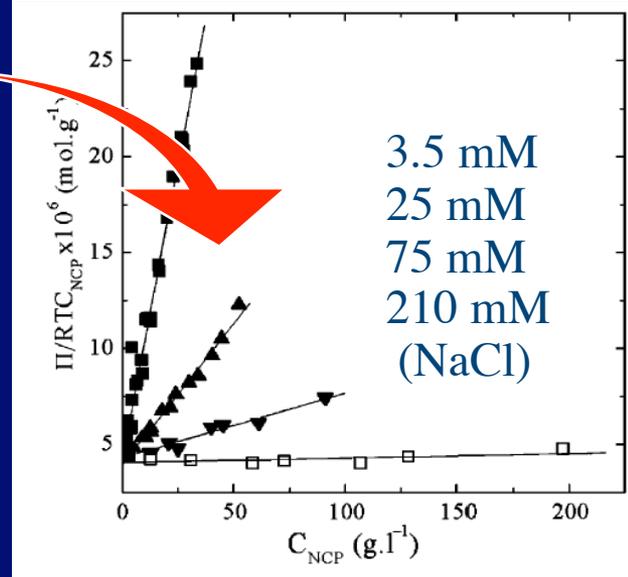
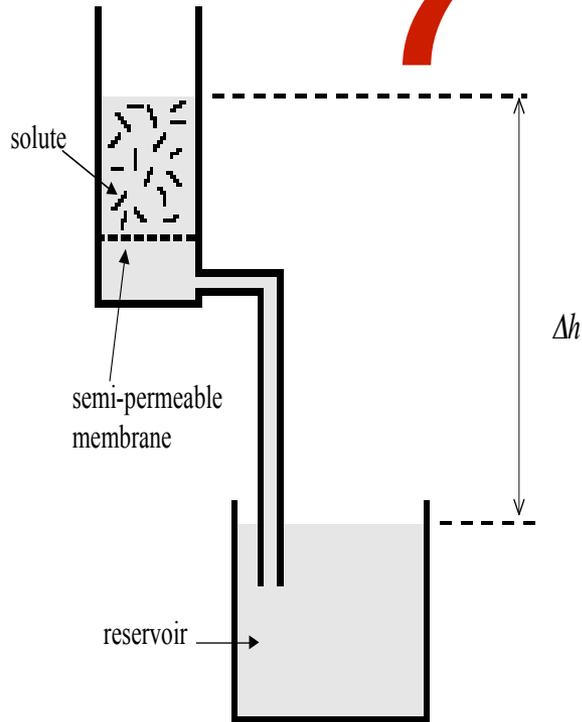
# High density mesophases and low density NCP solutions



(Mangenot, Livolant, Leforestier, Durand, de Frutos, Raspaud, 2001 - 2003)

# Low density NCP osmotic pressure

Manometric osmotic stress method  
(Raspaud, 2003)



Standard second virial coefficient:

$$\frac{\Pi}{RT} = \frac{C_{NCP}}{M} + A_2 C_{NCP}^2 + A_3 C_{NCP}^3 + \dots$$

A2 evidence of attractions.

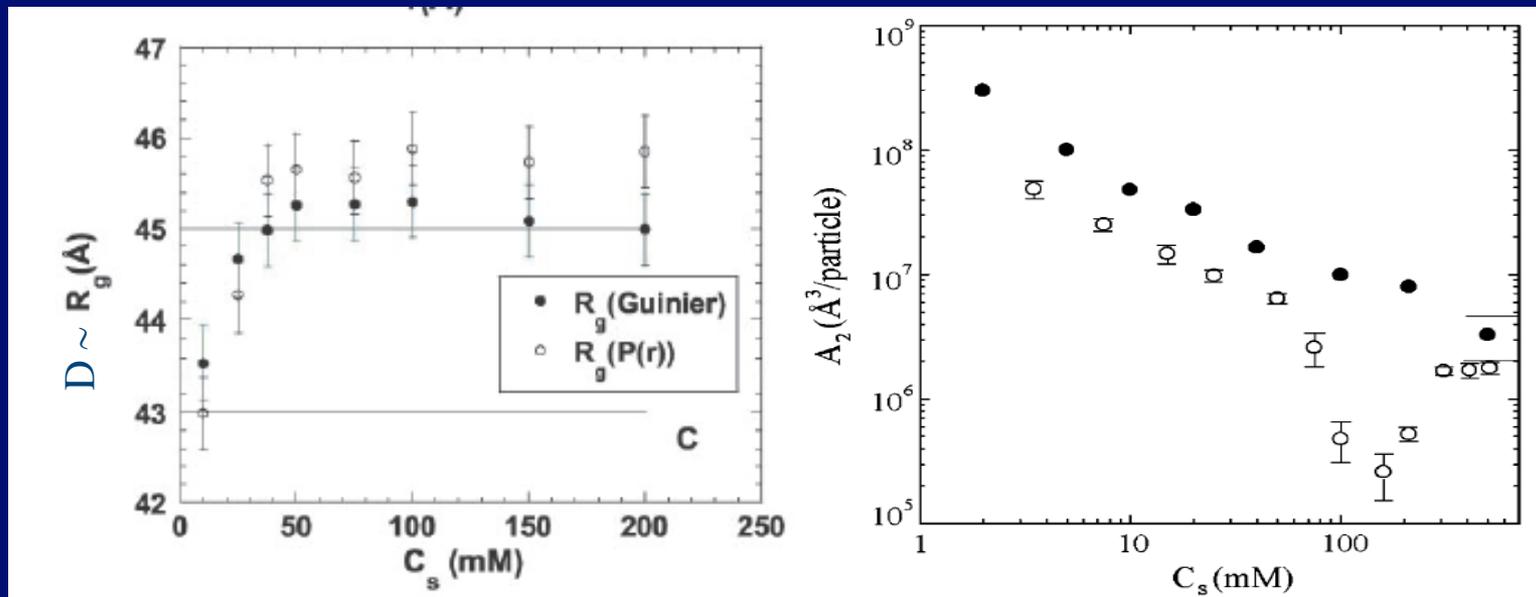
# Bridging of N-tails?

Raspaud et al. suggested that the attractions seen in A2 could be due to N-tail bridging.

Folded N-tails

Expanded N-tails

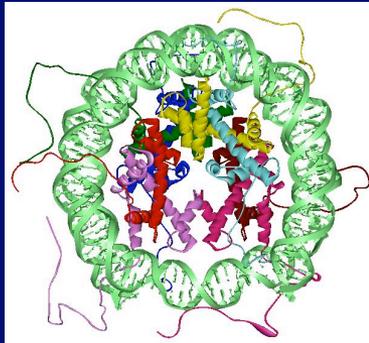
Folded tails below 50 mM and expanded from 50 mM and above.



# Bridging of N-tails?

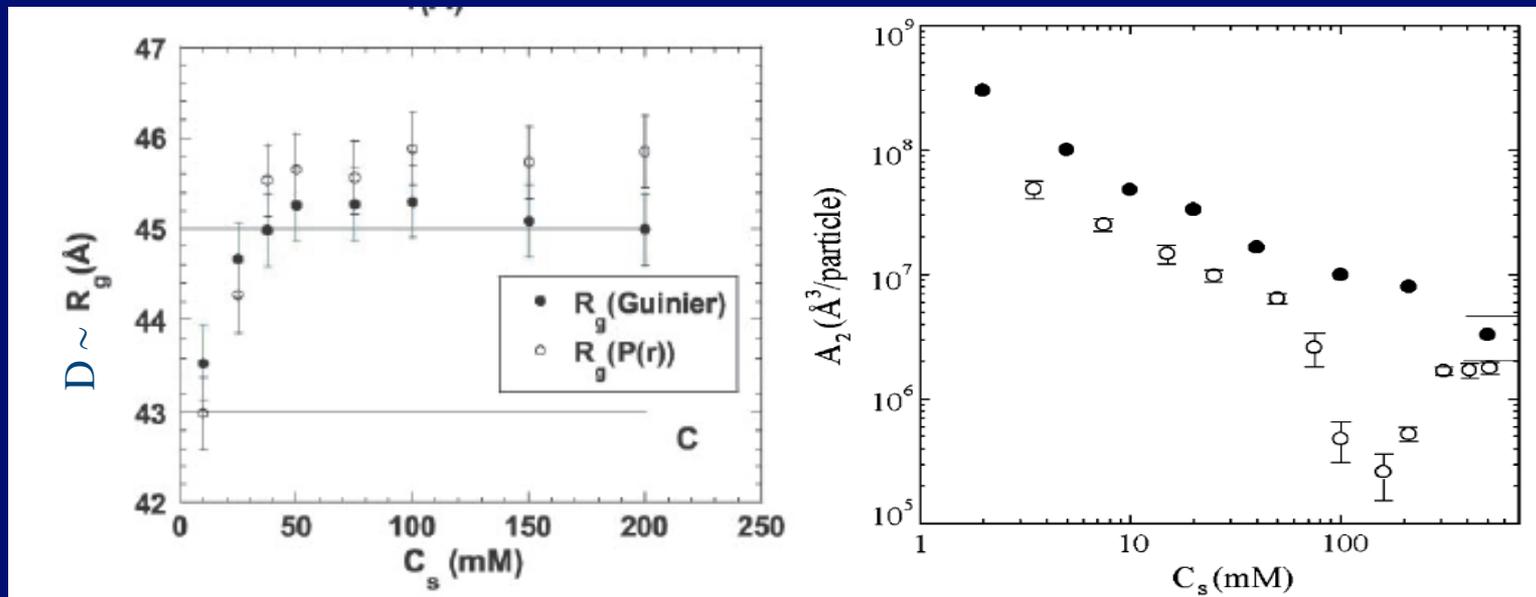
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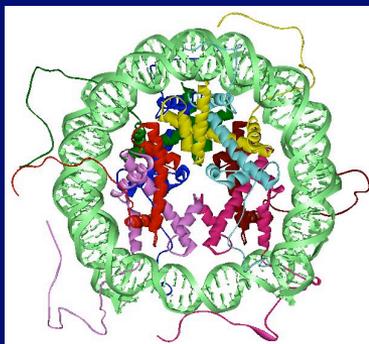
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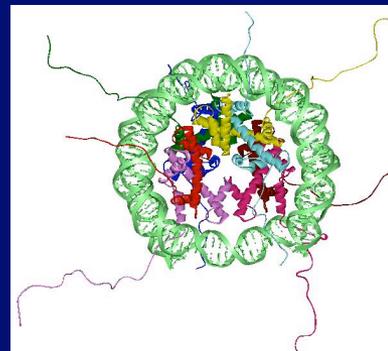
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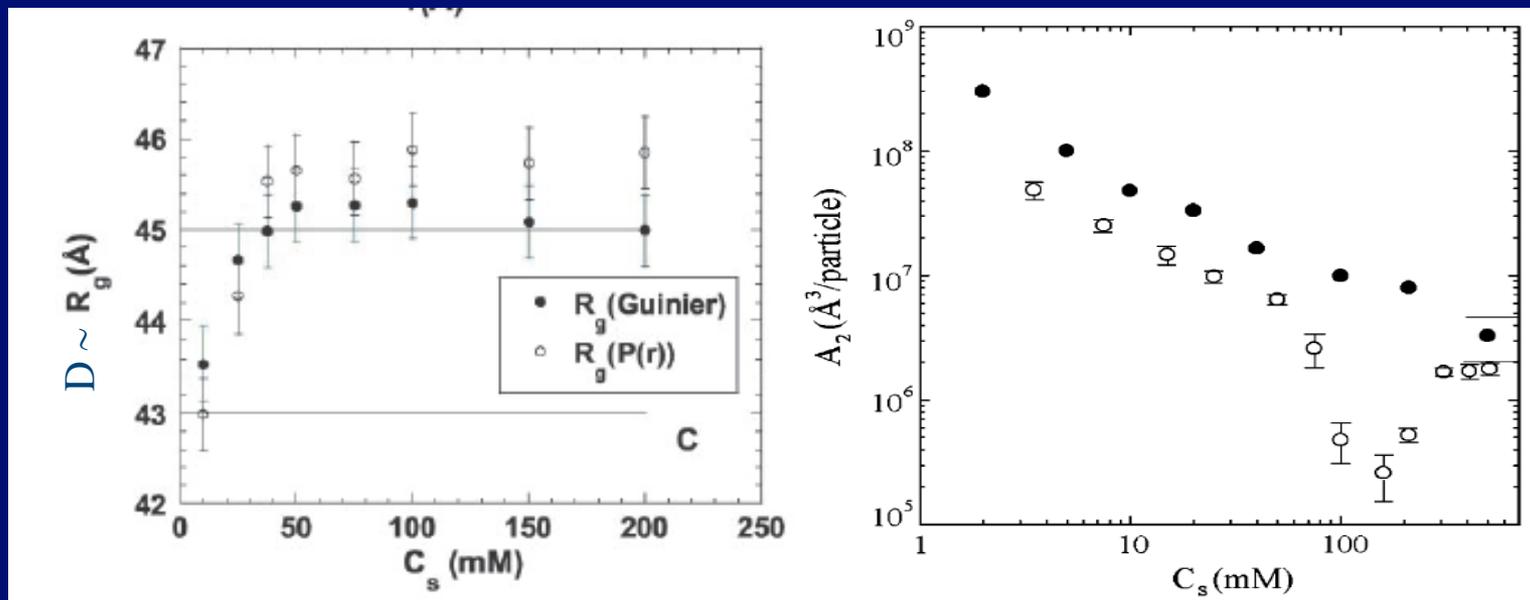
Folded N-tails



Expanded N-tails

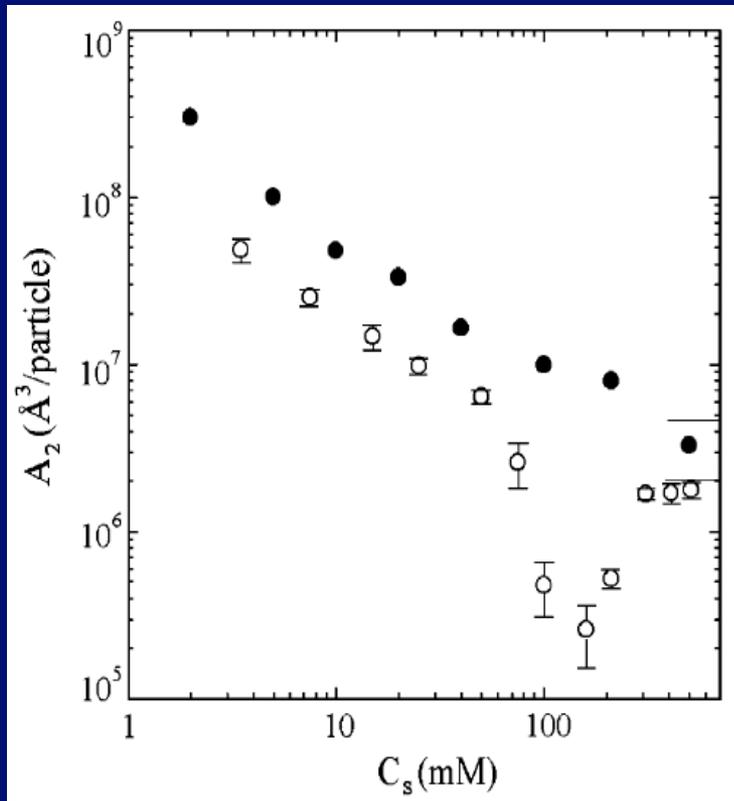


Folded tails below 50 mM and expanded from 50 mM and above.

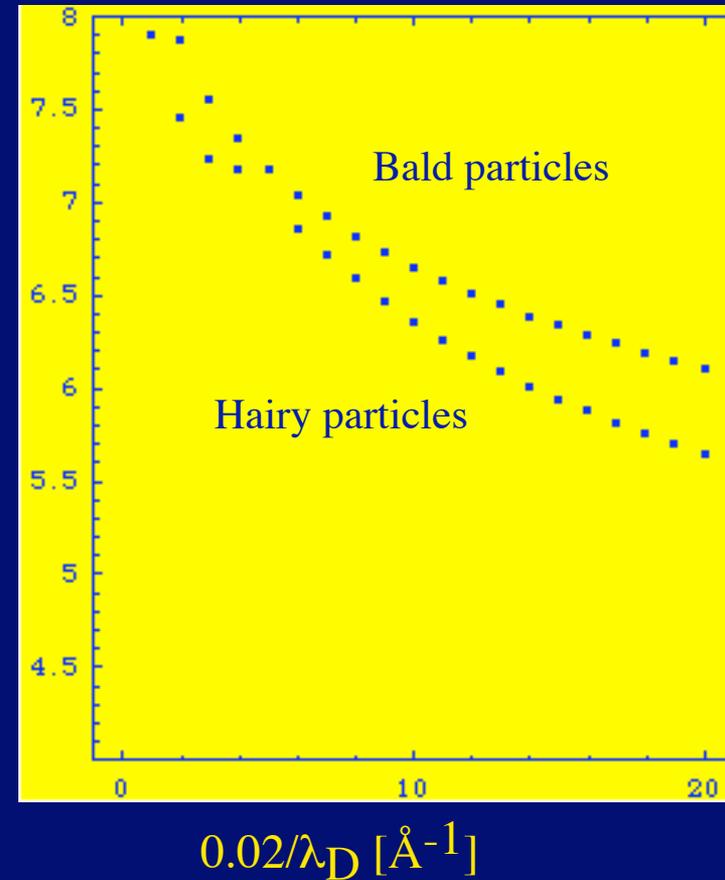


# Bridging of N-tails? Not directly.

Variational analytical theory as described before.



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



$R = 60 \text{ \AA}$ ,  $M = 143$ ,  $N = 50$ ,  $l = 6 \text{ \AA}$ , 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.

# Simulations of bridging of N-tails

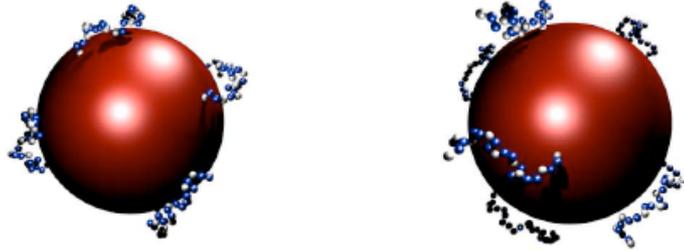
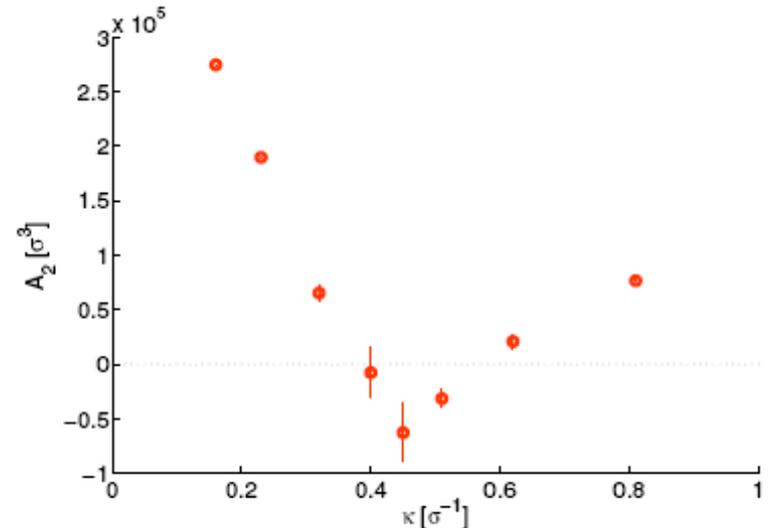
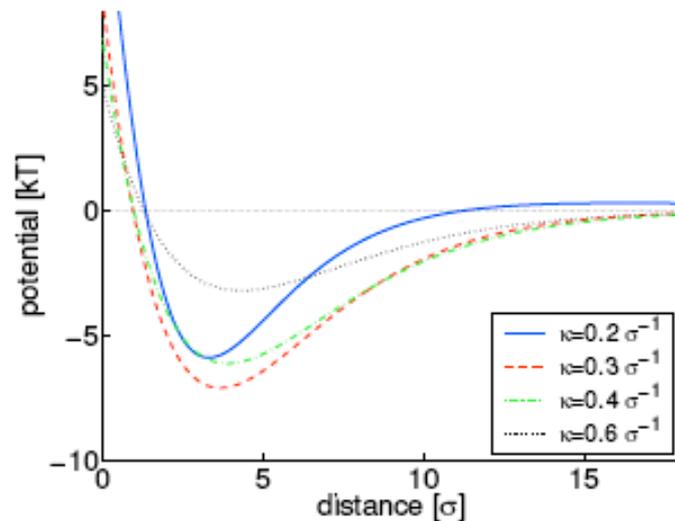


Figure 3.10: A typical conformation for  $k = 0$ ,  $Z = 100$  (left side) and  $k = 0.4 \sigma^{-1}$ ,  $Z = 250$  (right side)

Simulations of model NCP.  
Coarse grained bead-spring model.  
Muehlbacher, Schiessel and Holm, (2005).

Typical configurations.



Bridging interactions can be stronger than electrostatics and can lead to association of nominally equally charged colloids. They also depend on orientation. Important also at large densities of NCPs where they make condensed mesophases...

Same conclusions from all atoms simulations.  
Lyubartsev et al. (2006)

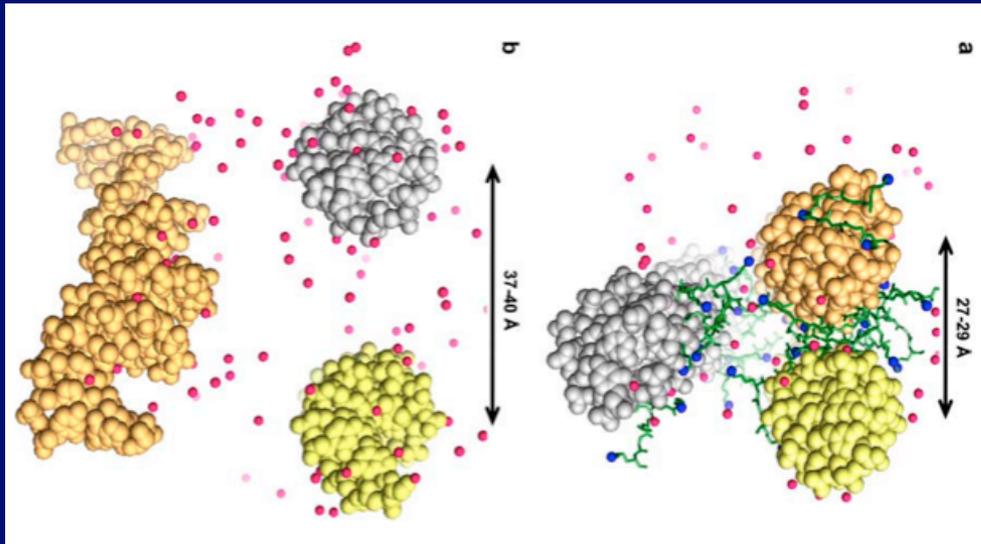


FIGURE 7 Snapshots from the all-atom MD simulations (view from top of the simulation cell along the DNA axes; pink spheres are  $K^+$ ). (a) Tail-1 system,  $t = 21.92$  ns; H4 histone tail fragments shown in sticks with NZ atoms of  $Lys^+$  as blue spheres. The two top DNA molecules (*yellow* and *beige*) lie with tails approximately parallel to each other, with axis-axis distance in the range 27–29 Å; several histone fragments bridge between these molecules. (b) No-Tail system,  $t = 16.00$  ns. DNA 22-mers repel each other and are separated by distances expected for evenly distributed rods (see also Figs. 5 and 7). PDB files with coordinates of all (excluding water) atoms of the snapshots shown in the figure are given in Supplementary Material.

Salt Free

Low Salt

Normal Salt

Mg Salt

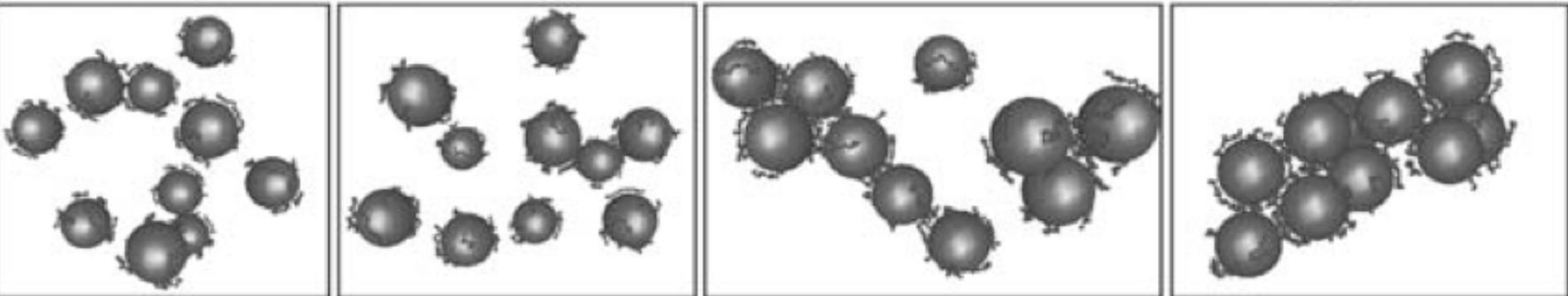


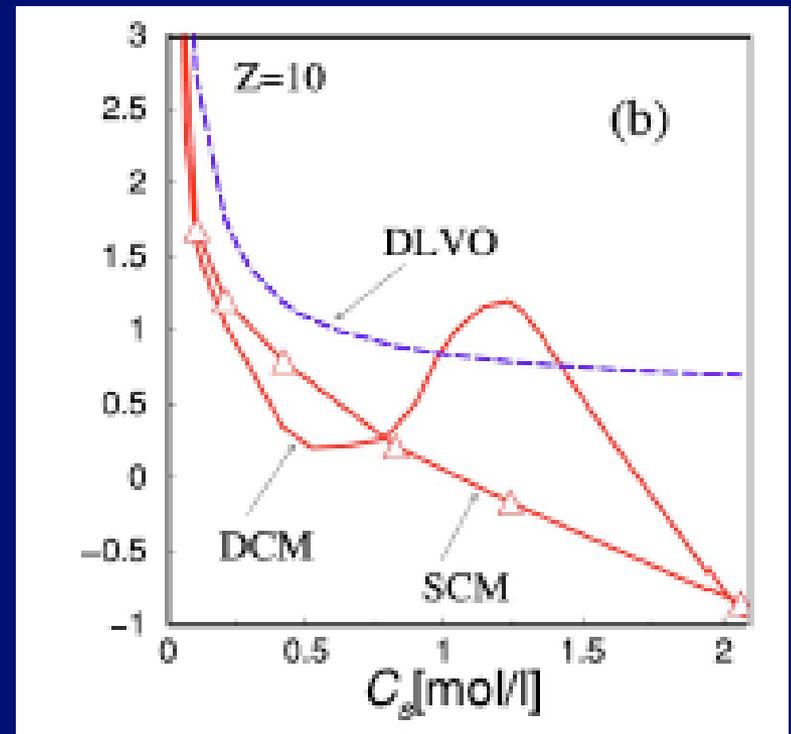
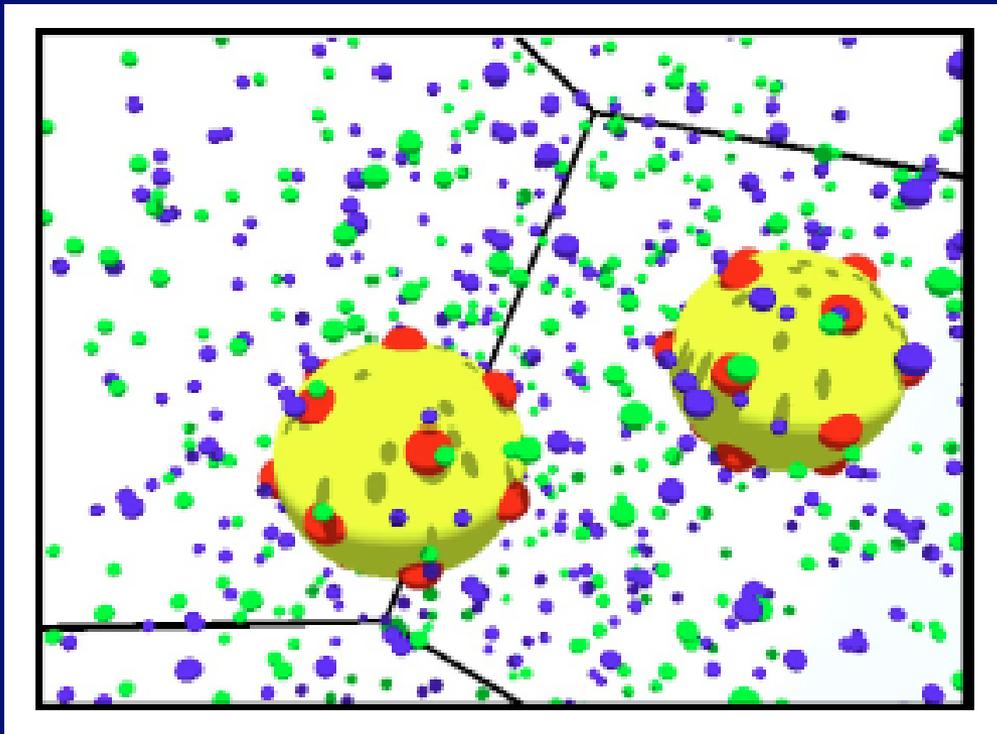
FIGURE 4 Snapshots showing distribution of the NCP particles at the end of the four coarse-grained MD simulations with different concentration of  $K^+$  (three pictures to the left) and in the presence of  $Mg^{2+}$  (right).

## Bridging can not be the only culprit

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

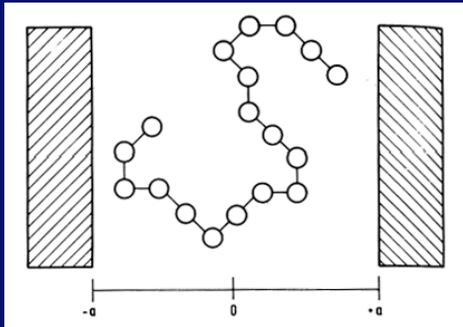
- lysozyme (Tessier et al. 2002)
- b-lactoglobulin (Piazza et al. 2002)
- apoferritin (Petsev et al. 2000) ...

Patchiness of the surfaces!



Allahyarov et al. (2003):

# Polyelectrolyte bridging between charged surfaces



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).

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

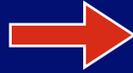
The standard PB equation for mobile counterions.

# Polyelectrolyte Poisson - Boltzmann theory

The Poisson - Boltzmann equation for PE.

$$-\epsilon\epsilon_0\nabla^2\phi = e_0n_0 e^{-\frac{e_0\phi}{kT}}.$$

simple counterions



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

polyelectrolyte counterions

Polyelectrolyte PB equation (Podgornik, 1990)

(Similar theory by Akesson et al. 1989.)

Ground state dominance ansatz  $N \gg 1$ .

Usual in polymer theory.

Edwards equation.

Monomer density.

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

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

Only the lowest lying eigenvalue remains in the energy spectrum.

This leads to the free energy:

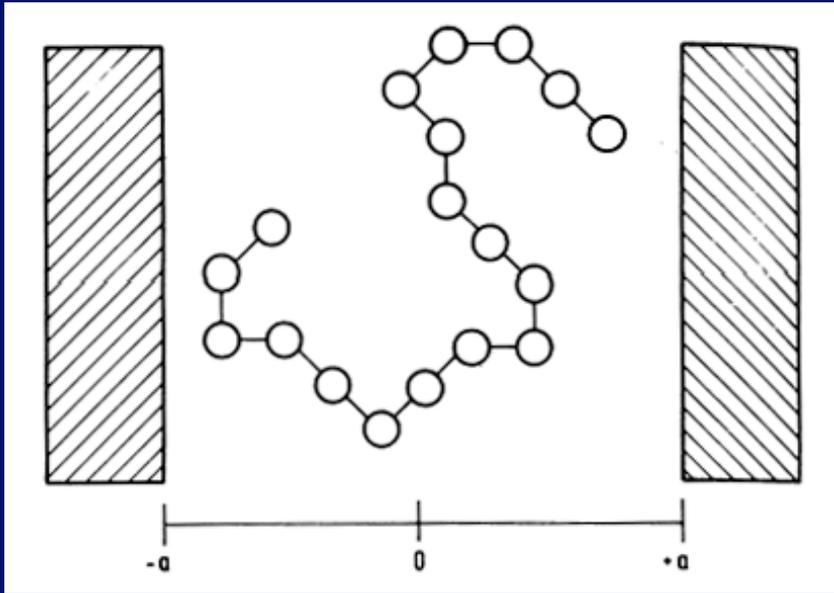
$$\mathcal{F} \cong k_B T E_0 N.$$

Free energy.

Solve the polyelectrolyte PB equation for the lowest energy eigenfunction.

# PE-PB

Polyelectrolyte Poisson - Boltzmann equation.



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

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

A **coupled** set of two equations for two fields: polymer density field and electrostatic potential.

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

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

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

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

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

# Single chain - numerics

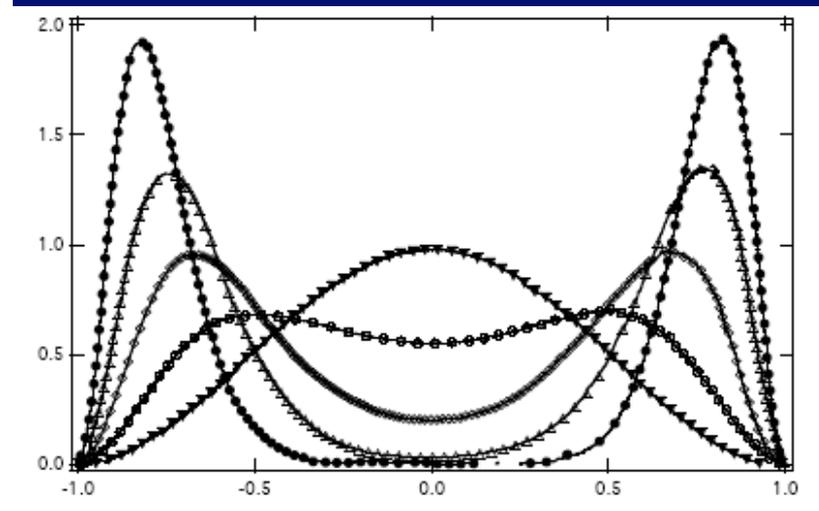
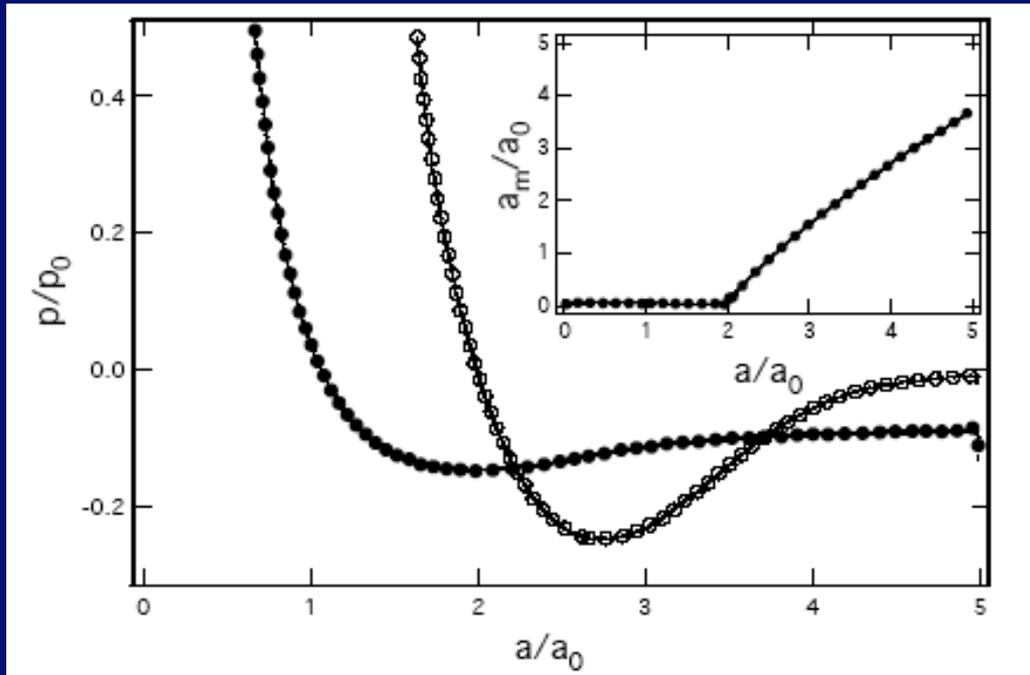
There are some nice analytical limits.

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:

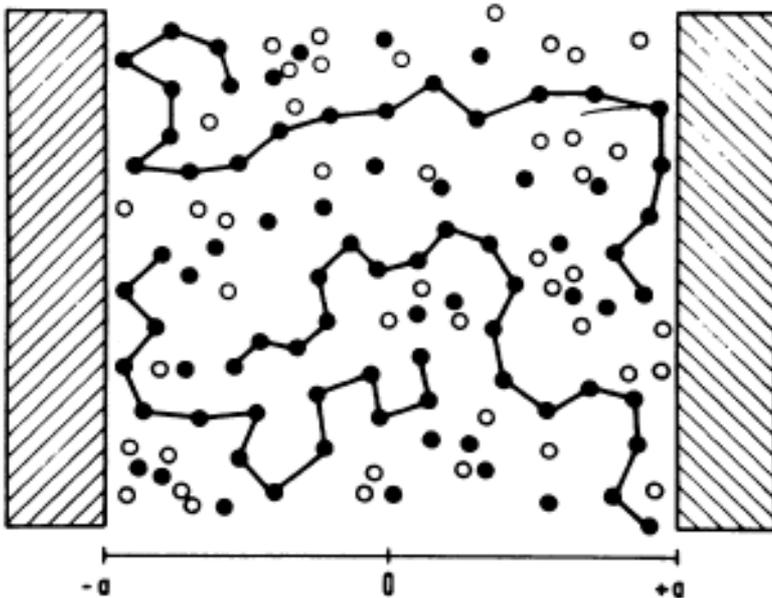
$$E_N = \frac{\ell^2}{6} \left( -\lambda_B^{1/3} a + ai_0 - \frac{1}{2} C(ai_0) \exp \left( -\frac{4}{3} \sqrt{\lambda_B a^3} \right) \right)$$



Monomodal-bimodal transition

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

# PE chain plus mobile ions



Polyelectrolyte plus mobile salt ions.  
Ground-state dominance:

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

Polyelectrolyte PB equation:

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

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

This is the standard PB part.

Dimensionless formulation  $\kappa \ell.$

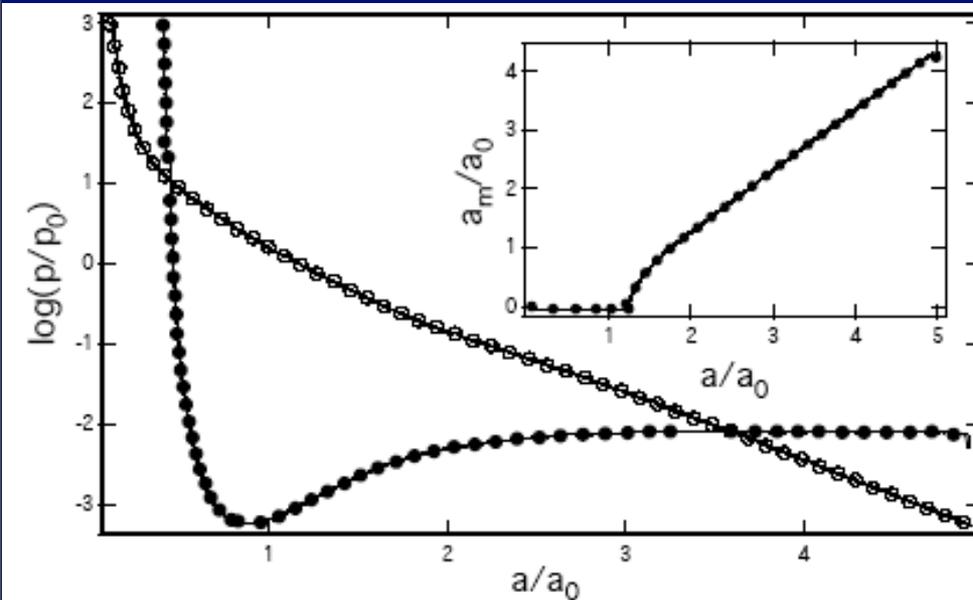
Large parameter space

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

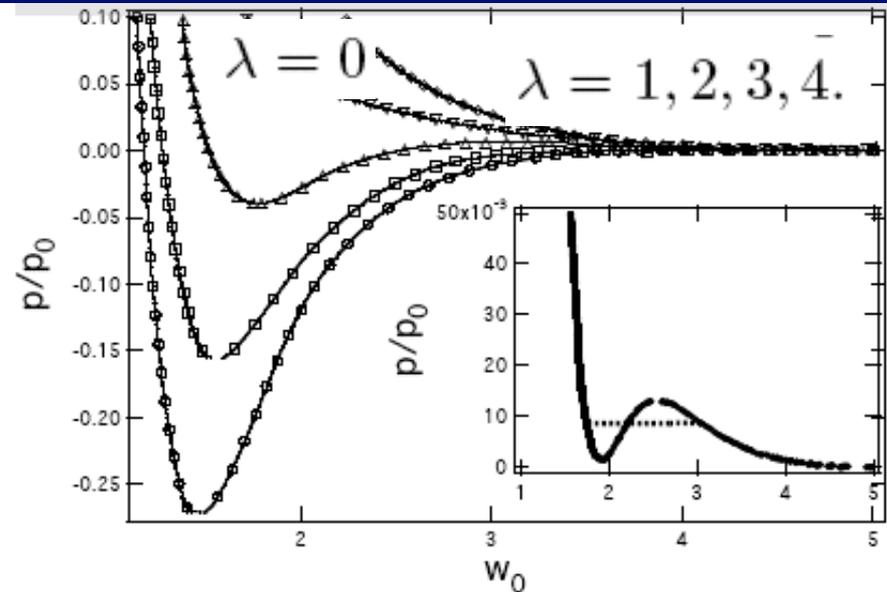
$$\lambda = \frac{\beta e_0^2 N}{\epsilon \epsilon_0 \kappa S} \quad \text{Monomer density}$$

$$w_0 = \kappa a \quad \text{Separation}$$

# Polyelectrolyte bridging with salt ions



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



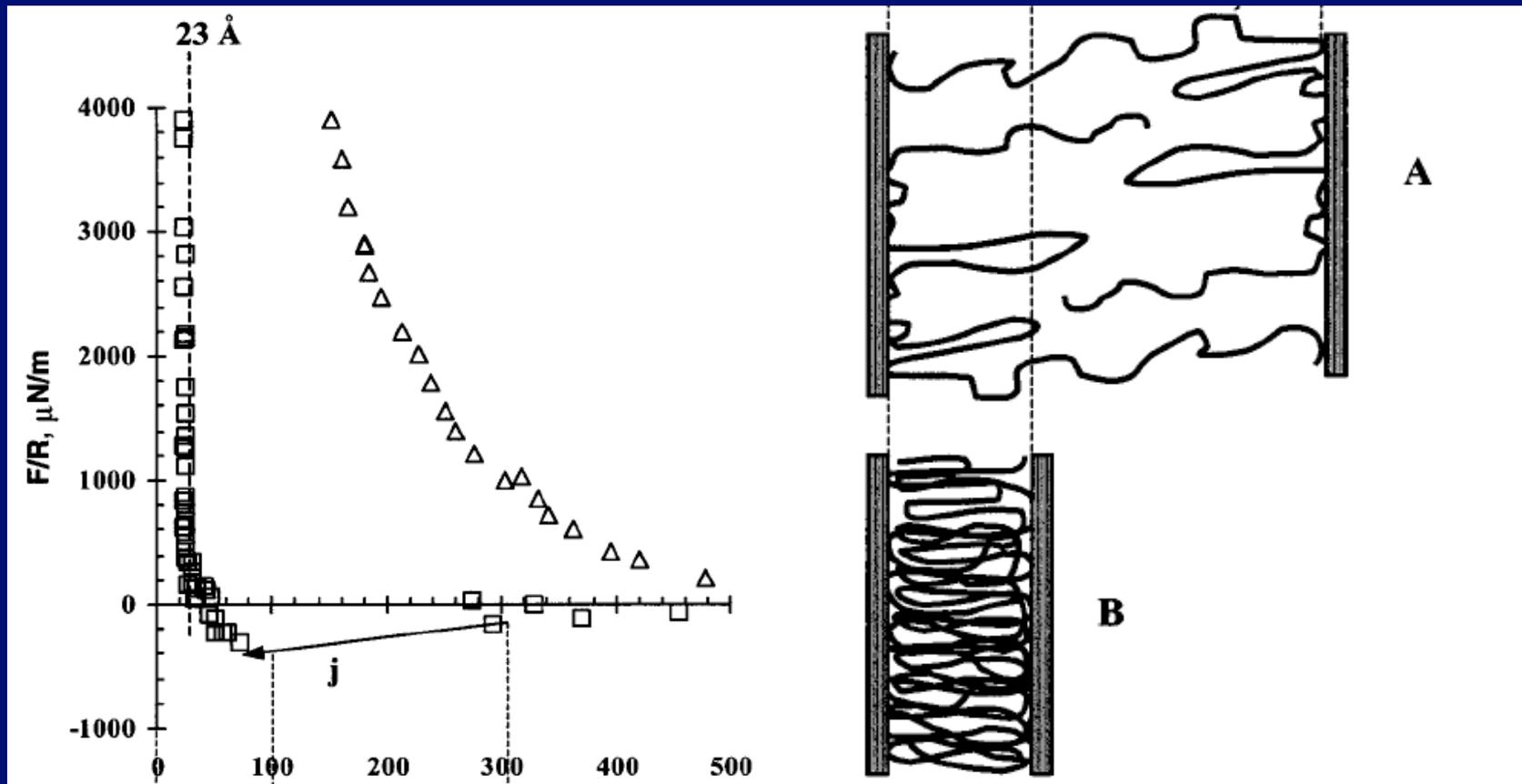
$\lambda = 2.5$  and  $\Gamma = 5.45$ .

$\Gamma = 5.45, l = 2.5$  (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)

# Carged surfaces with PE chains



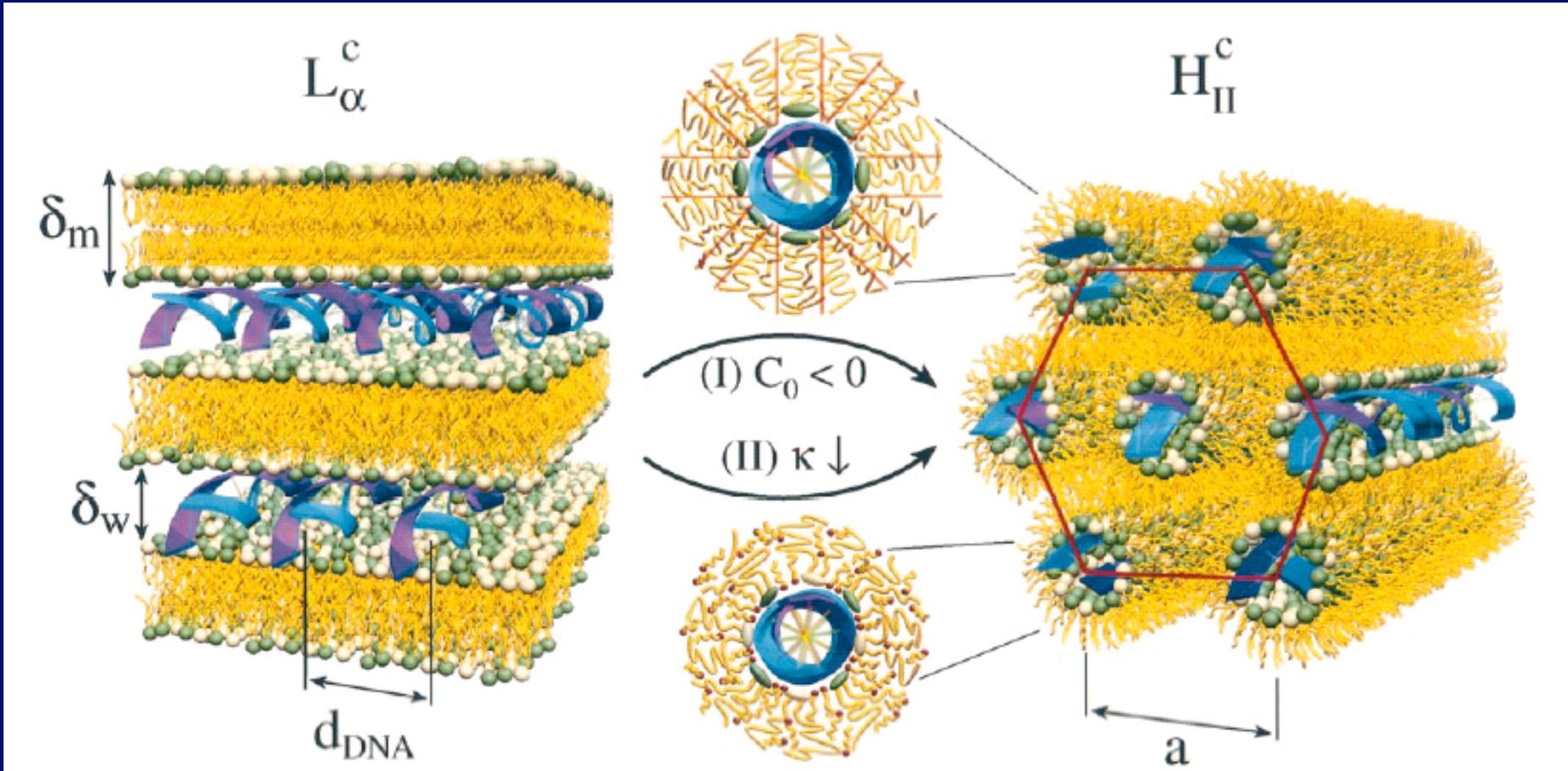
Abraham et al. (2001)

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.

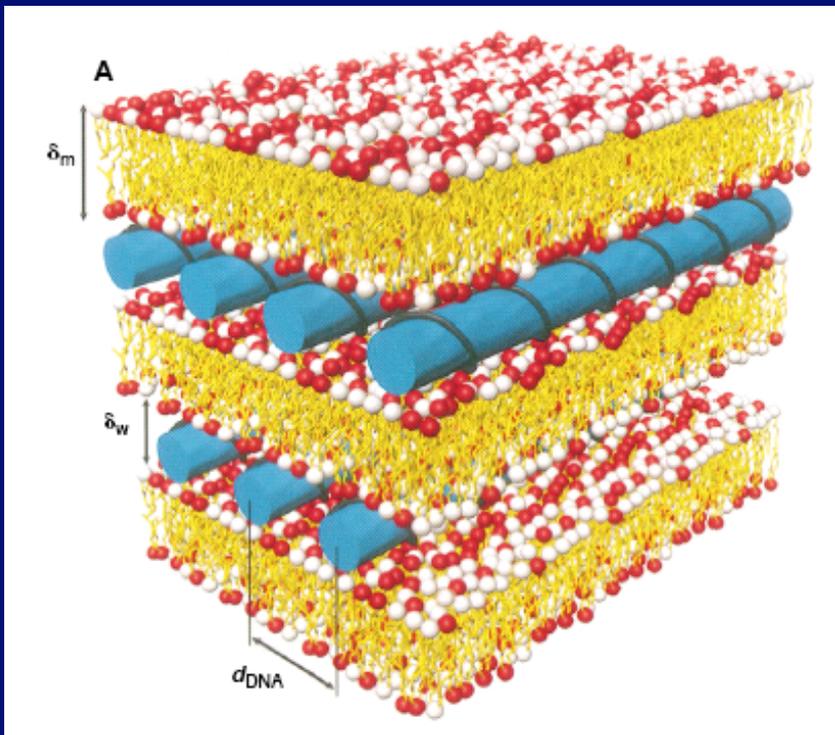
# Genosomes

Macromolecular complexes composed of DNA and lipids (Safinya et al. 2000 and later)

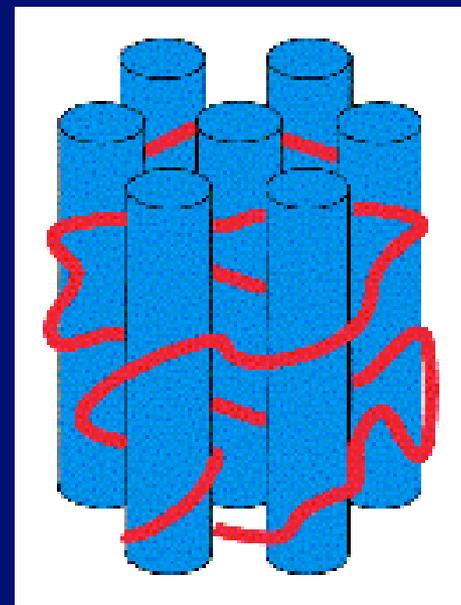
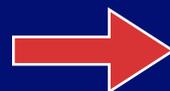


Raedler et al. 1997. Complexes of DNA and cationic lipids or cationic polymers. DOTAP(dioleoyltrimethylammoniumpropane)and the neutral helper-lipid DOPE(dioleoylphosphatidylethanolamine), or, DOPC(dioleoylphosphatidylcholine).

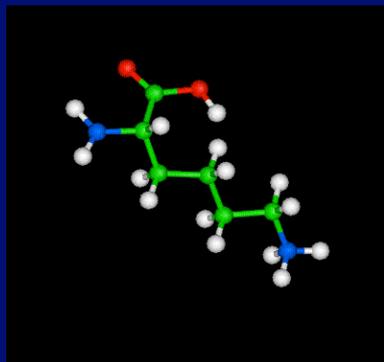
# DNA and cationic PE



Complexes of DNA and cationic lipids.  
DOTAP + helper lipid. (Safinya et al. 2003)

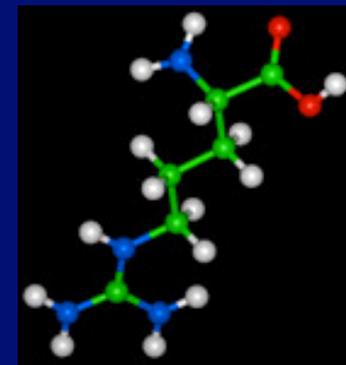


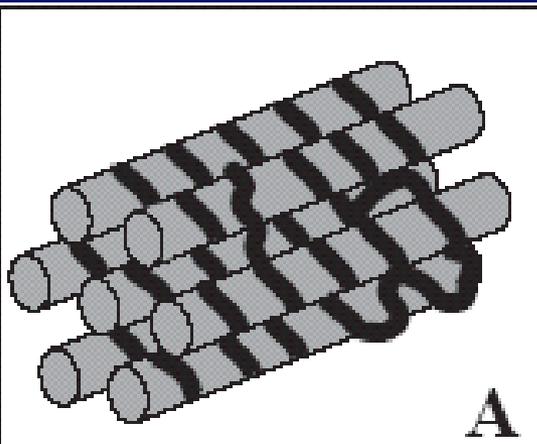
Complexes of DNA and cationic PE.  
poly-L-lysine (PL), poly-L-arginine (PA),  
spermine (Sp), and linear and branched  
polyethyleneimine (IPEI and bPEI).



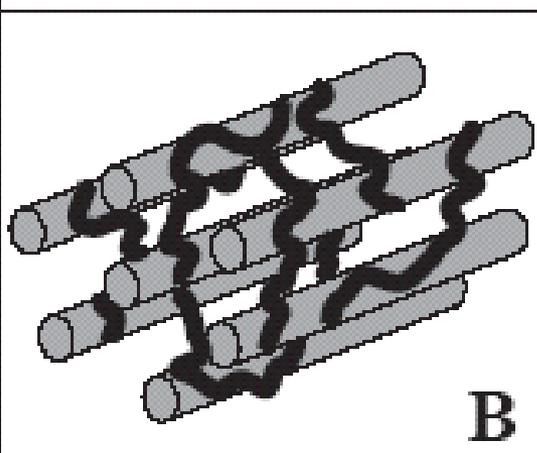
poly-L-lysine (PL)  
poly-L-arginine both of 30-100 units.

de Rouchey et al. 2004.

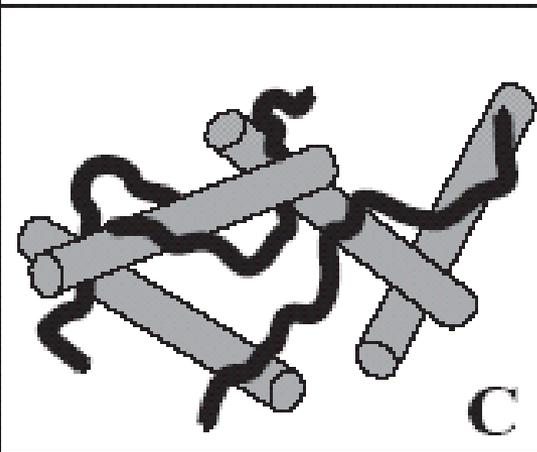




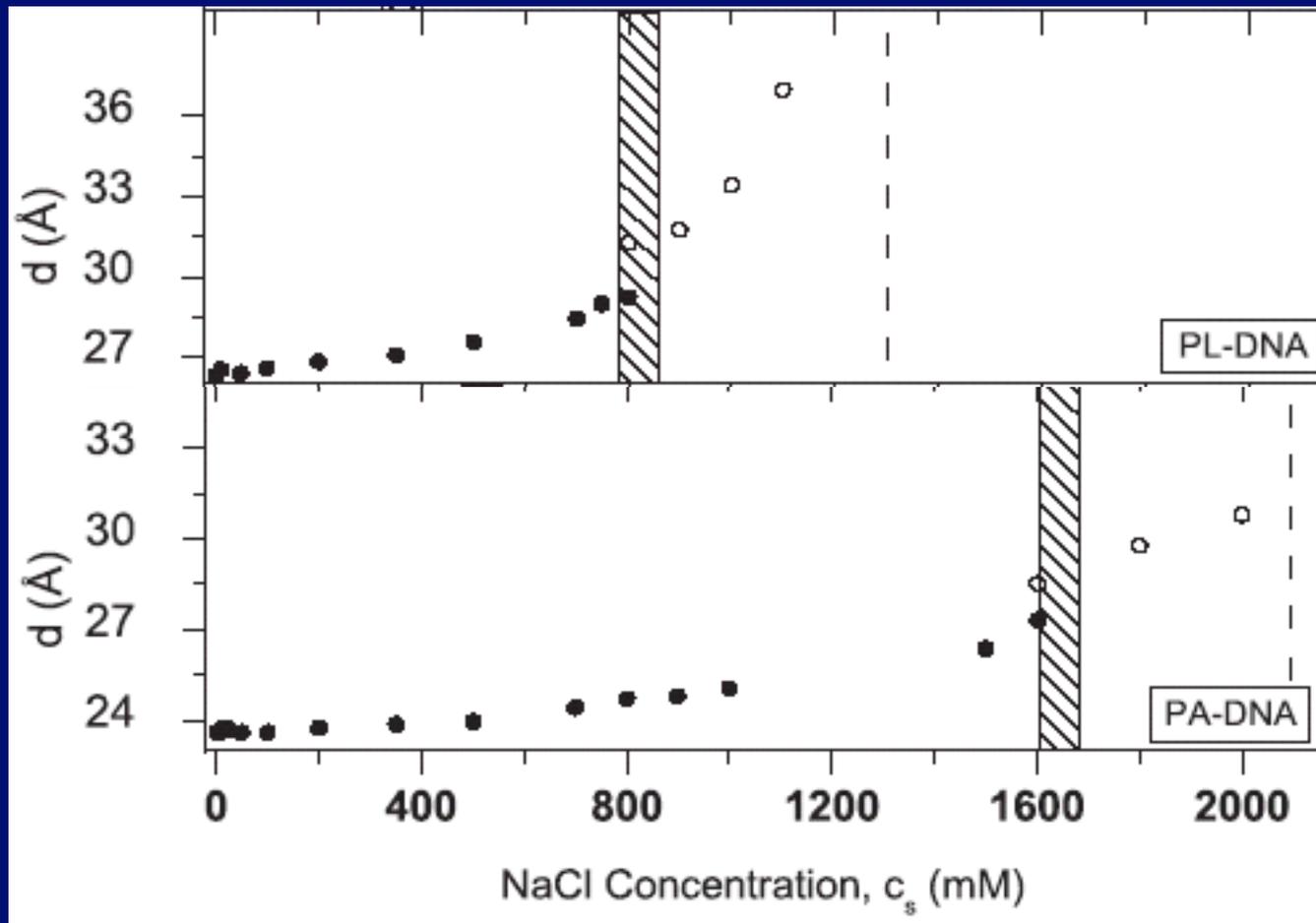
A



B



C

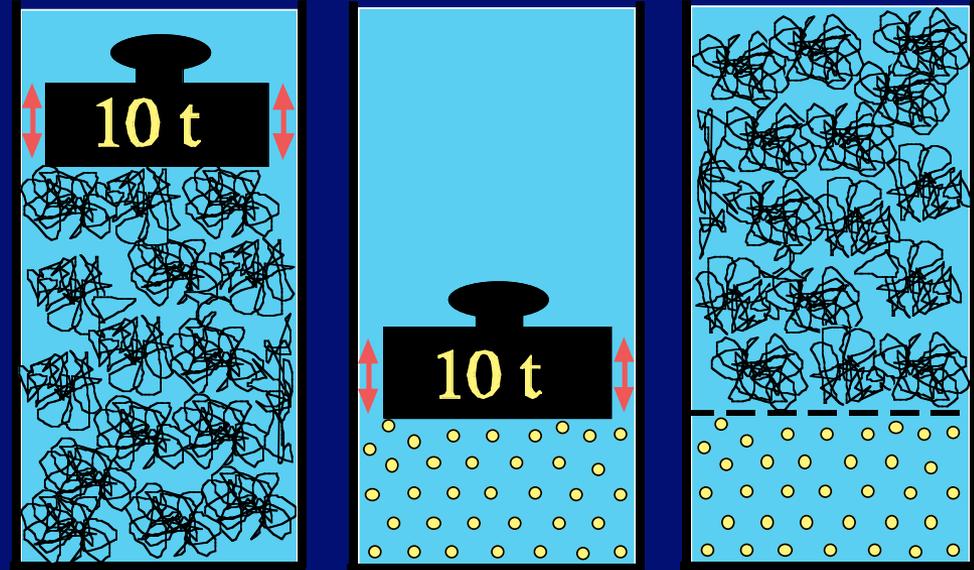
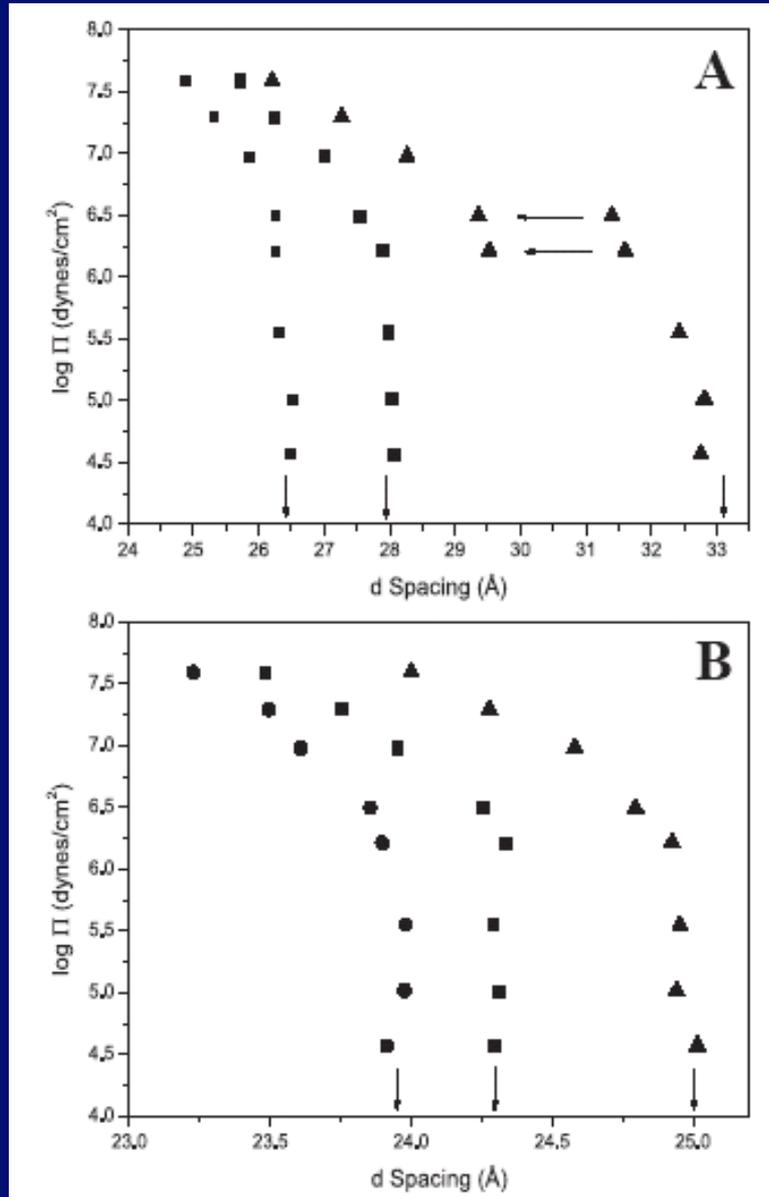


SAXS on PL-DNA and PA-DNA.  
Tight bundle, loose bundle and isotropic.

On concentrating the salt (screening)  
the system becomes unstable.

# Osmotic stress experiments

DeRouchey et al. osmotically compressed the genome.

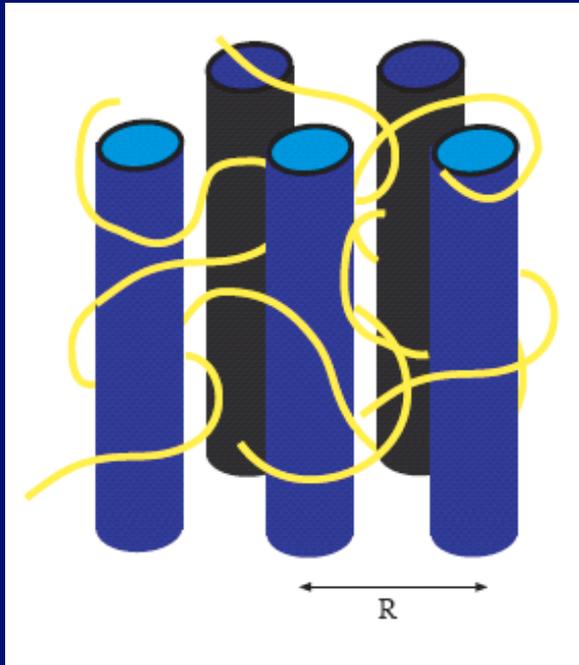


Evidence of attractions in the jumps  
(van der Waals isotherm!)

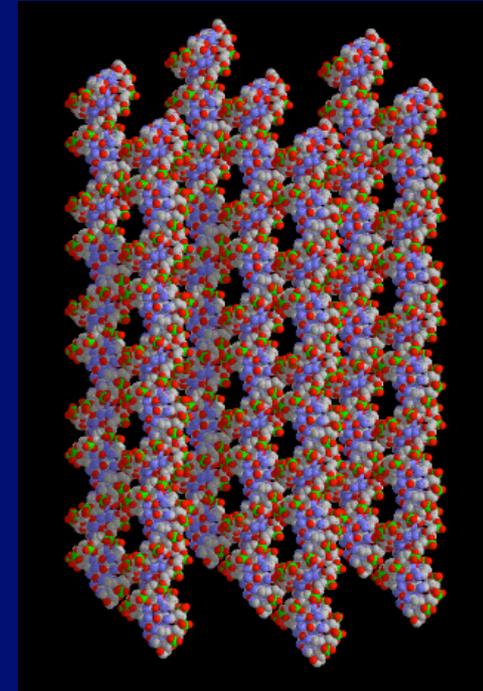
Osmotic pressure of DNA, stressed by solutions of PEG (Mw~20kDa) as a function of the d spacing for (A) PL-DNA and (B) PA-DNA polyplexes at three different salt concentrations.

Shown are (circle) 50mM, (square) 500mM, and (uptriangle) 900mM NaCl.

# A model of PE bridging



- hexagonal lattice of charged macroions
- infinitely rigid
- flexible, charged PE chains
- infinitely long
- Debye-Hueckel interactions
- ignore self-interactions
- ignore fluctuations (mean - field rules).



$$\beta\mathcal{H}[\mathbf{r}(n)] = \frac{3}{2\ell^2} \int_0^N \left( \frac{d\mathbf{r}(n)}{dn} \right)^2 dn + \beta \int_0^N V(\mathbf{r}(n)) dn,$$

Hexagonal symmetry of the interaction potential as well as of the PE density

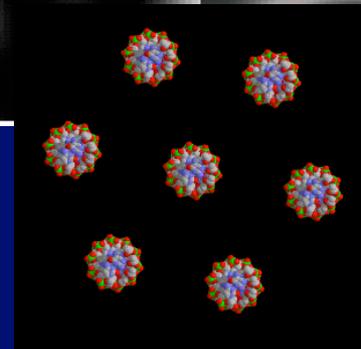
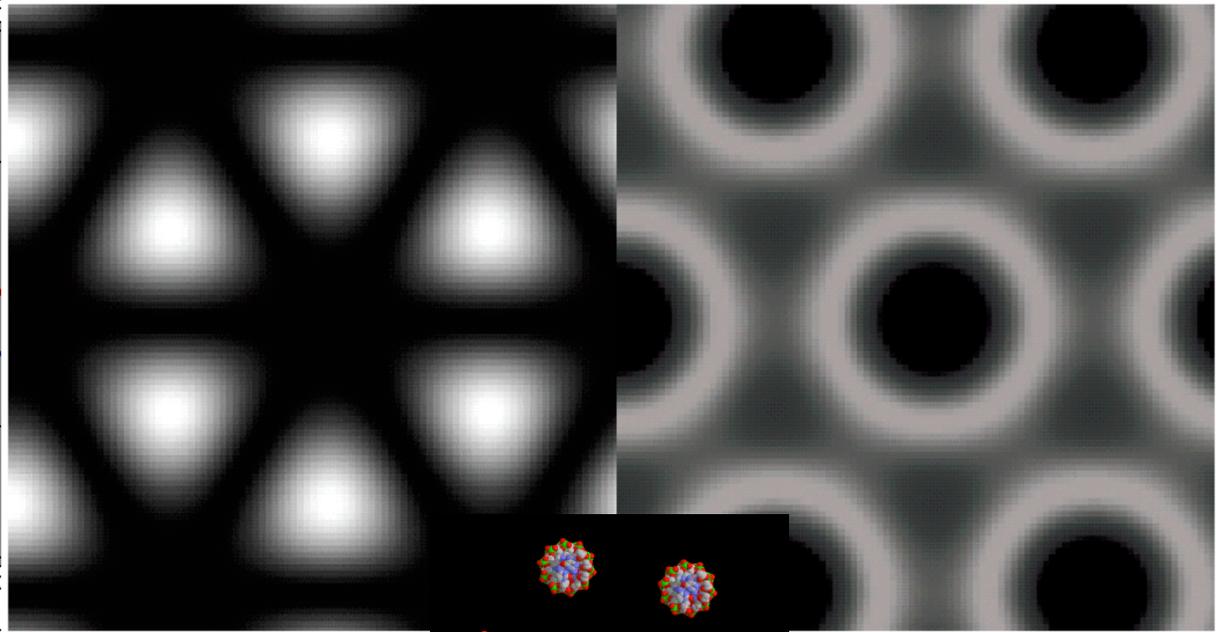
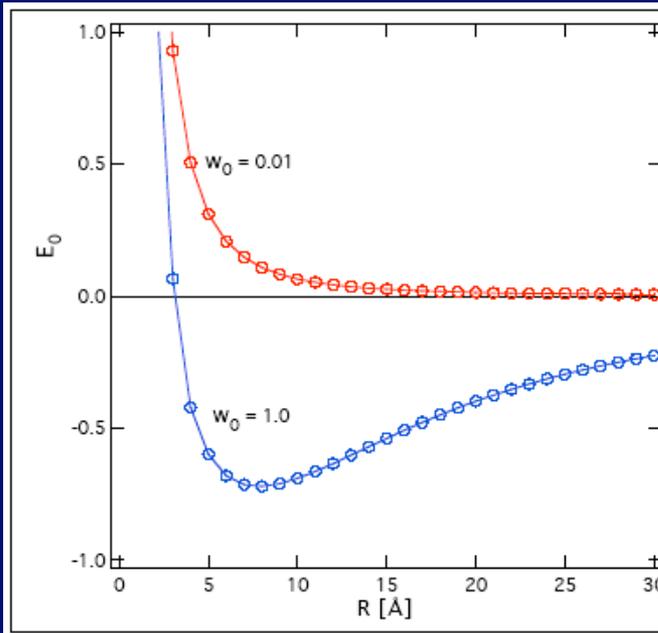
$$V(\boldsymbol{\rho}) = -k_B T w_0 \sum_i K_0(|\boldsymbol{\rho} - \boldsymbol{\rho}_i|).$$

$$V(\boldsymbol{\rho}) = \sum_{\mathbf{G}} e^{i\mathbf{G}\cdot\boldsymbol{\rho}} V(\mathbf{G}), \quad \sum_i e^{-i\mathbf{G}\cdot\boldsymbol{\rho}_i} = \mathcal{N},$$

Expand the interaction potential wrt the symmetry of the lattice.

# Analogy with electrons in a crystal

Two types of density distribution of PE monomers.



$$\frac{\ell^2}{6} G^2 u_n(\mathbf{G}) + \beta \sum_{\mathbf{G}'} V(\mathbf{G} - \mathbf{G}') u_n(\mathbf{G}') = E_n u_n(\mathbf{G}),$$

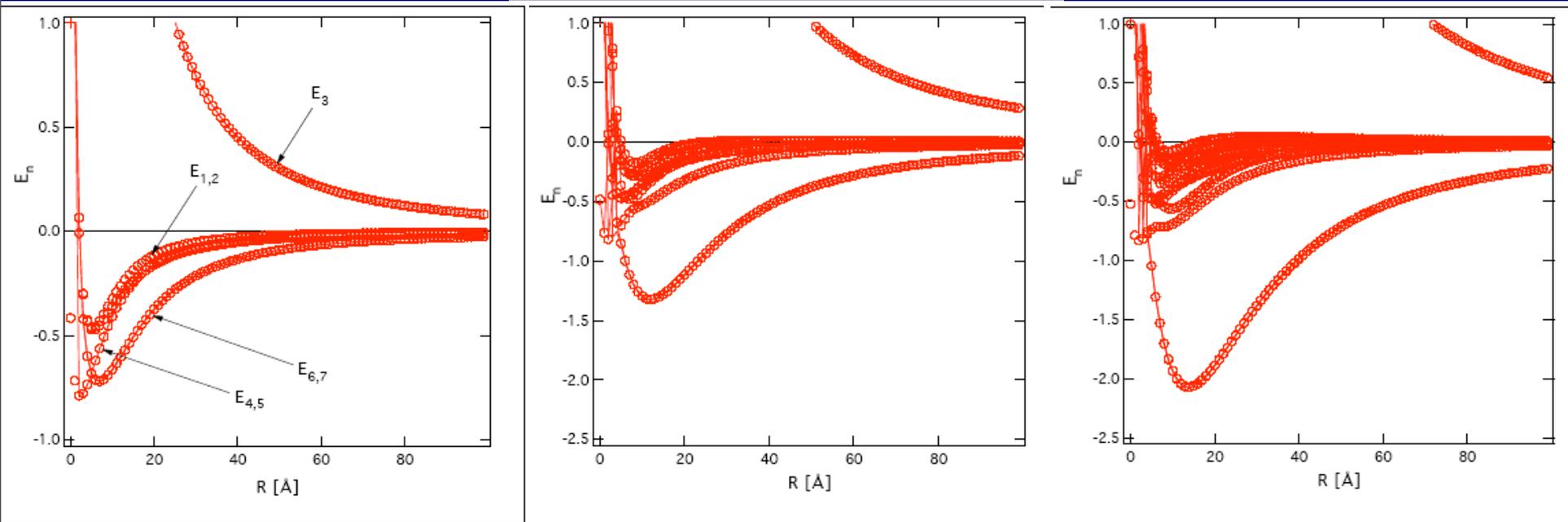
Eigenfunctions and eigenenergies.

$$V(\mathbf{G}) = -k_B T w_0 \frac{\mathcal{N}}{S} \int_S d^2 \rho e^{-i\mathbf{G} \cdot \rho} K_0(\kappa |\rho|) = -k_B T w_0 \frac{\mathcal{N}}{S} \frac{2\pi}{G^2 + \kappa^2}.$$

Interactions with hexagonal symmetry.

# Expanding reciprocal lattice space...

We simply follow the standard approach of solid state physics for electrons in a crystalline lattice...



Lowest eigenvalue determines the free energy

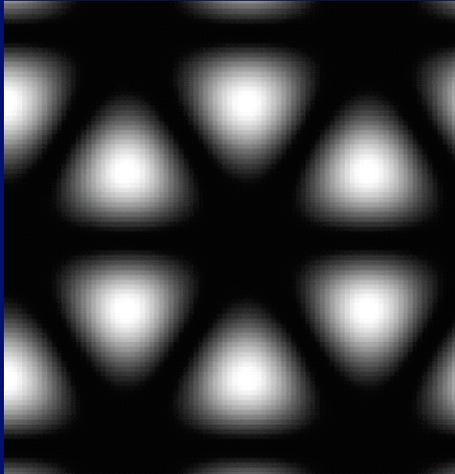
$$\mathcal{F} \cong k_B T E_0 N.$$

Asymptotic behavior of lowest eigenvalue, but ...

$$E_{4,5}(R \rightarrow 0) = \frac{8\ell^2\pi^2}{9R^2} - \frac{w_0N}{S\kappa^2} - \frac{5w_0NR^2}{64\pi^2S} + \mathcal{O}(R^4) \rightarrow \frac{8\pi^2}{9} \frac{\ell^2}{R^2}$$

$$E_{4,5}(R \rightarrow \infty) = \left( -\frac{64w_0\pi^2N}{S\kappa^4R^2} + \frac{8\ell^2\pi^2}{9R^2} \right) + \frac{2048w_0N\pi^4}{3S\kappa^6R^4} + \mathcal{O}(R^{-6}) \rightarrow -\left( \frac{64w_0N\pi^2}{S\kappa^2} - \frac{8(\kappa\ell)^2\pi^2}{9} \right) \frac{1}{(\kappa R)^2}.$$

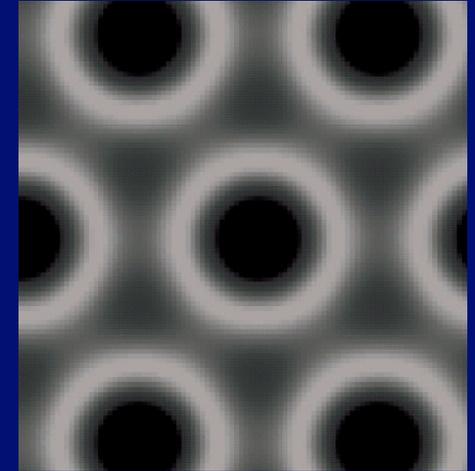
# Salient features of the interaction



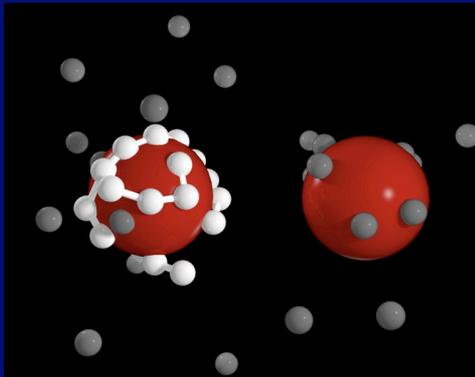
A branching point:

$$w_c = \frac{(\kappa\ell)^2 \kappa^2}{72 \frac{N}{S}},$$

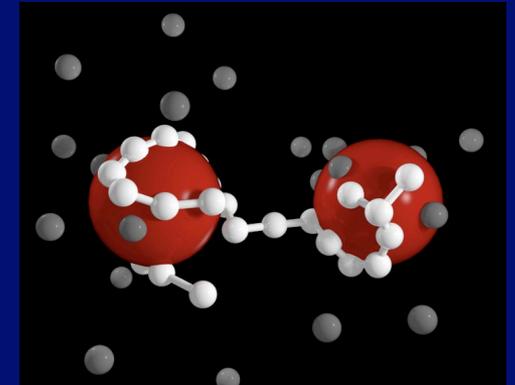
Bridging – no bridging



Separating the bridging configurations from the sterically compressed configurations of the chain.



How far does the bridging extend?



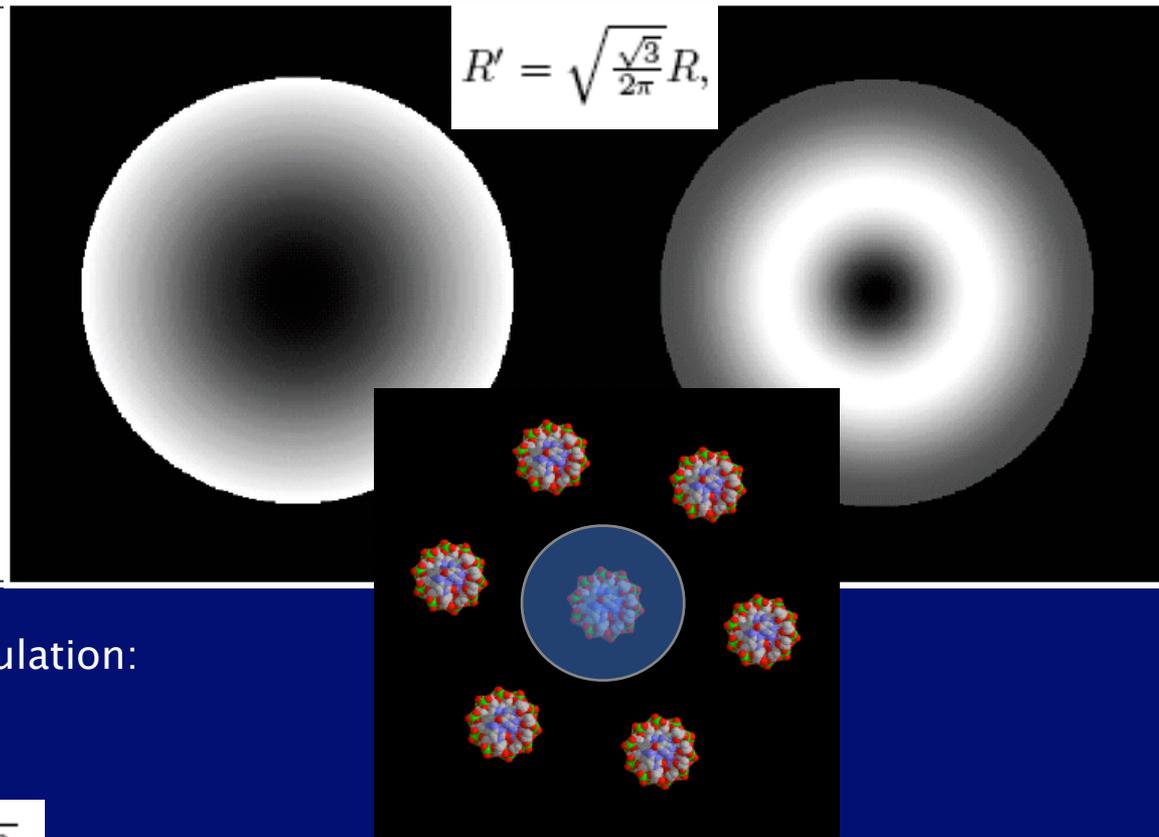
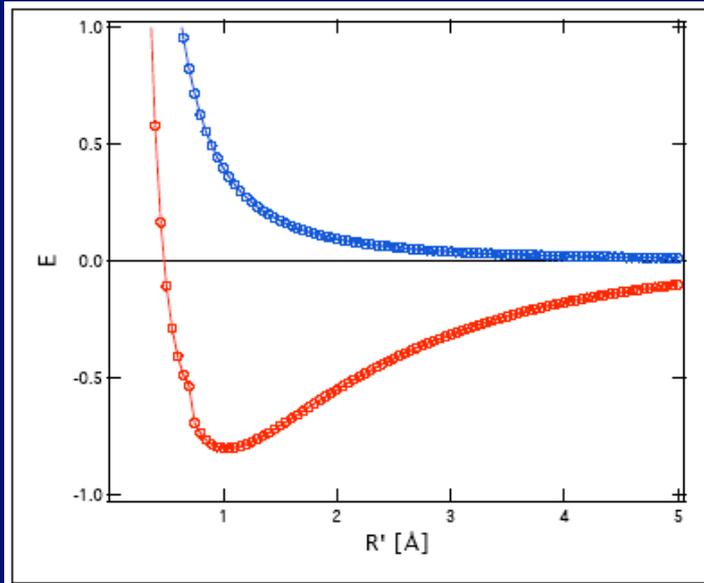
Long-range bridging effects:

$$- \left( \frac{64w_0 N \pi^2}{S \kappa^2} - \frac{8(\kappa\ell)^2 \pi^2}{9} \right) \frac{1}{(\kappa R)^2}.$$

Bridging interactions are not exponentially screened even on the MF level!

# Wigner - Seitz approximation

Since eigenfunction expansion is tedious and converges poorly.



Similar behavior as for RLV calculation:

A branching point:

$$\int_0^{R'} \sqrt{w_0 K_0(\kappa\rho)} d\rho = \frac{\pi}{2} \sqrt{\frac{\ell^2}{6}}.$$

$$w_c = (\mu/e)_c \ell_B \approx \frac{\pi^2}{0.1} (\kappa\ell)^2.$$

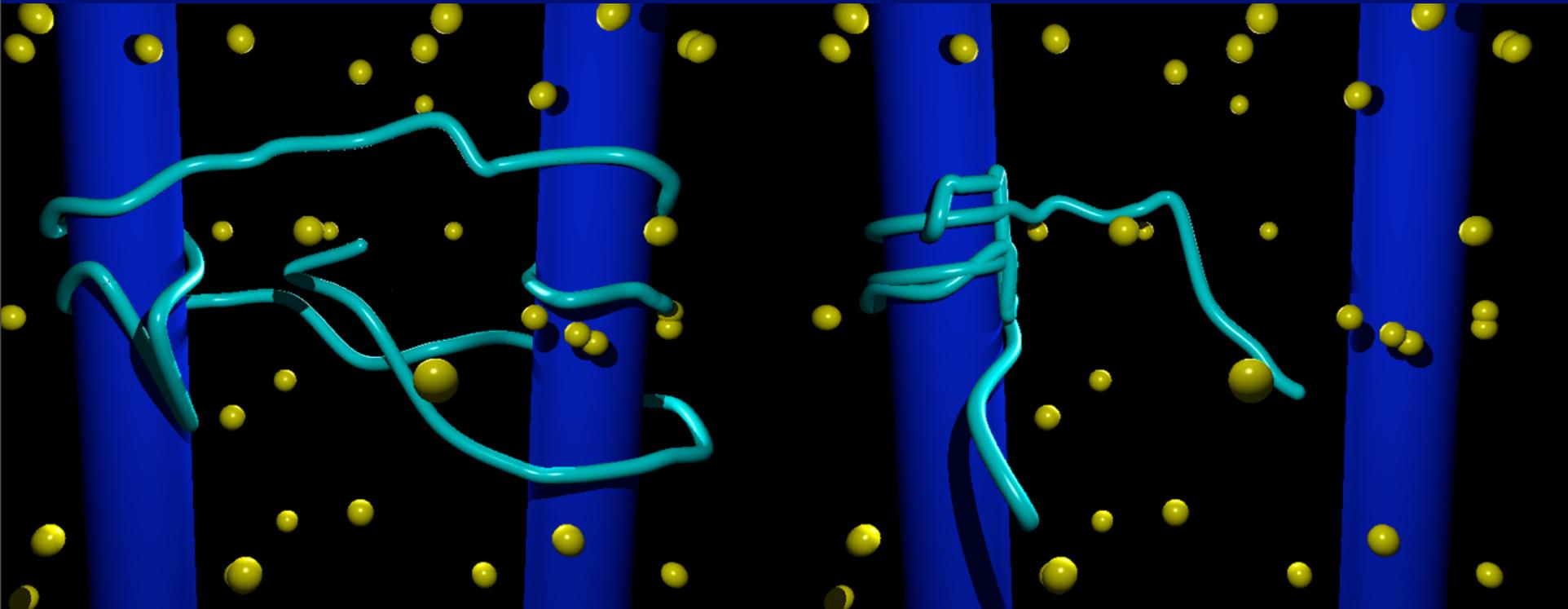
Long-range bridging effects:

$$E \simeq -\gamma (\ell^2 \rho_M) \quad \text{where} \quad \frac{3\pi^3}{32} < \gamma < \frac{25\pi^3}{216}.$$

$$\rho_M = 1/\pi R'^2$$

# Polyelectrolyte bridging

Appears to be a very common effect with charged polymers.



One should apparently differentiate between two very different cases:

PE bridging between pairs of macroions and  
PE bridging in a lattice of macroions

The strength and the range of PE bridging is very different in these two cases. A nice correspondence with standard solid state theory.