Fluctuation and correlation forces in Coulomb fluids: An Overview

Ali Naji & Rudolf Podgornik
(KITP/UCSB, Sept 2008)

In two parts:

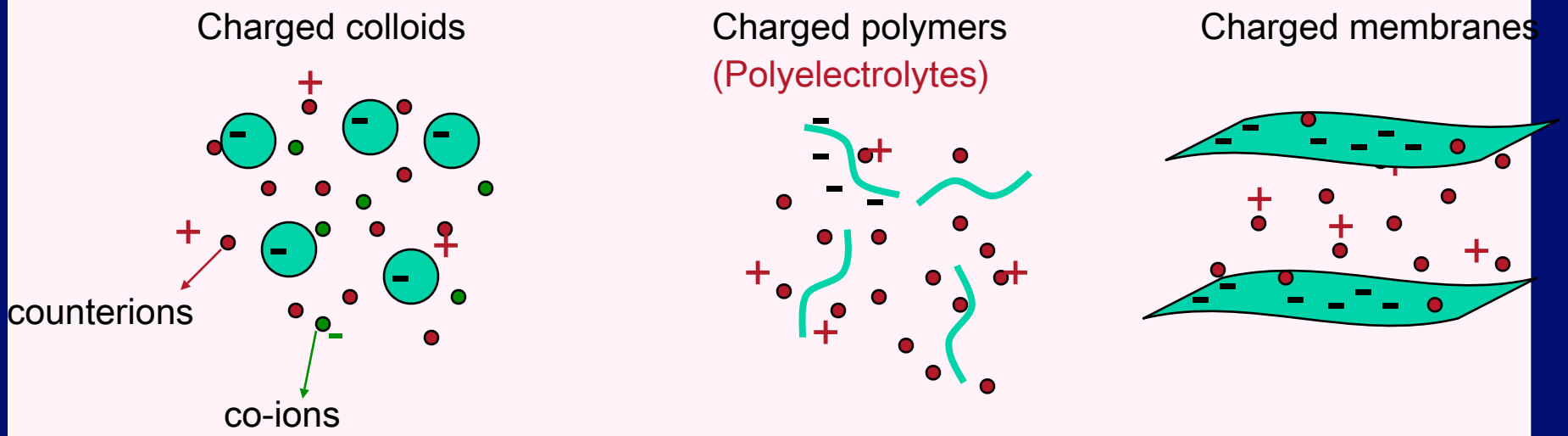
Ali:

- Introduction: Classical charged systems
- Field-theoretical formalism: weak--strong coupling paradigm
- Uniformly charged planar surfaces: fluctuations & correlations
- Disorder in the surface charge distribution

Rudi:

- Asymmetrically charged surface (planar)
- Dielectric discontinuity effects
- Disorder-induced fluctuation forces vs van-der-Waals

Charged Soft Matter:

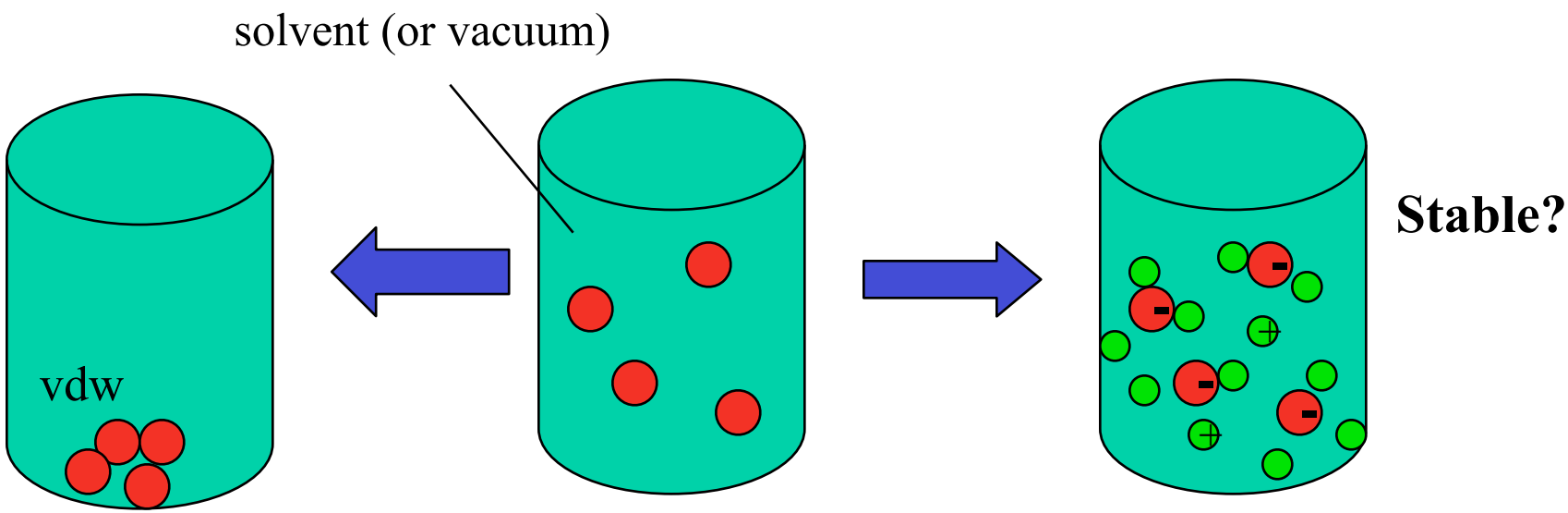


- structural properties and phase behavior (aggregation, crystallization, ...), equation of state, electrokinetics, etc.

Effective interaction between charged objects ('macroions')

charge fluctuations in bulk and on the boundaries

Stability of charged systems



counterions make the system globally **electroneutral**

DLVO theory **(Derjaguin, Landau, Verwey and Overbeek)**

Earnshaw, S., On the nature of the molecular forces which regulate the constitution of the luminferous ether, Trans. Camb. Phil. Soc., 7, pp 97-112 (1842)

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)

Derjaguin & Landau (1941)
"disjoining pressure"

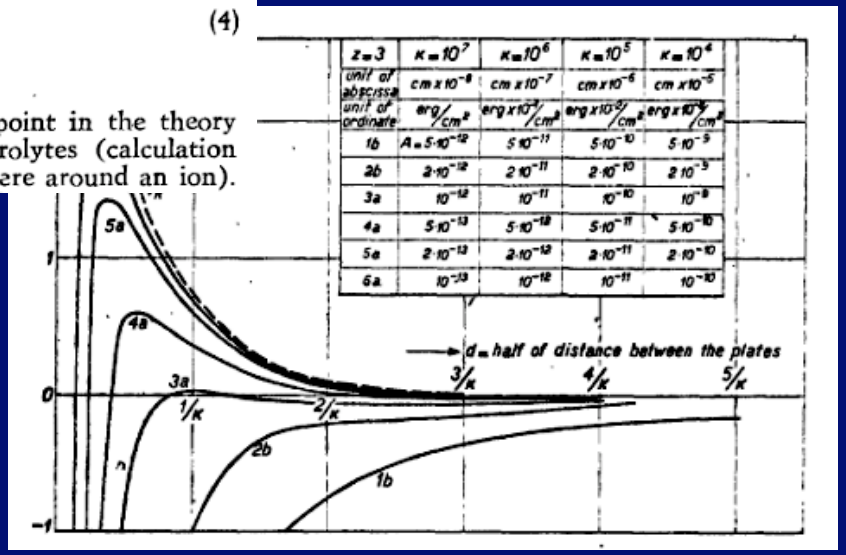
Hence we now have an expression for the charge density which may be inserted into eq. (1), when we obtain the *fundamental differential equation:*

$$\Delta\psi = \frac{8\pi nve}{\varepsilon} \sinh\,(ve\psi/kT) \qquad (3)$$

For small values of ψ this equation simplifies to

$$\left.\begin{aligned} \Delta\psi &= \frac{8\pi ne^2v^2\psi}{\varepsilon kT} = \varkappa^2\psi \\ \text{with: } \varkappa^2 &= \frac{8\pi ne^2v^2}{\varepsilon kT} \end{aligned}\right\} \qquad (4)$$

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.

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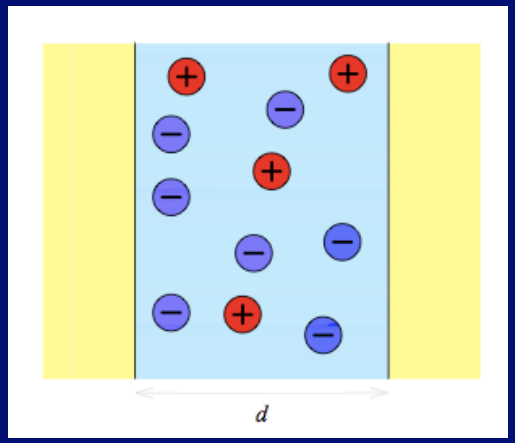
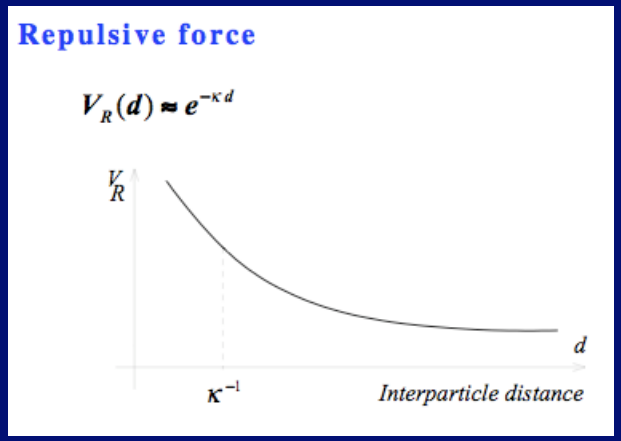
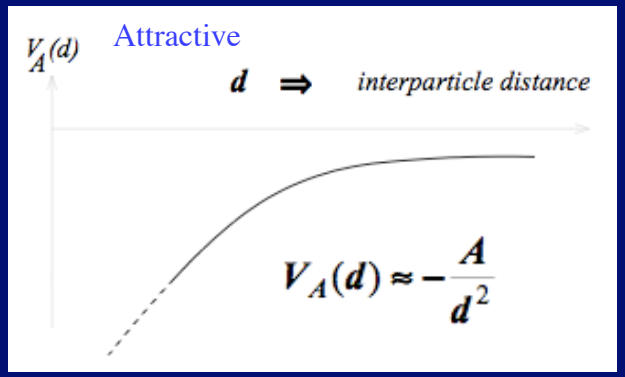
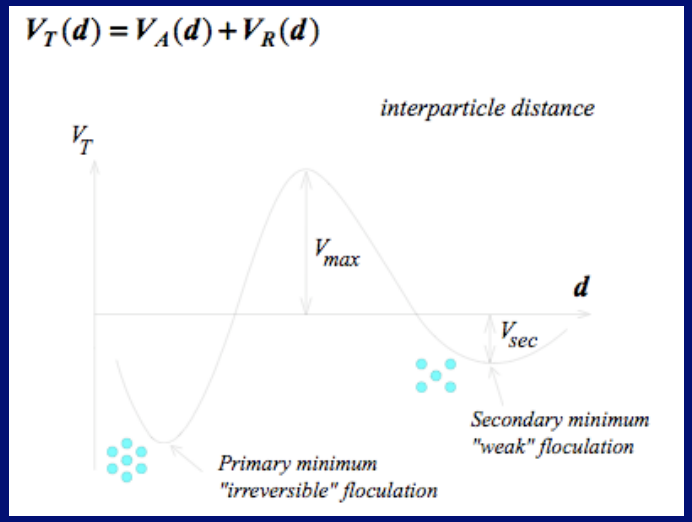
Electrostatics plus van der Waals.

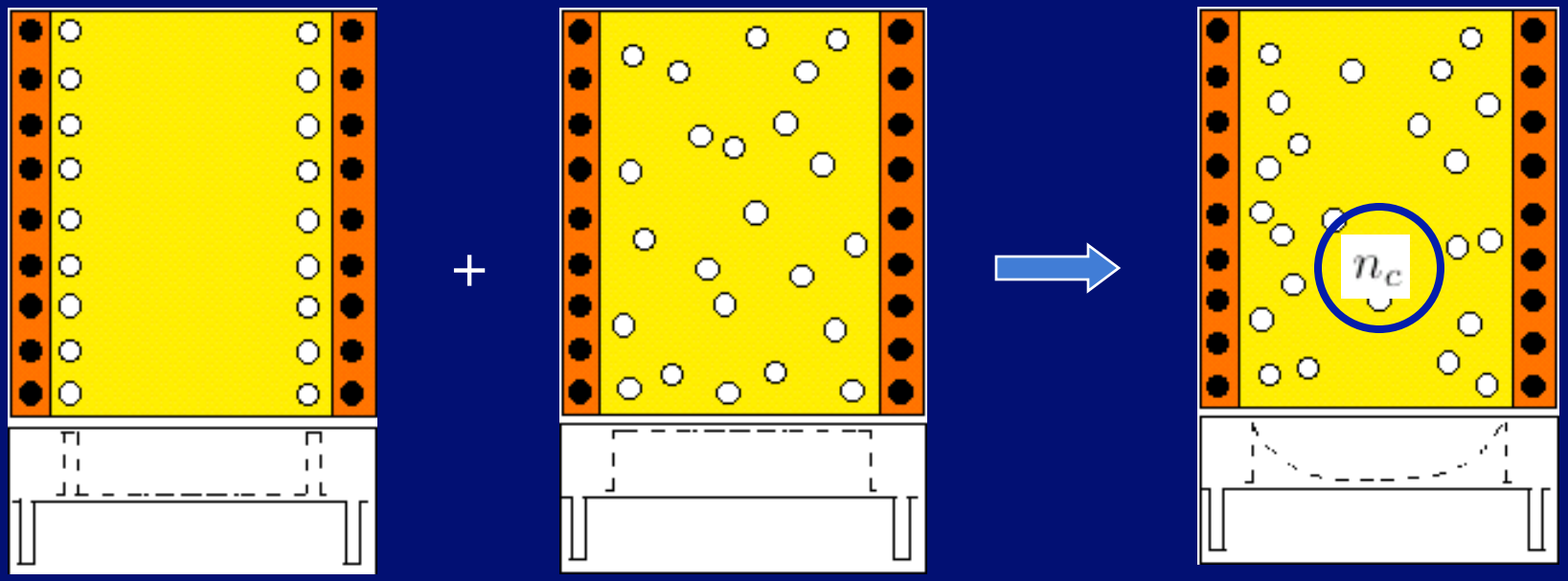








The Poisson - Boltzmann equation - collective description



electrostatic energy

ideal gas entropy

minimize to get equilibrium

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

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

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

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

plus electroneutrality

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

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

$$P = n_{\mathrm{mid}}\, k_{\mathrm{B}} T$$

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 double-layer 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.

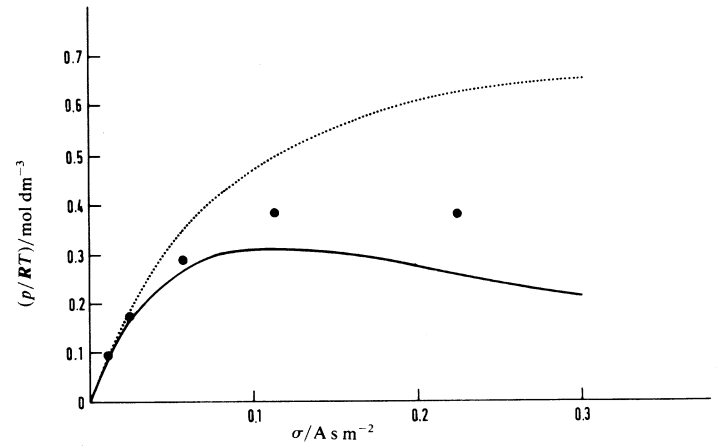


Fig. 4. The pressure in the counterion-only system at the intersurface separation $2a = 2.1$ nm as a function of the surface charge density. The counterions are monovalent. The PB approximation (· · ·) and the simulation results[4] (●) are also presented for comparison.

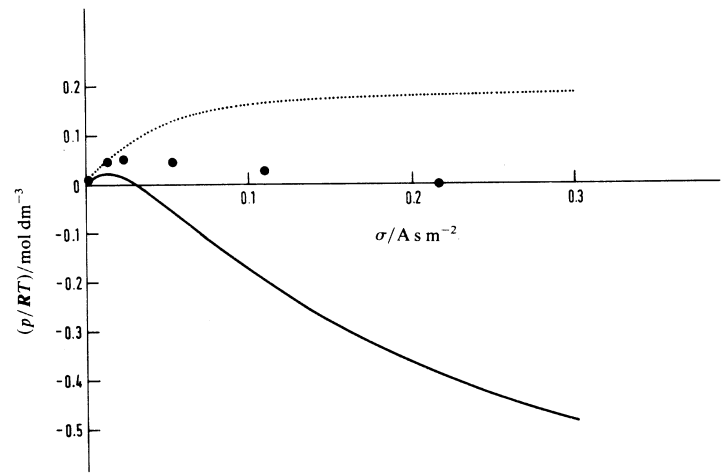
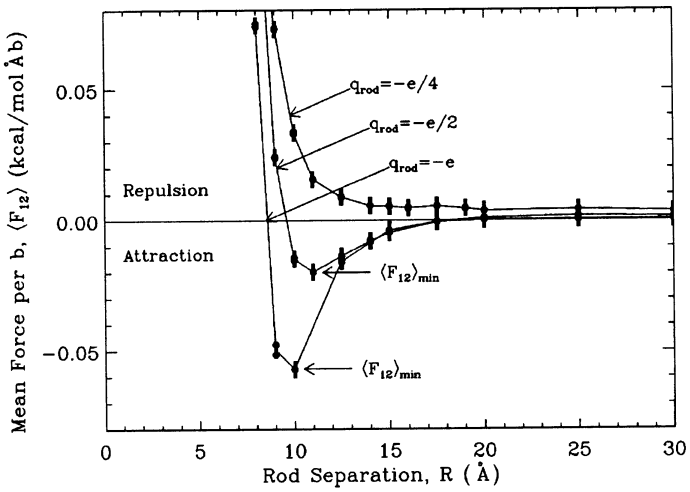


Fig. 5. As fig. 4 except that here the counterions are divalent.

Probably the biggest advance in colloid science since DLVO.

Getting worse and worse...



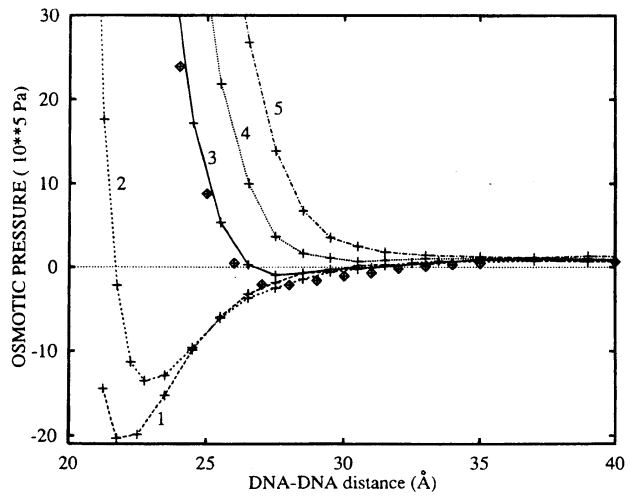
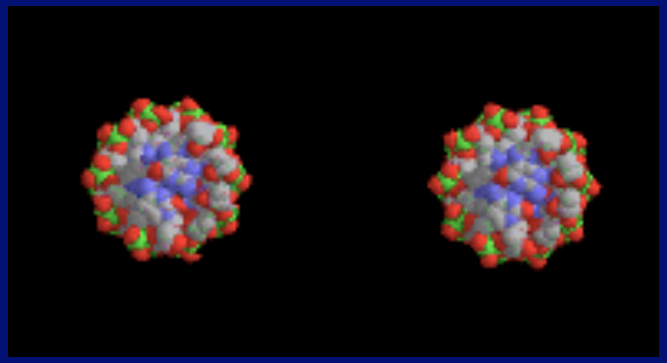


Figure 7. Osmotic pressure in the ordered DNA system with +2 counterions. Lines: one DNA in the cell and ion diameter $\sigma = 0$ (1), $\sigma = 1$ Å (2), $\sigma = 4$ Å (3), $\sigma = 5$ Å (4), $\sigma = 6$ Å (5). Points: seven DNA's in the cell and $\sigma = 4$ Å.

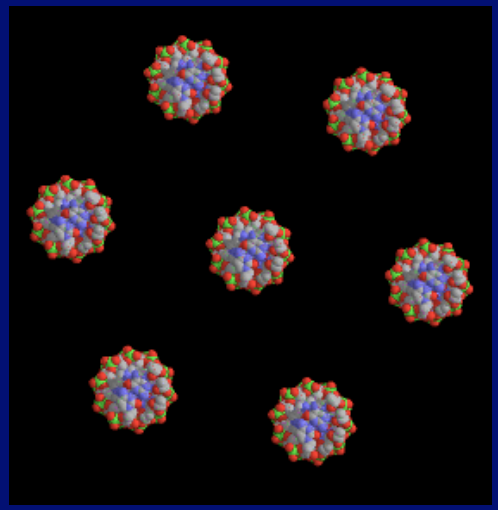
Attractions seem to be everywhere!

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

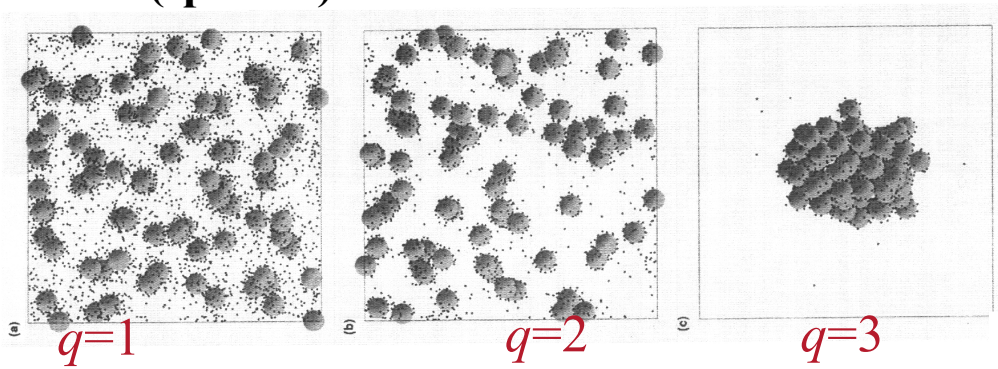


Screening. Debye length ~ 3.05 Å /$\sqrt{M}$

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



• **Colloids (spheres):**



Per Linse et al. (1999)

• **Microtubules (cylinders):**

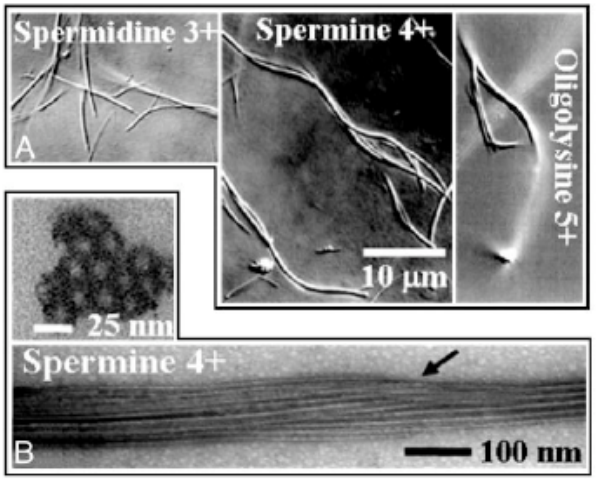


Fig. 2. Micron and nanometer scale images of the hexagonal bundle phase of microtubules. (*A*) DIC optical micrographs of hexagonal MT bundles with 3+ (20 mM spermidine), 4+ (5 mM spermine), and 5+ (2.5 mM oligolysine-five) counterions. (*B*) Plastic-embedded TEM cross section (*Upper*) and whole-mount TEM side view of hexagonal MT bundles (10 mM spermine) (*Lower*). A 3D schematic is shown in Fig. 1 *Left*.

D. Needleman-C. Safinya et al. (2004)

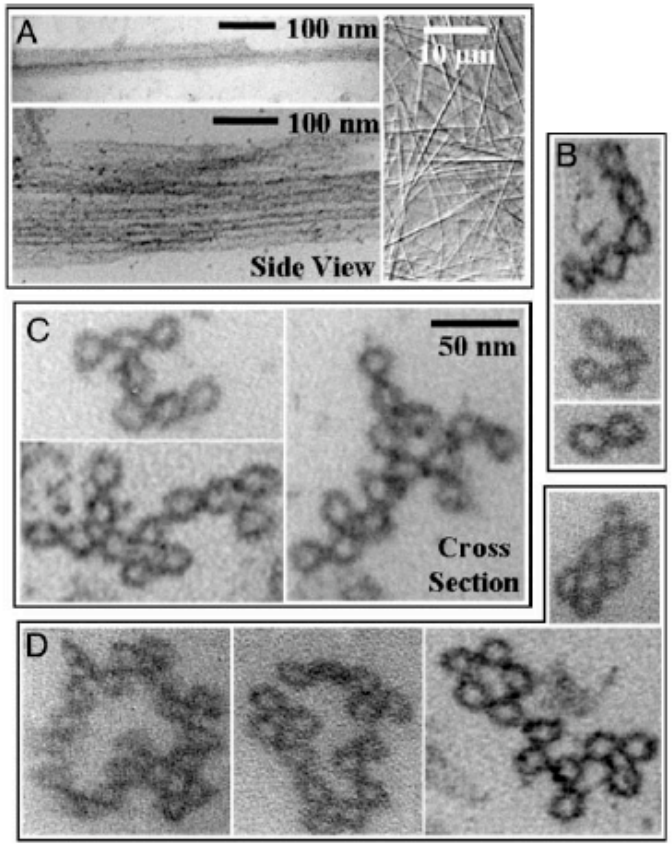


Fig. 3. Micron and nanometer scale images of the necklace bundle phase of microtubules. (*A*) DIC (*Right*), whole-mount TEM side view (*Upper Left*), and plastic-embedded TEM side view (*Lower Left*) of MT necklace bundles with 100 mM $BaCl_2$. (*B–D*) Plastic-embedded TEM cross sections of bundles with 100 mM $BaCl_2$ showing linear (*B*), branched (*C*), and loop-like (*D*) morphologies. A 3D schematic is shown in Fig. 1 *Right*.

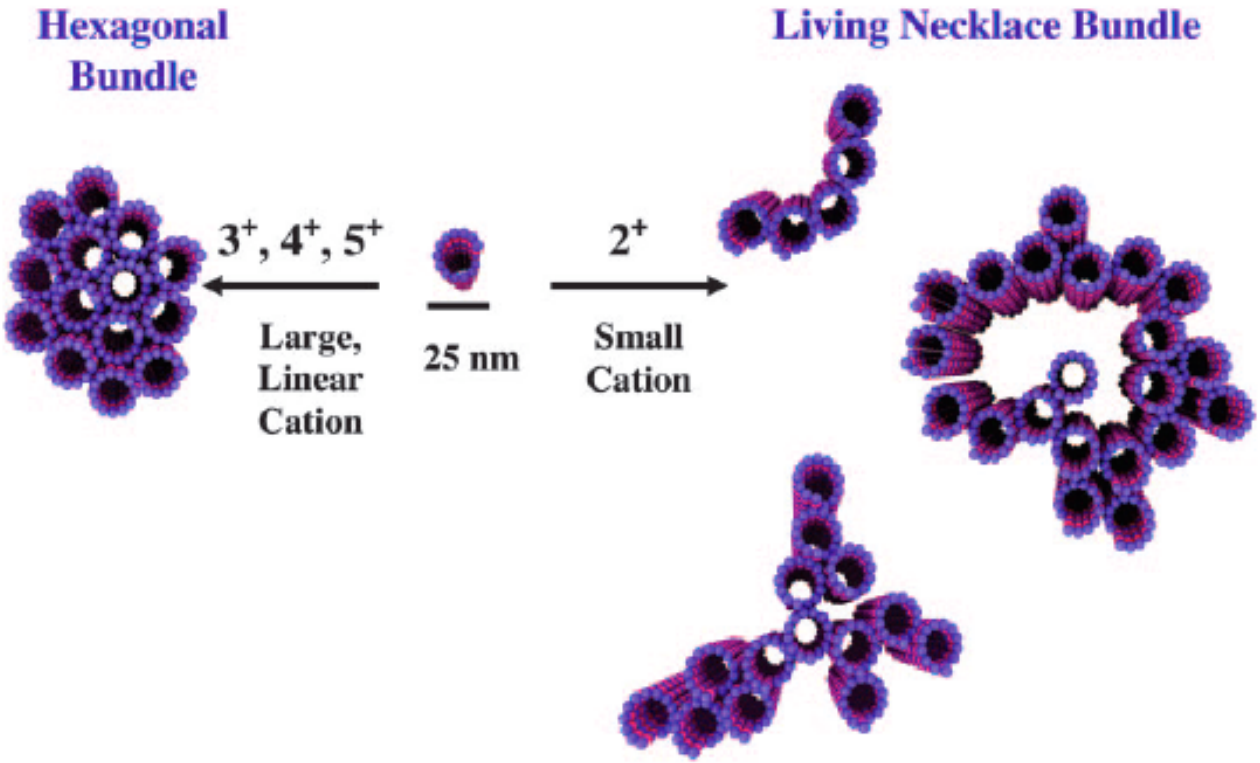
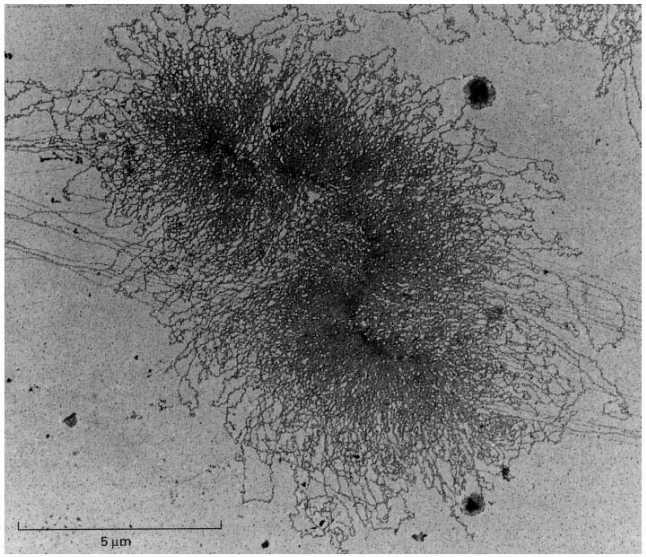


Fig. 1. 3D schematics of higher-order assembly of nanometer-scale MTs. Large trivalent, tetravalent, and pentavalent cations lead to the formation of hexagonal bundles (*Left*). Small divalent cations lead to the living necklace bundles with linear, branched, and loop morphologies (*Right*). The distinct bundle phases allow for tailored applications in miniaturized materials requiring high volume (hexagonal bundles) or high surface area (necklace bundles).

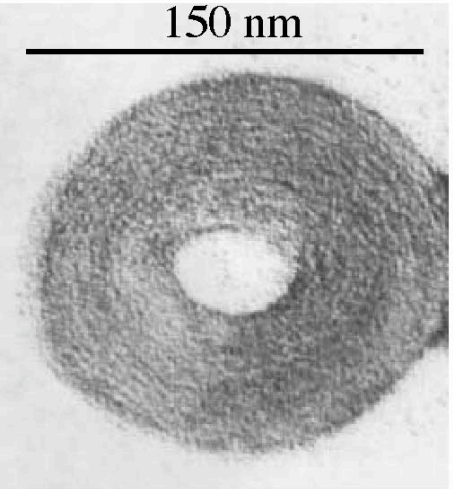
spontaneous compactification of DNA



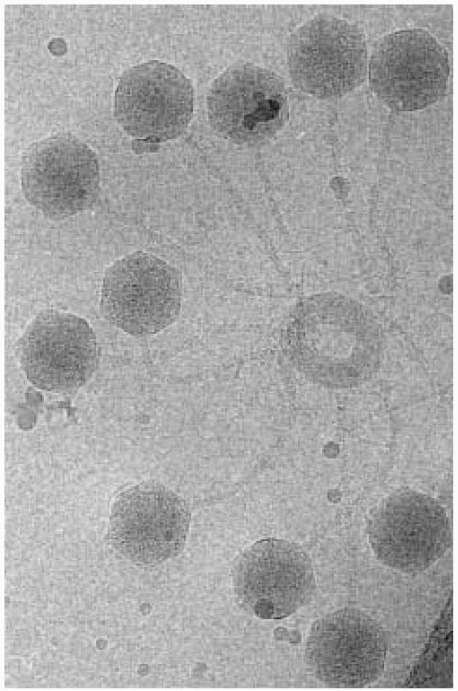
"normal" DNA:
a swollen,
disordered coil

(Kleinschmidt et al., 1962)

viral DNA after adding spermin
(four-valent positive ion):

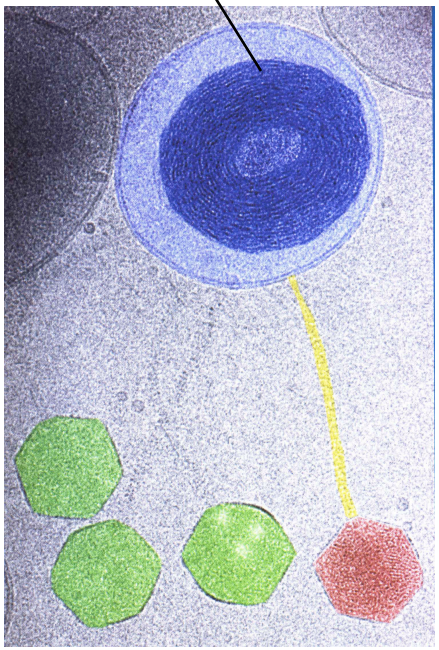


Sikorav

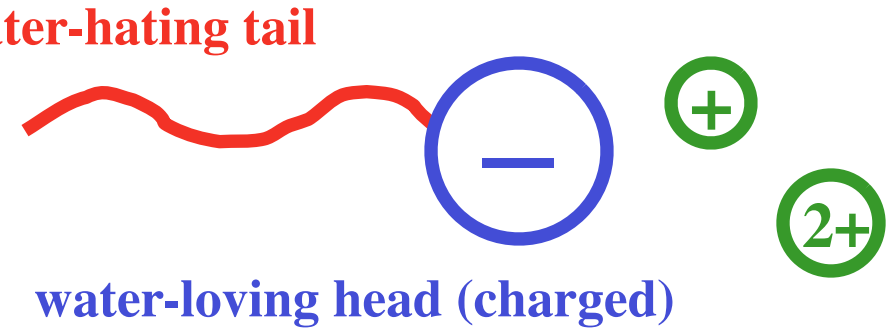


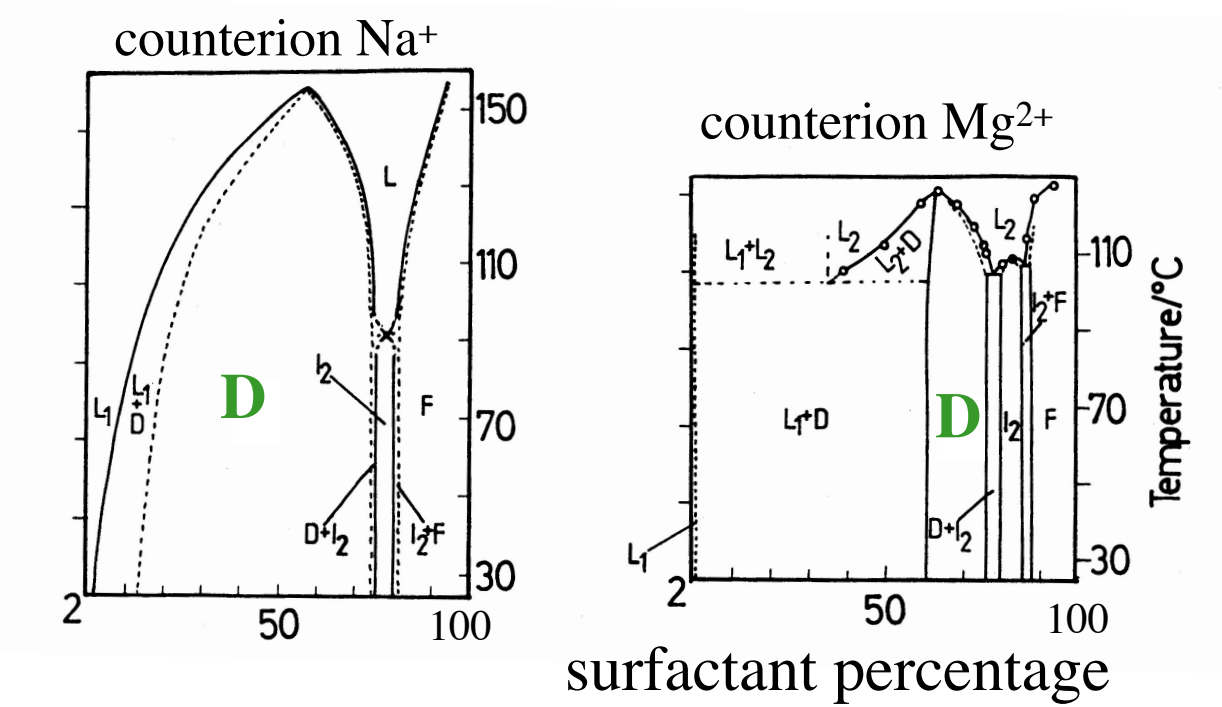
Lambert

DNA condensates

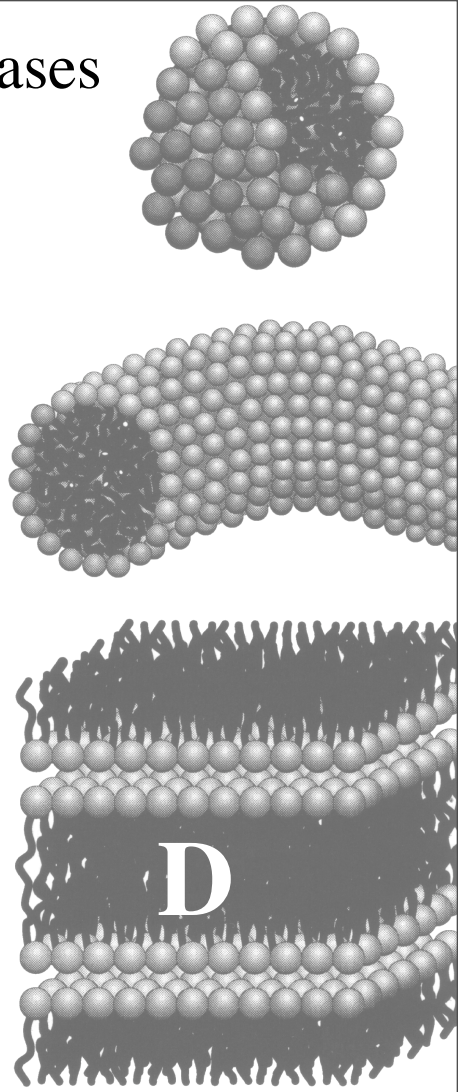


charged surfactants in water form different ordered phases





Khan, Wennerström, Lindman



lamellar phase

increasing the counterion valency induces attraction between lamellae

(similar effects seen for spheres, cylinder ...)

A historical guide to the correlation effect

Oosawa (1971)
(counterion fluctuations)

Gulbrand, Jonsson, Wennerstrom and Linse
(1984)

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

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

Rouzina and Bloomfield (1996)
(checkerboard model)

Podgornik et al. (1988-1991)
Attard et al. (1988)
Pincus, Safran (1995)
Podgornik and Parsegian (1999)
Kardar, Golestanian (1999)
.....
(Gaussian fluctuations)

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

Shklovskii et al. (1999-2002)
Lau and Pincus (2001)
Levin et al (2000)
(Wigner crystal model)

Netz et al (2000-...)
(General analysis of Coulomb fluids + simulations)

Weeks et al (2006)
Santangelo (2006)
AN, RP et al
(various extensions)

High-T approach

Low-T approach

Weak--Strong coupling paradigm
(planar charged surfaces)

Weak and strong coupling electrostatic interactions

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)
$\Xi \rightarrow \infty$

``

Charged object	σ_s (e/nm^2)	R(Å)	q	μ(Å)	Ξ	$\tilde{R}$
charged membranes	~ 1	–	1	2.2	3.1	–
			2	1.1	24.8	–
			3	0.7	83.7	–
DNA	0.9	10	1 (Na^+)	2.4	2.8	4.1
			2 (Mn^{2+})	1.2	22.4	8.2
			3 (spermidine)	0.8	75.6	12.3
			4 (spermine)	0.6	179	16.4
highly charged colloids (surfactant micelles)	~ 1	20	3	0.7	85	28
weakly charged colloids (polystyrene particles)	~ 0.1	$\sim 10^3$	1	~ 2	~ 0.1	$\sim 5 \times 10^2$

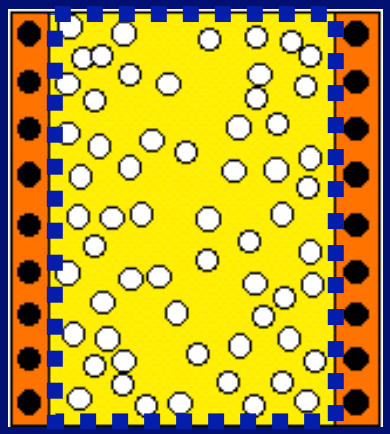
Table 2.1: Typical values of physical parameters for realistic charged systems: σ_s and R denote the surface charge density and the radius of curvature of charged objects. q is the charge valency of counterions, $\mu = 1/(2\pi q \ell_B \sigma_s)$ is the Gouy-Chapman length, $\Xi = q^2 \ell_B/\mu$ is the coupling parameter, and $\tilde{R} = R/\mu$ is the Manning parameter (Section 2.3). The Bjerrum length is taken here as $\ell_B \simeq 7.1$Å corresponding to an aqueous medium of dielectric constant $\varepsilon = 80$ at room temperature.

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

Coupling parameter

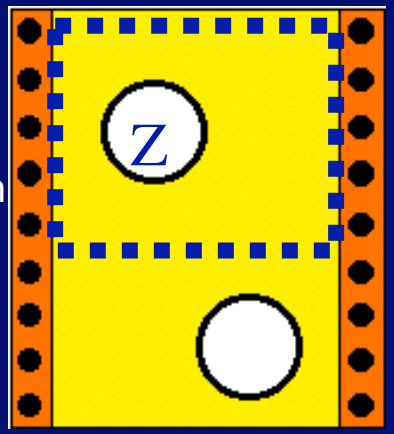
$$\Xi = 2\pi Z^3 \ell_B^2 \sigma$$

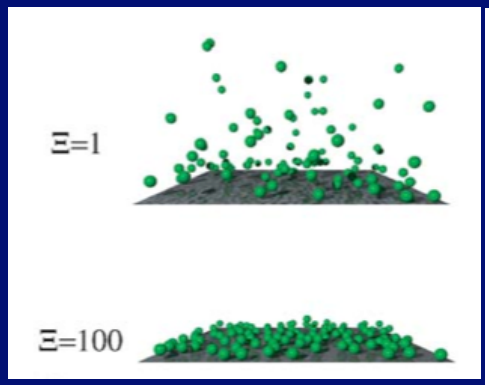
Strong coupling limit
(Netz - Moreira)
$\Xi \rightarrow \infty$



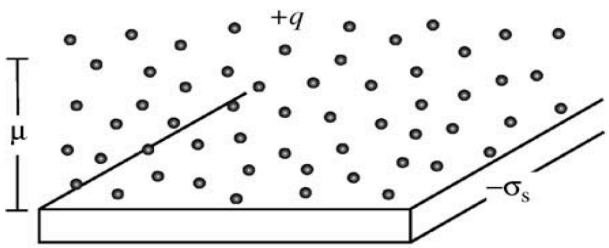
Collective description
(Poisson - Boltzmann "N" description
Screened Debye-Hueckel)

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



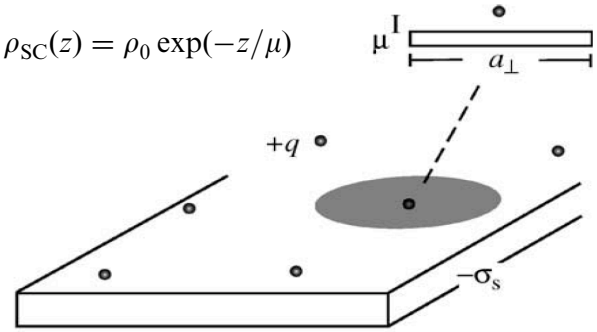


$$\frac{\rho_{PB}(z)}{2\pi\ell_B\sigma_s^2} = \frac{1}{(z/\mu+1)^2}$$

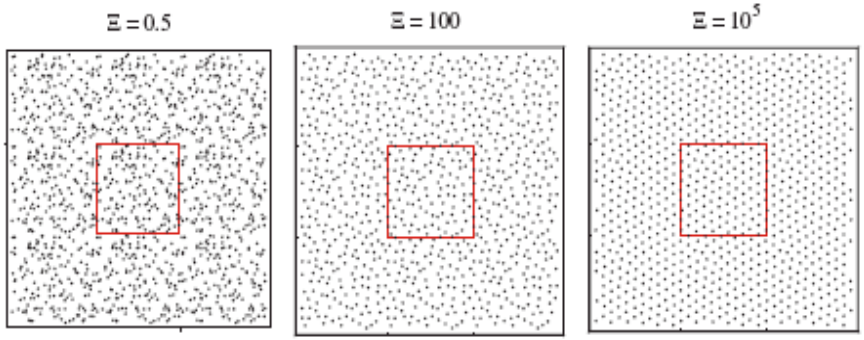


(a)

$$\rho_{SC}(z) = \rho_0 \exp(-z/\mu)$$



(b)



$$a_\perp^2 \sim q/\sigma_s$$

$$\frac{a_\perp}{\mu} \sim \sqrt{\Xi}$$

$$\Gamma = \frac{q^2 \ell_B}{a_\perp} \sim \Xi^{1/2}$$

How was that accomplished?

Field-Theoretical Approach 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

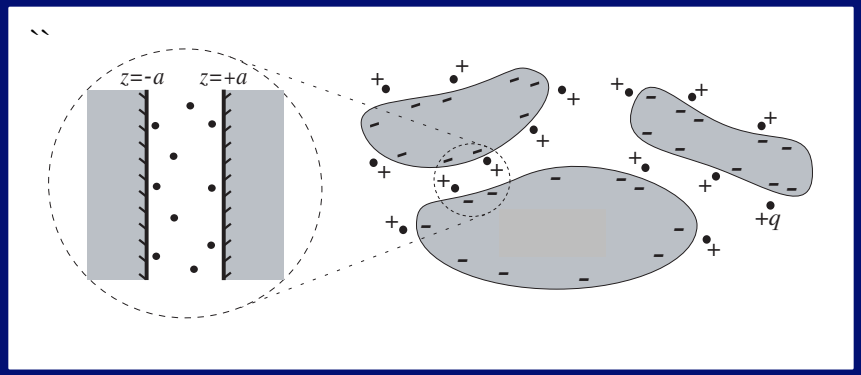
S. F. EDWARDS
Department of Theoretical Physics, Manchester University, Manchester, England
AND
A. LENARD*
Plasma Physics Laboratory, Princeton University, Princeton, New Jersey
(Received January 11, 1962)

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

Coulomb fluid = an ensemble of interacting Coulomb charges.

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

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



Grand canonical partition function can be written as

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

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

Exactly solvable for 1D Coulomb gas. “Schroedinger equation” (Dean, Horgan et al)
In 3D, only asymptotic cases can handled analytically

``

Dimensionless representation

$$\mathcal{Z}_\lambda = \int \frac{\mathcal{D}\varphi}{Z_v} \exp\left\{ -\frac{\tilde{\mathcal{S}}[\varphi]}{\Xi} \right\}$$

$$\tilde{\mathcal{S}}[\varphi] = \frac{1}{2\pi} \int_{\tilde{\mathbf{x}}} \left[\frac{1}{4} \left(\nabla_{\tilde{\mathbf{x}}} \varphi(\tilde{\mathbf{x}}) \right)^2 - \mathrm{i}\tilde{\sigma}(\tilde{\mathbf{x}})\varphi(\tilde{\mathbf{x}}) - \Lambda\tilde{\Omega}(\tilde{\mathbf{x}})\, e^{-\mathrm{i}\varphi} \right]$$

``

- for $\Xi \to 0$: loop expansion in powers of Ξ (e.g. for interaction)

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

``

- for $\Xi \to \infty$: expansion in powers of Ξ^{-1} (virial expansion)

$$P(\Delta) = P_{\mathrm{SC}}(\Delta) + \frac{1}{\Xi} P^{(1)}_{\mathrm{SC}}(\Delta) + \mathcal{O}(\Xi^{-2})$$

PB equation and saddle point $\Xi \to 0$

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Inhomogeneous Coulomb Fluid

A Functional Integral Approach

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

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)

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

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

= 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 or the classical Casimir effect

Strong-coupling theory $\Xi \to \infty$

On the SC level the image corrections exist for the external potential as well as for the image self-energy!

$$Z_G = Z_G^{(0)} + \lambda' Z_G^{(1)} + \mathcal{O}(\lambda'^2).$$

Zero order SC: Coulomb interaction between charged surfaces

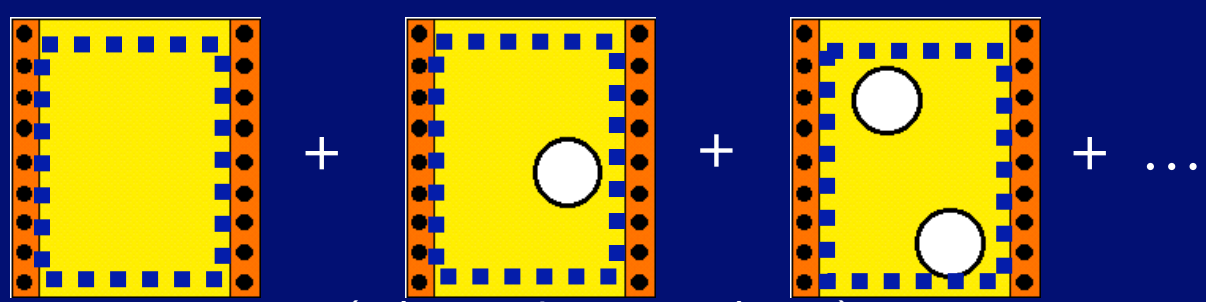
$$Z_G^{(0)} = e^{-\frac{1}{2}\beta \iint d^3\mathbf{r} d^3\mathbf{r}' u(\mathbf{r},\mathbf{r}')\rho_0(\mathbf{r})\rho_0(\mathbf{r}')}.$$

...and the first order (SC proper) correction:

$$U = \int \exp\left(-\frac{1}{2}\beta e_0^2 q^2 u \quad (\mathbf{R},\mathbf{R}) - \beta e_0 q \int u(\mathbf{r},\mathbf{R})\rho_0(\mathbf{r}) d^3\mathbf{r}\right) d^3\mathbf{R}$$

$$Z_G = Z_G^{(0)}(1 + \lambda U)$$

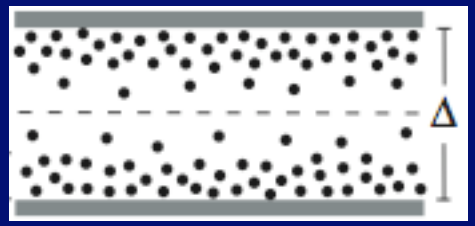
$$\mathcal{F} = \mathcal{E}_0 - kT\,\Xi\, N \log \int_{(V)} d^3\mathbf{r} \exp - \frac{\mathcal{E}_1(\mathbf{r})}{kT}.$$



(a lot easier to evaluate)

Interaction between *identical* planar charged surfaces

- Weak coupling (Poisson - Boltzmann + Gaussian flucts)



Total pressure (PB+ flucts)

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

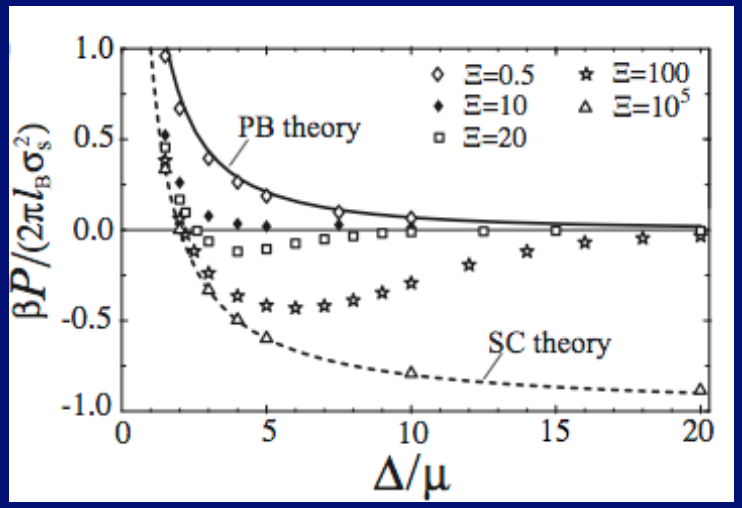
Poisson - Boltzmann (analytic)

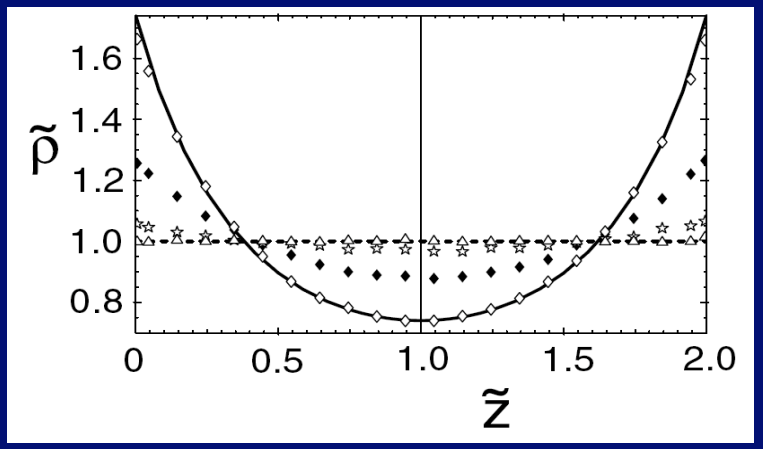
$$\frac{\beta P_{\rm PB}(\Delta)}{2\pi\ell_{\rm B}\sigma_{\rm s}^2} \approx \left(\frac{\pi\mu}{\Delta}\right)^2$$

net attraction not possible!!

Fluctuational (analytic)

$$\frac{\beta P^{(1)}_{\rm PB}}{2\pi\ell_{\rm B}\sigma_{\rm s}^2} \approx -\left(\frac{\mu}{\Delta}\right)^3 \left[\frac{\zeta(3)}{4} + \frac{\pi^3}{4} + \pi^2 \ln(\Delta/\pi\mu)\right].$$





- Strong coupling

mosaic binding

$$\frac{\beta P_{\rm SC}(\Delta)}{2\pi\ell_{\rm B}\sigma_{\rm s}^2} = -1 + \frac{2\mu}{\Delta}.$$

equilibrium distance

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

Regimes of validity of asymptotic theories

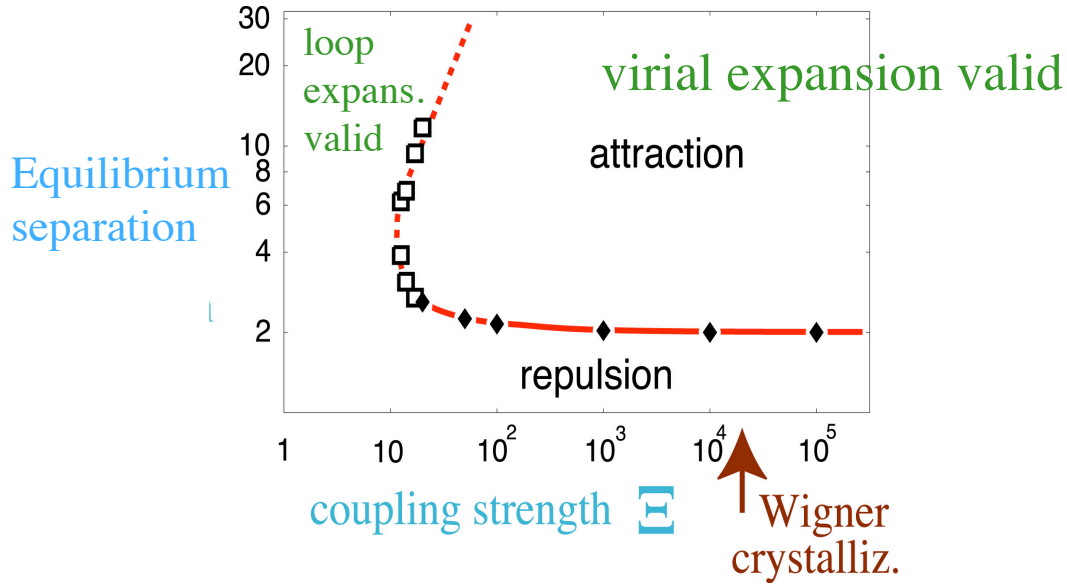
WC regime:

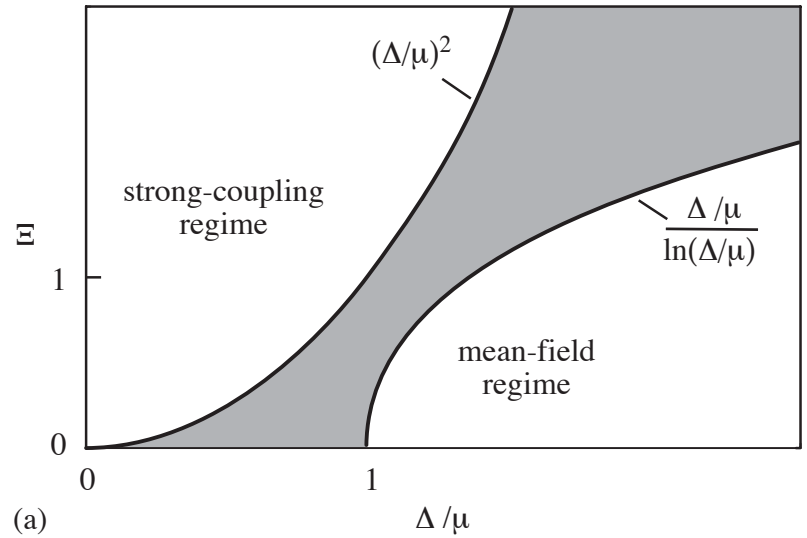
$$\frac{\Delta/\mu}{\ln(\Delta/\mu)} > \Xi$$

SC regime:

$$\Delta < a_\perp$$

$$\left(\frac{\Delta}{\mu}\right)^2 < \Xi$$

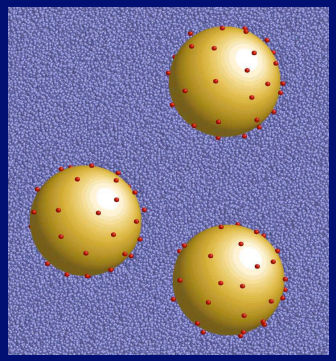




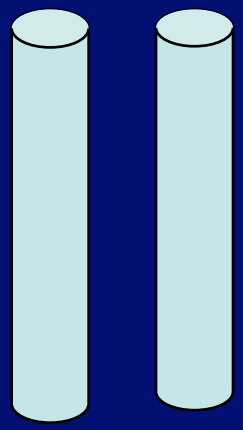
Beyond the ‘standard model’

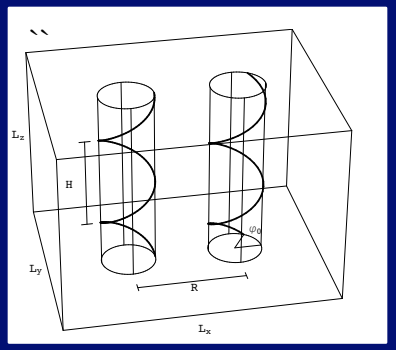
Generalization to more realistic and refined models if compared to the “primitive model”.

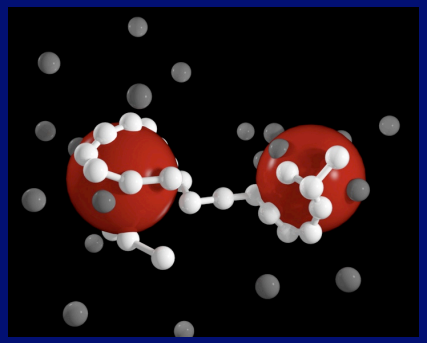
- Geometry of ‘macroions’



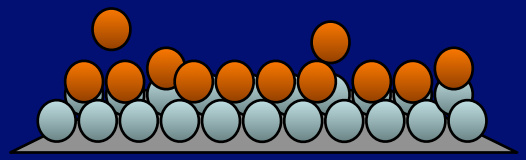
picture: Barbosa (2005)



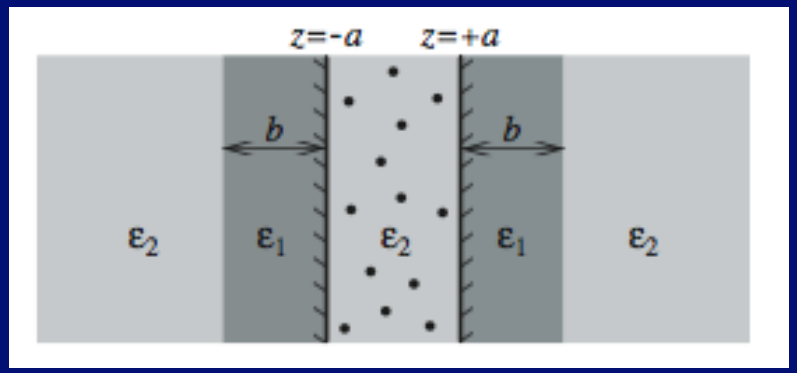




- Additional salt (co + counterions)
- Discreteness of surface charges

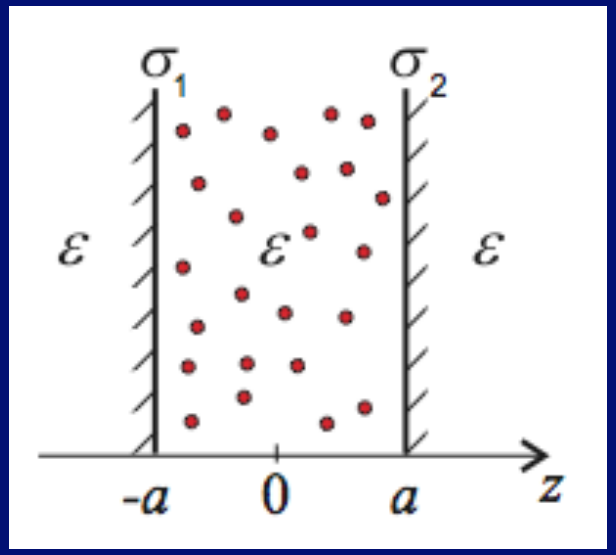


- Discontinuous dielectric constant (vdw vs. charge fluctuations)
- Asymmetrically charged surfaces
- Disordered charge distributions
- ....



Electrostatic image effects

What happens when there are dielectric inhomogeneities in the system?



A model system composed of couterions with dielectric discontinuity at the boundary.

The dielectric discontinuity is quantified by:

$$\Delta = \frac{\varepsilon - \varepsilon'}{\varepsilon + \varepsilon'}$$

Electrostatic interactions are composed of two parts:

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

Direct electrostatic interactions and image interactions:

$$\begin{aligned} u_0(Q, z; z') &= \frac{1}{2\varepsilon\varepsilon_0 Q} e^{-Q|z-z'|}, \\ u_{\mathrm{im}}(Q, z; z') &= \frac{1}{\varepsilon\varepsilon_0 Q} \frac{\operatorname{ch} Q(z+z') + \Delta\, e^{-2Qa} \operatorname{ch} Q(z-z')}{\Delta^{-1} e^{2Qa} - \Delta\, e^{-2Qa}}, \end{aligned}$$

Electrostatic image effects on the WC level

The mean-field (PB) solution depends only on the transverse coordinate.
By definition then, the image effects are non-existant on the PB level!

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

Saddle point = mean-field (MF)
With homogeneous charge distribution depends only on z-coordinate

They do however exist in the 2nd order correction to the mean-field.

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

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

Small separation limit:

$$\tilde{p} = \tilde{p}_0 + \tilde{p}_2 \sim \frac{1}{\tilde{a}} - \frac{1}{3} - \Xi\,\frac{\mathrm{Li}_3(\Delta^2)}{32\,\tilde{a}^3}\,.$$

Large separation limit:

$$\tilde{p} = \tilde{p}_0 + \tilde{p}_2 \sim \frac{\pi^2}{4\tilde{a}^2} - \frac{\Xi}{32\,\tilde{a}^3}\left[2\pi^2\left(\ln\frac{2\tilde{a}^2}{\pi^2} + 2\frac{1+\Delta}{\sqrt{1+2\Delta}}\,\mathrm{arctg}\sqrt{1+2\Delta} - -(1+\Delta)\ln(1+\Delta)\right) + \zeta(3)\right]. \qquad (24)$$

Electrostatic image effects on the SC level

On the SC level the image corrections exist for the external potential as well as for the image self-energy!

$$Z_G = Z_G^{(0)} + \lambda' Z_G^{(1)} + \mathcal{O}(\lambda'^2).$$

Zero order SC: Coulomb interaction between charged surfaecs

$$Z_G^{(0)} = e^{-\frac{1}{2}\beta \iint d^3\mathbf{r} d^3\mathbf{r}' u(\mathbf{r},\mathbf{r}')\rho_0(\mathbf{r})\rho_0(\mathbf{r}')}.$$

...adn the first order (SC proper) correction:

$$Z_G = Z_G^{(0)}(1 + \lambda U),$$

$$U = \int \exp\left(-\frac{1}{2}\beta e_0^2 q^2 u_{\rm im}(\mathbf{R},\mathbf{R}) - \beta e_0 q \int u(\mathbf{r},\mathbf{R})\rho_0(\mathbf{r}) d^3\mathbf{r}\right) d^3\mathbf{R}$$

Small separation limit:

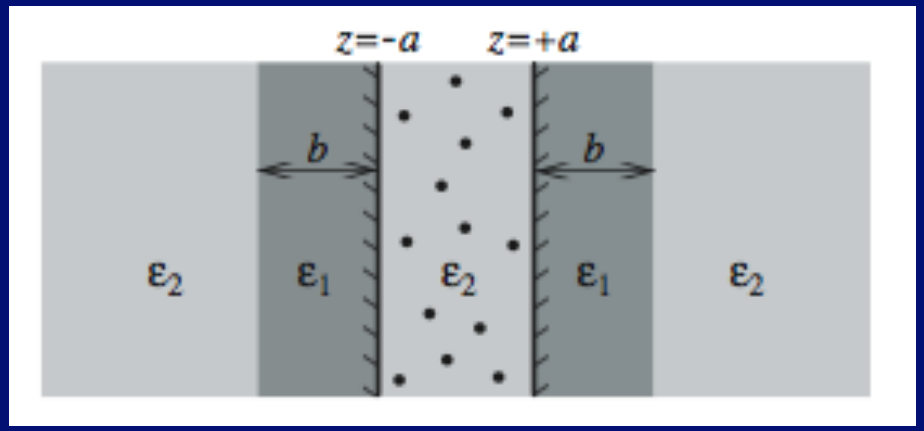
$$\tilde{p}(\tilde{a}, \Delta > 0) \sim -\left(\frac{1+\Delta}{1-\Delta}\right)^2 - \frac{\Xi}{2\tilde{a}^2}\ln(1-\Delta) + \frac{3}{2\tilde{a}} + \mathcal{O}(\tilde{a}).$$

Large separation limit:

$$\tilde{p} \sim -\left(\frac{1+\Delta}{1-\Delta}\right)^2 - \frac{\Xi}{4\tilde{a}^2}\ln(1-\Delta^2) + \frac{1}{\tilde{a}} + \mathcal{O}(\tilde{a}^{-3}).$$

Theory vs. simulations

Compare SC analytical results with simulations at large electrostatic coupling!



Explicit expressions for the counterion density and the interaction free energy.

$$\tilde{\rho}_{\rm SC}(\tilde{z}) = A(\tilde{a})\; e^{-\Xi \int_0^\infty {\rm d}Q \, \frac{\cosh 2Q\tilde{z}}{\Delta_Q^{-1} e^{2Q\tilde{a}} - \Delta_Q \, e^{-2Q\tilde{a}}}} \,,$$

$$\tilde{\mathcal{F}}_{\rm SC} = \tilde{a} - \ln \int_0^{\tilde{a}} {\rm d}\tilde{z} \; e^{-\Xi \int_0^\infty {\rm d}Q \, \frac{\cosh 2Q\tilde{z} + \Delta_Q \, e^{-2Q\tilde{a}}}{\Delta_Q^{-1} e^{2Q\tilde{a}} - \Delta_Q \, e^{-2Q\tilde{a}}}} \,.$$

The range of validity of the SC theory is extended and remains valid for larger values of the intersurface separation then in the case of no images.

$$\tilde{a}^3 \ll \tilde{a}\,\Xi + \Delta\,\Xi^2 .$$

Yong-Seok Jho (MRL) produced an extended set of simulations and thoroughly explored the parameter space for this problem. The approximate SC theory fares extremely well in the regime where it is supposed to work!

Theory vs. simulations

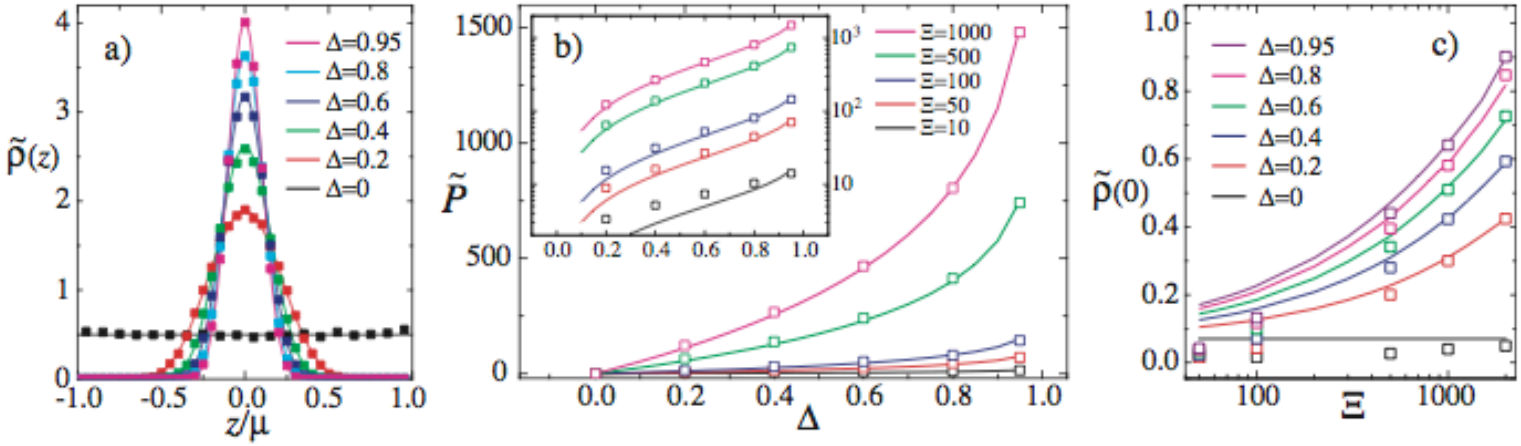


FIG. 2: a) Rescaled counterion density profile between two like-charged dielectric membranes for $\Xi = 100$, $b/\mu = 100$, $a/\mu = 1$ and as the dielectric mismatch Δ is increased (from bottom to top at $z = 0$). b) Rescaled inter-membrane pressure as a function of Δ for $b/\mu = 100$, $a/\mu = 1$ and as Ξ is increased (bottom to top); inset shows the details in the logarithmic scale. c) The mid-plane ($z = 0$) counterion density, $\tilde{\rho}(0)$, as a function of the coupling parameter Ξ for $a/\mu = 7$, $b/\mu = 100$ and as Δ is increased (bottom to top). In a)-c) lines are the SC predictions (see the text) and symbols are simulation data.

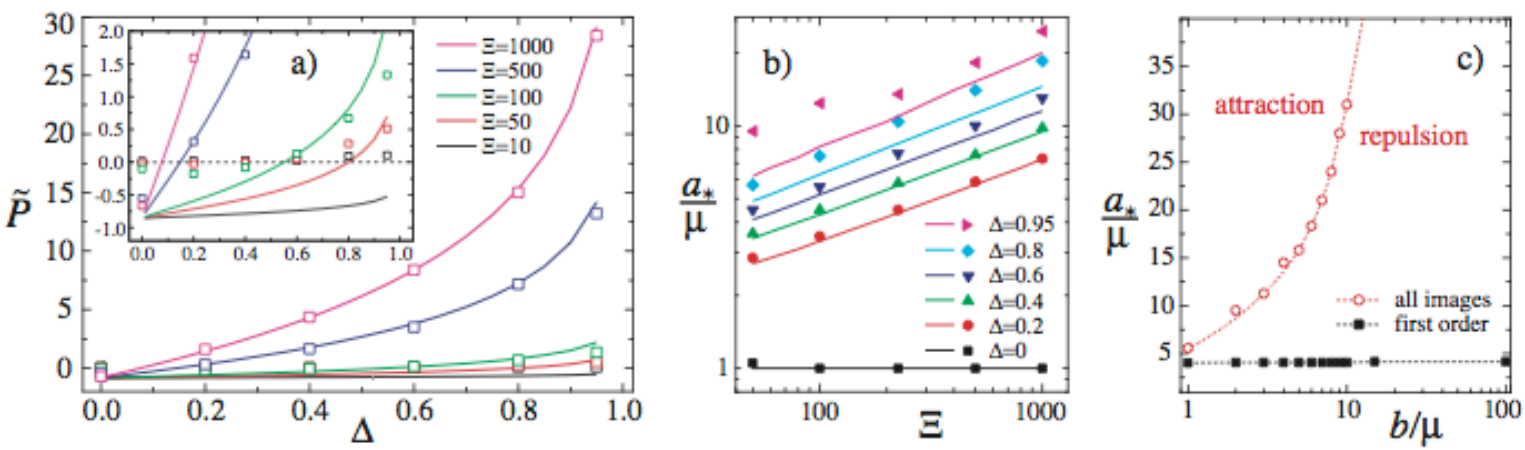
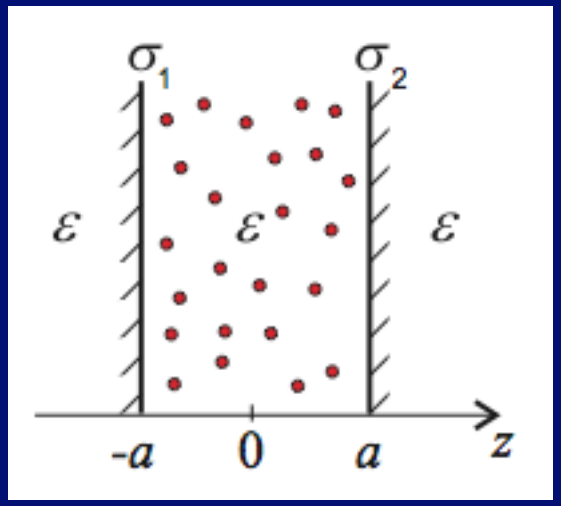


FIG. 3: a) Same as Fig. 2b but for $a/\mu = 7$. Inset shows the details for small pressures. b) Simulated equilibrium half-distance, a_*, as a function of Ξ for $b/\mu = 2$ and as Δ is increased. Lines are SC predictions (from minimization of Eq. (3)). c) Simulation results with all images (circles) and the first-order images only (squares) showing a_* as a function of b for $\Xi = 50$ and $\Delta = 0.95$; here lines are guides to the eye. The surfaces attract for $a > a_*$ and repel for $a < a_*$.

Electrostatic interactions in asymmetric systems

Parsegian and Gingell formulated a linearized PB theory of the interactions in the presence of salt. The linearization ansatz was later generalized in the work of Lau and Pincus and Ben-Yaakov et al.

V.A. Parsegian and D. Gingell, Biophys. J. 12, 1193 (1972).
A.W.C. Lau and P. Pincus, Eur. Phys. J. B 10, 175 (1999).
D. Ben-Yaakov, Y. Burak, D. Andelman and S.A. Safran, Europhys. Lett. 79, 48002 (2007).



$$\sigma_1 + \sigma_2 < 0, \quad \text{and} \quad \sigma_2 > \sigma_1, \quad \text{so that} \quad \sigma_1 < 0.$$

Electroneutrality:

$$N e_0 q + (\sigma_1 + \sigma_2) S = 0,$$

The mean field pressure can be calculated in full and depends on the value of zeta, giving attractions as well as repulsions.

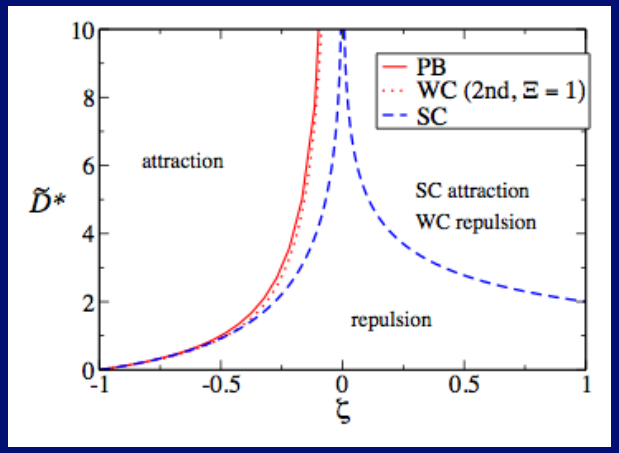
$$\frac{\mathrm{d}^2 \tilde{\psi}_0(z)}{\mathrm{d}z^2} = -(4\pi \ell_B q^2) \lambda_0 e^{-\tilde{\psi}_0(z)},$$

with boundary conditions

$$\left.\frac{\mathrm{d}\tilde{\psi}_0}{\mathrm{d}z}\right|_{-a} = \frac{2}{\mu},$$

$$\left.\frac{\mathrm{d}\tilde{\psi}_0}{\mathrm{d}z}\right|_{a} = -\frac{2\zeta}{\mu}.$$

$$\zeta = \frac{\sigma_2}{\sigma_1} > -1.$$



Fluctuations around mean-field in an asymmetric system (the classical Casimir effect)

One needs to calculate the tracelog of the Hessian of the Coulomb action:

$$H(\mathbf{r},\mathbf{r}') = u^{-1}(\mathbf{r},\mathbf{r}') + \beta(e_0 q)^2 n_0(z)\,\delta^3(\mathbf{r}-\mathbf{r}'),$$

With mean-filed couunterion density:

$$(4\pi\ell_{\mathrm{B}}q^2)n_0(z) = \begin{cases} \dfrac{2\alpha^2}{\cos^2\alpha(z-z_0)} & p_0 > 0, \\[2ex] \dfrac{2}{(z-z_0)^2} & p_0 = 0, \\[2ex] \dfrac{2\alpha^2}{\sinh^2\alpha(z-z_0)} & p_0 < 0. \end{cases}$$

The tracelog of the Hessian equals the trace of the log of the secular determinant

$$\beta\mathcal{F}_2 = \frac{1}{2}\mathrm{Tr}\ln H(\mathbf{r},\mathbf{r}') = \frac{S}{4\pi}\int_0^\infty Q\ln\frac{\mathcal{D}_1(Q)}{\mathcal{D}_0(Q)}\,\mathrm{d}Q.$$

$$\left(\frac{\partial^2}{\partial z^2} - Q^2 - \lambda(4\pi\ell_{\mathrm{B}}q^2)n_0(z)\right)f_\lambda(\mathbf{Q},z) = 0.$$

General result in the Lifshitz theory first shown to be valid by Barash and Ginzburg.

Different results in different limits:

$$\tilde{p}_2(\tilde{D}) \simeq -\Xi\,\pi^2\frac{\ln\tilde{D}}{8\tilde{D}^3}.$$

for D >> 2(1 + 1/ζ) (repulsive MF)

$$\tilde{p}_2(\tilde{D}) \simeq -\Xi\,\pi^2\frac{\ln\tilde{D}}{\tilde{D}^3},$$

for 1/ζ >> D >> 1 (repulsive MF)

$$\tilde{p}_2(\tilde{D}) \simeq \Xi\,f(\zeta)\,e^{2\zeta\tilde{D}},$$

for D >> 1 (attractive MF)

$$\Xi < \frac{\tilde{D}}{\ln\tilde{D}}.$$

$$\Xi < \frac{\zeta^2}{|f(\zeta)|}e^{-2\zeta\tilde{D}}.$$

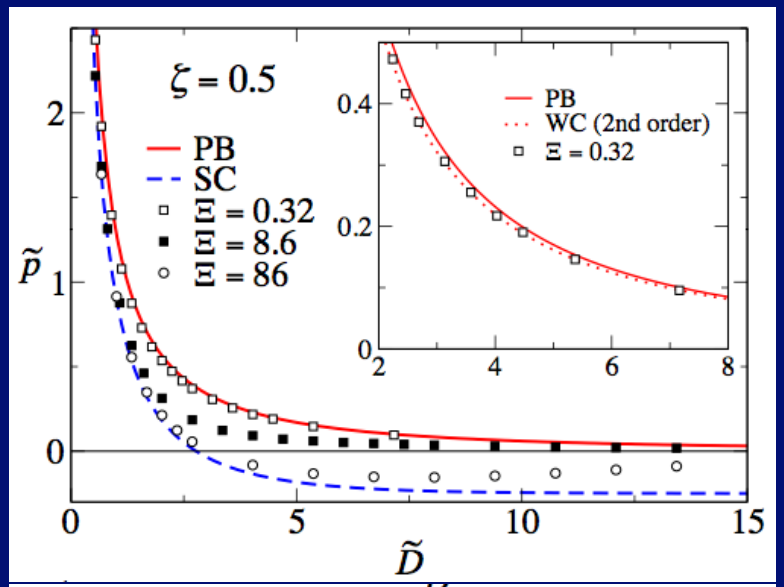
$$f(\zeta) = \zeta^3\frac{1+\zeta}{1-\zeta}\left(\frac{2\arctan\sqrt{1-2\zeta^2}}{\sqrt{1-2\zeta^2}} + \ln\frac{1-\zeta^2}{2\zeta^2}\right)$$

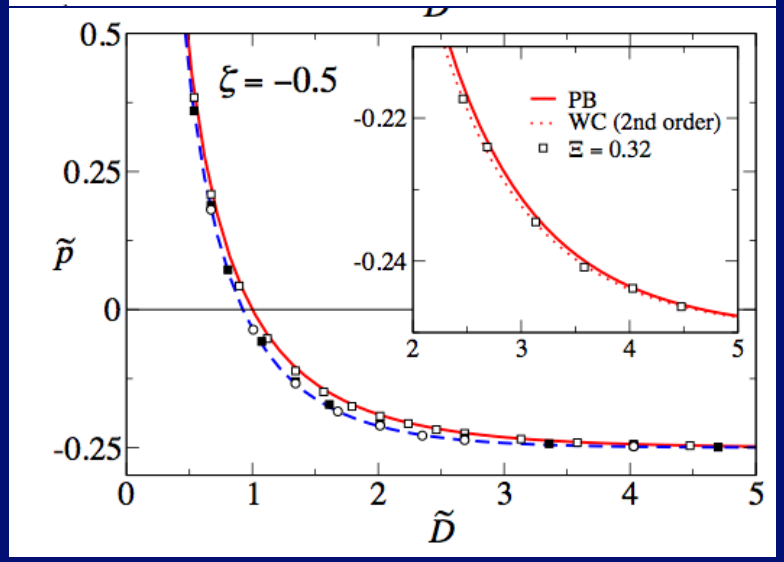
For negative ζ.

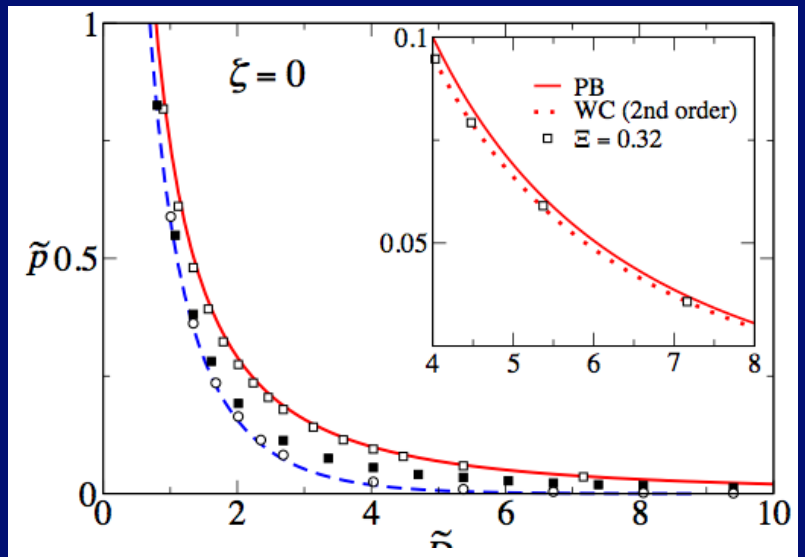
Range of validity

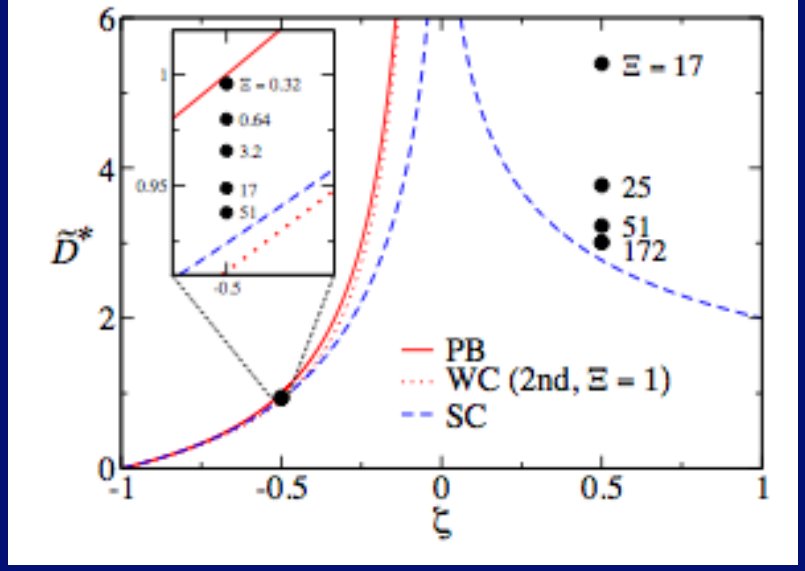
Theory vs. simulations (WC)

Compare WC + 2nd order fluctuations analytical results with extensive simulations (Martin Trulsson).









Quantitative comparison for pressure only if classical Casimir taken into account!

Strong coupling in an asymmetric system

Mean-field no longer valid. SC limit again analytical.

Exact form for pressure:

$$\tilde{p}(\tilde{D}) = -\frac{1}{2}(1+\zeta^2) + \frac{1}{2}(1-\zeta^2)\coth\left[(1-\zeta)\frac{\tilde{D}}{2}\right].$$

$$\tilde{p}(\tilde{D}) \simeq \frac{1+\zeta}{\tilde{D}},$$ for D << 1

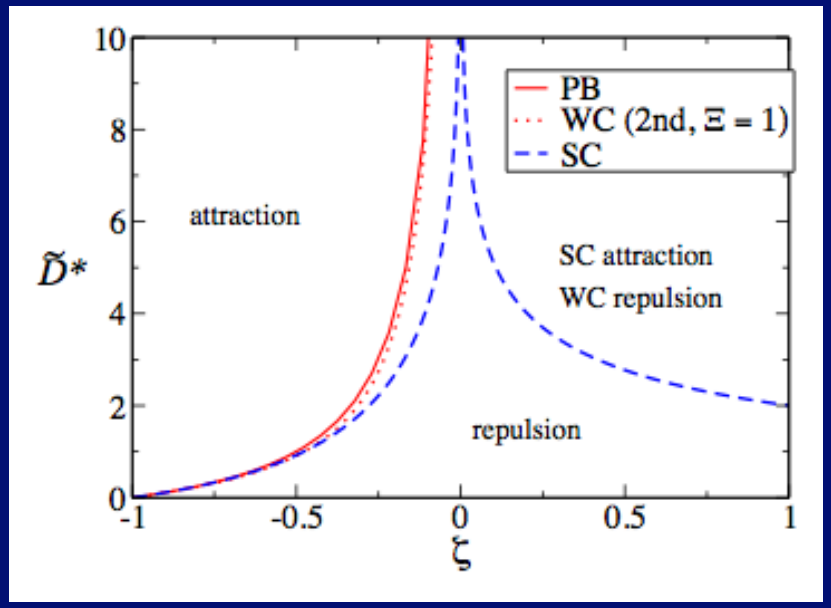
$$\tilde{p}(\tilde{D}) \simeq -\zeta^2.$$ for D >> 1

$$\tilde{D}^* = -\frac{2\ln|\zeta|}{1-\zeta},$$

Exact form for counterion density:

$$\tilde{n}(z) = \frac{1-\zeta^2}{2}\frac{e^{-(1-\zeta)\tilde{z}}}{\sinh\left[(1-\zeta)\tilde{D}/2\right]},$$

In the SC limit there is always an equilibrium spacing for the system. For any value of ζ.



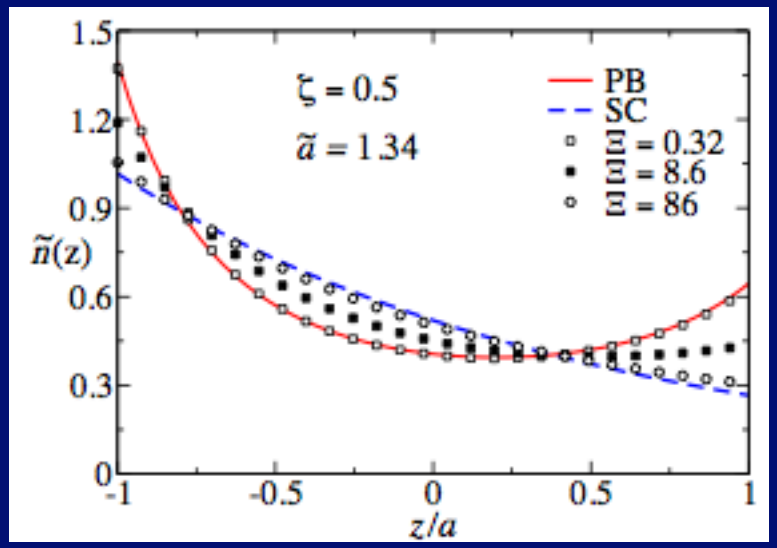
The validity of the SC approximation is limited to small enough separations. The following criterion holds:

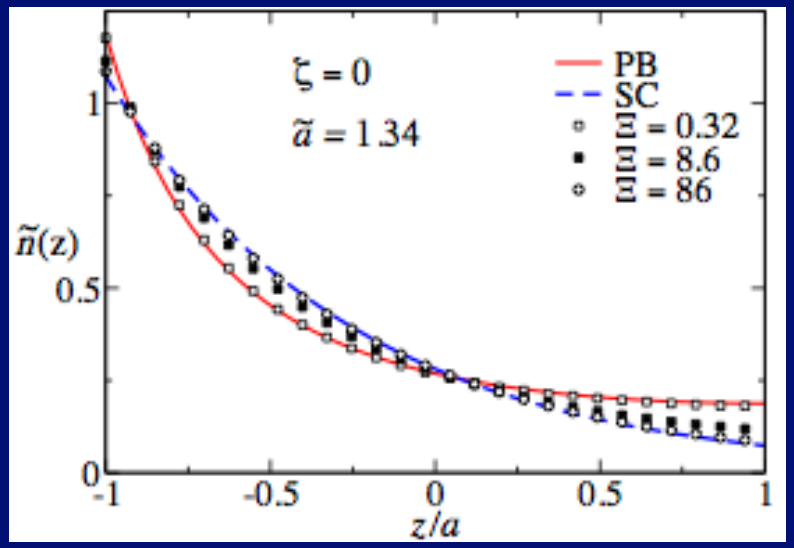
$$\tilde{D} \ll \sqrt{(1+\zeta)\Xi},$$

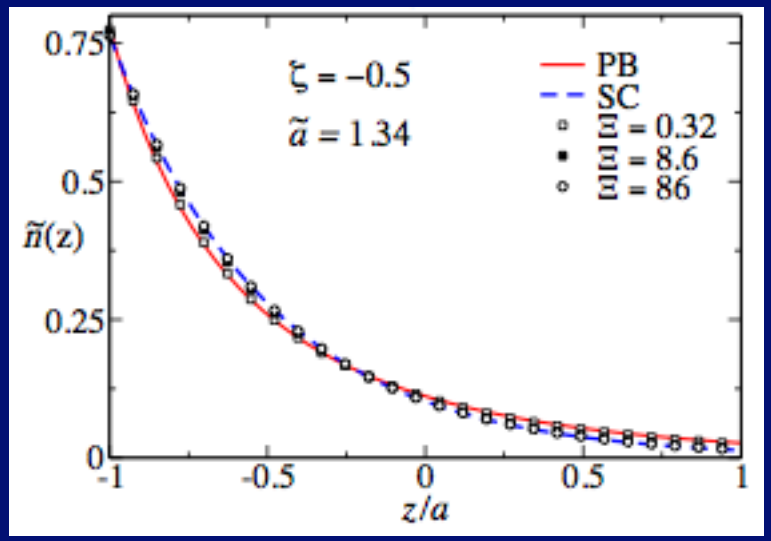
Remember: SC is the virial expansion to the first order in the absolute activity or equivalently in the inverse coupling constant.

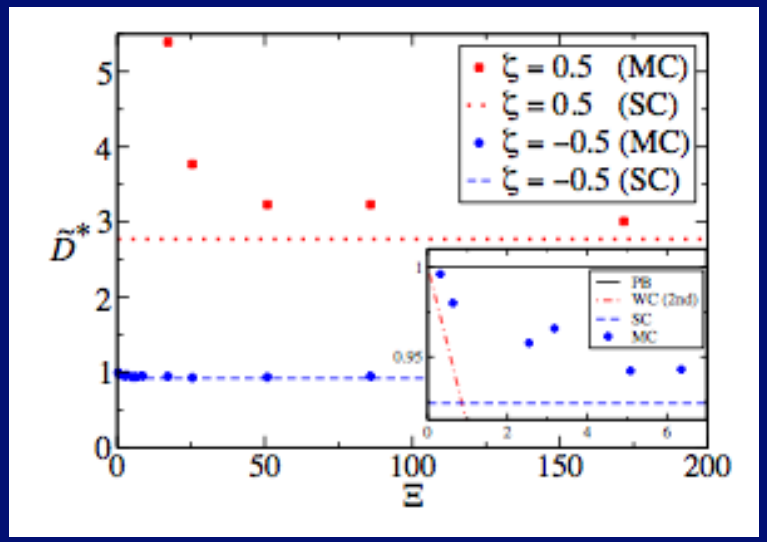
Theory vs. simulations (SC)

Compare SC analytical results with extensive simulations (Martin Trulsson).







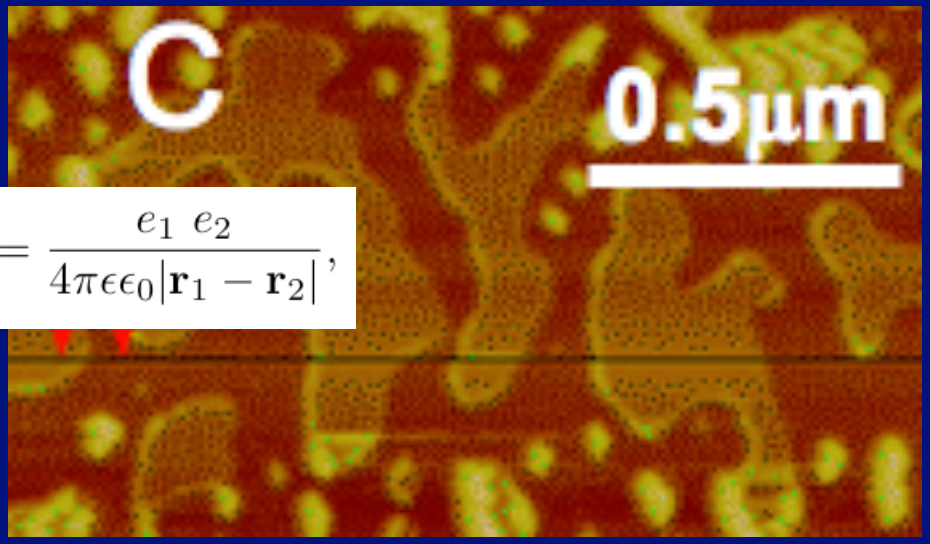


Quantitative comparison for WC as well as SC in their respective ranges of validity!

Patching together disorder & coulomb interactions

Disorder is seen or inferred (lecture of Andy Kim!) experimentally.

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



Perkin et al. (2005)

Surface charge disorder - patchy surfaces.
Probably ubiquiteous in many contexts and important when small interactions are measured..

"Mean" coupling parameter

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

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

?

Disorder coupling parameter

$$\chi = \frac{Z^2(\beta e_0)^2 g}{8\pi(\epsilon\epsilon_0)^2} = 2\pi Z^2 \ell_B^2 g.$$

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

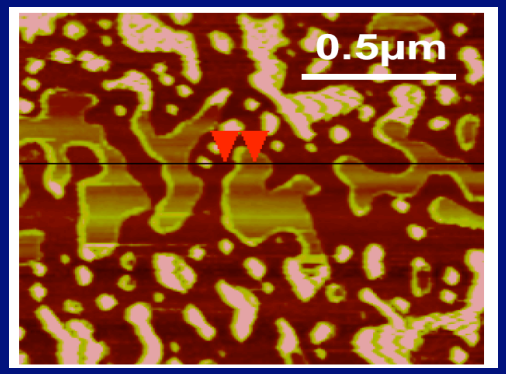
?

Consider only surface charge disorder:

$$g(\mathbf{r}) = g(z,\rho) = g\,\delta(z-a) + g\,\delta(z+a).$$

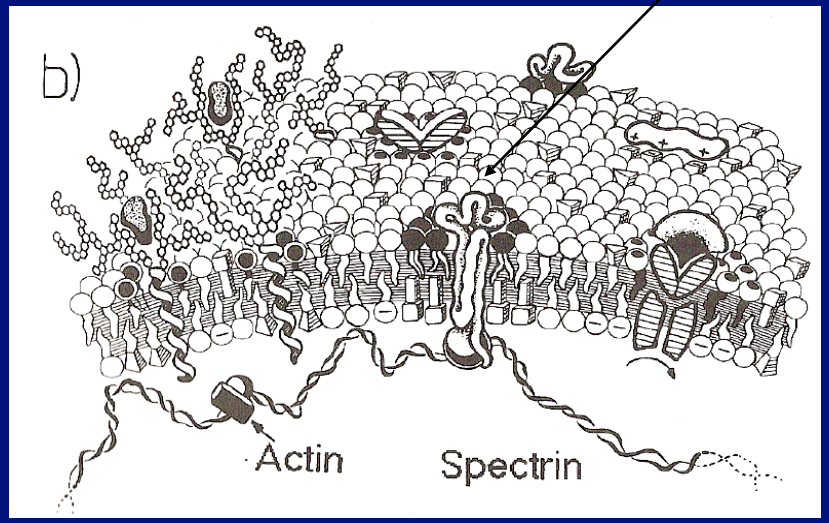
Quenched vs. annealed disorder

- Quenched disorder:
  surfactant-coated surfaces (?)



- Annealed disorder:
  fluid membranes (mobile charges and surface fluctuations)
  charge regulating surfaces (dissociation/association of weak acids)
  DNA microarrays
  polyampholytes

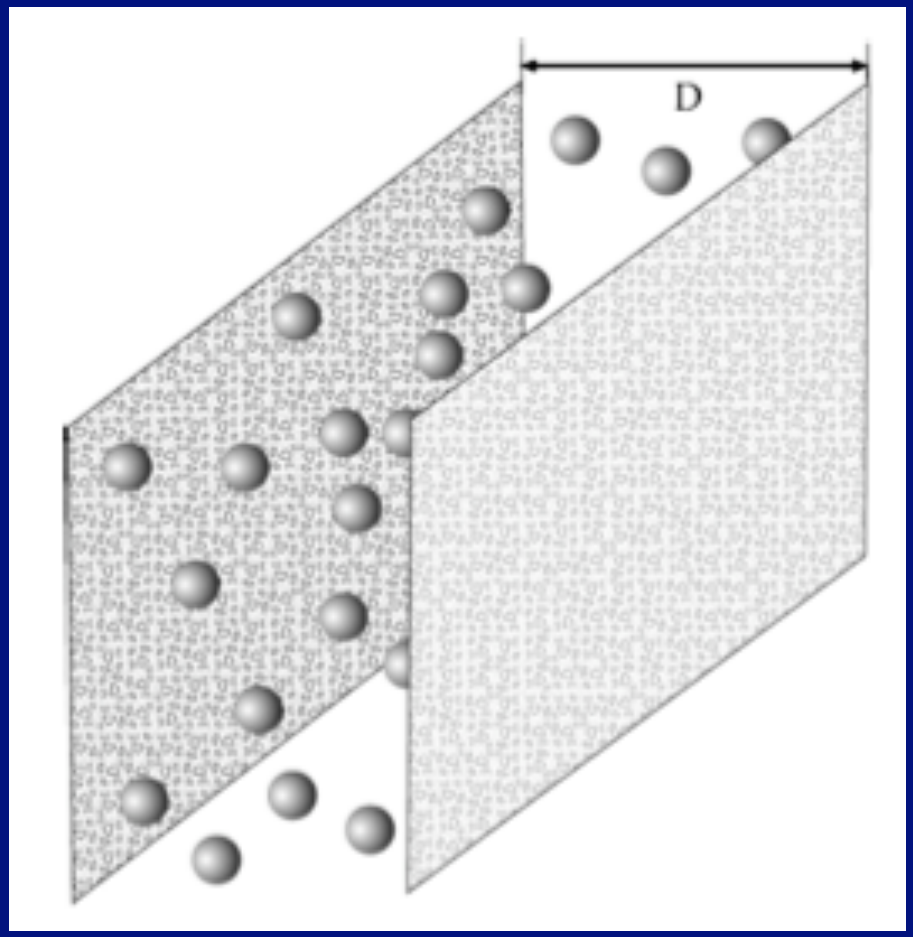
mobile charges



- Partially annealed disorder: nonequilibrium

Quenched surface charge disorder & coulomb interactions

Generalize the model system from homogeneously charged interfaces to interfaces with disordered charge distribution.



Gaussian ansatz for the charge disorder

$$\text{const} \times e^{-(1/2)\int d\mathbf{r}\, g^{-1}(\mathbf{r})[\rho(\mathbf{r})-\rho_0(\mathbf{r})]^2}.$$

The free energy:

$$\mathcal{F} = -k_B T\, \overline{\log \mathcal{Z}} = -k_B T \lim_{n\to 0} \frac{\overline{\mathcal{Z}^n} - 1}{n},$$

Replica formalism but also alternatives:

$$\overline{(\ldots)} = \int \mathcal{D}[\rho(\mathbf{r})](\cdots) e^{-(1/2)\int d\mathbf{r}\, g^{-1}(\mathbf{r})[\rho(\mathbf{r})-\rho_0(\mathbf{r})]^2}.$$

Does the quenched charge distribution have any effect on intersurface interactions?
Henri Orland (private communication,1999): not in the PB limit!

Strong coupling disorder effects

$$g(\mathbf{r}) = g(z,\rho) = g\,\delta(z-a) + g\,\delta(z+a).$$

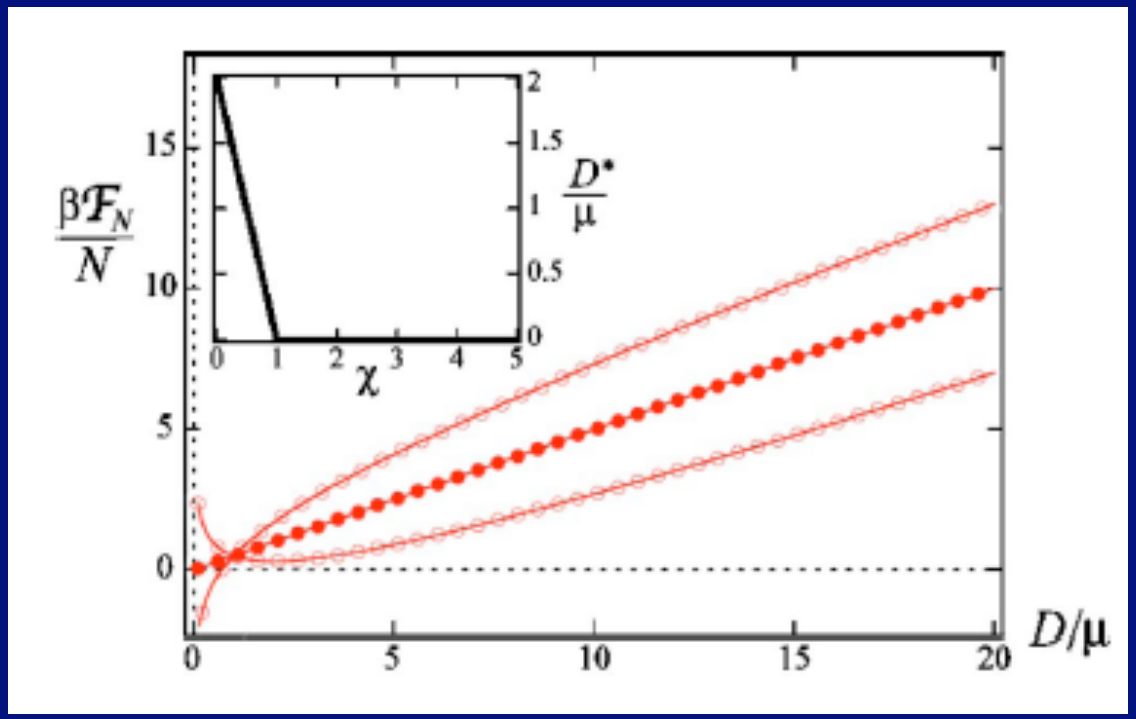
In this limit one can obtain very simple analytical results. Two charged surfaces with non-zero average and non-zero mean square average.

$$\frac{\beta\mathcal{F}_N}{N} = \tfrac{1}{2}\frac{\beta Z e_0 \sigma}{2\epsilon\epsilon_0} D + (\chi-1)\ln D - I(\chi)$$

$$= \tfrac{1}{2}\frac{D}{\mu} + (\chi-1)\ln D - I(\chi),$$

$$\chi = \frac{Z^2(\beta e_0)^2 g}{8\pi(\epsilon\epsilon_0)^2} = 2\pi Z^2 \ell_B^2 g.$$

Disorder coupling parameter.



Disappeearance of the entropic minimum for large enough disorder.

Attraction even if the surfaces carry very small NET charge!!!

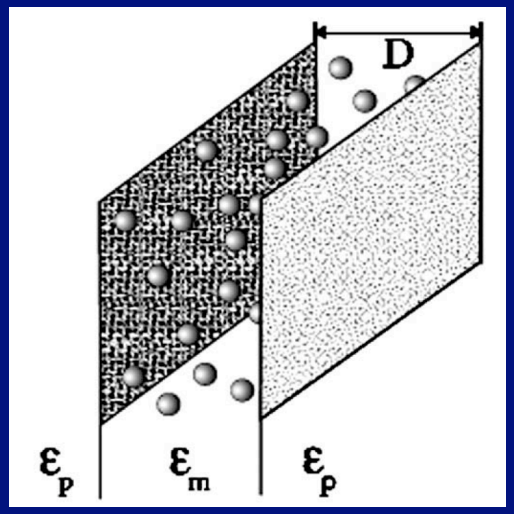
Disorder effects with dielectric inhomogeneities

$$\mathcal{Z} = \int \mathcal{D}[\phi(\boldsymbol{r})]\; e^{-\mathcal{S}[\phi(\boldsymbol{r})]}$$

Standard FT representation of the partition function.

$$\mathcal{S}[\phi(\boldsymbol{r})] \cong \frac{\beta\varepsilon_0}{2}\int \mathrm{d}\boldsymbol{r}\varepsilon(\boldsymbol{r})\Big[(\boldsymbol{\nabla}\phi(\boldsymbol{r}))^2 + \kappa^2(\boldsymbol{r})\phi^2(\boldsymbol{r})\Big] + i\beta\int \mathrm{d}\boldsymbol{r}\rho(\boldsymbol{r})\phi(\boldsymbol{r})$$

$$\beta\varepsilon_m\varepsilon_0(-\nabla^2 + \kappa^2)\mathcal{G}(\boldsymbol{r},\boldsymbol{r}') = \delta^3(\boldsymbol{r}-\boldsymbol{r}')$$



When one does the disorder average one ends up with another term in the free energy:

$$\mathcal{F} = -k_{\mathrm{B}}T\;\overline{\ln\mathcal{Z}} = \frac{\beta}{2}\;\mathrm{Tr}\;g(\boldsymbol{r})\mathcal{G}(\boldsymbol{r},\boldsymbol{r}') + \frac{k_{\mathrm{B}}T}{2}\;\mathrm{Tr}\ln\mathcal{G}^{-1}(\boldsymbol{r},\boldsymbol{r}') + \frac{\beta}{2}\iint \mathrm{d}\boldsymbol{r}\,\mathrm{d}\boldsymbol{r}'\rho_0(\boldsymbol{r})\mathcal{G}(\boldsymbol{r},\boldsymbol{r}')\rho_0(\boldsymbol{r}')$$

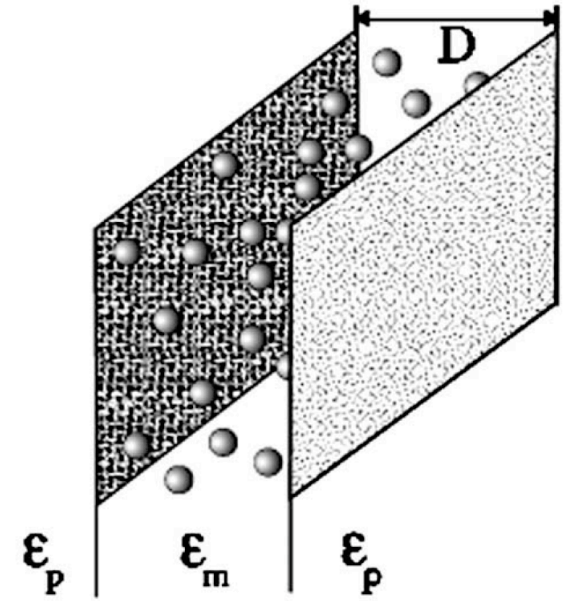
Standard vdw term

Standard mean-field term

Disorder induced term
(fluctuational in origin)

$$\mathcal{Z} = \int \mathcal{D}[\phi(\boldsymbol{r})]\; e^{-\mathcal{S}[\phi(\boldsymbol{r})]}$$

$$\mathcal{S}[\phi(\boldsymbol{r})] \cong \frac{\beta\varepsilon_0}{2} \int \mathrm{d}\boldsymbol{r}\varepsilon(\boldsymbol{r})\Big[(\boldsymbol{\nabla}\phi(\boldsymbol{r}))^2 + \kappa^2(\boldsymbol{r})\phi^2(\boldsymbol{r})\Big] + i\beta \int \mathrm{d}\boldsymbol{r}\rho(\boldsymbol{r})\phi(\boldsymbol{r})$$



$$\beta\varepsilon_m\varepsilon_0(-\nabla^2 + \kappa^2)\mathcal{G}(\boldsymbol{r},\boldsymbol{r}') = \delta^3(\boldsymbol{r}-\boldsymbol{r}')$$

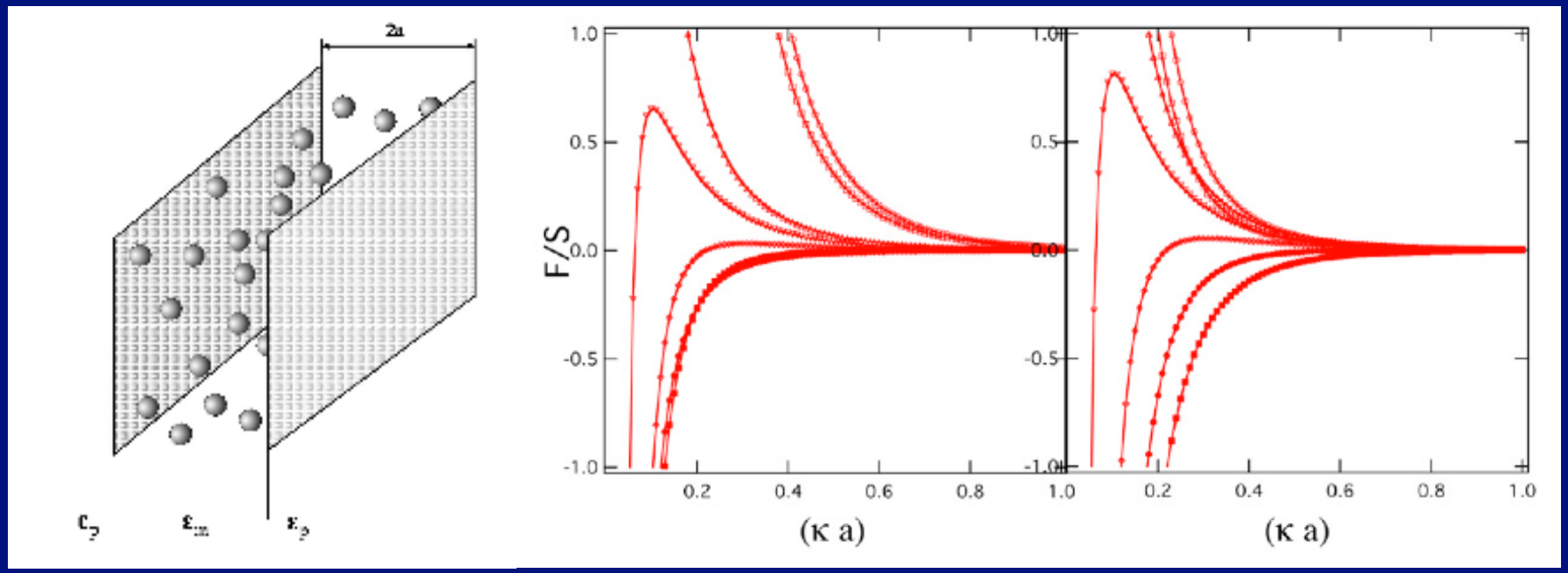
$$\mathcal{F} = -k_{\mathrm{B}}T\;\overline{\ln\mathcal{Z}} = \frac{\beta}{2}\;\mathrm{Tr}\;g(\boldsymbol{r})\mathcal{G}(\boldsymbol{r},\boldsymbol{r}') + \frac{k_{\mathrm{B}}T}{2}\;\mathrm{Tr}\ln\mathcal{G}^{-1}(\boldsymbol{r},\boldsymbol{r}') + \frac{\beta}{2}\iint \mathrm{d}\boldsymbol{r}\,\mathrm{d}\boldsymbol{r}'\rho_0(\boldsymbol{r})\mathcal{G}(\boldsymbol{r},\boldsymbol{r}')\rho_0(\boldsymbol{r}')$$

Standard vdw term

Standard mean-field term

Disorder induced term
(fluctuational in origin)

Weak coupling disorder effects with images



Disorder effect are clearly there and can be repulsive as well as attractive, for 0 < κa < 1 and the ratios εm/εp = 0.2, 0.4, 0.6, 0.8, 1.0, 5.0 and 10.0 (from top to bottom).

Small separation:

$$\frac{\mathcal{F}}{S} \simeq \frac{\sigma^2}{\epsilon_m \epsilon_0 \kappa^2 a}\left(1 + \frac{G\,\epsilon_m^2(\epsilon_m - \epsilon_p)\kappa^2}{4\pi\sigma^2(\epsilon_m + \epsilon_p)^3}\,F\left(\frac{\epsilon_m - \epsilon_p}{\epsilon + \epsilon_p}\right)\right).$$

Disorder does NOT renormalize charge. It gives a non-zero interactions even for electroneutral surfaces.

Large separation:

$$\frac{\mathcal{F}}{S} = \frac{G\,e^{-4\kappa a}}{\pi\epsilon_0\epsilon_m\,4a} - \frac{kT\,\kappa^2}{16\pi\,(\kappa a)}\,e^{-4\kappa a} + 2\frac{\sigma^2}{\epsilon\epsilon_0\kappa}\,e^{-2\kappa a}.$$

Disorder renormalizes zero frequency van der Waals.

Fascinating world of Coulomb fluids:

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

Coulomb says:

Opposites attract and equals repel!
In line with the common wisdom.

Weak coupling electrostatics says:

Opposites attract and equals repel but not quite so much!

Strong coupling electrostatics says:

Opposites repel and equals attract but only if everybody is very charged!

Quenched disorder electrostatics says:

Neutrals can attract
but only if everybody in between is very charged!

Of course, only if free mobile charges are present in solution.