From Charge Inversion to Like-charge Attraction at Debye Scale

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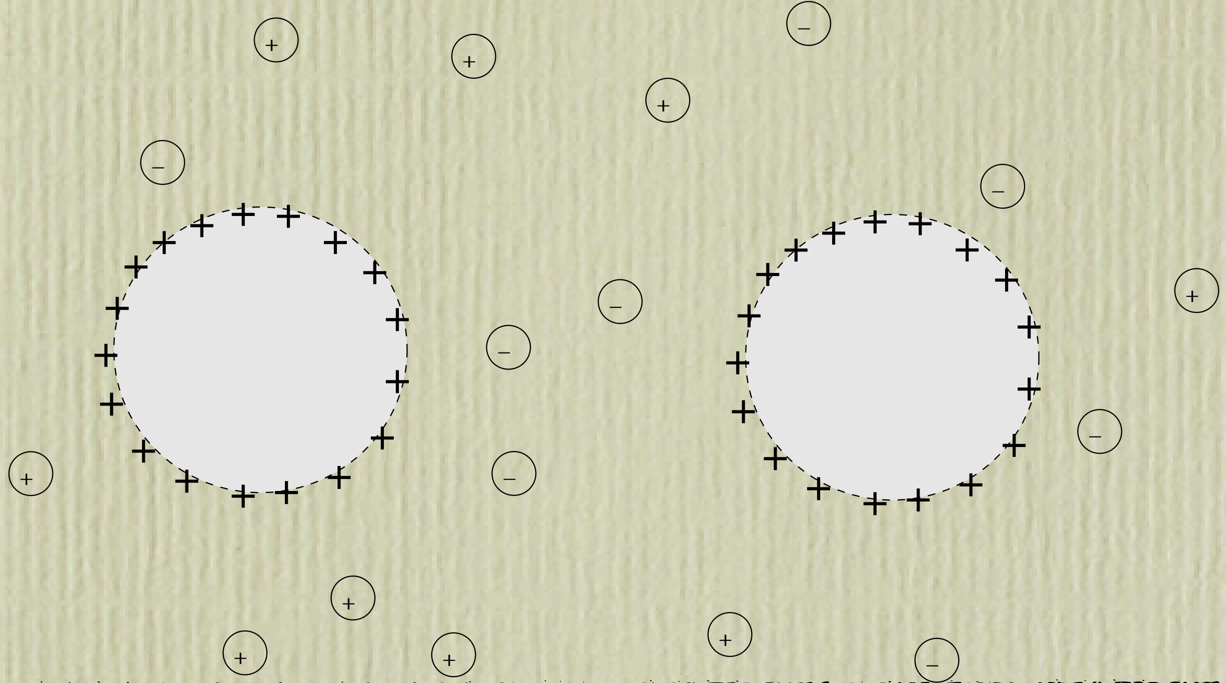
Outline

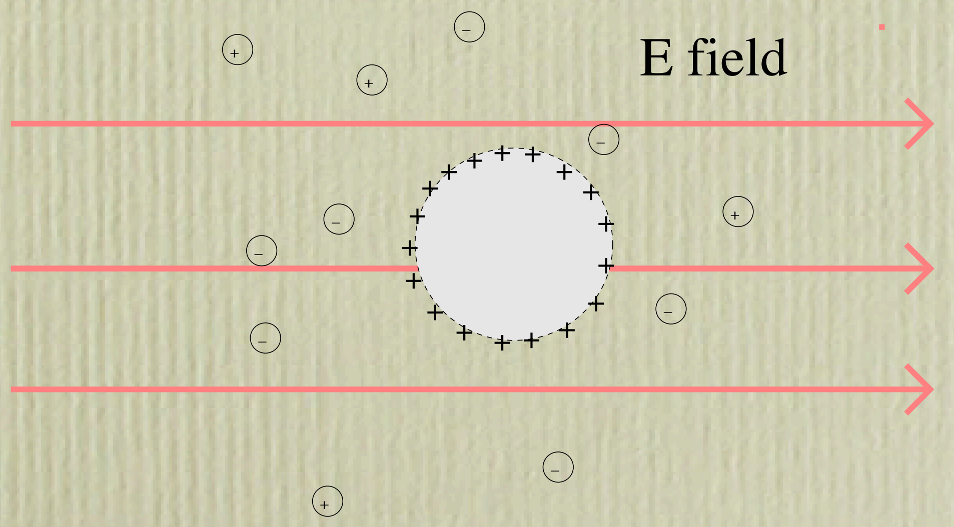
- Experiments on Like-charge Attraction
- Poisson-Boltzmann and DLVO and gap between them
- Previous Theories beyond Poisson-Boltzman
- Two Fluid Model and Interaction between two likely charged plates

Two Simple Questions about Electrolytes



attract or repel?

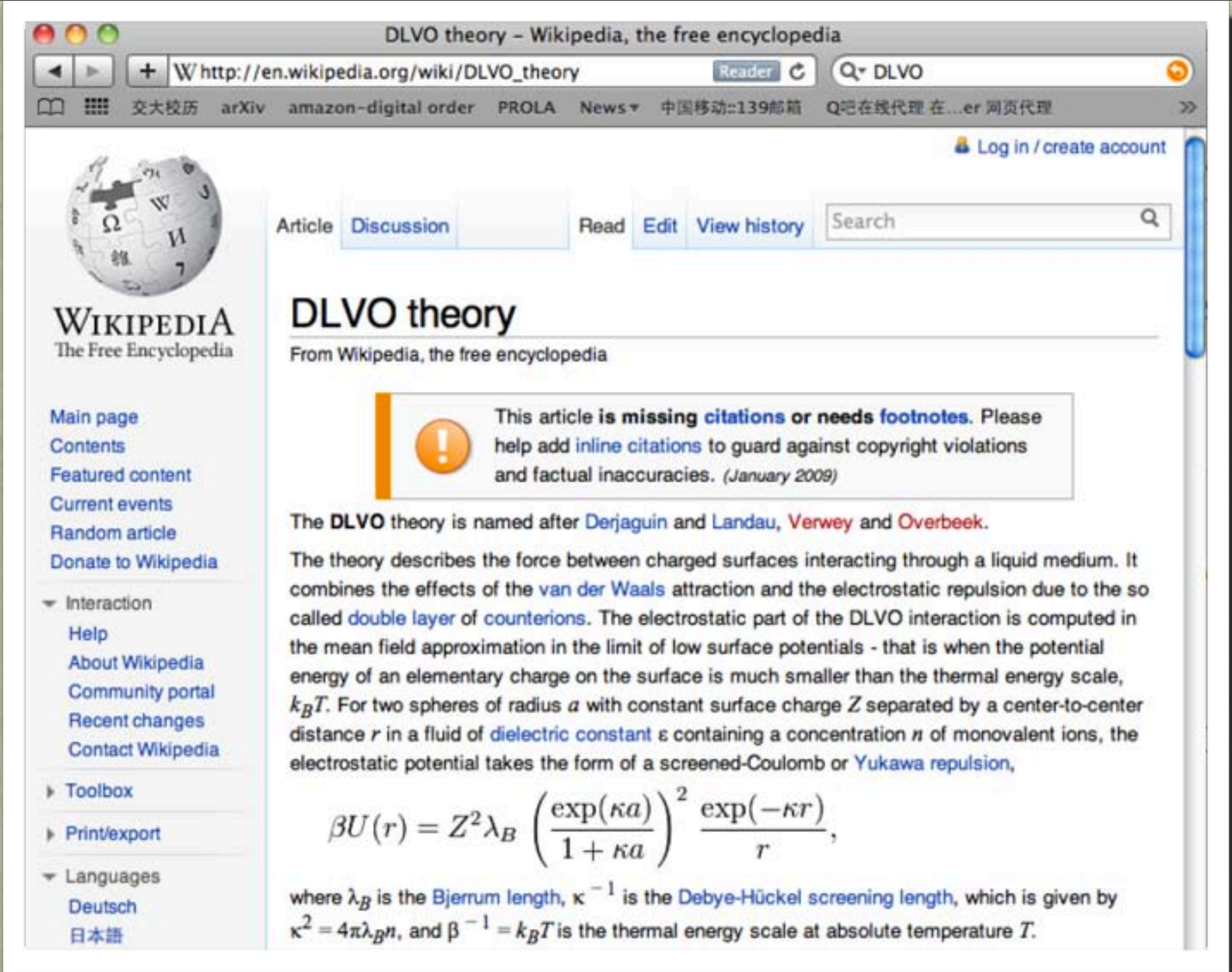
Classical DLVO Theory $U = \frac{Q_1^* Q_2^*}{4\pi\epsilon r} e^{-\kappa r}$



moving right or left?

Electrophoresis: more difficult

These two questions have remained controversial for long time.



DLVO theory

From Wikipedia, the free encyclopedia

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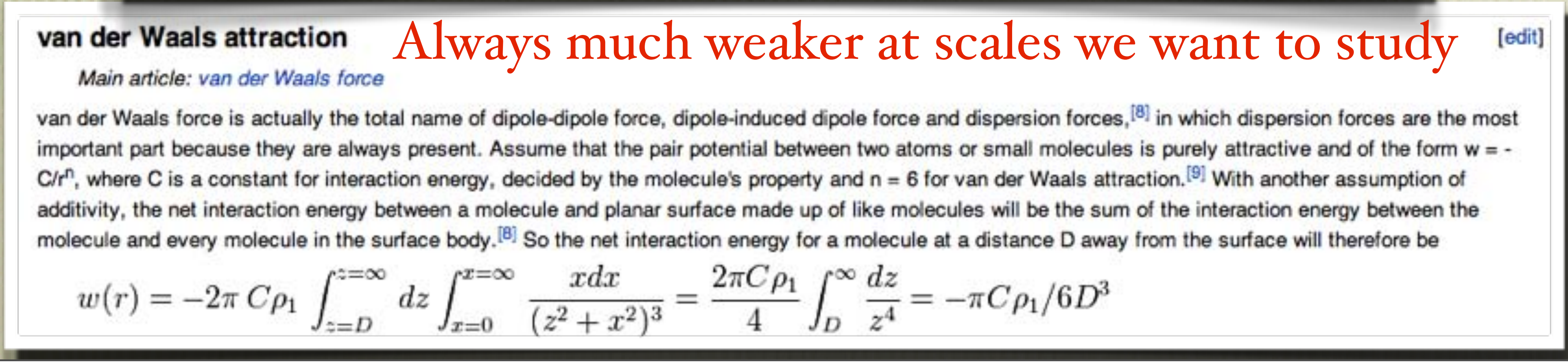
The **DLVO** theory is named after Derjaguin and Landau, Verwey and Overbeek.

The theory describes the force between charged surfaces interacting through a liquid medium. It combines the effects of the van der Waals attraction and the electrostatic repulsion due to the so called double layer of counterions. The electrostatic part of the DLVO interaction is computed in the mean field approximation in the limit of low surface potentials - that is when the potential energy of an elementary charge on the surface is much smaller than the thermal energy scale, $k_B T$. For two spheres of radius a with constant surface charge Z separated by a center-to-center distance r in a fluid of dielectric constant ε containing a concentration n of monovalent ions, the electrostatic potential takes the form of a screened-Coulomb or Yukawa repulsion,

$$\beta U(r) = Z^2 \lambda_B \left(\frac{\exp(\kappa a)}{1+\kappa a}\right)^2 \frac{\exp(-\kappa r)}{r},$$

where λ_B is the Bjerrum length, κ^{-1} is the Debye-Hückel screening length, which is given by $\kappa^2 = 4\pi\lambda_B n$, and $\beta^{-1} = k_B T$ is the thermal energy scale at absolute temperature T.



van der Waals attraction

[edit]

Always much weaker at scales we want to study

Main article: van der Waals force

van der Waals force is actually the total name of dipole-dipole force, dipole-induced dipole force and dispersion forces,[8] in which dispersion forces are the most important part because they are always present. Assume that the pair potential between two atoms or small molecules is purely attractive and of the form $w = -C/r^n$, where C is a constant for interaction energy, decided by the molecule's property and n = 6 for van der Waals attraction.[9] With another assumption of additivity, the net interaction energy between a molecule and planar surface made up of like molecules will be the sum of the interaction energy between the molecule and every molecule in the surface body.[8] So the net interaction energy for a molecule at a distance D away from the surface will therefore be

$$w(r) = -2\pi C\rho_1 \int_{z=D}^{z=\infty} dz \int_{x=0}^{x=\infty} \frac{x\,dx}{(z^2+x^2)^3} = \frac{2\pi C\rho_1}{4}\int_D^{\infty} \frac{dz}{z^4} = -\pi C\rho_1/6D^3$$

Attraction between Like-Charged Colloids


NATURE | VOL 385 | 16 JANUARY 1997

articles

Like-charge attractions in metastable colloidal crystallites

Amy E. Larsen* & David G. Grier

The James Franck Institute and Department of Physics, The University of Chicago, 5640 S. Ellis Avenue, Chicago, Illinois 60637, USA

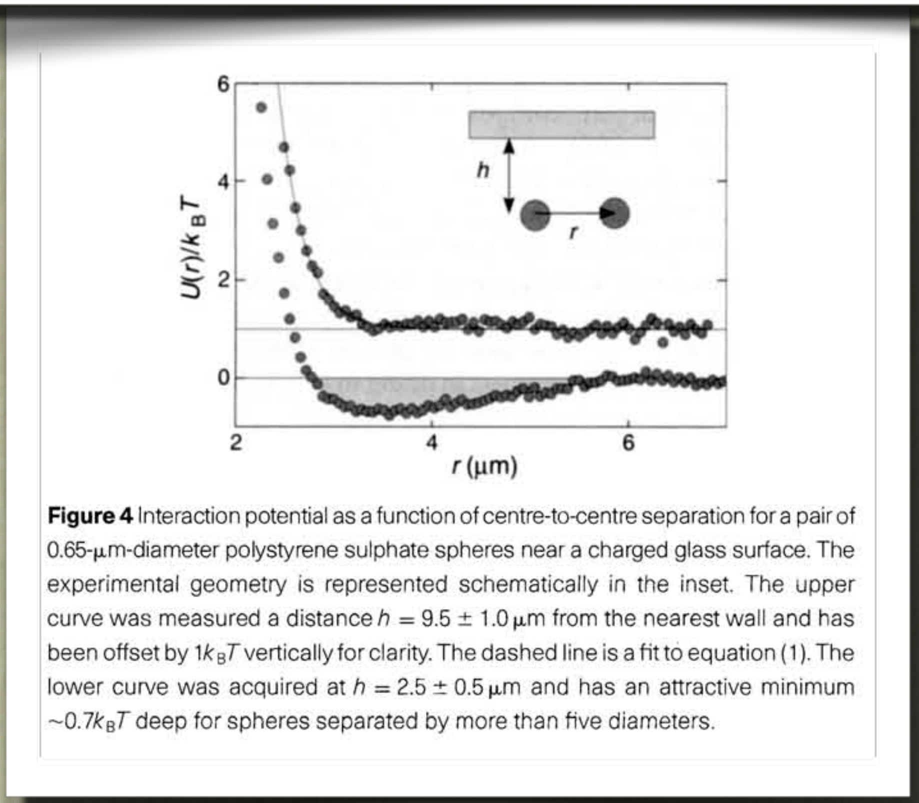
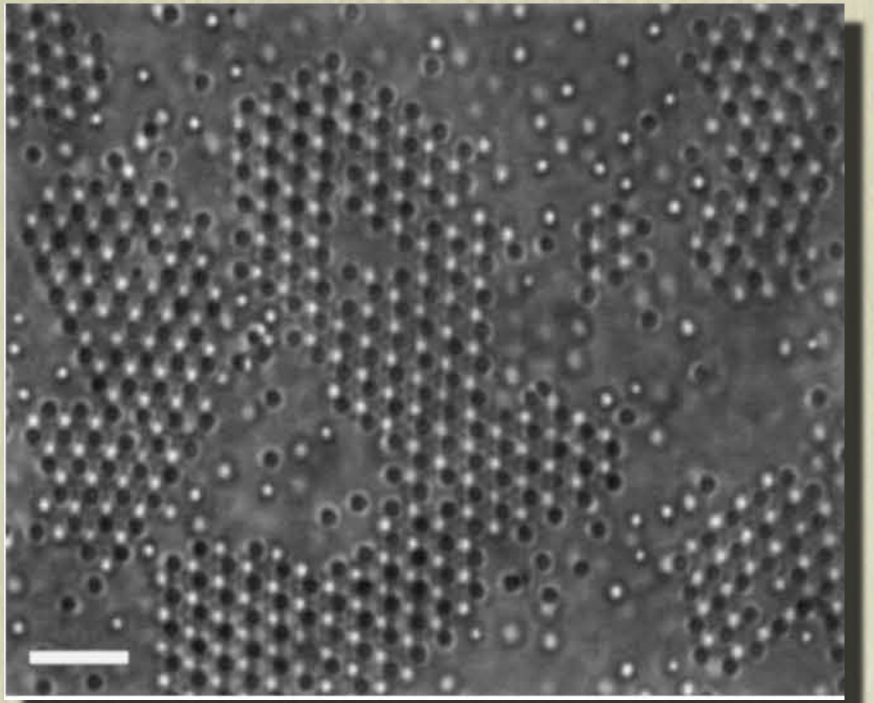


Figure 4 Interaction potential as a function of centre-to-centre separation for a pair of 0.65-μm-diameter polystyrene sulphate spheres near a charged glass surface. The experimental geometry is represented schematically in the inset. The upper curve was measured a distance $h = 9.5 \pm 1.0$ μm from the nearest wall and has been offset by $1k_BT$ vertically for clarity. The dashed line is a fit to equation (1). The lower curve was acquired at $h = 2.5 \pm 0.5$ μm and has an attractive minimum $\sim 0.7k_BT$ deep for spheres separated by more than five diameters.



Coupling parameter

$$\Xi = 2\pi q^3 \ell_B^2 \sigma_s$$

polystyrene, monovalent counter-ions

Particle diameter $600nm$
Debye length $400nm$
$28\mu m$ between two plates
$\sigma = 0.1e/nm^2$
$\ell_{GC} = 1.14nm, \quad \Xi \approx 0.3$

Monovalence Ions

Weak coupling regime!
"Confinement induced attraction"?

Direct Imaging of Bound States

polystyrene, monovalent counter-ions

particle diameter: $600nm$
Debye length: $500nm$
More than $200\mu m$ away from wall

Sample 1
$\sigma_1 = 2.7\mu C/cm^2 = 0.17e/nm^2$
$\ell_{GC} = 0.67nm, \quad \Xi = 0.5$

Sample 2
$\sigma_2 = 0.3\mu C/cm^2 = 0.019e/nm^2$
$\ell_{GC} = 6.1nm, \quad \Xi =$

Sample 3
$\sigma_3 = 0.004\mu C/cm^2 =$
$\ell_{GC} = 455nm$

No bound states seen

In sample 1 & 2, bou
seconds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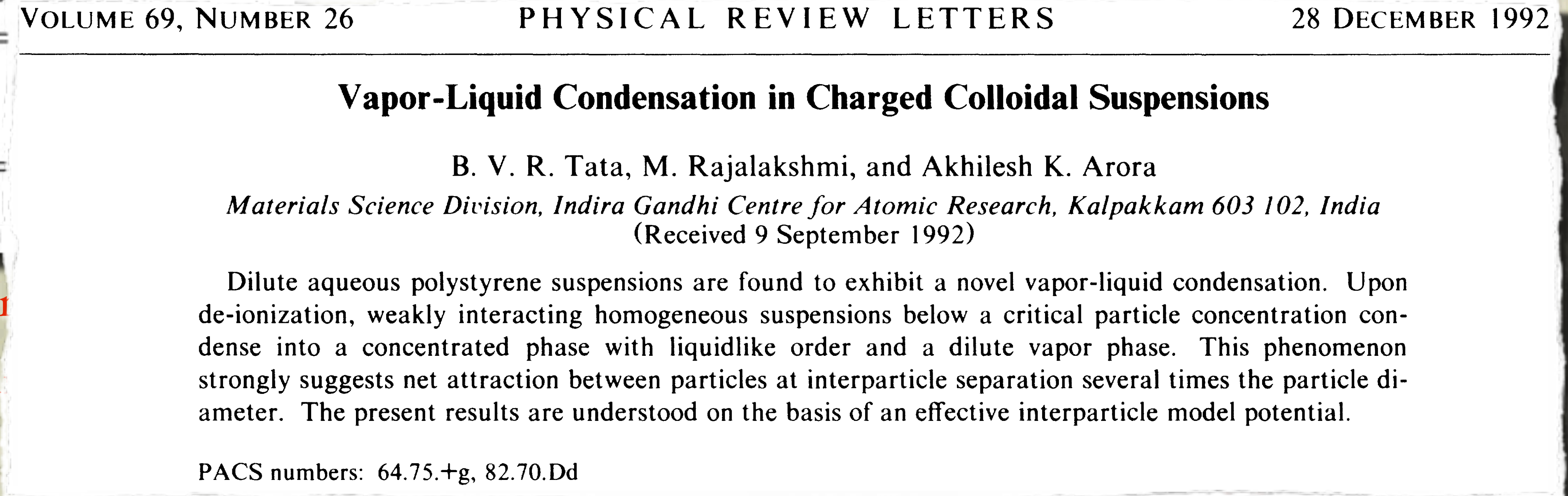
Bound pairs: Direct evidence for long-range attraction between like-charged colloids

B.V.R. Tata*, P.S. Mohanty, M.C. Valsakumar

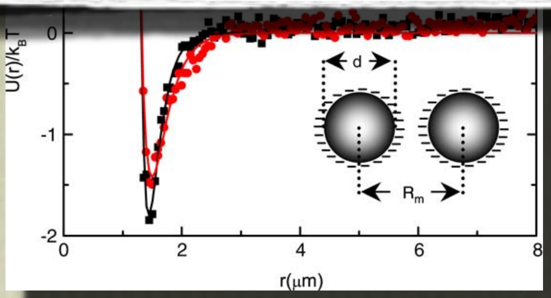

VOLUME 69, NUMBER 26 PHYSICAL REVIEW LETTERS 28 DECEMBER 1992

Vapor-Liquid Condensation in Charged Colloidal Suspensions

B. V. R. Tata, M. Rajalakshmi, and Akhilesh K. Arora
Materials Science Division, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, India
(Received 9 September 1992)

Dilute aqueous polystyrene suspensions are found to exhibit a novel vapor-liquid condensation. Upon de-ionization, weakly interacting homogeneous suspensions below a critical particle concentration condense into a concentrated phase with liquidlike order and a dilute vapor phase. This phenomenon strongly suggests net attraction between particles at interparticle separation several times the particle diameter. The present results are understood on the basis of an effective interparticle model potential.

PACS numbers: 64.75.+g, 82.70.Dd



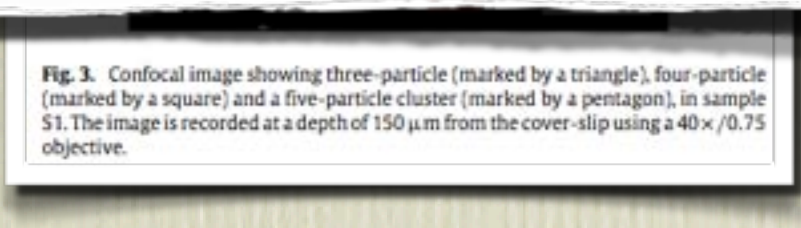
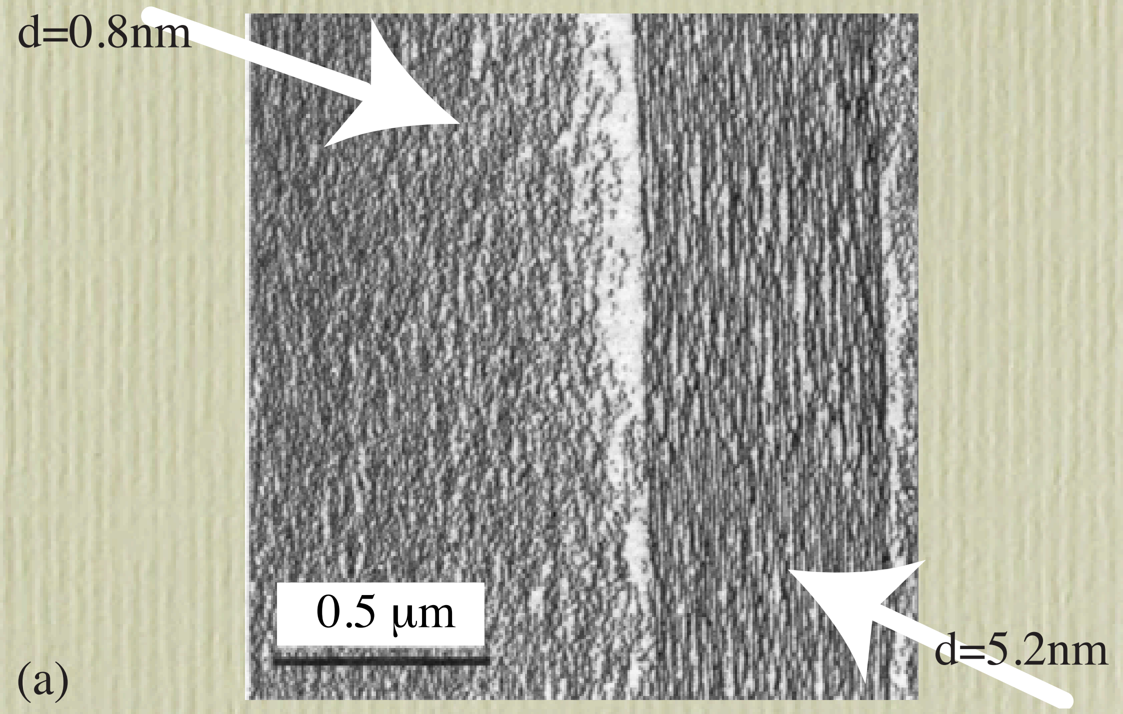


Fig. 3. Confocal image showing three-particle (marked by a triangle), four-particle (marked by a square) and a five-particle cluster (marked by a pentagon), in sample S1. The image is recorded at a depth of 150 μm from the cover-slip using a 40× /0.75 objective.

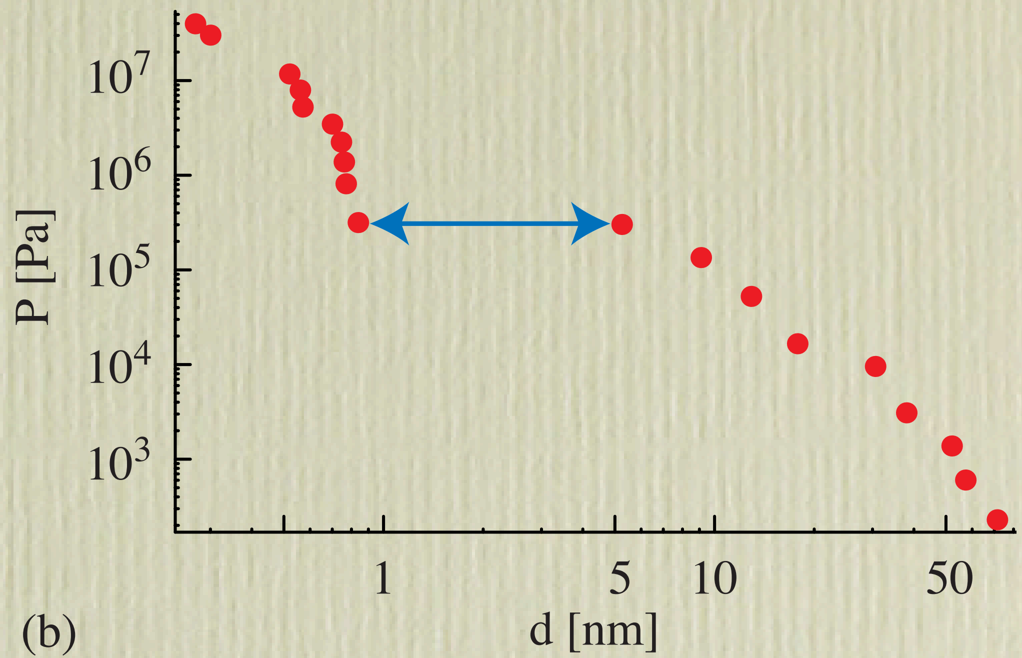
Coupling parameter

$$\Xi = 2\pi q^3 \ell_B^2 \sigma_s$$

Likely-Charged Lipid Layers



(a)



(b)

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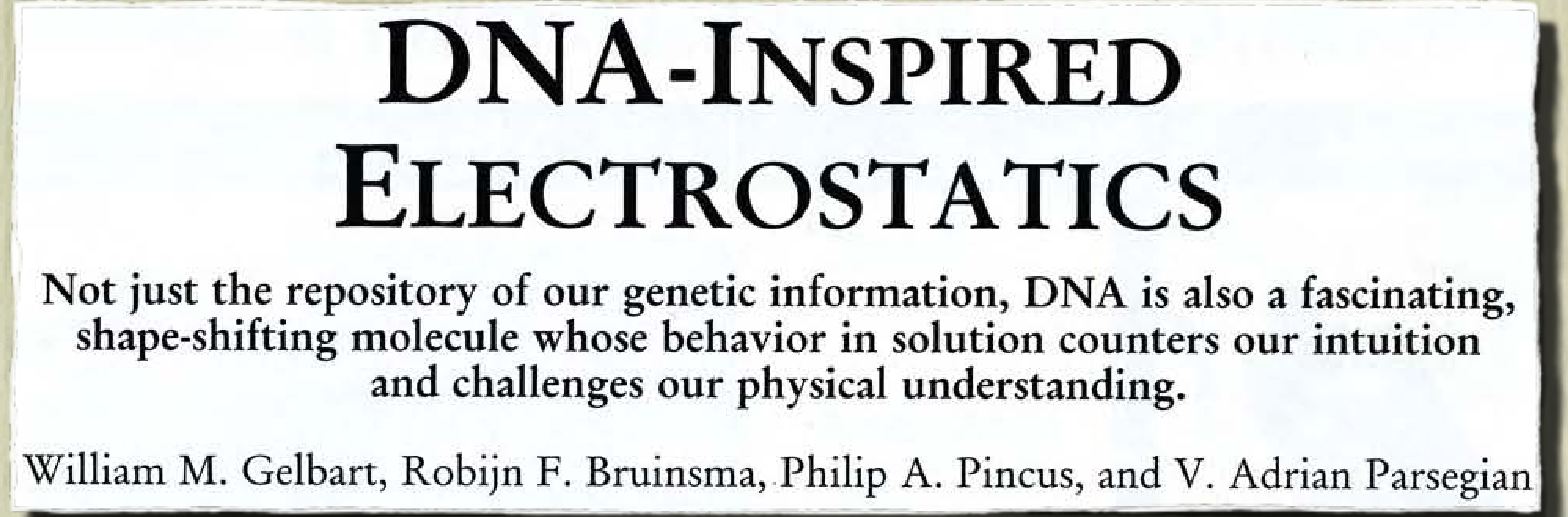
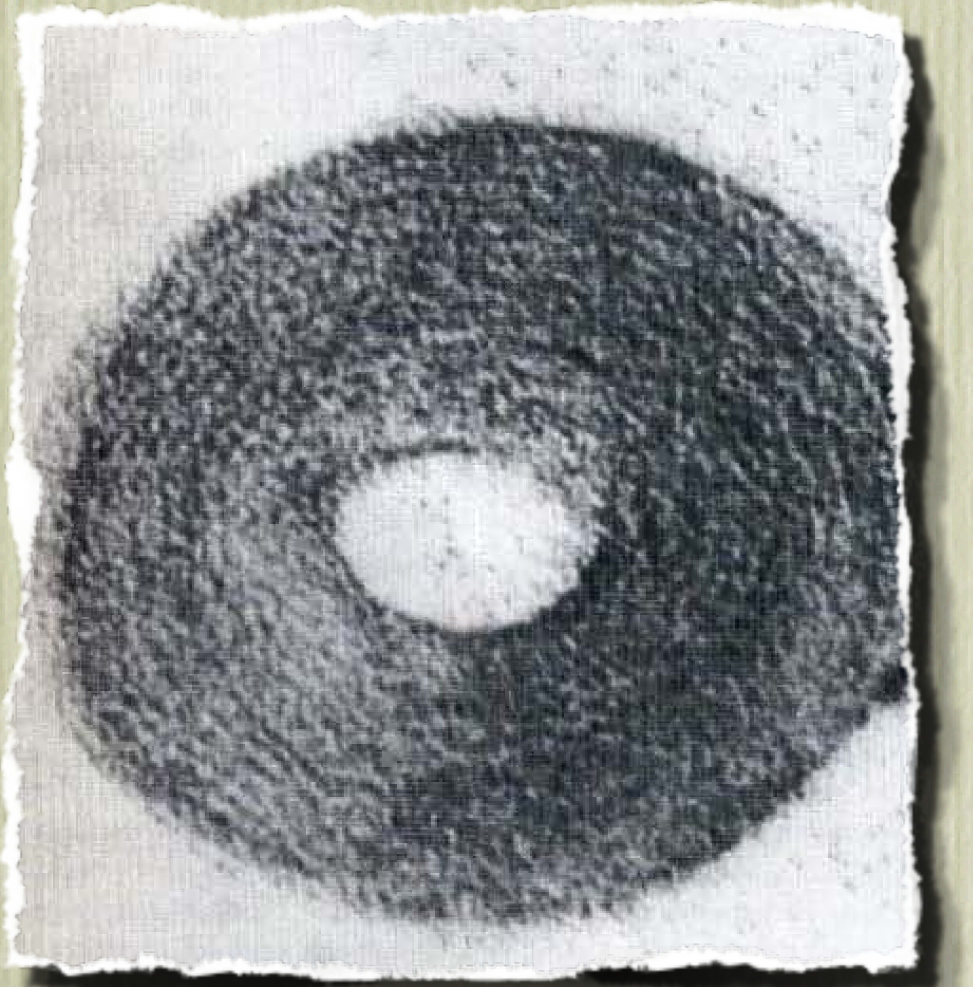
surface charge density:
0.6 e/nm^2
No data on Debye length



DNA-INSPIRED ELECTROSTATICS

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

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



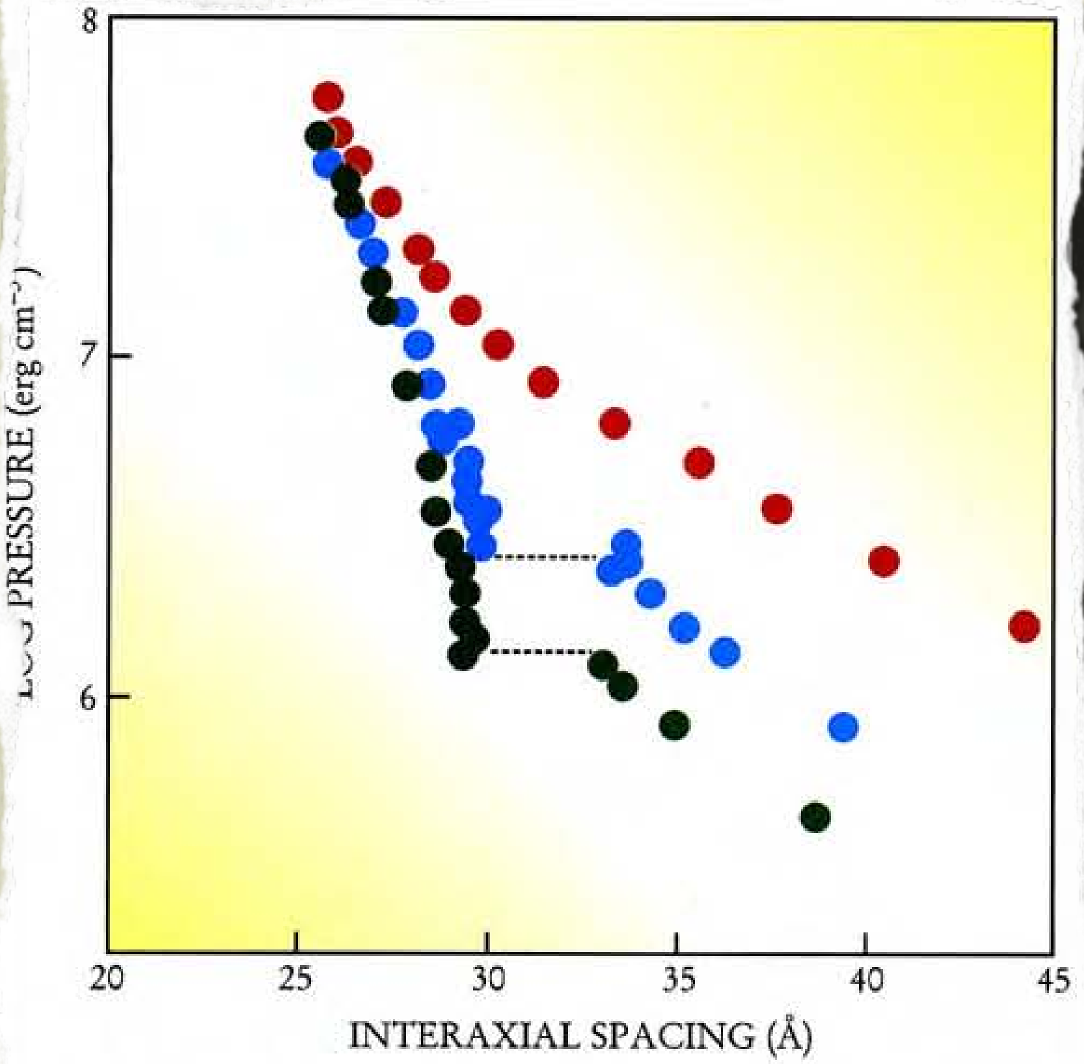
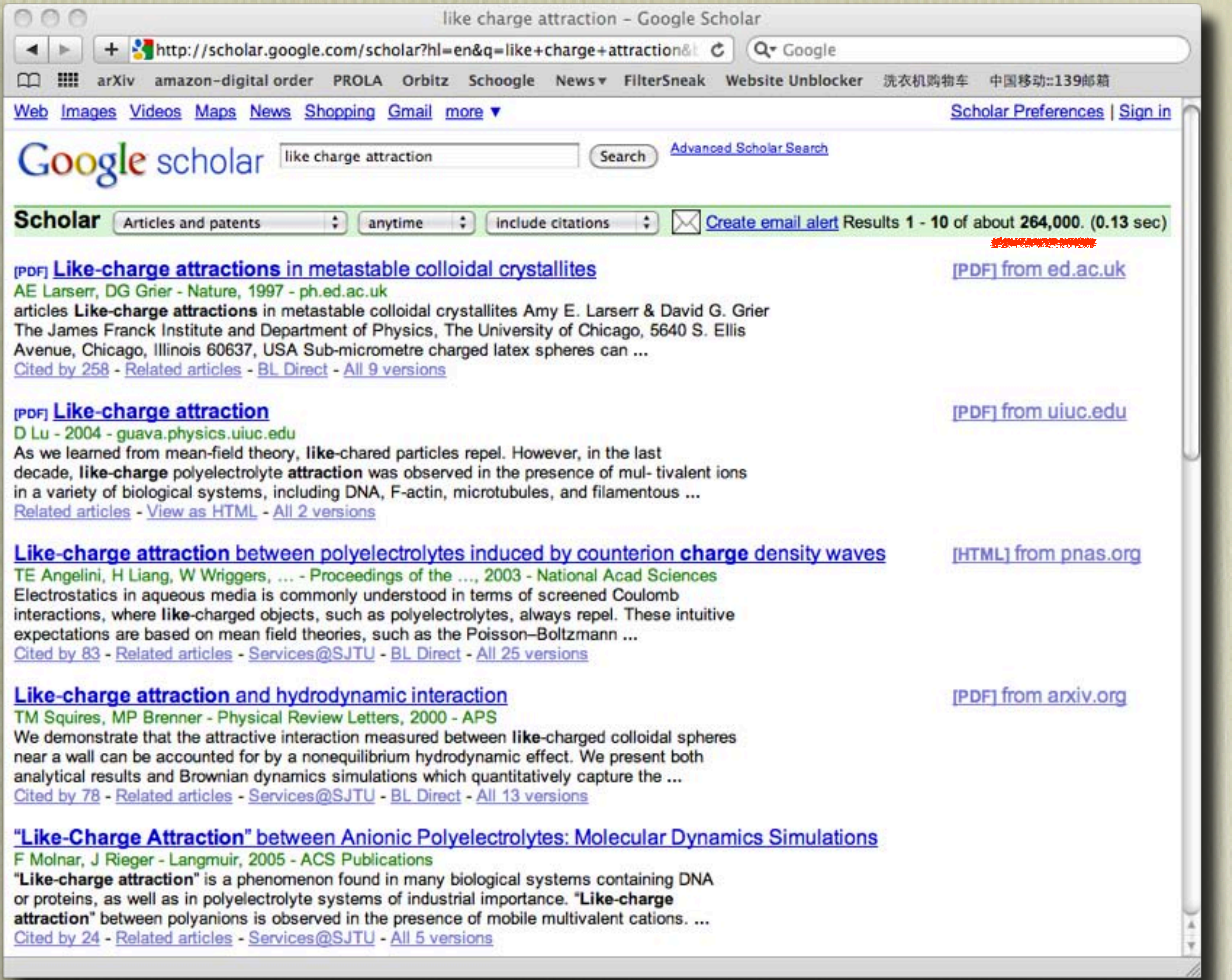


FIGURE 2. MEASURED INTERMOLECULAR FORCE as a function of interaxial separation for DNA in simple salt solutions (0.25 molar NaCl) that contain increasing concentrations (2 mM, red; 8 mM, blue; 12 mM; green) of the trivalent cation $Co(NH_4)_6^{+3}$. (Adapted from ref. 2, Rau *et al.*)



like charge attraction

Results 1 - 10 of about **264,000**. (**0.13** sec)

[PDF] **Like-charge attractions** in metastable colloidal crystallites — [PDF] from ed.ac.uk
AE Larsen, DG Grier - Nature, 1997 - ph.ed.ac.uk
articles **Like-charge attractions** in metastable colloidal crystallites Amy E. Larsen & David G. Grier The James Franck Institute and Department of Physics, The University of Chicago, 5640 S. Ellis Avenue, Chicago, Illinois 60637, USA Sub-micrometre charged latex spheres can ...
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D Lu - 2004 - guava.physics.uiuc.edu
As we learned from mean-field theory, **like**-chared particles repel. However, in the last decade, **like-charge** polyelectrolyte **attraction** was observed in the presence of mul- tivalent ions in a variety of biological systems, including DNA, F-actin, microtubules, and filamentous ...
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Like-charge attraction between polyelectrolytes induced by counterion **charge** density waves — [HTML] from pnas.org
TE Angelini, H Liang, W Wriggers, ... - Proceedings of the ..., 2003 - National Acad Sciences
Electrostatics in aqueous media is commonly understood in terms of screened Coulomb interactions, where **like**-charged objects, such as polyelectrolytes, always repel. These intuitive expectations are based on mean field theories, such as the Poisson–Boltzmann ...
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Like-charge attraction and hydrodynamic interaction — [PDF] from arxiv.org
TM Squires, MP Brenner - Physical Review Letters, 2000 - APS
We demonstrate that the attractive interaction measured between **like**-charged colloidal spheres near a wall can be accounted for by a nonequilibrium hydrodynamic effect. We present both analytical results and Brownian dynamics simulations which quantitatively capture the ...
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"**Like-Charge Attraction**" between Anionic Polyelectrolytes: Molecular Dynamics Simulations
F Molnar, J Rieger - Langmuir, 2005 - ACS Publications
"**Like-charge attraction**" is a phenomenon found in many biological systems containing DNA or proteins, as well as in polyelectrolyte systems of industrial importance. "**Like-charge attraction**" between polyanions is observed in the presence of mobile multivalent cations. ...
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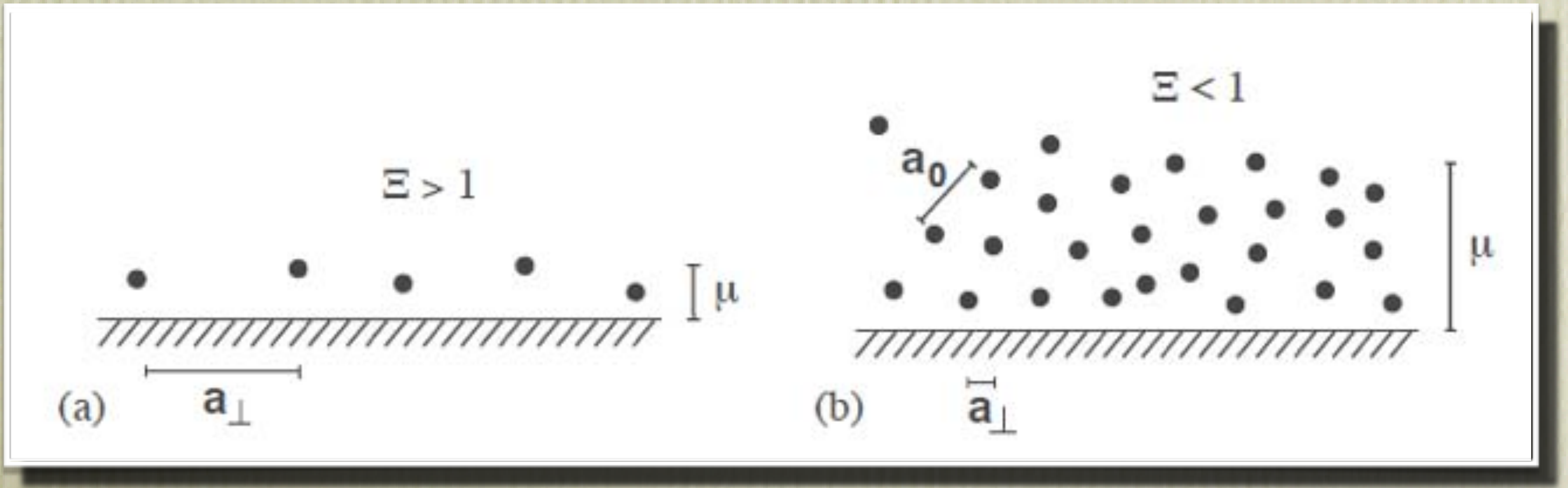
The Primitive Model of Electrolyte

with unknown origin

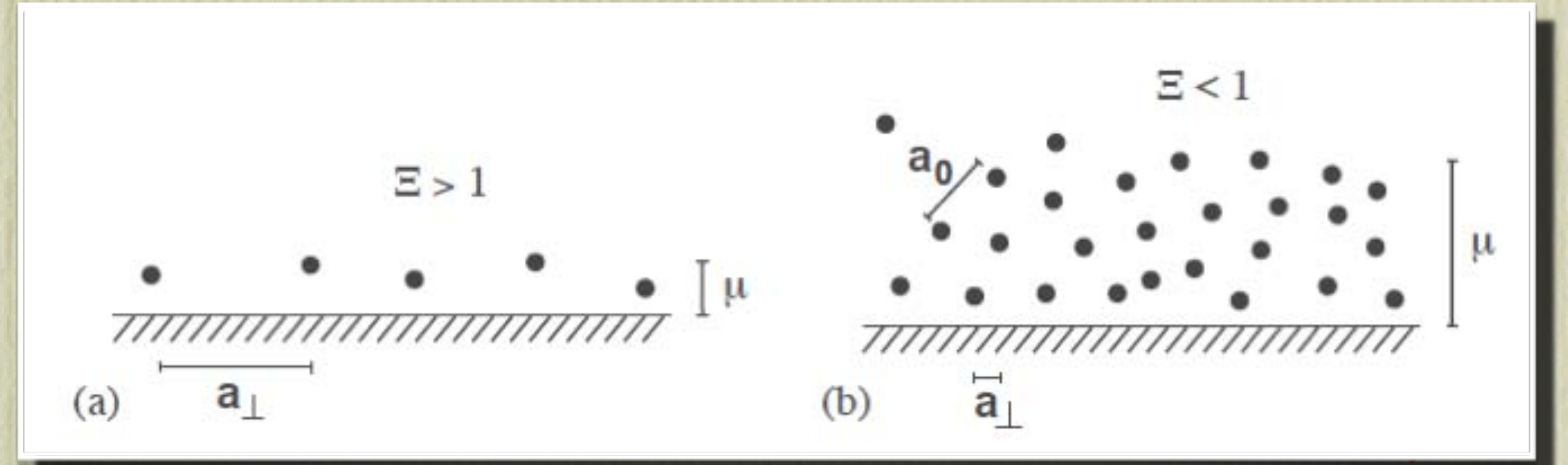
- Uniform surface charge density σ. (just for convenience, not essential)
- Ions with charge q, radius a.
- Temperature T.
- Dielectric constant of solid ~ 1, water $\epsilon \sim 80 \gg 1$.

Strong image charge effects due to surface

- Debye length $\ell_{DB} = \kappa^{-1}$, decay length of potetial in water.



Some Important Length Scales



- Gouy-Chapmann $\ell_{GC} \sim \frac{\epsilon}{\beta q \sigma}$

  Interaction with charged surface $\epsilon^{-1}\sigma q \ell_{GC}$

  balances thermal energy $1/\beta = k_B T$

  Typically a few Angstroms to a few nms.

- Bjerrm length $\lambda_{Bj} = \frac{q^2}{4\pi\epsilon k_B T} \approx 0.7nm$

  Interaction between ions $\frac{q^2}{4\pi\epsilon\lambda_{Bj}}$

  balances thermal energy $k_B T$.

- Coupling parameter $\Xi = \frac{\lambda_{Bj}}{\ell_{GC}}$
- $\Xi \gg 1$, strong coupling.

  lateral correlation between ions important

- $\Xi \leq 1$, weak coupling

  Mean field (Poisson-Boltzmann) valid

Where are the difficulties

- Lack of translational symmetry
    - Simple geometry is desirable
- Long range Coulomb interaction
    - Mean field theory (Poisson-Boltzmann) is not enough
    - How to go beyond MFT without going crazy?
- Lack of proper understanding of short scale details
    - Specific interactions: chemistry may matter
    - Is it a physics problem or chemistry problem?

Poisson-Boltzmann Theory

1. Every ion interact with a mean field ϕ

   $\rho(x) = qn\, e^{-q\beta\phi} - qn\, e^{q\beta\phi}$ ← Mean field theory

2. The mean field ϕ is determined self-consistently

   $-\Delta\phi(x) = \rho(x)$

3. Nonlinear Poisson-Boltzmann

   $\Delta\Psi + \kappa^2 \sinh\Psi = 0, \quad \Psi = \beta q\phi$

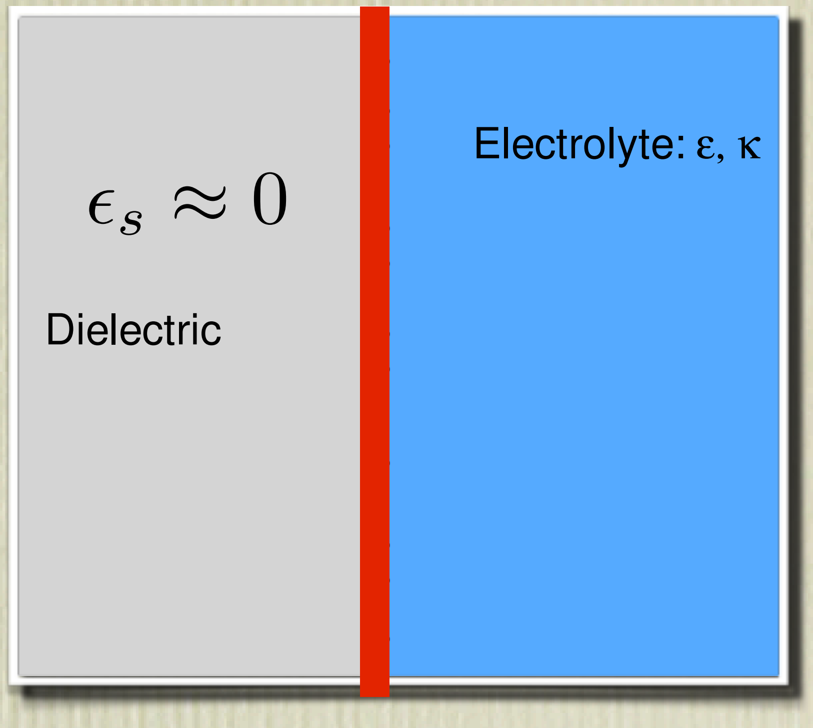
4. Linearization: $\Psi \ll 1$, $\sinh\Psi \approx \Psi$

   $-\Delta\phi + \kappa^2\phi = 0$

Boundary Conditions

- Standard electrostatic BC $\epsilon_l \frac{\partial \phi}{\partial n}\Big|_l - \epsilon_s \frac{\partial \phi}{\partial n}\Big|_s = \sigma$
- If $\epsilon_l (\approx 80) >> \epsilon_s (\sim 1)$, we can set $\epsilon_s = 0$,
- reduce to Neumann BC: $\epsilon_s \frac{\partial \phi}{\partial n}\Big|_s = \sigma$

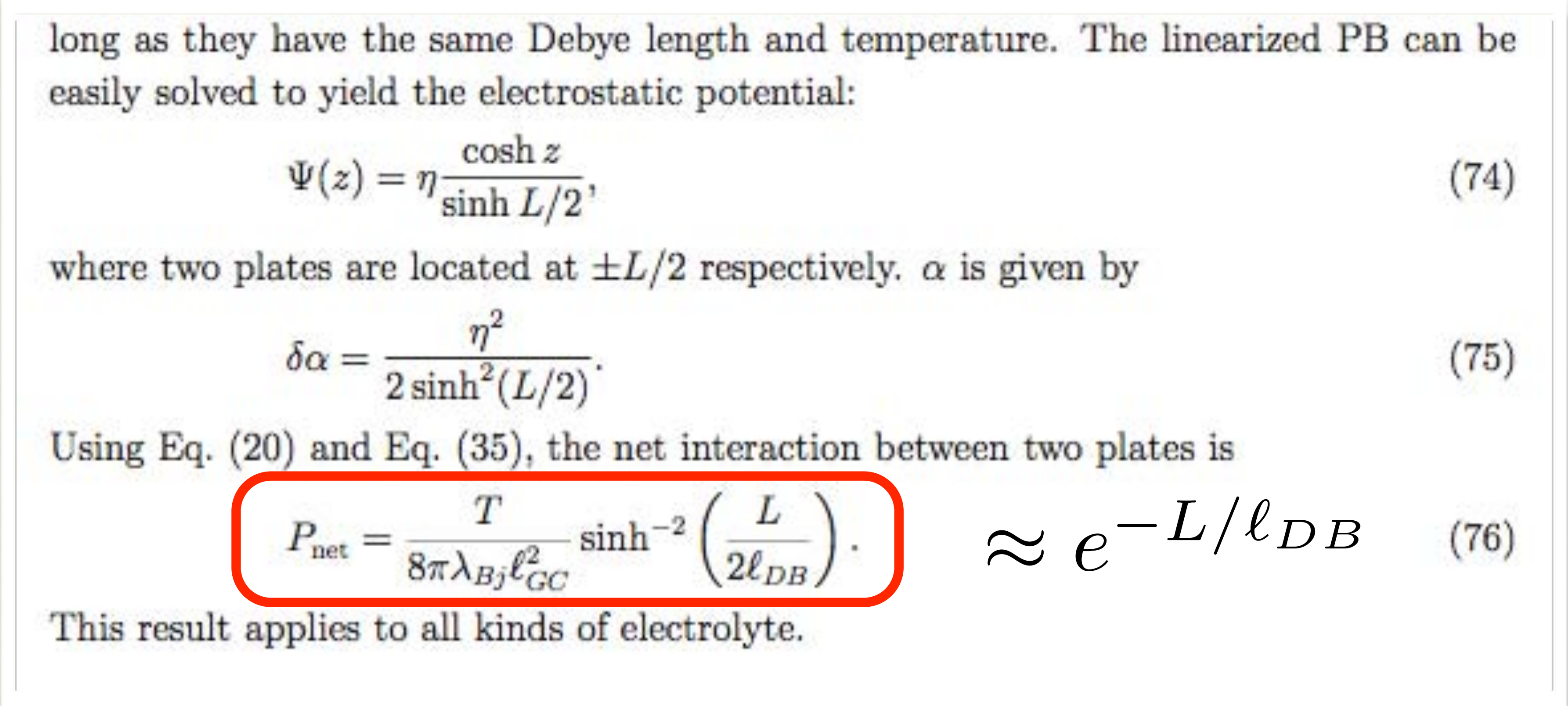
$$\Delta \Psi - \kappa^2 \sinh \Psi = 0$$



- Potential in two regions decouple from each other
- What is left is a mathematical problem!
- Linear Elliptic PDE with Neumann BC

  Solution exists and unique, smooth

Linearized PB: Two-Plate Problem



long as they have the same Debye length and temperature. The linearized PB can be easily solved to yield the electrostatic potential:

$$\Psi(z) = \eta \frac{\cosh z}{\sinh L/2}, \tag{74}$$

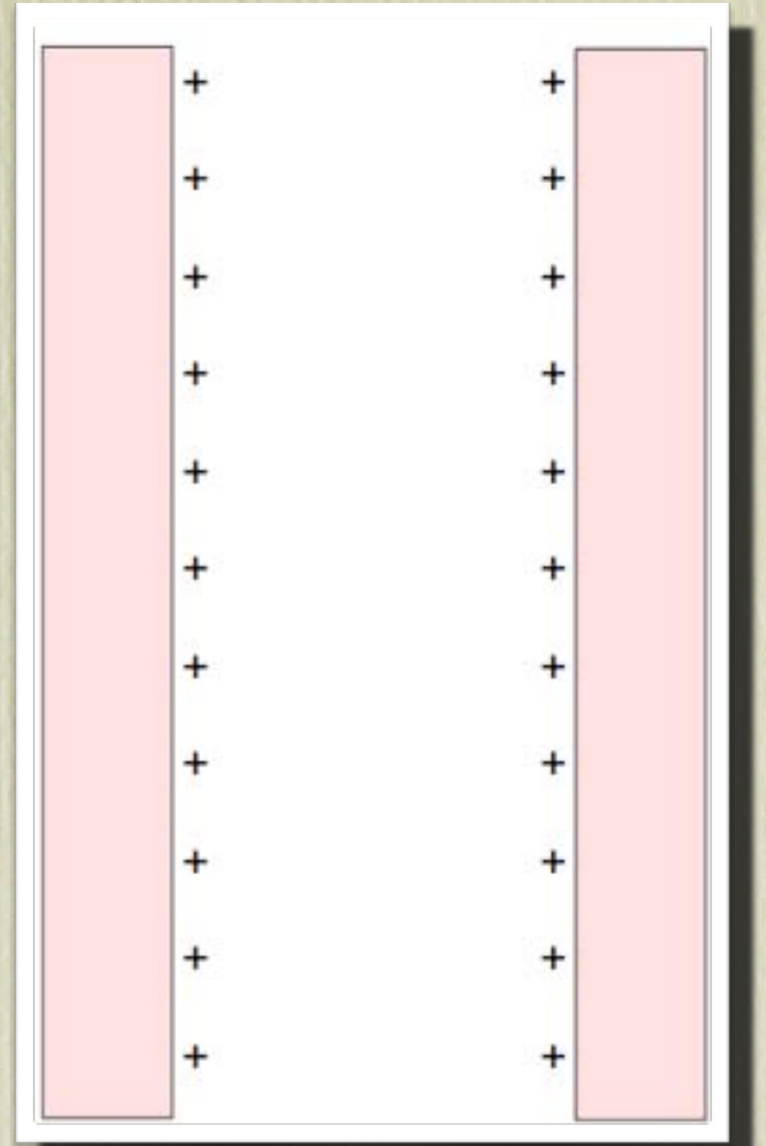
where two plates are located at $\pm L/2$ respectively. α is given by

$$\delta\alpha = \frac{\eta^2}{2\sinh^2(L/2)}. \tag{75}$$

Using Eq. (20) and Eq. (35), the net interaction between two plates is

$$\boxed{P_{\text{net}} = \frac{T}{8\pi\lambda_{Bj}\ell_{GC}^2}\sinh^{-2}\left(\frac{L}{2\ell_{DB}}\right).} \quad \approx e^{-L/\ell_{DB}} \tag{76}$$

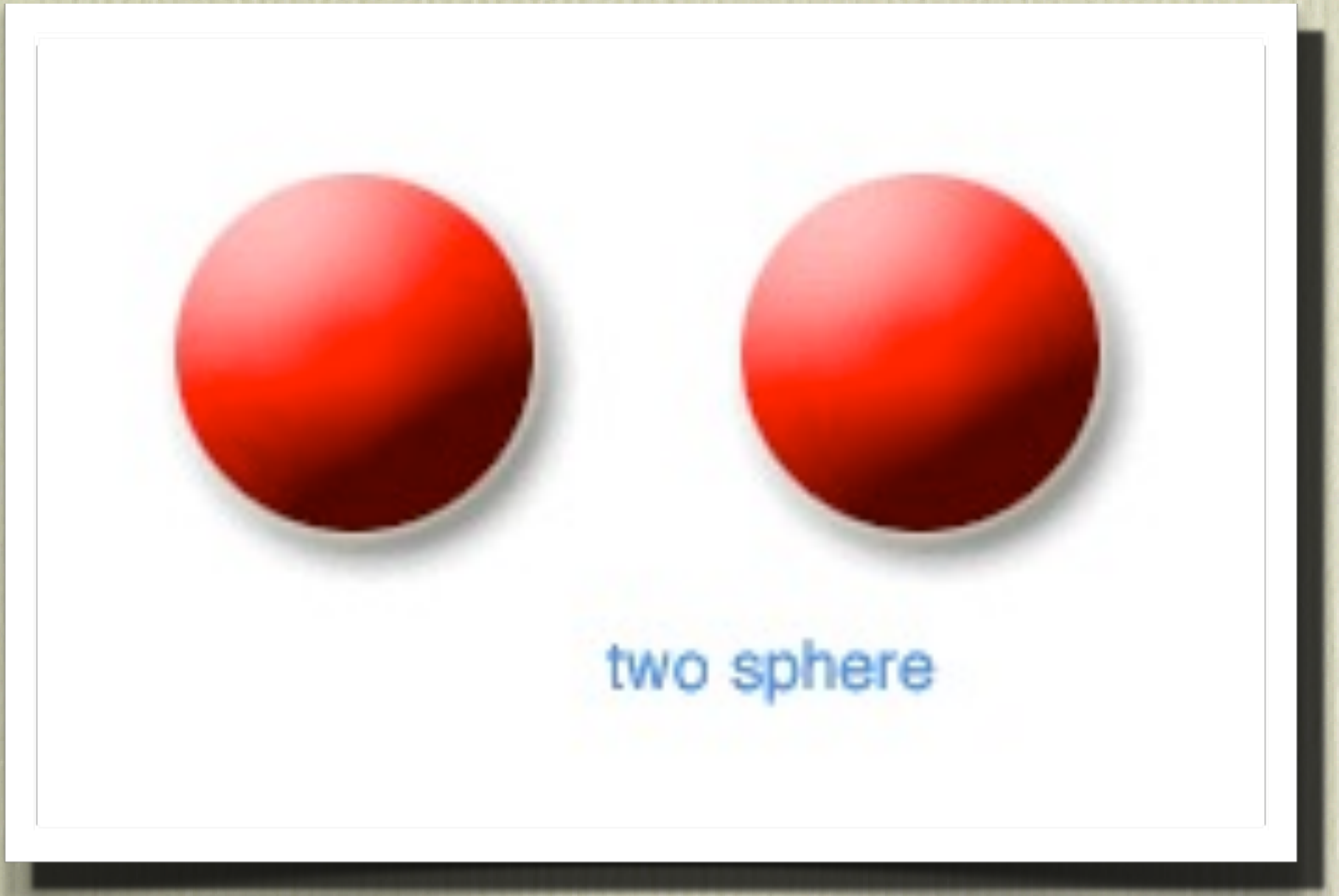
This result applies to all kinds of electrolyte.



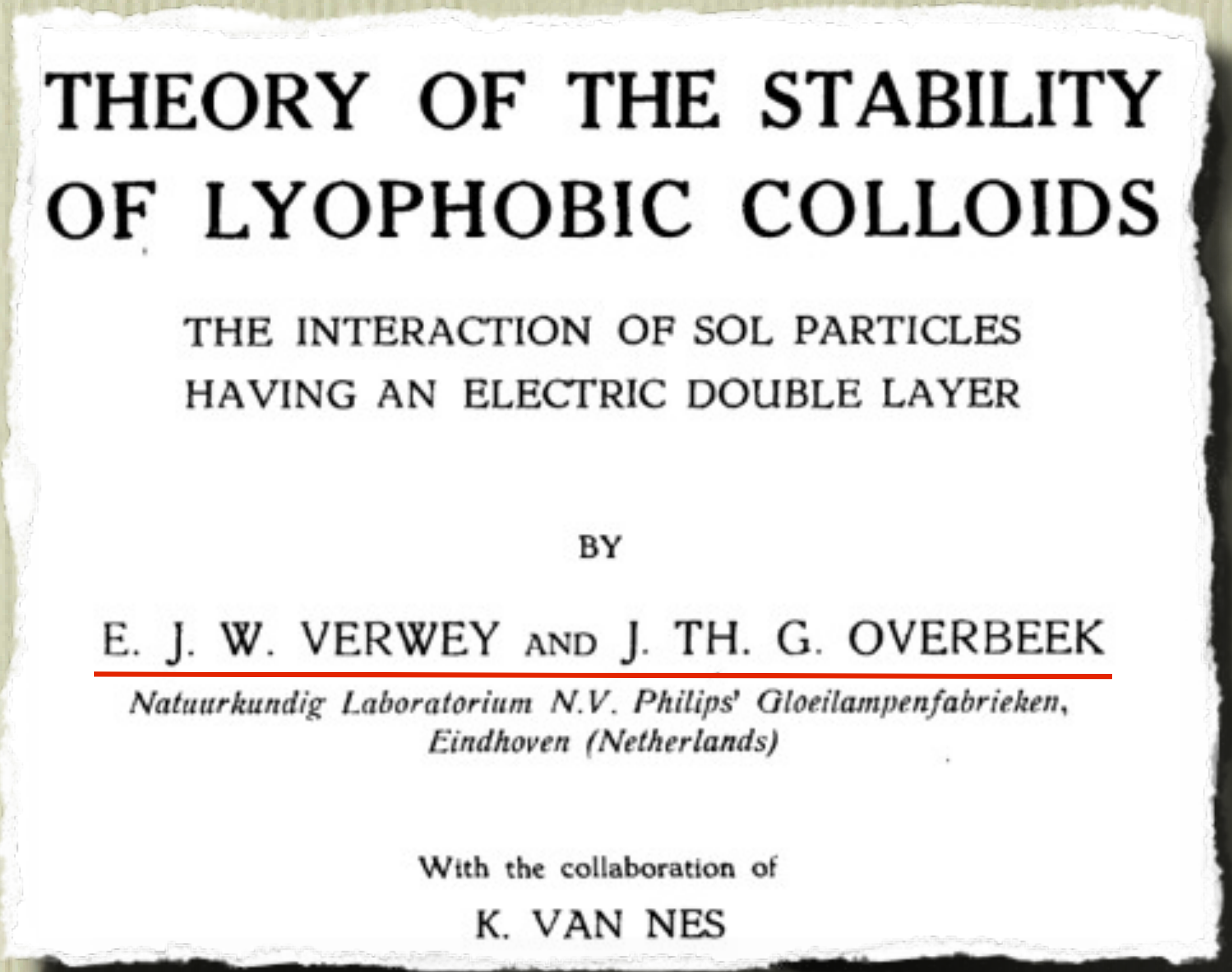
We can either assume potential is constant or charge density is constant on plates, they are equivalent

Two Sphere Problem

- Difficult boundary value problem (but mathematical problem!)
- Constant potential and constant charge density are inequivalent



Derjaguin & Landau



THEORY OF THE STABILITY OF LYOPHOBIC COLLOIDS

THE INTERACTION OF SOL PARTICLES HAVING AN ELECTRIC DOUBLE LAYER

BY

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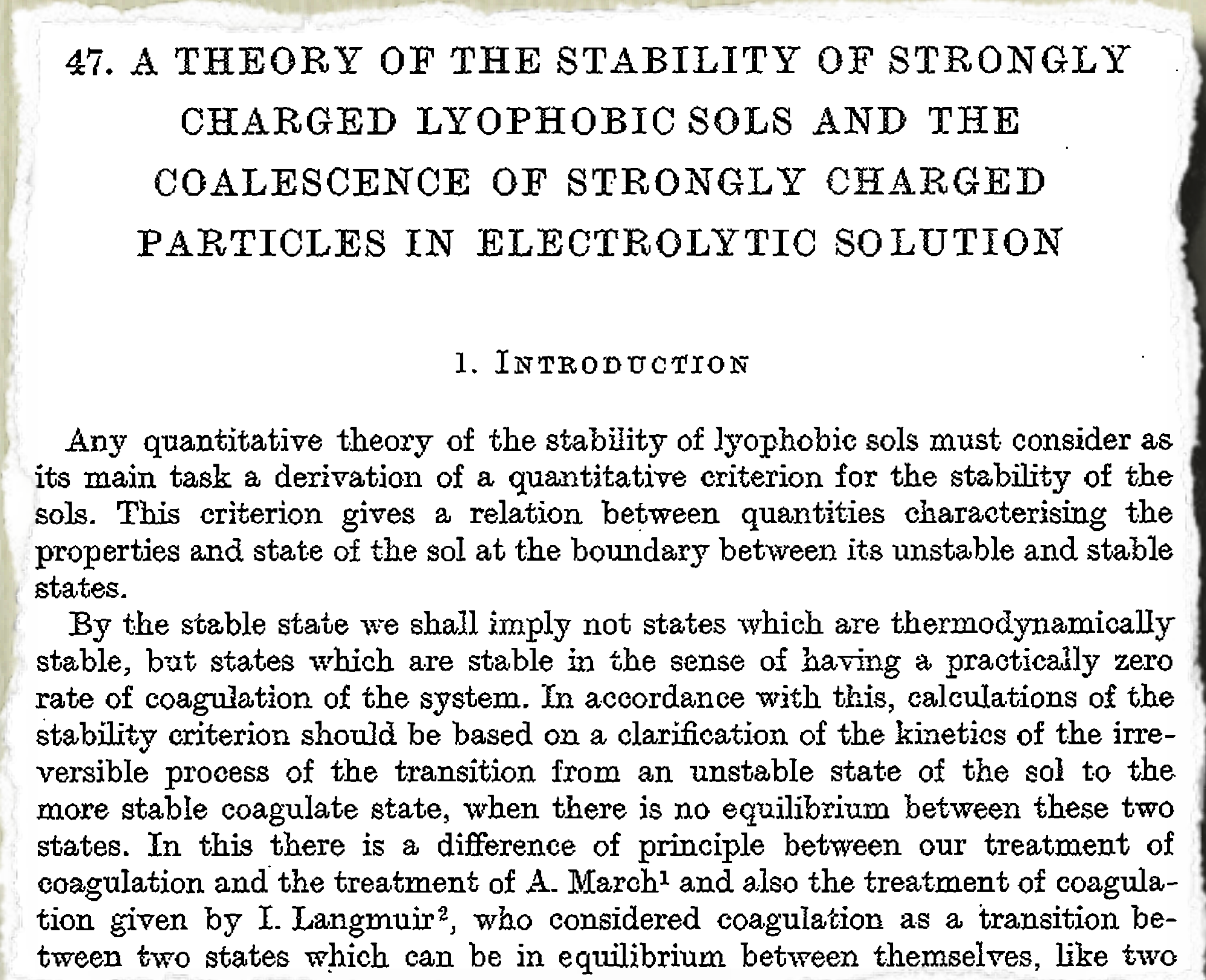
Natuurkundig Laboratorium N.V. Philips' Gloeilampenfabrieken, Eindhoven (Netherlands)

With the collaboration of

K. VAN NES



47. A THEORY OF THE STABILITY OF STRONGLY CHARGED LYOPHOBIC SOLS AND THE COALESCENCE OF STRONGLY CHARGED PARTICLES IN ELECTROLYTIC SOLUTION

1. INTRODUCTION

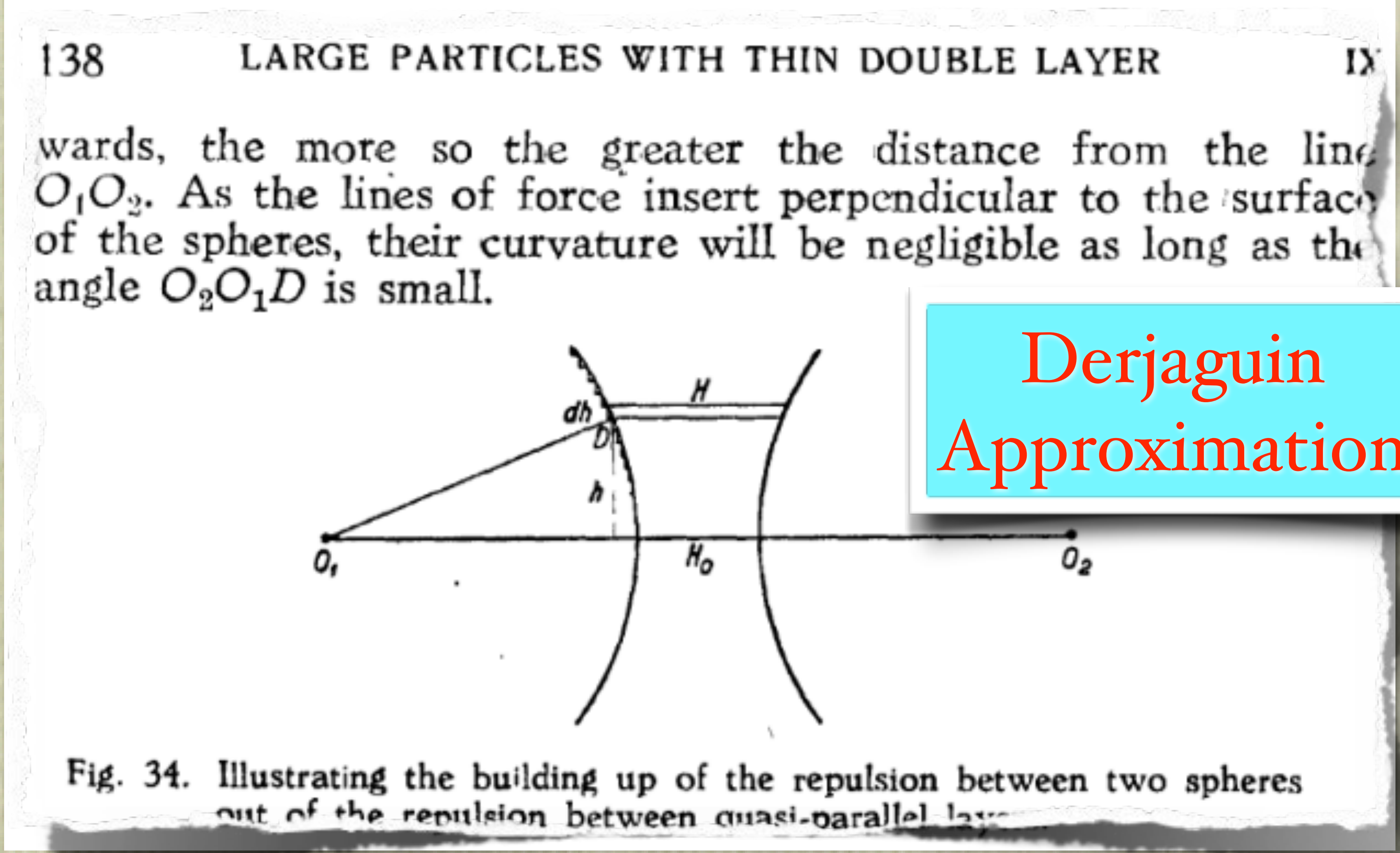
Any quantitative theory of the stability of lyophobic sols must consider as its main task a derivation of a quantitative criterion for the stability of the sols. This criterion gives a relation between quantities characterising the properties and state of the sol at the boundary between its unstable and stable states.

By the stable state we shall imply not states which are thermodynamically stable, but states which are stable in the sense of having a practically zero rate of coagulation of the system. In accordance with this, calculations of the stability criterion should be based on a clarification of the kinetics of the irreversible process of the transition from an unstable state of the sol to the more stable coagulate state, when there is no equilibrium between these two states. In this there is a difference of principle between our treatment of coagulation and the treatment of A. March[1] and also the treatment of coagulation given by I. Langmuir[2], who considered coagulation as a transition between two states which can be in equilibrium between themselves, like two

It is generally perceived that
DLVO is equivalent to linearized PB
The reality: a serious gap between them

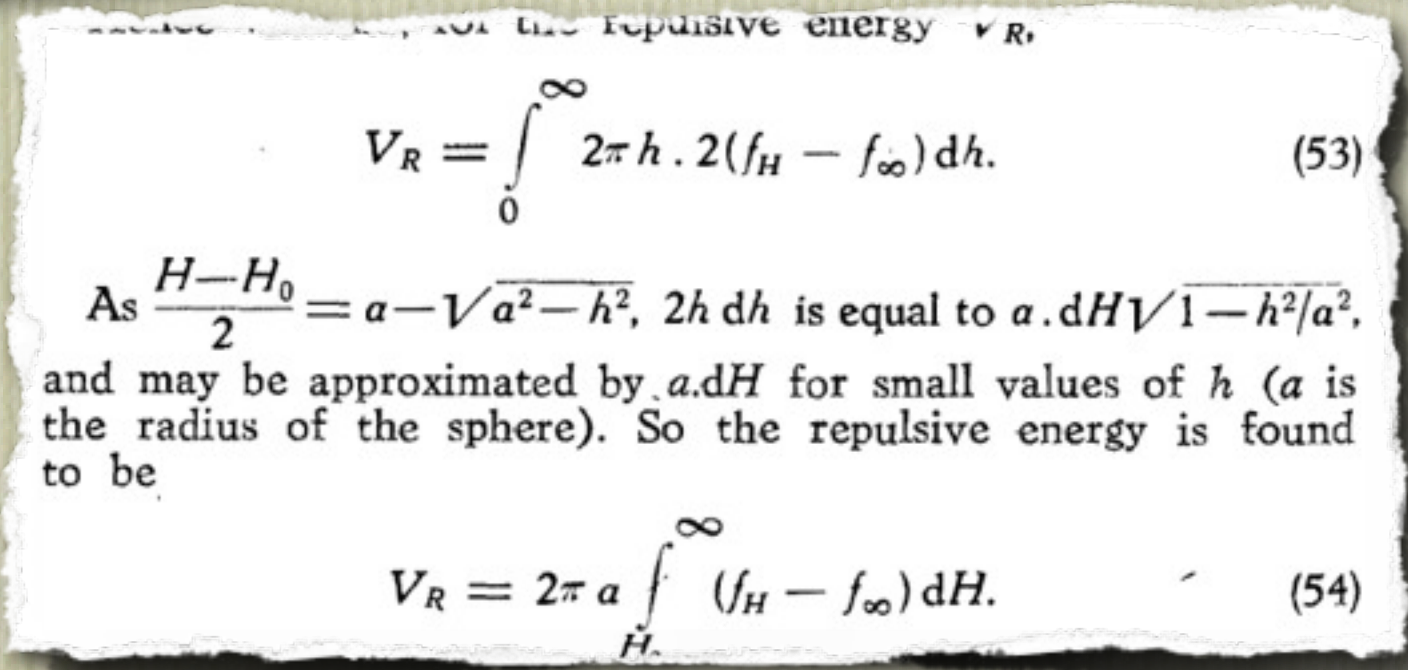
Derjaguin Approximation

Fundamentally wrong in math point of view



wards, the more so the greater the distance from the line O_1O_2. As the lines of force insert perpendicular to the surface of the spheres, their curvature will be negligible as long as the angle O_2O_1D is small.

Fig. 34. Illustrating the building up of the repulsion between two spheres out of the repulsion between quasi-parallel lay



for the repulsive energy V_R,

$$V_R = \int_0^\infty 2\pi h \,.\, 2(f_H - f_\infty)\, dh. \qquad (53)$$

As $\dfrac{H-H_0}{2} = a - \sqrt{a^2 - h^2}$, $2h\,dh$ is equal to $a\,.\,dH\sqrt{1-h^2/a^2}$, and may be approximated by $a.dH$ for small values of h (a is the radius of the sphere). So the repulsive energy is found to be

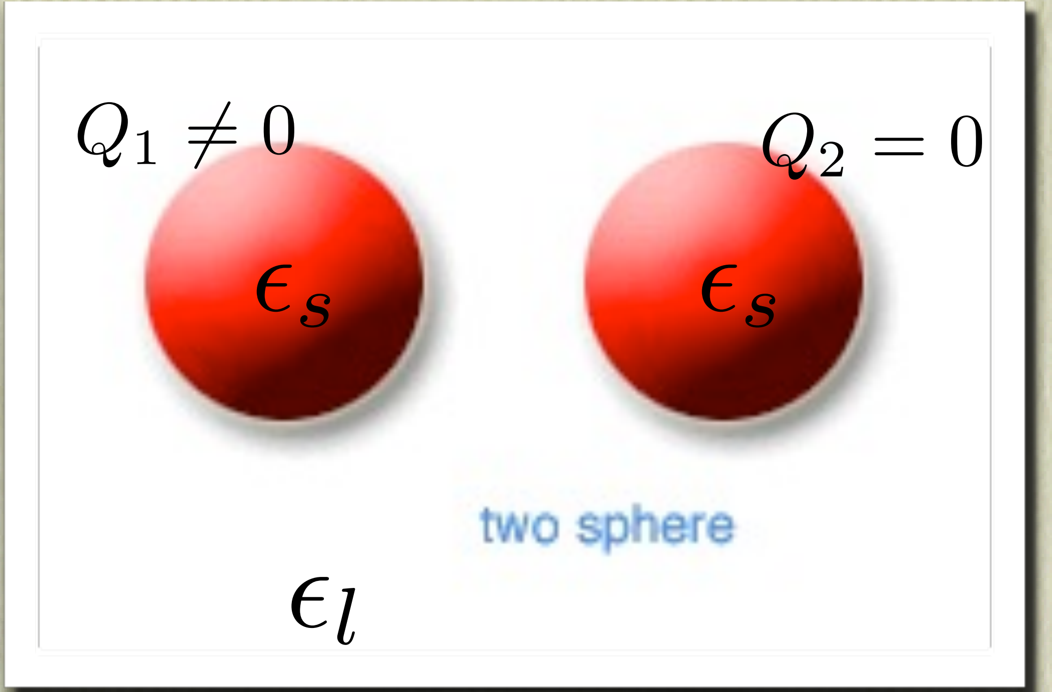
$$V_R = 2\pi a \int_{H_0}^\infty (f_H - f_\infty)\, dH. \qquad (54)$$

$$U = \frac{Q_1^* Q_2^*}{4\pi\epsilon r} e^{-\kappa r}$$

What does DLVO miss?

No interaction between charged objects and neutral objects according to DLVO, obviously wrong

$$U = \frac{Q_1^* Q_2^*}{4\pi\epsilon r} e^{-\kappa r}$$



Two missing aspects:

- Image charge effects
  (attractive only if $\epsilon_l < \epsilon_s$)
- Blocking of screening clouds
  (always repulsive)

Therefore DLVO is incorrect even at the level of linearized PB.

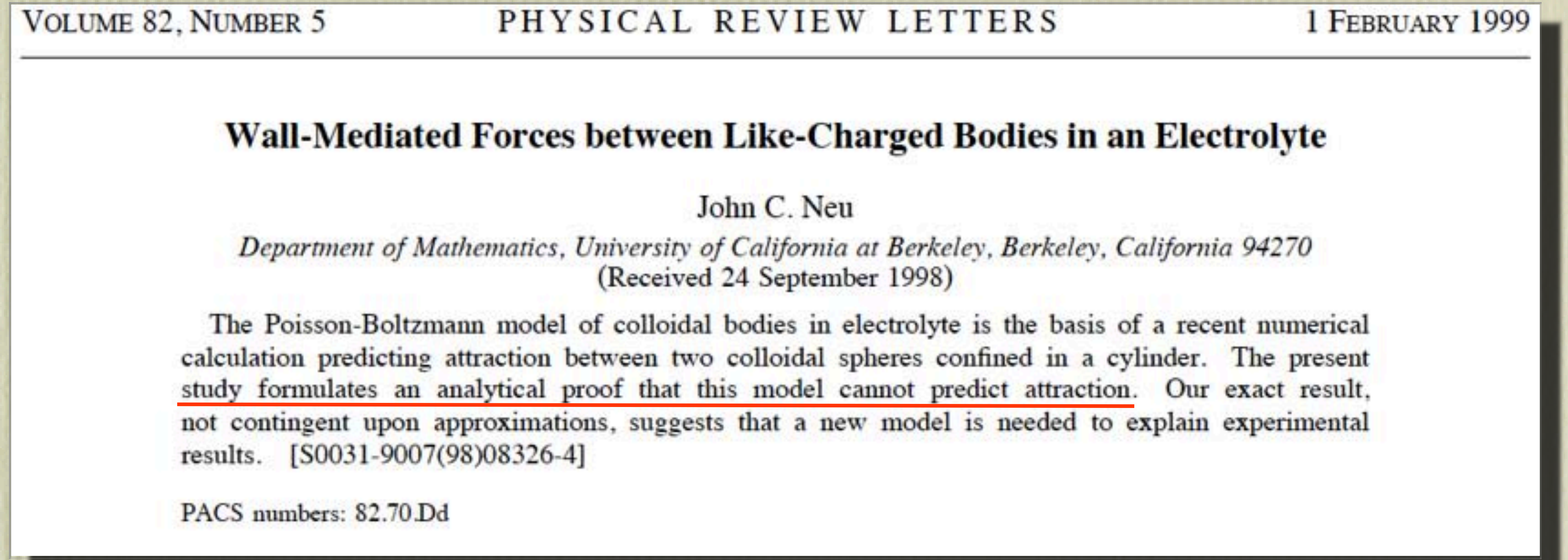
Landau Expansion of two particle free energy

$$F_{\text{eff}}(Q_\alpha, a_\alpha, R) = \Phi_0 + \Psi_1 Q_1 + \Psi_2 Q_2 + \frac{1}{2}\left(\mho_{11} Q_1^2 + 2\mho_{12} Q_1 Q_2 + \mho_{22} Q_2^2\right).$$

Does not work for strongly charged particles

Even after these two errors being corrected, DLVO can't explain like charge attraction in water

No Like-charge Attraction in Nonlinear PB



VOLUME 82, NUMBER 5 PHYSICAL REVIEW LETTERS 1 FEBRUARY 1999

Wall-Mediated Forces between Like-Charged Bodies in an Electrolyte

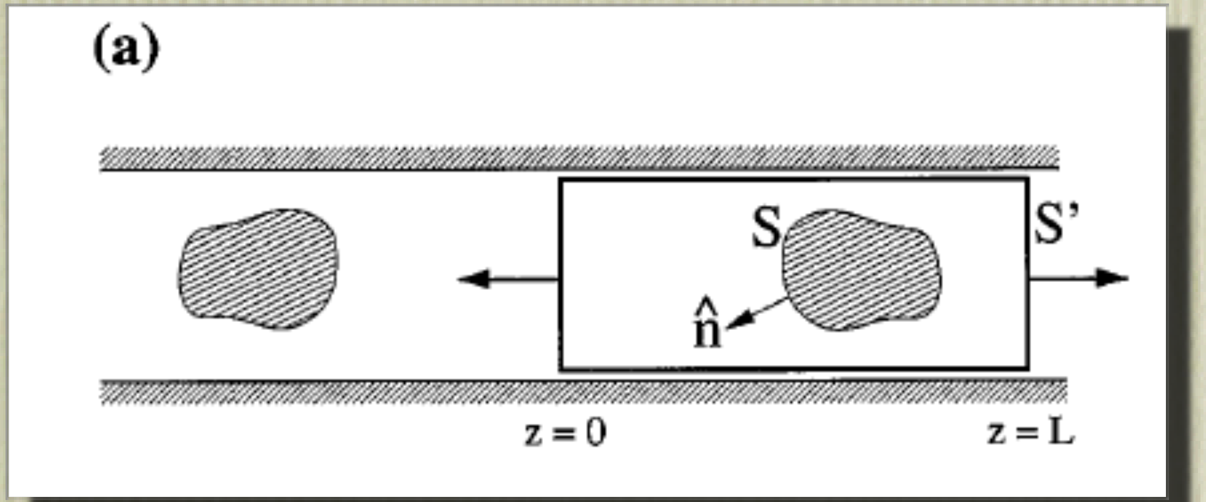
John C. Neu

Department of Mathematics, University of California at Berkeley, Berkeley, California 94270

(Received 24 September 1998)

The Poisson-Boltzmann model of colloidal bodies in electrolyte is the basis of a recent numerical calculation predicting attraction between two colloidal spheres confined in a cylinder. The present study formulates an analytical proof that this model cannot predict attraction. Our exact result, not contingent upon approximations, suggests that a new model is needed to explain experimental results. [S0031-9007(98)08326-4]

PACS numbers: 82.70.Dd



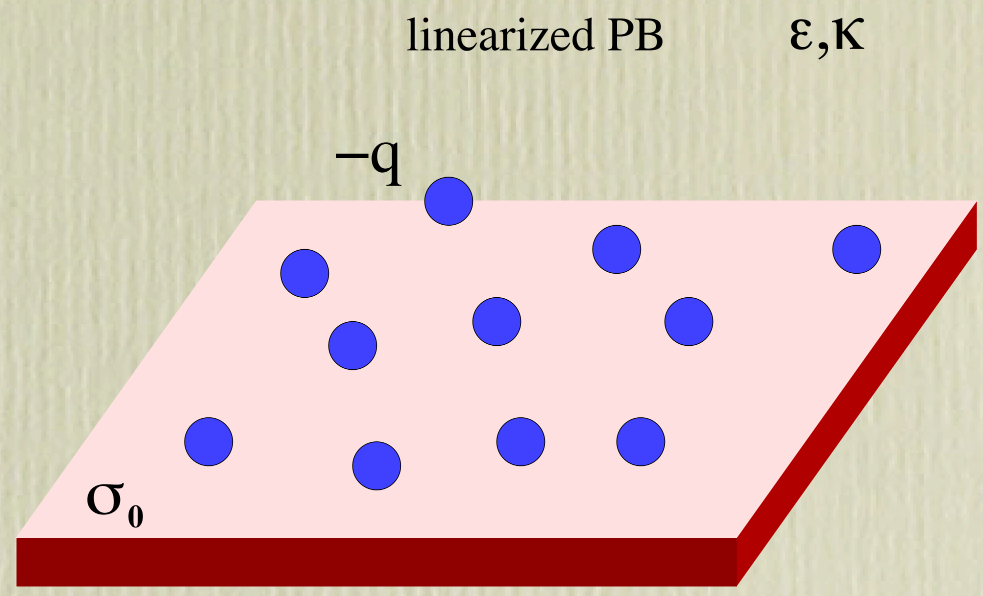
- The result follows because certain function is concave in terms of potential
- The concavity follows from PB assumption
- Correlation presumably destroys concavity, which may leads to like charge attraction

Why PB fails for strongly charged surface and two-fluids model

- Counter-ions are so close to surface that they do not see screening effects of others
- They only see the uniform field by surface
- Their density distribution is exponential

$$n(x) = n_s \exp -x/\ell_{GC}$$

- A thin layer of counter-ions condensed onto the charged surface, treated as a 2d fluid



Chemical equilibrium between condensed ions and free ions

$$\underbrace{\mu_{id}+\mu_{WC}}_{\text{correlation energy}}+\underbrace{Ze\psi(0)}_{\text{electrostatic repulsion}}=\mu_b$$

- Overcharging appear when μ_{WC} is large enough $\Xi \gg 1$
- Overcharging does not imply like-charge attraction

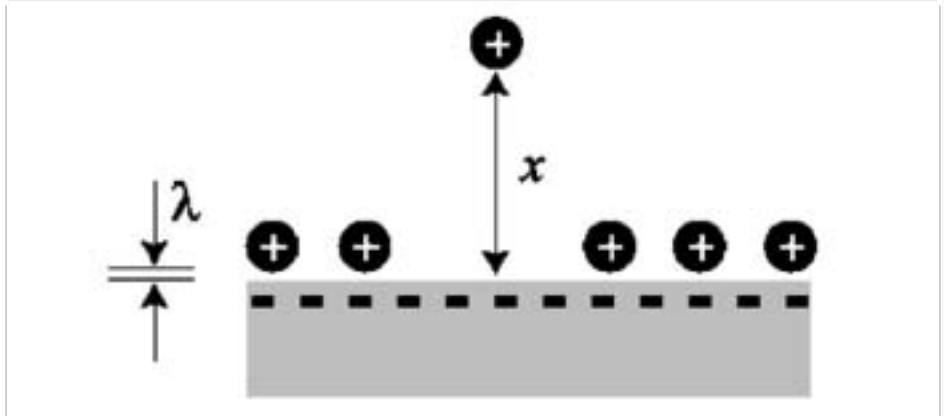
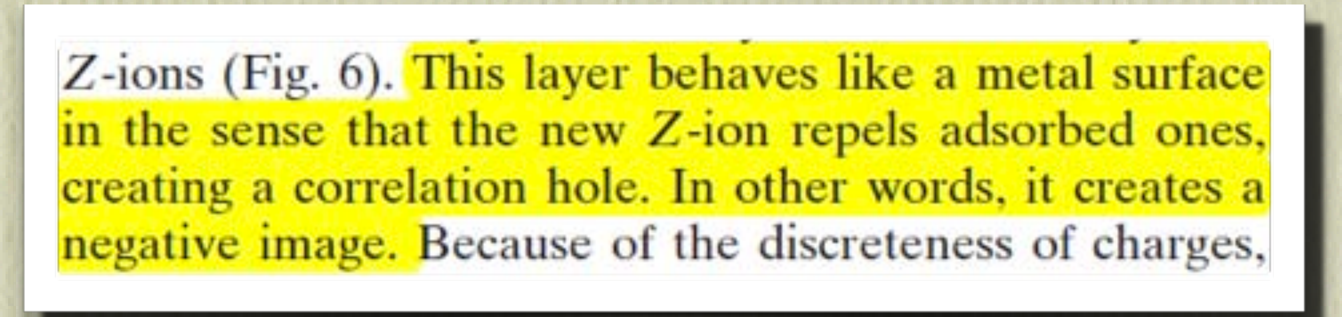


FIG. 6. The origin of attraction of a new positive *Z*-ion to the already neutralized surface. *Z*-ions are shown by solid circles. The new *Z*-ion creates its negative correlation hole.

Heuristic Explanation of Over-charging



Z-ions (Fig. 6). This layer behaves like a metal surface in the sense that the new Z-ion repels adsorbed ones, creating a correlation hole. In other words, it creates a negative image. Because of the discreteness of charges,

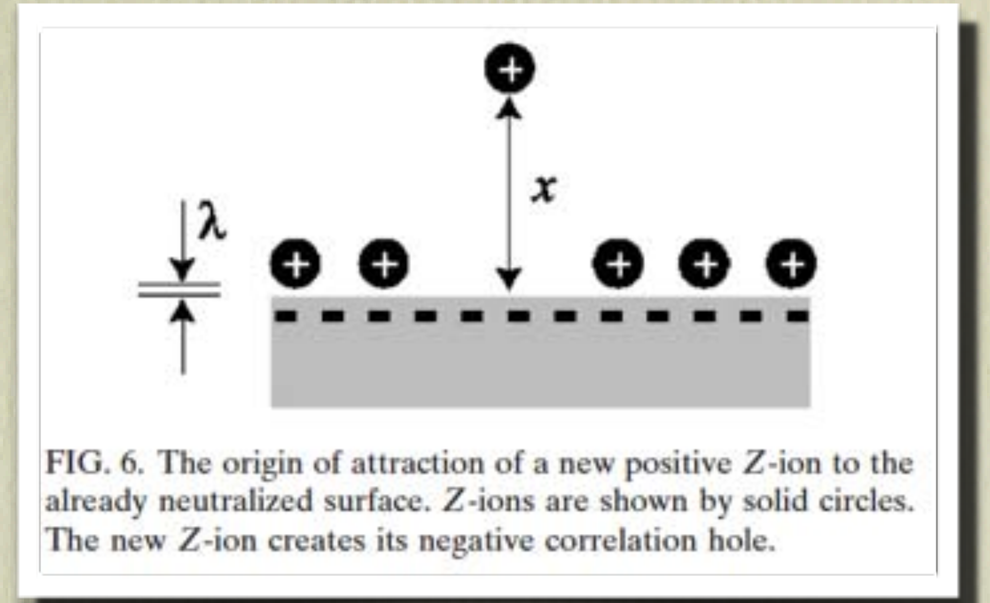
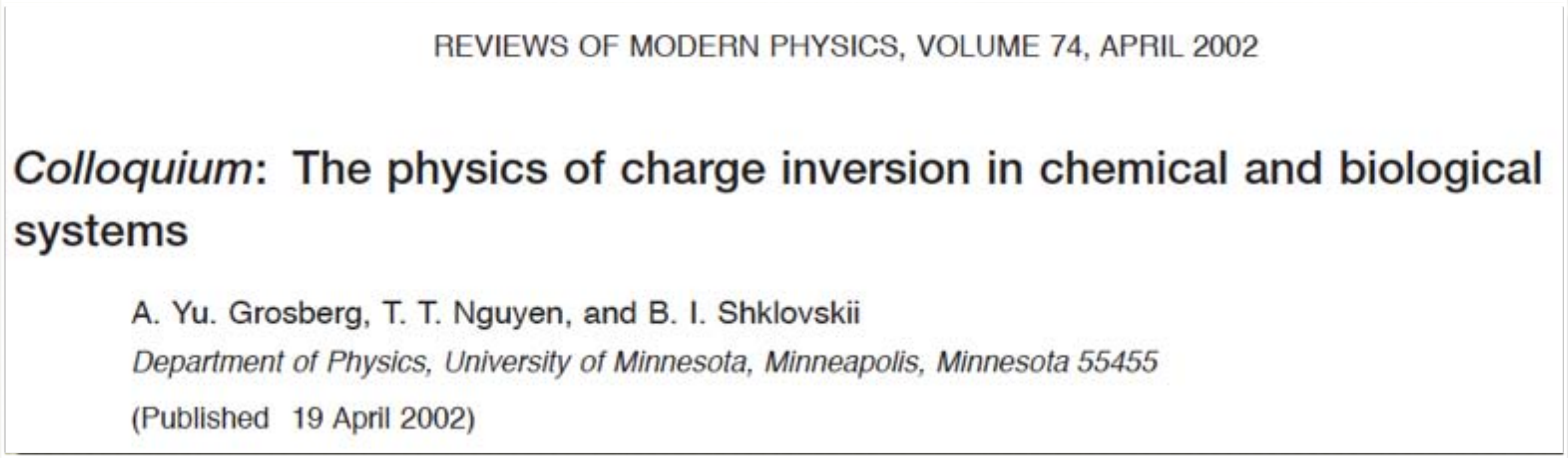


FIG. 6. The origin of attraction of a new positive Z-ion to the already neutralized surface. Z-ions are shown by solid circles. The new Z-ion creates its negative correlation hole.



REVIEWS OF MODERN PHYSICS, VOLUME 74, APRIL 2002

Colloquium: The physics of charge inversion in chemical and biological systems

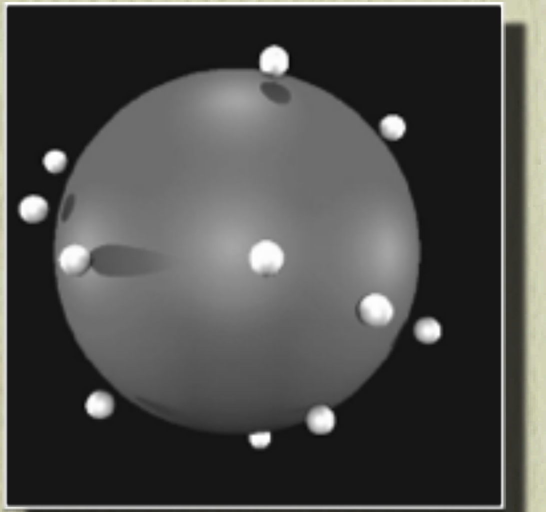
A. Yu. Grosberg, T. T. Nguyen, and B. I. Shklovskii

Department of Physics, University of Minnesota, Minneapolis, Minnesota 55455

(Published 19 April 2002)

- We will calculate this image charge effect later

Over Charging at Zero Temperature



- Z q charge uniformly distributed on sphere
- n discrete αq ions adsorbed on sphere

$$E_n = \frac{Z^2 q^2}{2\epsilon a} - \frac{Z\alpha n q^2}{\epsilon a} + F_n^{\alpha\alpha}.$$

Self energy of surface charges

Interaction between surface charge and ions

Interaction between ions

$$F_n^{\mathrm{OCP}} = F_n^{\alpha\alpha} - \frac{\alpha^2 n^2 q^2}{\epsilon a} + \frac{\alpha^2 n^2 q^2}{2\epsilon a}.$$

$$E_n = \frac{(Z - \alpha n)^2 q^2}{2\epsilon a} + F_n^{\mathrm{OCP}}.$$

$$F_n^{\mathrm{OCP}} = -M \frac{\alpha^2 q^2 n^{3/2}}{2\epsilon a}.$$

The effective charge of the polyion–counterion complex in units of $-q$ is

$$Z_{\mathrm{eff}} = Z - \alpha n^*.$$

where n^* is the number of condensed α-ions which minimize the electrostatic energy:

$$\left.\frac{\mathrm{d}E_n}{\mathrm{d}n}\right|_{n^*} = 0.$$

$$Z_{\mathrm{eff}} = -\frac{1 + \sqrt{1 + 4\gamma^2 Z}}{2\gamma^2},$$

$$\gamma = \frac{4}{3M\sqrt{\alpha}}.$$

- Zero temperature argument
- No screening effects

PHYSICAL REVIEW E, VOLUME 64, 021405

Strong electrostatic interactions in spherical colloidal systems

René Messina,* Christian Holm,† and Kurt Kremer‡
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(Received 17 January 2001; published 20 July 2001)

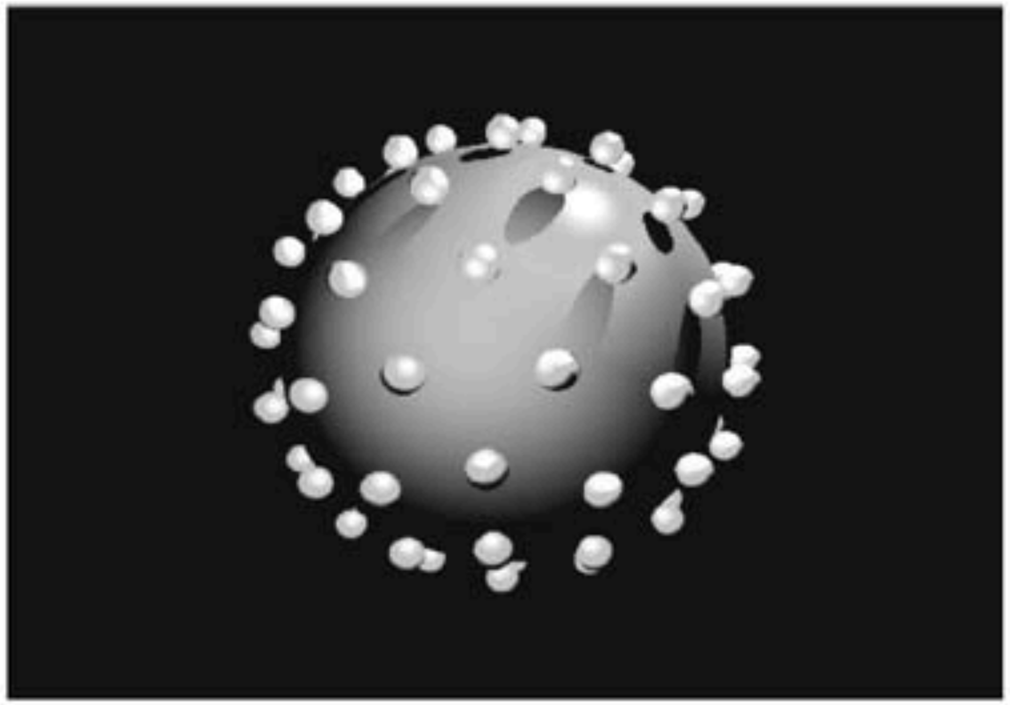
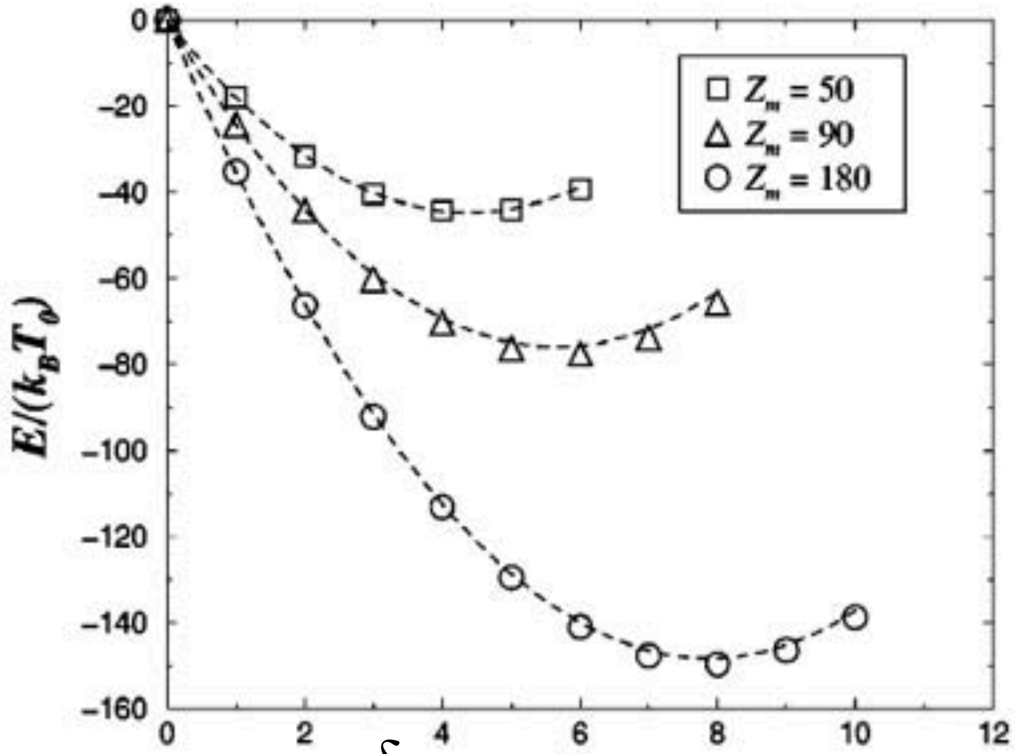


FIG. 3. Snapshot of the ground state structure of the neutral state ($n=0$) with a macroion charge $Z_m=180$ [see Fig. 2 for the corresponding $g(r)$].

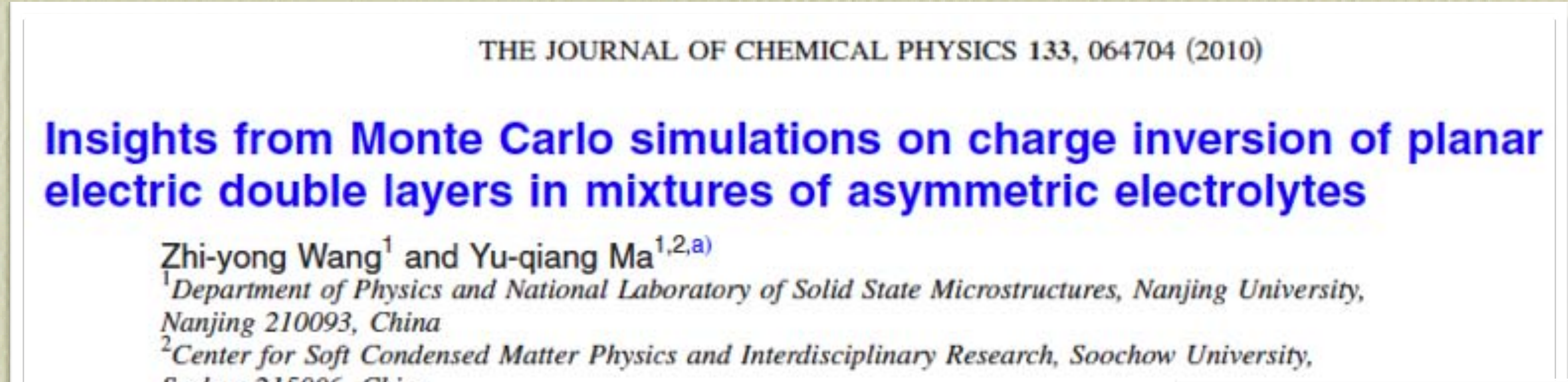
lomb coupling parameter [24,25] $\Gamma = Z_c^2 l_B / a_{cc}$, where a_{cc} is the average distance between counterions, we have $\Gamma \approx 13$ for $Z_m=180$.



$$\delta n = n - n_0$$

FIG. 5. Electrostatic energy (in units of k_BT_0) for *ground state* configurations of a single charged macroion of as a function of the number of *overcharging* counterions n for three different bare charges Z_m. The neutral case was chosen as the potential energy origin, and the curves were produced using the theory of Eq. (13), compare text.

Over-charging at Weak Coupling Regime



THE JOURNAL OF CHEMICAL PHYSICS 133, 064704 (2010)

Insights from Monte Carlo simulations on charge inversion of planar electric double layers in mixtures of asymmetric electrolytes

Zhi-yong Wang[1] and Yu-qiang Ma[1,2,a)]
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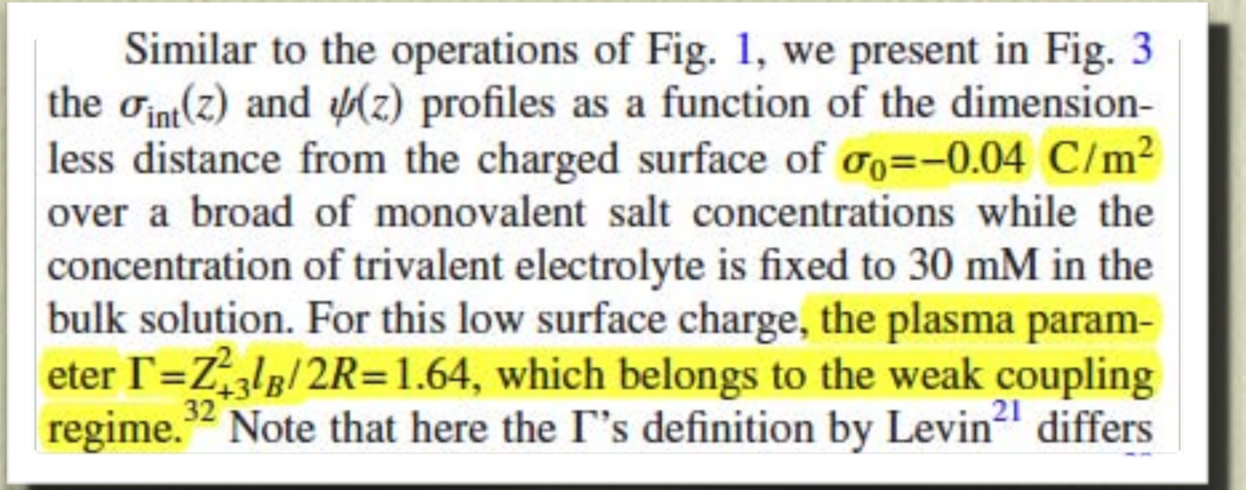
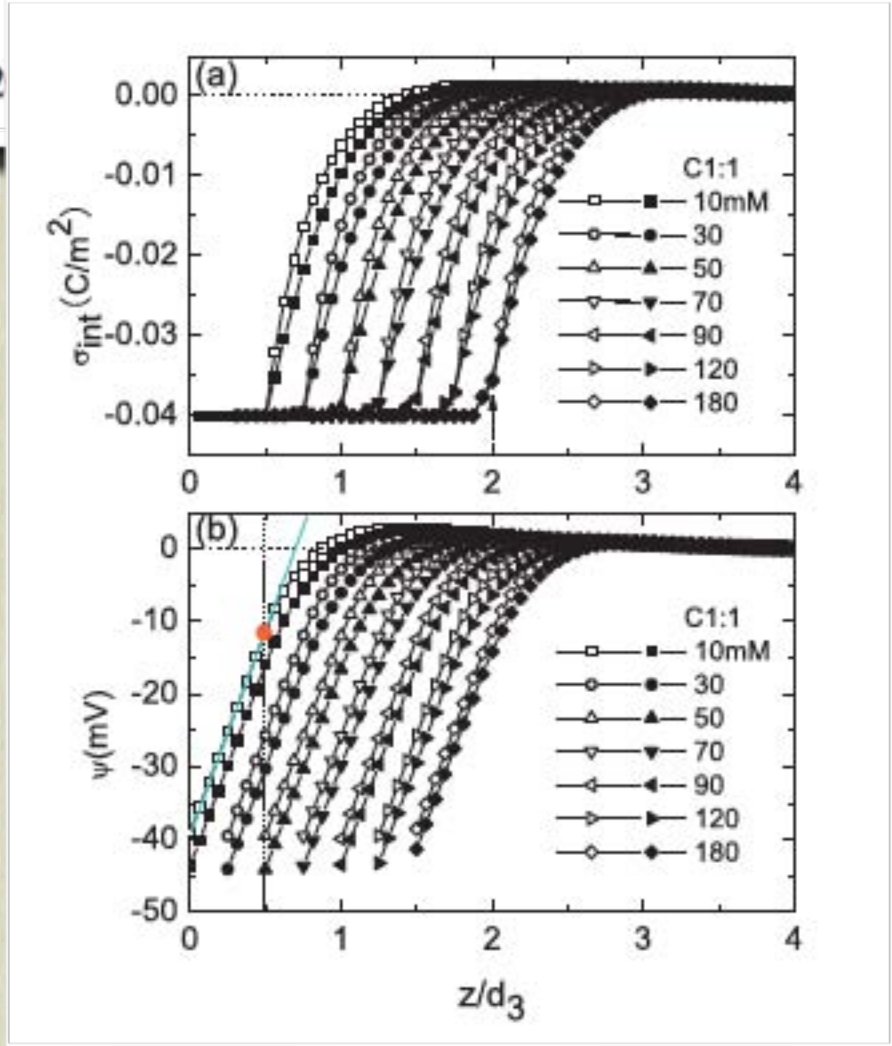
(Received 1 June 2010; accepted 5 July 2010; published online 11 August 2



Similar to the operations of Fig. 1, we present in Fig. 3 the $\sigma_{\text{int}}(z)$ and $\psi(z)$ profiles as a function of the dimensionless distance from the charged surface of $\sigma_0=-0.04$ C/m^2 over a broad of monovalent salt concentrations while the concentration of trivalent electrolyte is fixed to 30 mM in the bulk solution. For this low surface charge, the plasma parameter $\Gamma=Z_{+3}^2 l_B/2R=1.64$, which belongs to the weak coupling regime.[32] Note that here the Γ's definition by Levin[21] differs



No theory capable of describing over charging
in weakly coupled regime
We do not understand over-charging yet!

Strong Coupling Theory

Physics Reports 416 (2005) 129–199

Statics and dynamics of strongly charged soft matter

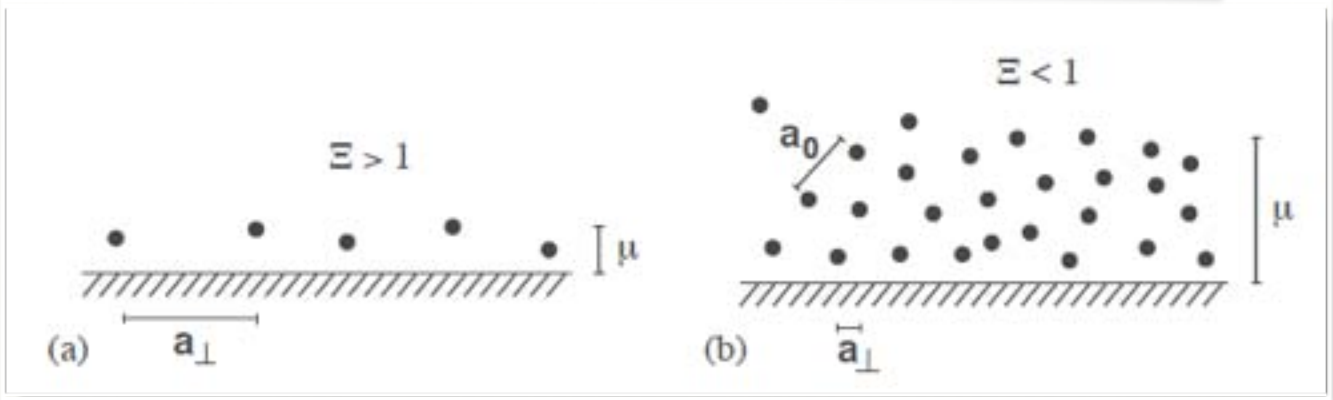
H. Boroudjerdi, Y.-W. Kim, A. Naji, R.R. Netz*, X. Schlagberger, A. Serr

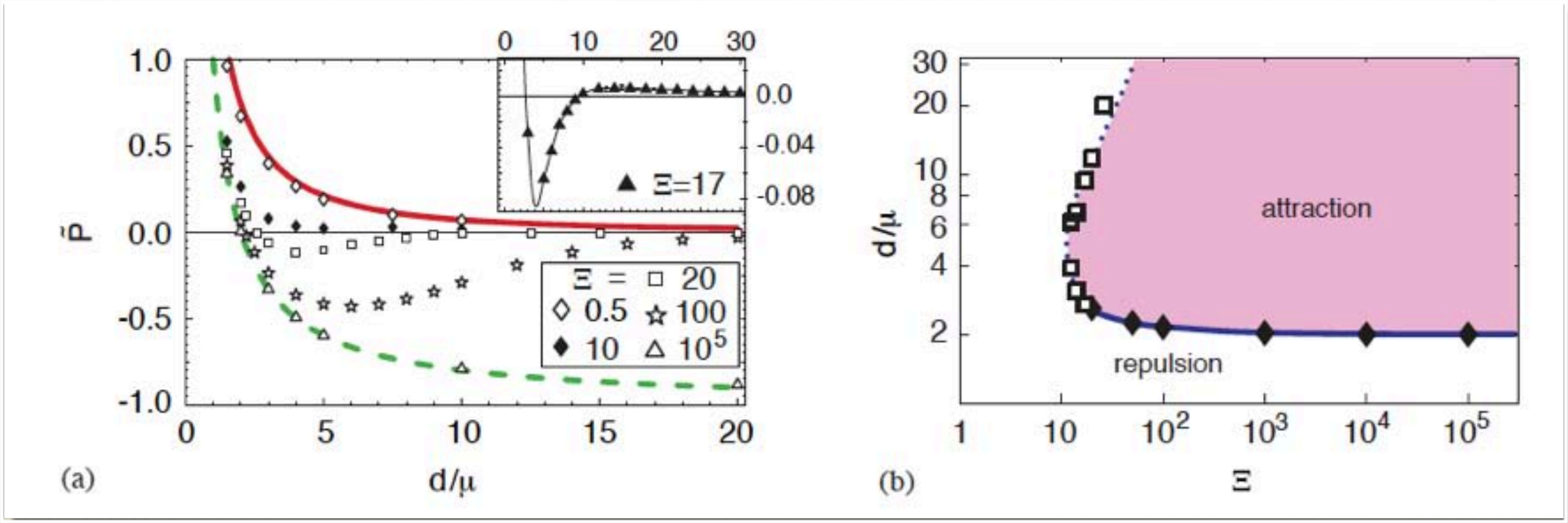
Physics Department, TU Munich, 85748 Garching, Germany

Coupling parameter

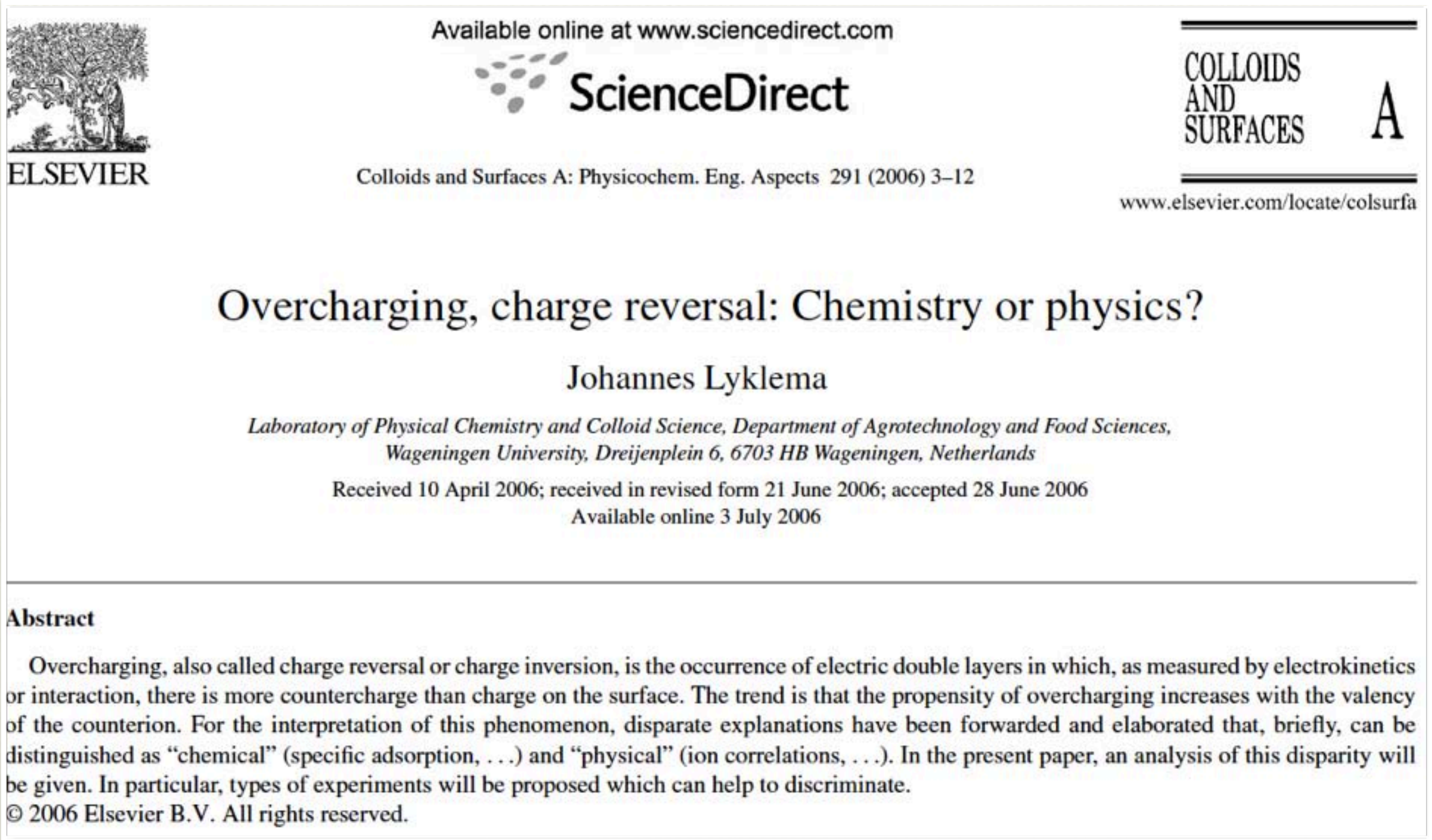
$$\Xi = 2\pi q^3 \ell_B^2 \sigma_s \sim \frac{q^3 \sigma_s}{T^2}$$

$$\mathscr{H} = \sum_{j=1}^{N-1} \sum_{k=j+1}^{N} \frac{\Xi}{|\tilde{\mathbf{r}}_j - \tilde{\mathbf{r}}_k|} + \sum_{j=1}^{N} \tilde{z}_j$$





Overcharging is far from being understood



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Colloids and Surfaces A: Physicochem. Eng. Aspects 291 (2006) 3–12

COLLOIDS AND SURFACES A

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Overcharging, charge reversal: Chemistry or physics?

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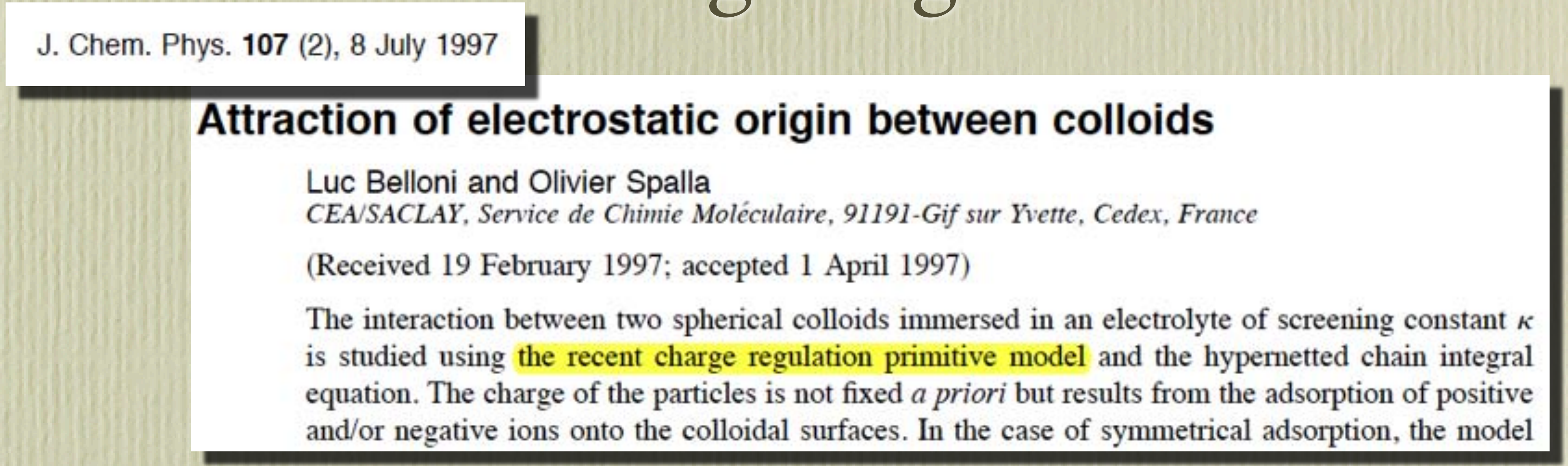
Received 10 April 2006; received in revised form 21 June 2006; accepted 28 June 2006
Available online 3 July 2006

Abstract

Overcharging, also called charge reversal or charge inversion, is the occurrence of electric double layers in which, as measured by electrokinetics or interaction, there is more countercharge than charge on the surface. The trend is that the propensity of overcharging increases with the valency of the counterion. For the interpretation of this phenomenon, disparate explanations have been forwarded and elaborated that, briefly, can be distinguished as "chemical" (specific adsorption, . . .) and "physical" (ion correlations, . . .). In the present paper, an analysis of this disparity will be given. In particular, types of experiments will be proposed which can help to discriminate.

Beyond Primitive Model:
Charge Regulation



J. Chem. Phys. **107** (2), 8 July 1997

Attraction of electrostatic origin between colloids

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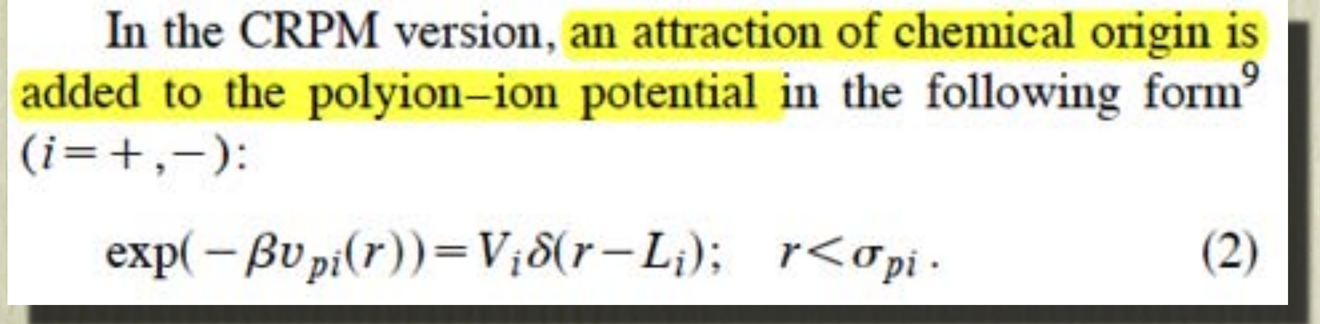
(Received 19 February 1997; accepted 1 April 1997)

The interaction between two spherical colloids immersed in an electrolyte of screening constant κ is studied using the recent charge regulation primitive model and the hypernetted chain integral equation. The charge of the particles is not fixed *a priori* but results from the adsorption of positive and/or negative ions onto the colloidal surfaces. In the case of symmetrical adsorption, the model



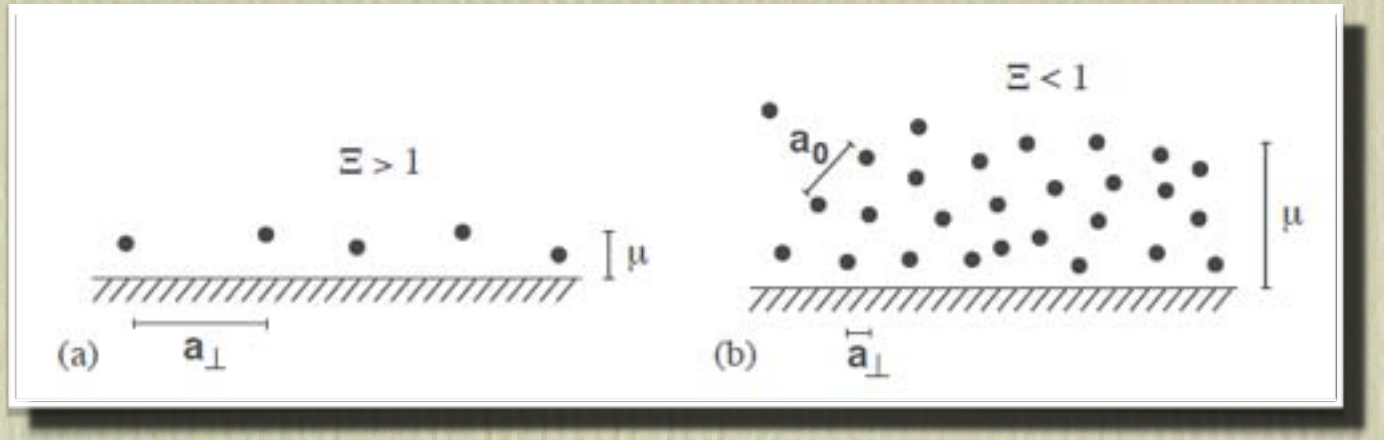
In the CRPM version, an attraction of chemical origin is added to the polyion–ion potential in the following form[9] $(i=+,-)$:

$$\exp(-\beta v_{pi}(r))=V_i\delta(r-L_i);\quad r<\sigma_{pi}. \qquad (2)$$

- The surface charge density is variable and should be determined by minimization of total free energy.
- The sign of charge on colloids depends their environment.
- "Charge inversion" loses its significance. Is it really a chemistry problem ?
- Doubly screened attraction between two such overall neutral colloids.

Summary of Status Quo

- Overcharging in weak coupling regime is not understood
    - Charge regulated primitive model looks promising
- Link between overcharging and like charge attraction missing
- Like charge attraction at Debye scale is mysterious
    - Main theme of our work

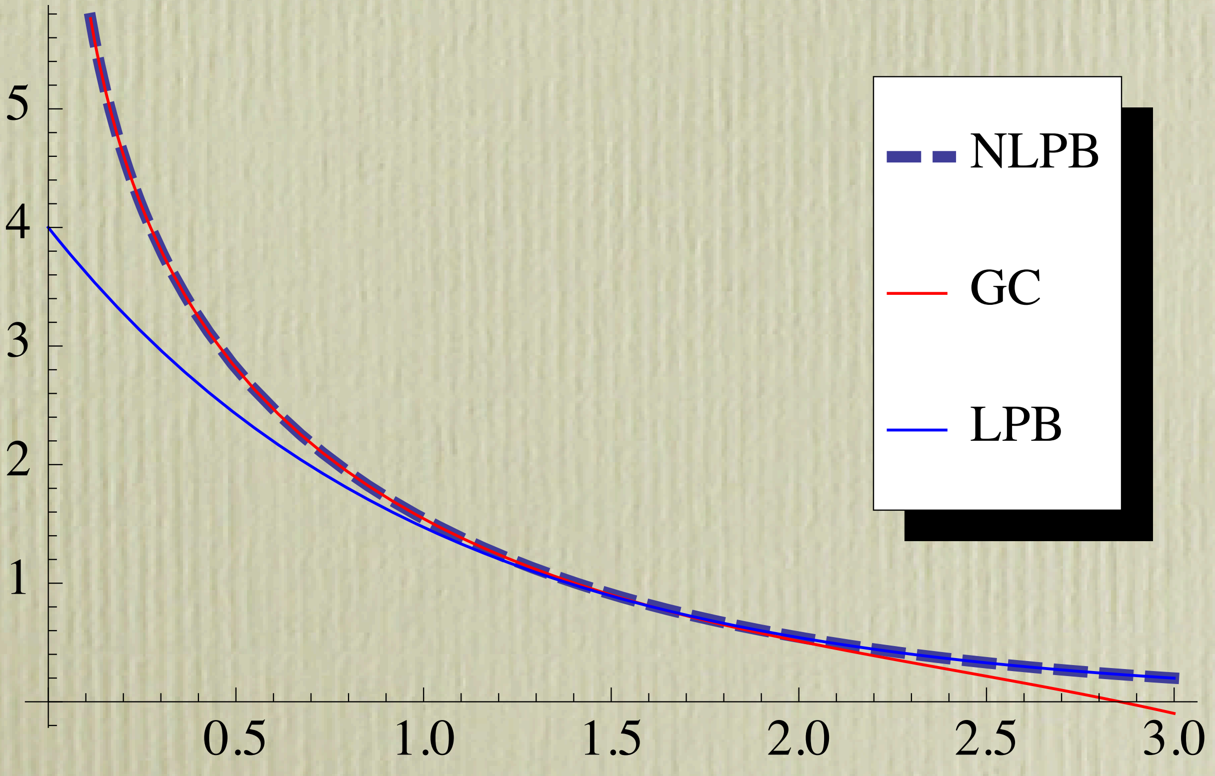


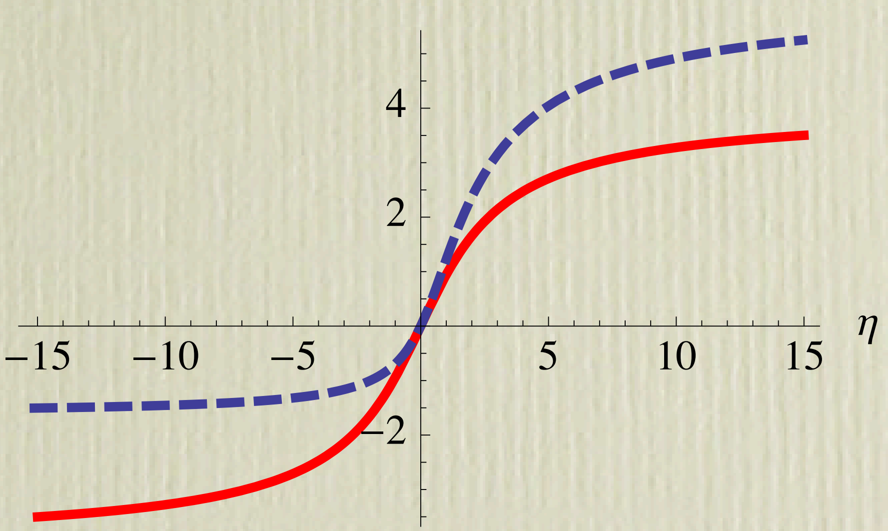
- The physics near charged surface is very complicated
- Linearized PB works far away from charged surface
- Effective charge density is different: charge renormalization $\Psi = \eta_R \, e^{-z/\ell_{DB}}$
- Interaction must be transmitted via the bulk
- We must be able to describe attraction within linearized PB

$$\Psi = \beta q \phi \qquad \Psi^{+}_{q:-q}(z) = 2 \ln \frac{1+e^{-z}}{1-e^{-z}},$$

$$\eta = \frac{\beta q \sigma}{\epsilon \kappa} = \frac{\ell_{DB}}{\ell_{GC}}, \qquad \Psi^{\text{linear}}(z) = \eta_R \, e^{-\delta z}.$$

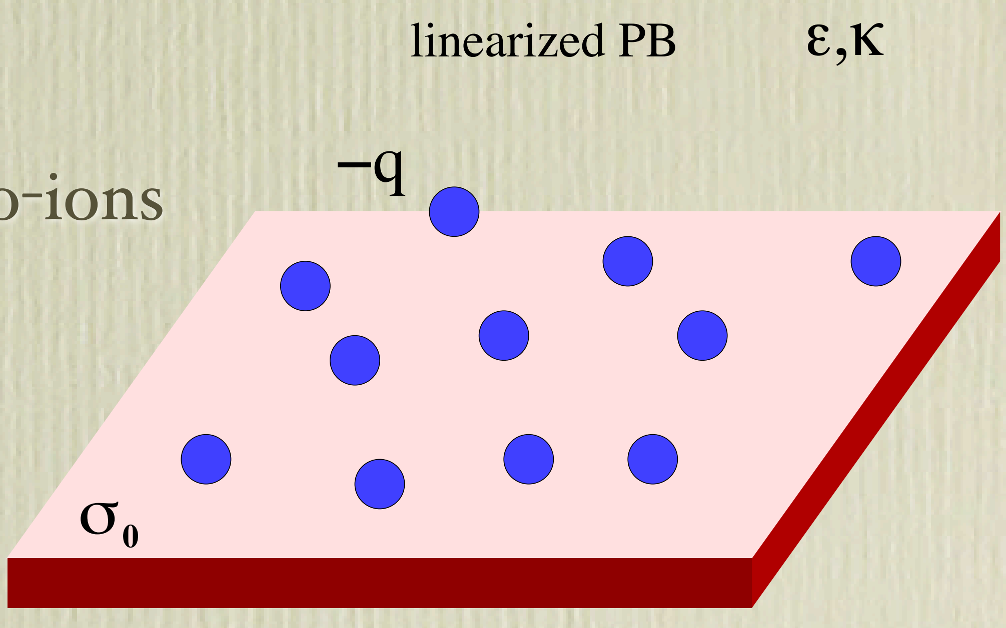
Linear PB works if $\ell_{DB} \le \ell_{GC}$





Dichotomy between Condensed and Free Counter-ions

- Stop worrying about overcharging and take it as a fact.
- Condensed counter-ions as 2d liquid, free in lateral direction
  - "Stern or Helmholtz layer"
- Free counter-ions by linearized PB, together with co-ions
- "Two-fluids Model" (Studied by many researchers)
- Effective surface charge density $\sigma_R = \sigma_0 - \sigma_c$
  - Difficult to calculate! No good understanding so far
- Equally important, but not yet analyzed: how condensed counter-ions respond to external perturbations?
- The key to understand like-charge attraction at Debye scale



Condensed Counter-ions as Effective Boundary Conditions

- Boundary conditions $\epsilon' \frac{\partial \phi'}{\partial n} - \epsilon \frac{\partial \phi}{\partial n} = \sigma_{\text{net}}$
- $\epsilon' \to 0, \qquad -\epsilon \frac{\partial \phi}{\partial n} = \sigma_{\text{net}}$
- $\sigma_{\text{net}} = \sigma_0 + \sigma_c$

Fixed surface charge

mobile counter-ions

- Mean field theory $\sigma_c = q\, n_c e^{-\beta q \phi}$
- at threshold of over-charging, $\sigma_0 + q n_c = 0$

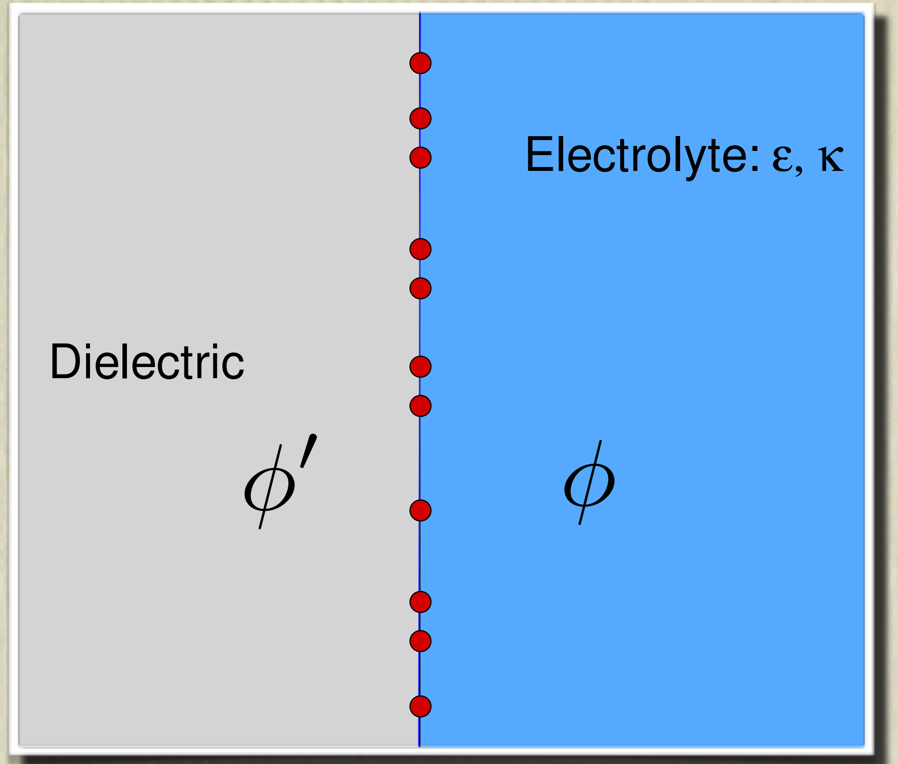
Iso-electric Point

- Linearization of exponential: $\epsilon \frac{\partial \Phi}{\partial n} = n_0 \beta q^2 \Phi(x).$

$$\ell_{GC} \frac{\partial \Phi}{\partial n} = \Phi(x),$$

$$\ell_{GC} = \frac{\epsilon}{n_0 \beta q^2} = \frac{\epsilon}{\beta \sigma_0 q}$$

Gouy-Chapmann length

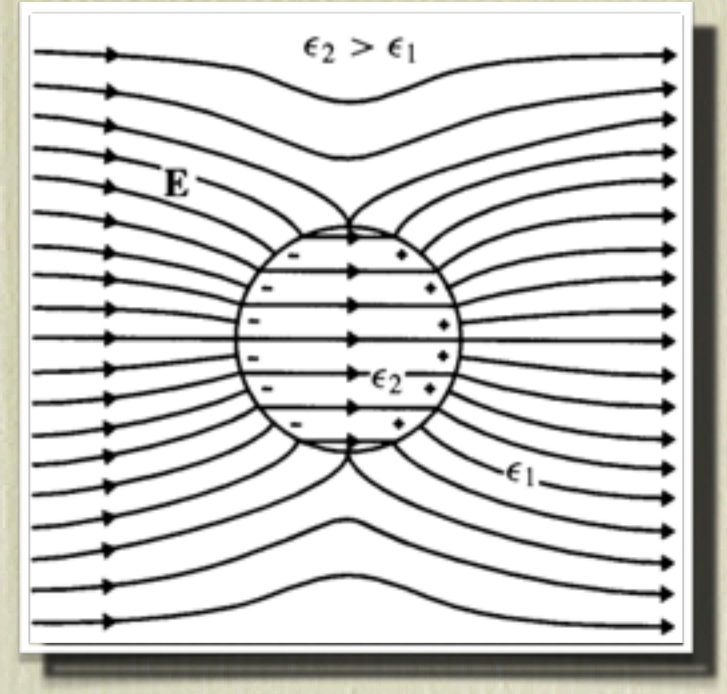


In the strongly charged limit, $\sigma_0 \to \infty, \ell_{GC \to 0}$

The BC reduces to $\Phi(x) = 0, \quad x \in \partial\Omega.$

Effectively a conductor!

Simple Example: Sphere in Uniform Field



- Potential can be expanded in Legendra polynomial

$$\Phi(x) = -E_0 r \cos\theta + \frac{p\cos\theta}{4\pi\epsilon r^2},$$

- Substituting into BC, we find $p = 4\pi a^3 \epsilon E_0 \frac{a - \ell_{GC}}{a + 2\ell_{GC}},$

a: spherical radius

- Comparing with a dielectric sphere in uniform field
- The effective dielectric constant becomes large for large sphere

$$\varepsilon_{\text{eff}} = \varepsilon \frac{a}{\ell_{GC}} \gg \varepsilon$$

- Condensed counter-ions make sphere looks like conductor!

Point Charge Near Overall Neutral Plate

- Total potential

reaction potential

$$\Phi(\vec{r}) = \frac{Q}{4\pi\epsilon r_1} e^{-\kappa r_1} + \chi(\vec{r}),$$

$$4\pi\epsilon\,\Phi(\vec{r}) = \frac{Q}{r_1} e^{-\kappa r_1} + \frac{Q'}{r_2} e^{-\kappa r_2}$$

point image

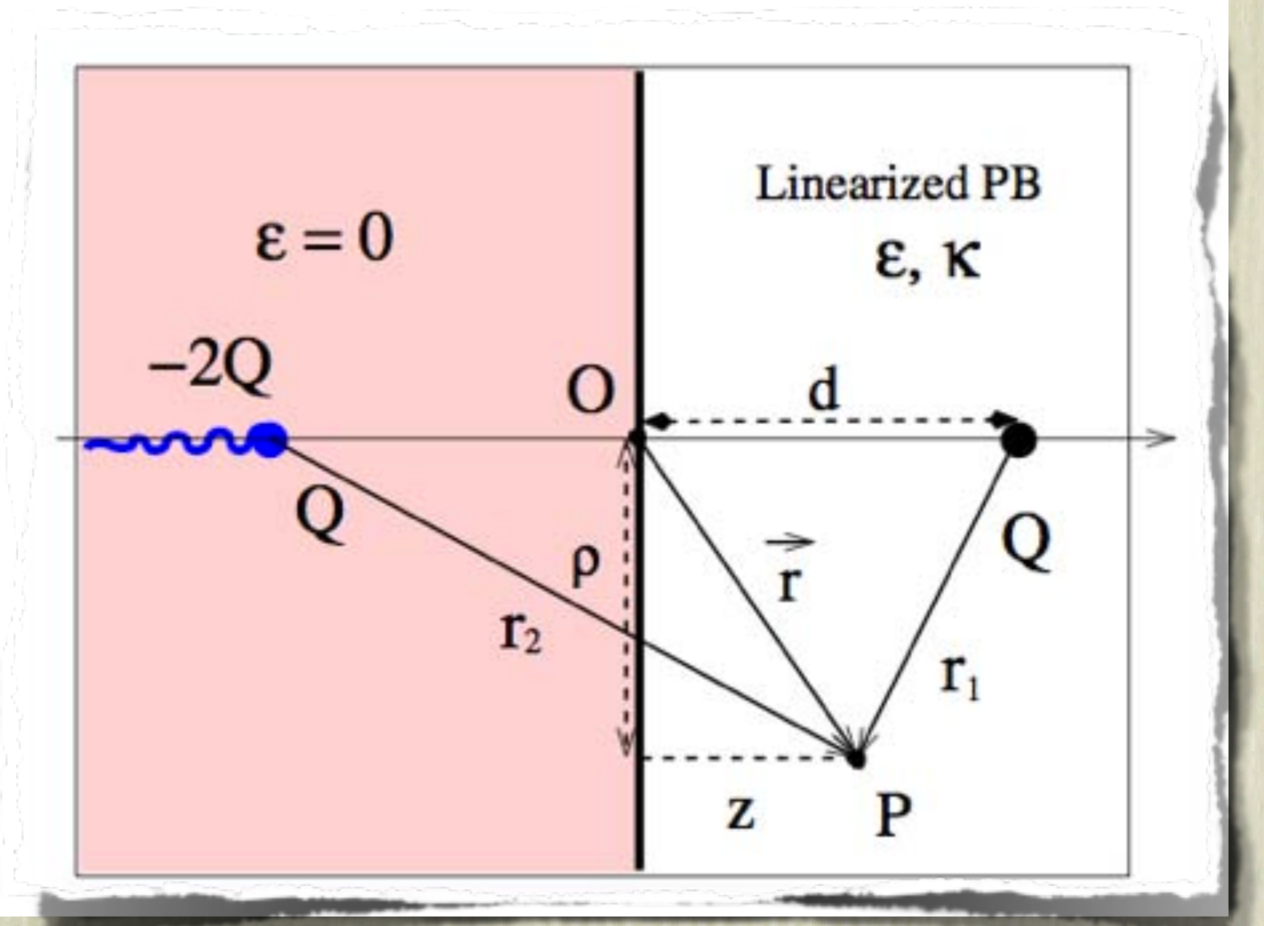
$$+ \int_{-\infty}^{-d} d\zeta \frac{\lambda(\zeta)}{\sqrt{(z-\zeta)^2+\rho^2}} e^{-\kappa r(z-\zeta)}$$

line image

$$\lambda(\zeta) = -\frac{2Q}{\ell_{GC}} e^{(\zeta+d)/\ell_{GC}}.$$

$$\int_{-\infty}^{-d} \lambda(\zeta) d\zeta = -2Q.$$

Image charge method



- Total charge of line image is -2Q
- Far away from the plate, the images appear as a point charge -Q
- Q is attracted towards plate, which looks like a conductor again!
- Tendency of over-charging becomes clear

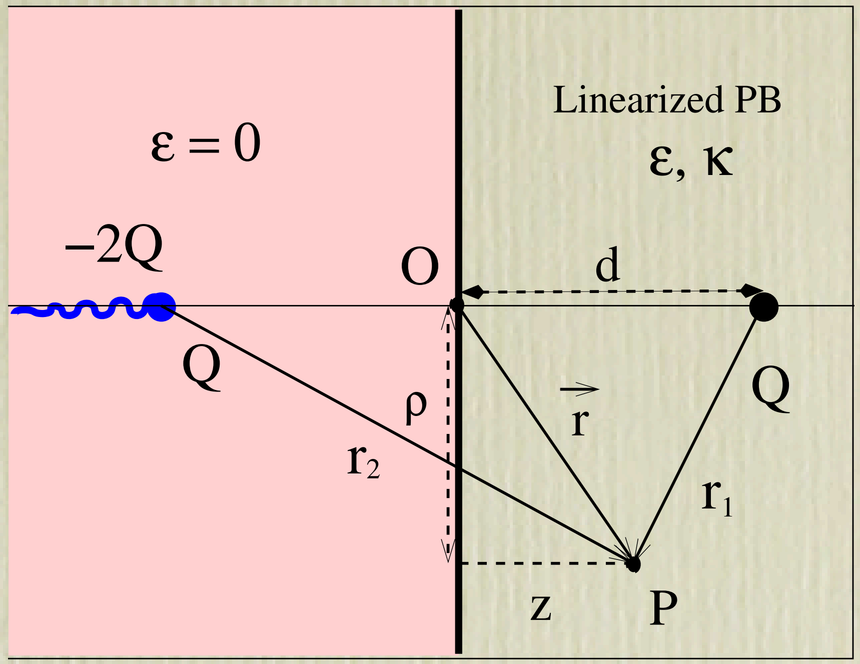
Our analysis here is essentially Debye-Huckel in a nontrivial geometry

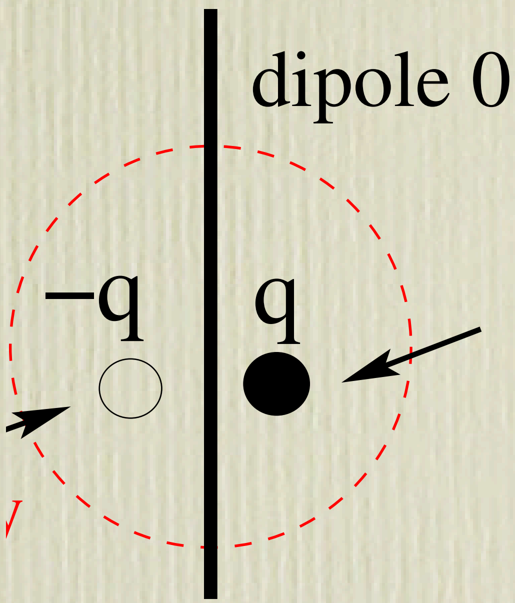
What if the charge is on the surface?

- Point image coincides with the source charge
- Repulsion between them diverges (nonsense)
- Short scale details become relevant, 2d fluid is no longer a fluid within scale of ion separation
- However, we only need the total potential far away
- From far away, source and all images form a dipole
- Dipole moment needs more careful calculation
- Crude estimate:

$$p = Max\{2q\ell_{GC}, 2qa_\perp\}$$

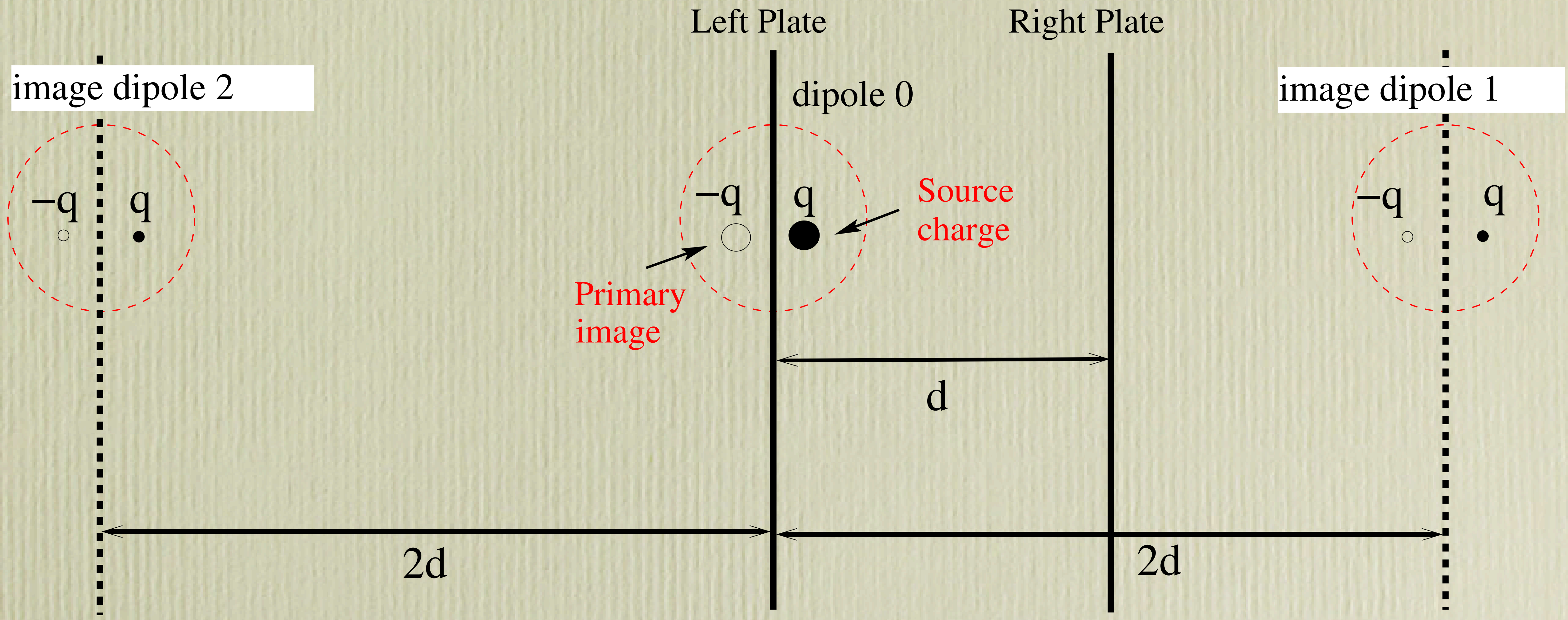
$a_\perp$ is the separation between neighboring counter-ions





Two-plate Problem:

correlation energy of one ion due to existence of the other plate



Correlation energy per condensed counter-ion

$$u = \frac{1}{4\pi\epsilon}(\vec{p}\cdot\nabla)(\vec{p}'\cdot\nabla')\frac{1}{|\vec{r}-\vec{r}'|}e^{-\kappa|\vec{r}-\vec{r}'|}.$$

$$u = -\frac{p^2}{4\pi\epsilon}\frac{1}{4d^3}\left(1+2\kappa d+2(\kappa d)^2\right)e^{-2\kappa d},$$

Including images at all orders (all attractive!)

$$\begin{aligned} u &= -\frac{p^2}{4\pi\epsilon}\sum_{k=1}^{\infty}\frac{1}{4(nd)^3}\left(1+2\kappa nd+2(\kappa nd)^2\right)e^{-2\kappa nd} \\ &= -\frac{p^2}{16\pi\epsilon d^3}\left[-2d^2\kappa^2\log\left(1-e^{-2d\kappa}\right)+2d\kappa\mathrm{Li}_2\left(e^{-2d\kappa}\right)\right. \\ &\quad \left.+\mathrm{Li}_3\left(e^{-2d\kappa}\right)\right] \qquad (4.3) \end{aligned}$$

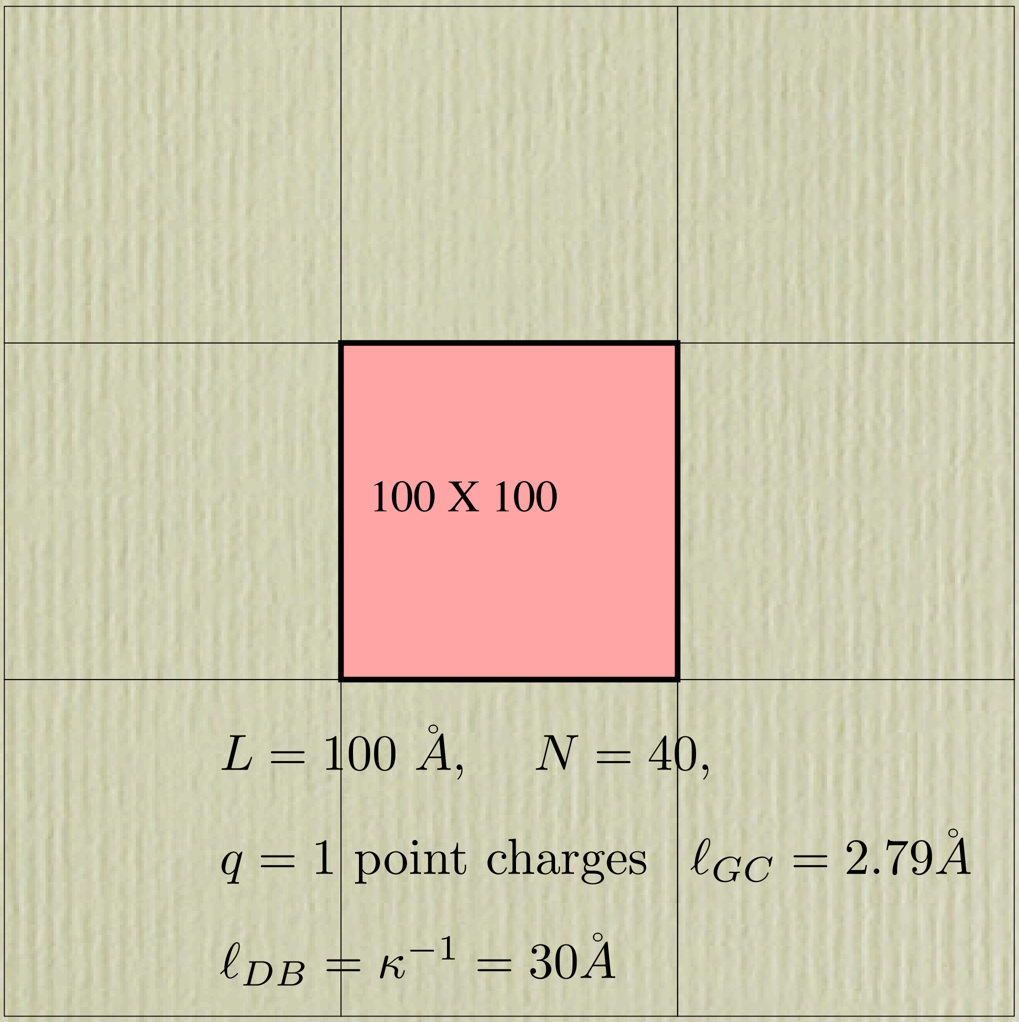
Correlation Energy between Two Plates

- Adding up correlation energy for all condensed counter-ions

$$U = -\frac{Np^2}{4\pi\epsilon}\frac{1}{4d^3}\left(1 + 2\kappa d + 2(\kappa d)^2\right)e^{-2\kappa d}$$

- with only one undetermined parameter p, which we can estimate.

Monte Carlo Simulation: One Plate Problem



$L = 100\ \mathring{A}$, $N = 40$,

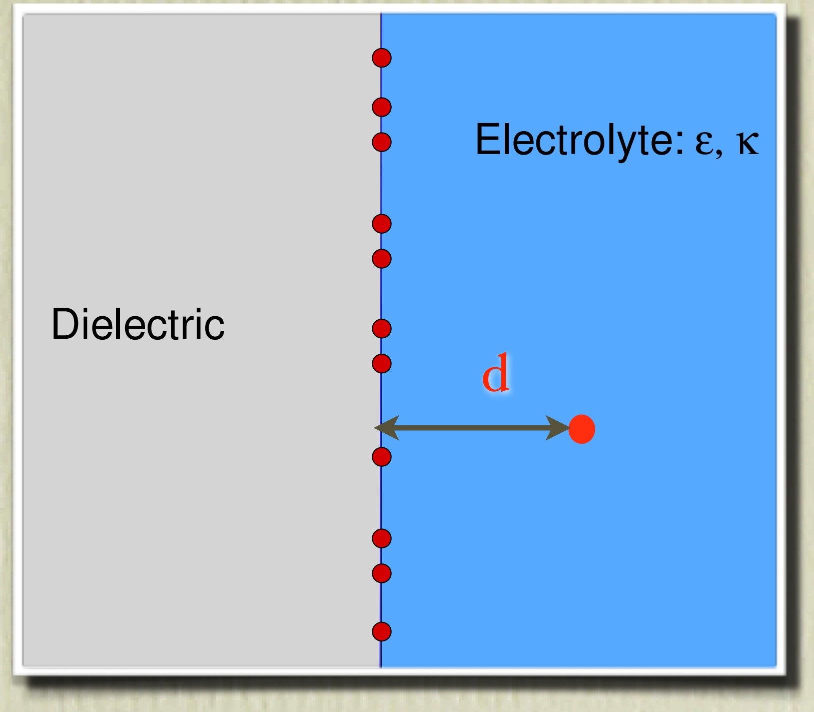
$q = 1$ point charges $\ell_{GC} = 2.79\mathring{A}$

$\ell_{DB} = \kappa^{-1} = 30\mathring{A}$

Average separation between ions: $10\mathring{A}$

Regions outside $300\mathring{A} \times 300\mathring{A}$ are ignored.

10 million MC steps



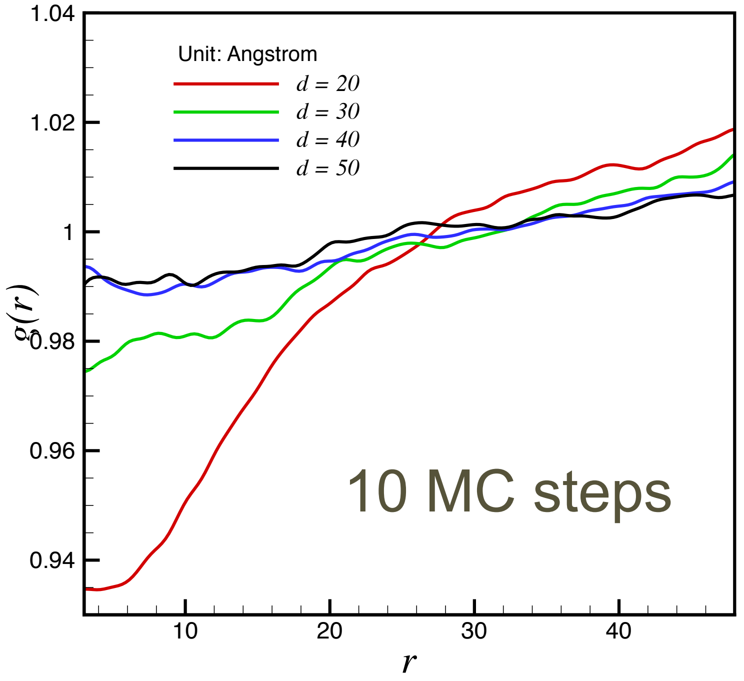


FIG. 5: Radial distribution functions for different distances.

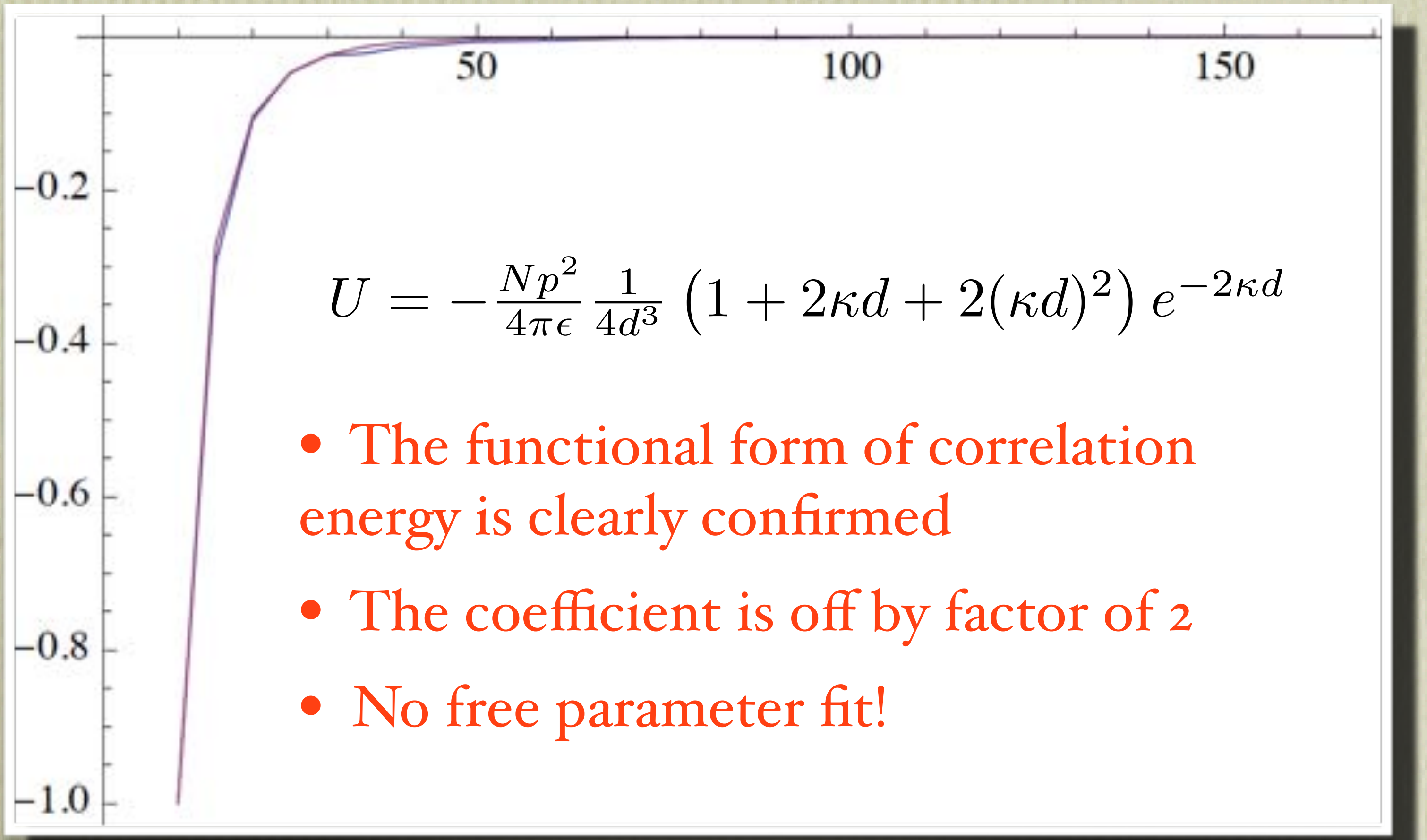
Monte Carlo Simulation: Two Plate Problem

- Multiple image charges (up to 10) are take care of
- Regions outside (300A)^2 are treated analytically, using mean field approximation
- Surface charges are treated using linearized PB

$$L = 100\ \mathring{A}, \quad N = 40,$$

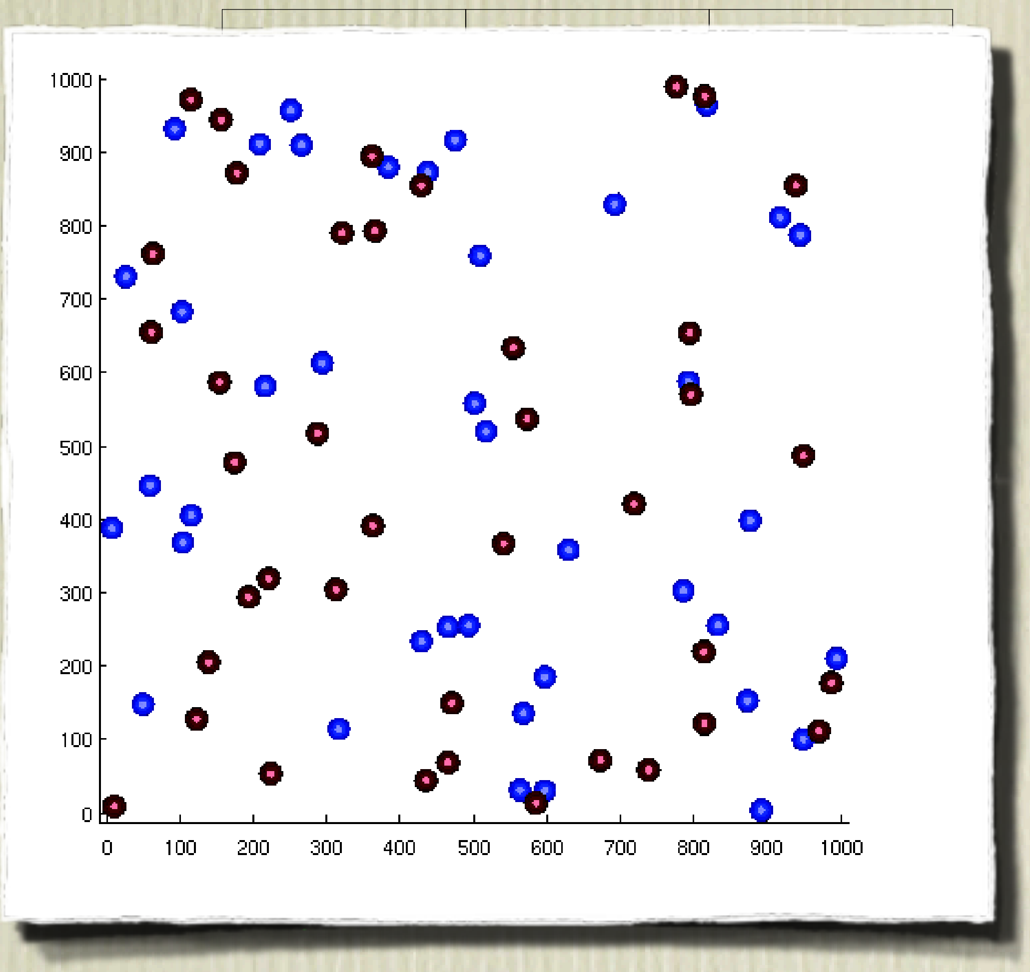
$$q = 1 \text{ point charges} \quad \ell_{GC} = 2.79\mathring{A}$$

$$\ell_{DB} = \kappa^{-1} = 30\mathring{A}$$



$$U = -\frac{Np^2}{4\pi\epsilon}\frac{1}{4d^3}\left(1+2\kappa d+2(\kappa d)^2\right)e^{-2\kappa d}$$

- The functional form of correlation energy is clearly confirmed
- The coefficient is off by factor of 2
- No free parameter fit!



Correlations of ions on two plates

Summary

- DLVO is intrinsically flawed, even at level of Linearized PB
- Two fluids model is useful
- Condensed counter-ions make colloids like conductors
- Counter-ions as effective boundary conditions
- Correlation energy calculated using generalized Debye-Huckel
- Like-charge attraction understood using linearized PB
- Excellent agreement with numerical simulation

Outlook

- More extensive simulation of two-fluids model
- Simulations of primitive model (maybe charge regulated)
- System slightly away from iso-electric point
- Comparing with experiments

Acknowledgement

- Thanks to Erik Luijten, Michael Brenner, Anatoly Kolomeisky, and Penger Tong for discussions on electrolytes and colloids
- Thanks to Shanghai Jiao Tong University for financial support and full freedom in scientific research