Electrostatic effects in soft matter
(after a long introduction to colloidal systems)

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*Introduction to colloidal systems*, in Soft and Fragile Matter, proceedings of the 53rd SUSSP, edited by M. Cates and M. Evans

W. Russel, D. Saville and W. Schowalter

*Colloidal dispersions*, Cambridge University Press 1989

J.L. Barrat and J.P. Hansen,

*Basic concepts for simple and complex liquids*, Cambridge University Press 2003

L. Belloni

What are colloidal systems?

Definition: size from $10^{-9}$ to $10^{-6}$ m
Dispersed entity, in a suspending medium
mesoscopic species / microscopic species
dust in fog, pigments, physiological DNA...

Involved in the vast majority of industrial processes
food industry, cosmetics, pharmaceutical industry...

Why such a definition (size criterion)?
Different types of colloidal dispersions

- Emulsion
- Aerosol
- Foam
Another type of colloid: opals

Hydrated silicon dioxide (amorphous)
Bell laboratories snapshot
Elise Beynon gallery...

The Scream, *Munch*
PMMA spheres of 400 nm
(electronic microscope)

L'Eglise d'Auvers, *van Gogh*
Columnar phase of Gibbsite platelets (polarization microscope)
Elise Beynon gallery II

Silicium rods / EM snapshots

Silica colloids / confocal microscope

EM snapshot

Gibbsite platelets / EM snapshots
Properties of colloidal systems: Tyndal effect
Properties of colloidal systems: Thixotropy...

... and the **blood** of St Januarius (Napoli)
The pair distribution function

Hard spheres; maximum at contact
For a Lennard-Jones fluid

Gas

Liquid

Solid

Au menu yesterday:

IA  What are colloids?
IB  Properties of colloidal systems
IC  Forces between colloids

- pair potential of mean force
- $N_c$ body potential of mean force...

... no effective potentials so far
Henderson theorem is nice... but in practice, $g(r) \rightarrow$ pair potential is (very) difficult

A. Louis (2002)

Does not violate Henderson theorem... \"same\" means \"close\"
The physico-chemistry of LE PASTIS

I. Grillo, small angle neutron scattering study,

Sambuca (Italy)
Raki (Turkey)
Generic phenomenon: The Ouzo effect


![Diagram](image)

Soluble in water

Insoluble in water

binodal: miscibility limit / spinodal: stability limit
The electric double-layer

Charged colloids $Ze$; micro-ions $\pm ze$; $|Z| \gg |z| \approx 1$

Globaly neutral system
The electric double-layer

Compromise *Boltzmann / Coulomb*: diffuse and inhomogeneous clouds around mesoscopic ions → the electric double-layer (central object for dispersions)

⇒ *Screening effect* (characteristic length $1/\kappa$)

\[
\frac{Z}{r} \rightarrow \frac{Z}{r} e^{-\kappa r}
\]

renormalization of ♦ charge  ♦ screening length
Last week...

IA  What are colloids?
IB  Properties of colloidal systems
IC  Forces between colloids

- potentials of mean force versus effective potential
- dominant forces between colloids
  hard core, dispersion, Coulomb

→ today: Focus on depletion forces
Depletion forces:
an exactly solvable lattice model

About the Ising Model...

Ernst Ising (1900-1998)
The excluded volume

Increasing the size of a tagged particle

after Barrat/Hansen
Sphere-sphere depletion potential

Mechanical and entropic interpretations fully coincide

Colloid-polymer mixture
Polymer induced flocculation

expected mechanism

PMMA spheres (70 nm) + polystyrene
The dark hand of entropy

10 fundamental stamps...
The dark hand of entropy

Entropic phase transition for hard spheres (NASA experiment)
Entropic phase transition for binary mixtures...

AB$_2$ super-structure
also observed in gem opals

AB$_{13}$ super-structure
also observed in gem opals

System: sterically stabilized PMMA spheres
Non spherical colloids...

Image from the International Committee on Taxonomy of Viruses database
Phase behaviour of hard spherocylinders

P. Bolhuis, 1996
Endless first chapter... 
...still not over!

IA  What are colloids?

IB  Properties of colloidal systems

IC  Forces between colloids
   - potentials of mean force versus effective potential
   - dominant forces between colloids
     - hard core, dispersion, Coulomb, depletion
   - colloidal phase behaviour
     - entropic phase transitions

→ today: back to colloid-polymer mixtures
The existence and general properties of solids and gases are relatively easy to understand once it is realized that atoms or molecules have certain typical properties and interactions that follow from quantum mechanics. **Liquids are harder to understand.** Assume that a group of intelligent theoretical physicists had lived in closed buildings from birth such that they never had occasion to see any natural structure [...] They probably would predict the existence of atoms, of molecules, of solid crystals, both metals and insulators, of gases, but most likely **not the existence of liquids**

Keep in mind:
\[ \rho_c^* = \rho \sigma^3 \] close to 0.3
\[ T_c^* = kT/\epsilon \] close to 1
\[ \rightarrow \text{no small parameter} \]
Phase diagram changing
the range of attraction

Liquid/vapor becomes metastable,
then unstable
The capillary length and the leaking tap

Snapshot N. Garnier, Ens Lyon
The capillary length and water striders
Water striders could also inspire artists!

PMMA spheres (70 nm) + polystyrene
...and imaging coalescence events


PMMA spheres (70 nm) + polystyrene
Tunable colloidal crystals

To some, the word colloidal conjures up visions of things indefinite in shape, indefinite in chemical composition and physical properties, fickle in chemical deportment, things generally unmanageable.

Hedges, *Colloids*, 1931
Interest for the physicist?

Experimentalist: compare with ordinary molecular systems

- Size $\sim \lambda_{\text{visible}}$
- Low density $\rightarrow$ fragile $\rightarrow$ soft matter
- Relaxation time $\rightarrow 10^{-1}$ rather than $10^{-12}$ second

Theoretician

- micro/meso scale separation (length + time)
  $\rightarrow$ eliminate microscopic degrees of freedom
  $\rightarrow$ develop effective approaches (for mesoscopic degrees of freedom)
- Fine tuning of effective potentials
  from short to long range (adding polymers, electrolyte...)
  impossible with molecular systems!
- Model systems described by few parameters
  ideal to test and refine statistical mechanics tools
In short... why study colloids?

- Soft
- Slow
- Seeable

(W. Poon)

large + small → dressed large
Scope of the (remaining) lectures
concentrate on fundamental Coulombic effects

- Symmetric electrolytes
- Poisson-Boltzmann theory
- DLVO and the stability of colloids
- *Strange* electrostatics
- Introduction to electrokinetic effects
Spectacular Coulombic effects

- Like charge attraction
  (beyond mean-field)
- Overcharging
- Anomalous electrophoresis
  (includes mean-field or (xor) non mean-field effects)
- DNA ejection from bacteriophages...

...
DNA ejection from bacteriophages
Statistical mechanics of charged systems: The pionneers

Michael Faraday (1830)

Swante Arrhenius (1884)
bad PhD but...

Peter Debye (1923)
Critical behaviour

Charge asymmetric but equisized primitive model \((z = \frac{e_+}{e_-})\)

Field theory results divided by 6 after S. Banergee and M. Fisher
First five lectures

I- Introduction
   IA  What are colloids ?
   IB  Properties of colloidal systems
   IC  Forces between colloids and phase behaviour

II- Symmetric electrolytes
   IIA  Background
   IIB  Ionized gases ans screening
   IIC  Critical behaviour within Debye-Huckel theory

III- Poisson-Boltzmann theory
   IIIA  Formal derivation
   IIIB  Solutions known
   IIIC  Properties
The Wigner-Seitz cell approach

Validity of the modelization...

$P = kT \text{ density}(R_{WS})$

Equation of state ($P$ in Pascal)
(bromopolystyrene dispersion)
spherical colloids a $\approx 51$nm
(Reus et al. 1997)
Comparison with Monte Carlo (Linse, 2000)
Charged hard spheres \((Z = 40)\)
+ point counter-ions \((z = 1)\)
Refined estimation of PB validity domain

coupling parameter \( \Gamma^2 \)

\[ \tilde{z} = z / (\text{Gouy length}) \]

Summary of relevant length scales

At least 5 independent and relevant scales

\[
\begin{array}{cccccc}
10^{-10} & 10^{-9} & 10^{-8} & 10^{-7} & 10^{-6} & \text{longueur (m)} \\
\bullet & \bullet & \bullet & \bullet & \bullet & \\
b & \ell_B & \kappa^{-1} & \rho^{-1/3} & a & \\
\end{array}
\]

\(b\) : Gouy
\(\ell_B\) : Bjerrum
\(\kappa^{-1}\) : Debye
\(\rho\) : density
\(a\) : size

\(-e\) \(-e\)

\(\ell_B\) : repulsion \(\sim k_B T\)
\(\ell_B = e^2 / (\epsilon k_B T)\)
Charge renormalisation

Multiple scale expansion, \((\kappa a)^{-1}\) small parameter
Spherical and cylindrical macro-ions

\[
Z_{\text{eff}} \frac{\ell_B}{a} = 4\kappa a t_z + 2 \left( 5 - \frac{t_z^4 + 3}{t_z^2 + 1} \right) t_z
\]

\[
t_z = T \left( \frac{Z_{\text{bare}} \ell_B / a}{2\kappa a + 2} \right)
\]

\[
T(x) = \frac{\sqrt{1 + x^2} - 1}{x}
\]

\[\text{SPHERES}\]

\[\text{ADN double brin}\]

Colloidal molecular crystals

CMC on triangular lattices

CMC on square lattices

Like charge attraction: An old controversy...

Professor London has informed us that he also obtained an approximate expression for the interaction energy of two colloidal particles which is similar to ours. [...] He got the peculiar result that on the basis of Debye-Hückel theory, two similarly charged colloidal particles attract each other at large distances. [...] His calculations have, so far, not been published due to certain objections raised by H. Kallmann, which we cannot consider to be valid any longer.

S. Levine et G. Dube, 1939

In a series of papers, Levine and Dube treated of the interactions of spherical particles [...] They derived —unfortunately using a wrong method— equations for the potential energy of interaction. [...] The attraction at relatively great distances is a result of a fallacious expression for the free energy. The general principles [...] were erroneous.

E. Verwey et J. Overbeek, 1948
Like-charge attraction, a simple argument
2 charged planes \( \sigma < 0 \), no electrolyte (counter-ions \( \oplus \) only)

\[
P = P_{\text{cin}} + P_{\text{el}}
\]

\[
P_{\text{el}} = -2 \pi \sigma^2 / \varepsilon, \text{ attractive}
\]

\[
P_{\text{cin}} = k_B T \rho_{\text{contact}}, \text{ repulsive}
\]

When \( h < a_{\perp} \), profile \( \rho(r) \) uniform

\[
\Rightarrow \rho_{\text{contact}} \approx \rho_{\text{mean}} \approx 2|\sigma|/h
\]

\[
\Rightarrow P \propto (1-h/b)
\]

\[
\Rightarrow \text{attraction if } h > b
\]

\[
0 \quad b \quad a_{\perp} \quad ? \quad h
\]

repulsion \hspace{1cm} attraction

Argument requires \( b < a_{\perp}, \sigma > \sigma_{\text{min}} \)

and \( h < h_{\text{seuil}} = \ell_B \approx 7 \text{ Å in water} \)

Field theory (Netz/high couplings) \( \rightarrow \) exact result!
Come back to failure of mean-field at short distances

\[ P = P_{\text{cin}} + P_{\text{el}} \]

When \( h < a_\perp \), profile \( \rho(\mathbf{r}) \) uniform

\[ \Rightarrow P \propto (1-h/b) \]

\[ \Rightarrow \text{attraction when } h > b, \text{ ALWAYS TRUE} \]

Within mean-field, discrete nature of microions neglected, only local density matters \( \Rightarrow a_\perp = 0 \)

when do profiles become uniform ?

\( h < b \)

and thus \( P \propto (1-h/b) > 0 \)!

mean-field correct for \( b > a_\perp \)

\( a_\perp / b \) defines the coupling parameter \( \Gamma \)

\[ a_\perp^2 = e / \sigma = b \ell_B \]

\[ b \propto 1/\sigma \]

In any case, mean-field valid for colloidal dispersions
A surprisingly attractive couple

Importance of confinement

Attraction beyond any « reasonable » length scale

ORIGIN ?

Larsen, Grier

Nature, 1997
Pitfalls in confined geometry...

Conclusion: do not mix up effective potentials and potentials of mean force.
Interpretation of experimental results?

- Attraction seems impossible at large distances (mean-field valid)

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mechanism with an adjustable parameter...
Thank you