File ISM04

Properties of Colloids I

Colloids

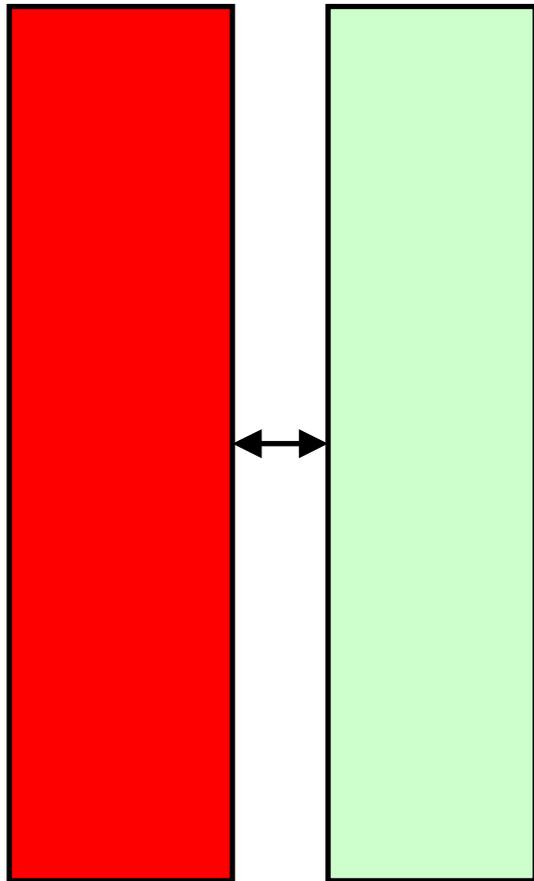Small things, but much bigger than a molecule

Background:
Foundations of Colloid Science Vol I & II, R.J. Hunter
Physical Chemistry, P.W. Atkins, Chapter 10 (electrostatics)
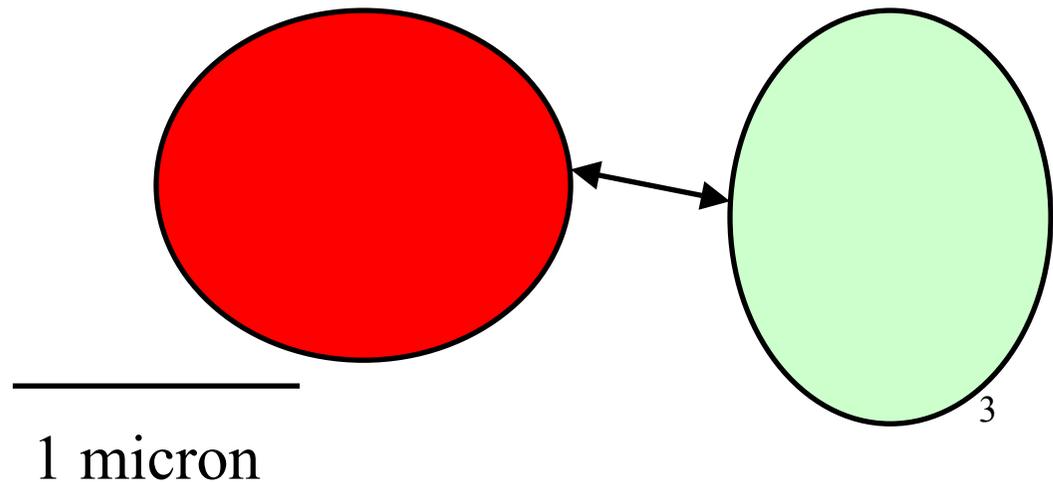And Chapter 23, Colloids

Colloidal forces
(Chapter 3 Hamley's book)
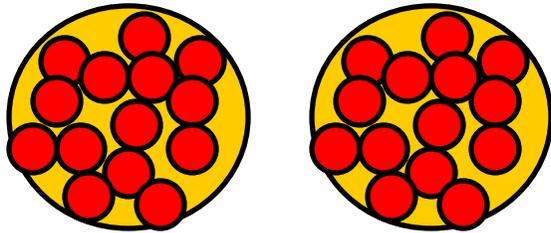
Two colloidal particles
in water.
The key question is:
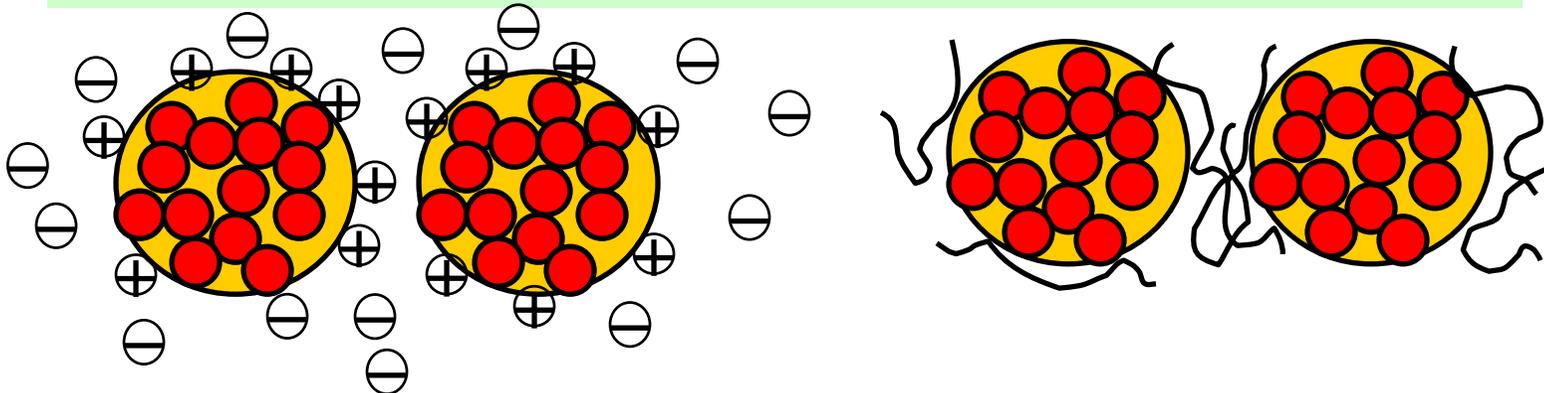do they stick together?

1 micron

Colloidal forces

There are two types of interactions

A volume force, derived from all interactions
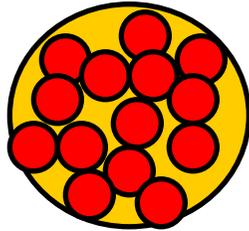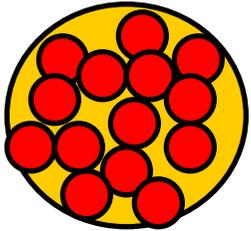between the constituting atoms of the colloids

Add up all interactions
between the 'red' atoms

A surface force, derived from the interactions
between things bound to the surfaces, for example ions or polymers

Colloidal forces: Hamaker constant

Add up all interactions
between the 'red' atoms

$$V(\mathbf{R}_1 - \mathbf{R}_2) = \sum_i \sum_j V(\mathbf{r}_i - \mathbf{r}_j)$$

$\mathbf{R}_1$ position colloid 1

$\mathbf{R}_2$ position colloid 2

$\mathbf{r}_i$ position atom i of colloid 1

$\mathbf{r}_i$ position atom i of colloid 1

$$V(\mathbf{r}_i - \mathbf{r}_j) = -cst.\frac{\alpha_i \alpha_j}{|\mathbf{r}_i - \mathbf{r}_j|^6} \text{ dispersion interaction}$$
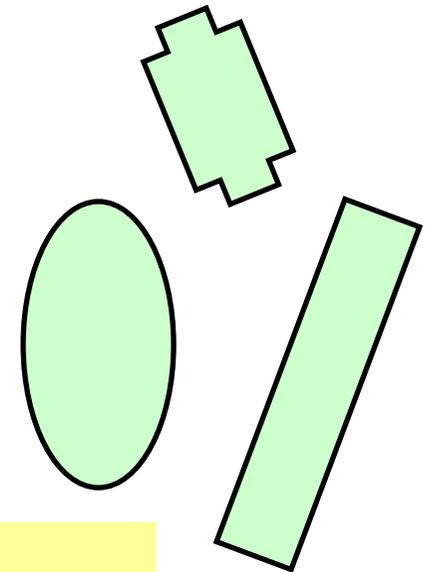
In analytical calculations,
the double sum is replaced by a double volume integral

The exact answer depends on the *shape* and *orientation* of
the colloids

vdW interaction: particle with half-body
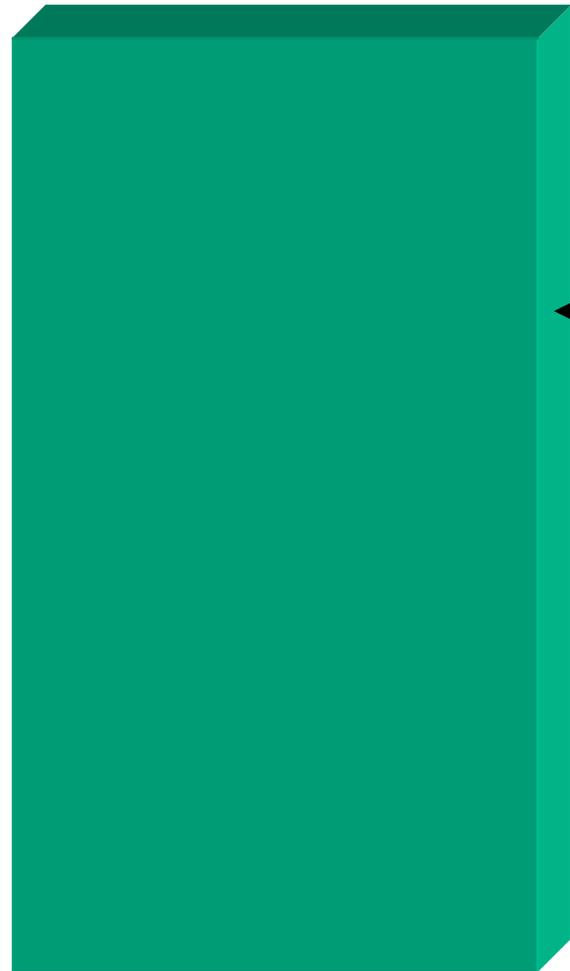
Density of atoms
in half-body: ρ

$$V_{11} = -\frac{C}{r^6}$$

$$V_{1S}(h) = \int_h^\infty \int_0^{2\pi} \int_0^\infty R\rho V_{11}(r)\,dr\,d\phi\,dz$$

$$r^2 = z^2 + R^2$$

$$V_{1S} = -\frac{\pi}{6}\rho C \frac{1}{h^3}$$

vdW interaction between two *half*-bodies
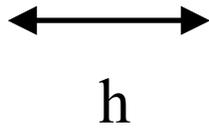
$$A\rho dz \quad \text{number of atoms in slab with thickness } dz$$

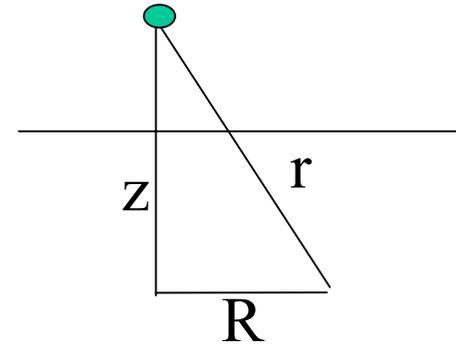$$V_{SS} = A \int_h^\infty \rho V_{1S}(z) dz$$

$$V_{SS} = -\frac{\pi}{6} A \rho^2 C \int_h^\infty \frac{1}{z^3} dz = -\frac{\pi}{12} A \rho^2 C \frac{1}{h^2}$$

$$\frac{V_{SS}}{A} = -\frac{\pi}{12} \rho^2 C \frac{1}{h^2} = -\frac{A_H}{12\pi} \frac{1}{h^2} \quad \text{pg 137 Hamley}$$

$$A_H \equiv \pi^2 \rho_1 \rho_2 C_{12} \quad \text{Hamaker constant}$$

vdW interaction between two spheres
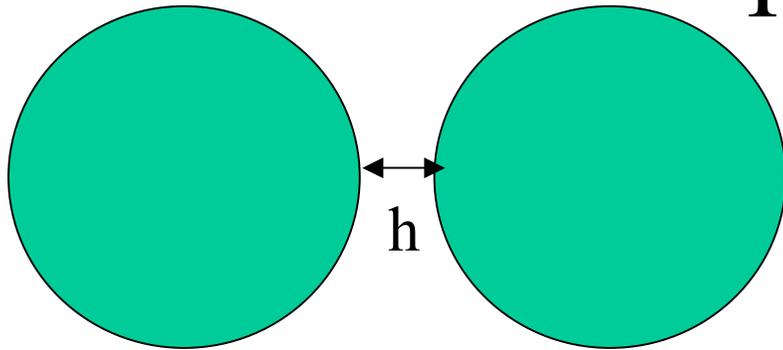
h<<R
Derjaguin approximation

h

$$\frac{V}{A} = -\frac{A_H}{48\pi R}\frac{1}{h} \quad \text{pg 137}$$

Various shapes vdW interaction

Motto: use a computer

Two spheres

$a_1, a_2 \gg H$

$$V_A = -\frac{A}{6H}\left(\frac{a_1 a_2}{a_1 + a_2}\right)$$

$a_1, a_2 \ll H$

$$V_A \doteq \frac{-16A}{9} a_1^3 a_2^3 / H^6$$

Sphere and half-space

$a \gg H$

$$V_A = \frac{-Aa}{6H}\left[1 + \frac{H}{2a+H} + \cdots\right]$$

$a \ll H$

$$V_A \propto -\frac{1}{H^3}$$

Parallel cylinders

$a_1, a_2 \gg H$

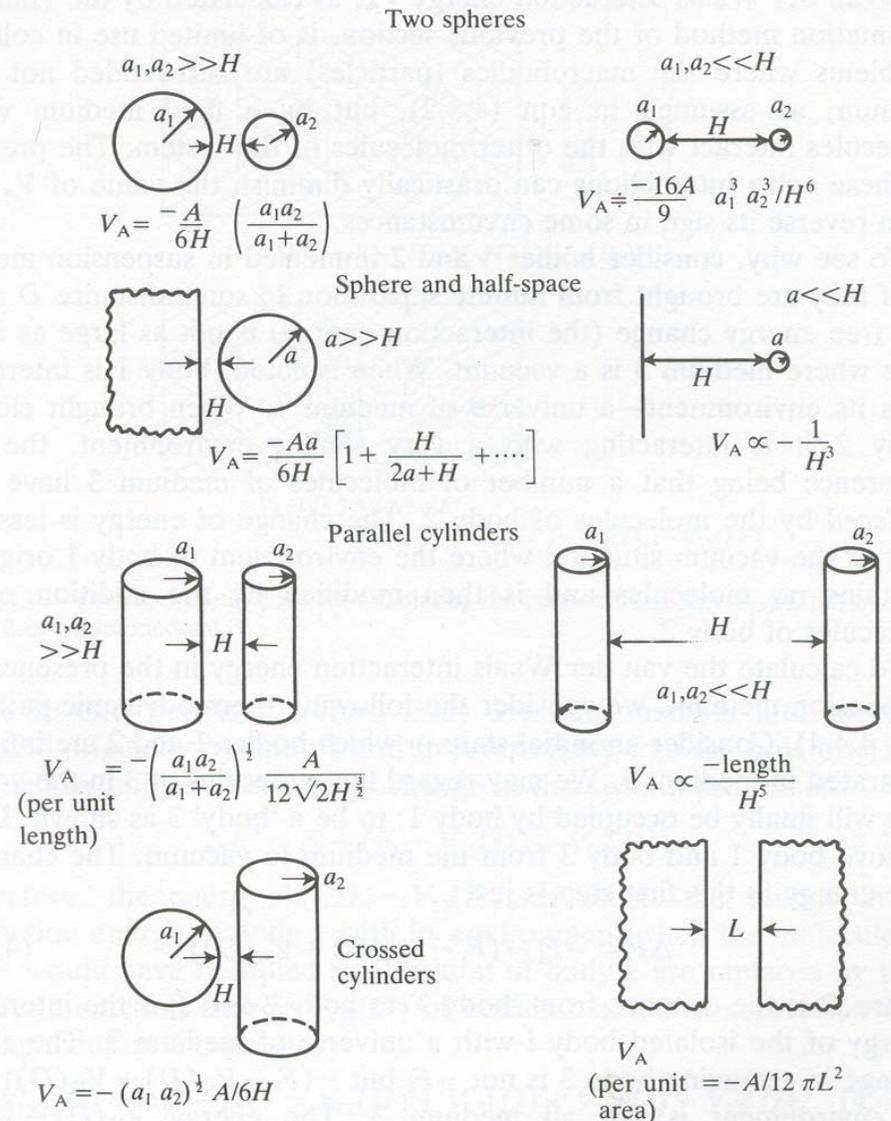$$V_A = -\left(\frac{a_1 a_2}{a_1 + a_2}\right)^{\frac{1}{2}} \frac{A}{12\sqrt{2}H^{\frac{3}{2}}}$$
(per unit length)

$a_1, a_2 \ll H$

$$V_A \propto \frac{-\text{length}}{H^5}$$

Crossed cylinders

$$V_A = -(a_1 a_2)^{\frac{1}{2}} A/6H$$

$$V_A \text{ (per unit area)} = -A/12\,\pi L^2$$

FIG. 4.4.3. Distance dependence of the *non-retarded* potential energy between pairs of solid surfaces of various geometries. The retarded interaction has a distance dependence $1/H$ times that and the proportionality constant then changes. In some cases the integration process yields quite messy results and these have not been included explicitly. Mahanty and Ninham (1976) remark that it is preferable in many cases to do the integration over the volumes of the particles by numerical methods rather than try to find analytical representations that are bound to be complicated for all but the simplest geometries.

9

Hamaker constants

Material (M)	M |air| M	M |water| M
Alkanes		
$n = 5$	3.75	0.336
6	4.07	0.360
7	4.32	0.386
8	4.50	0.410
9	4.66	0.435
10	4.82	0.462
11	4.88	0.471
12	5.04	0.502
13	5.05	0.504
14	5.10	0.514
15	5.16	0.526
16	5.23	0.540
Fused quartz	6.50	0.833
Cryst. quartz	8.83	1.70
Water	3.70	0
Fused silica	6.55	0.849
Calcite	10.1	2.23
Calcium fluoride	7.20	1.04
Sapphire	15.6	5.32
Poly(methylmeth-acrylate)	7.11	1.05
Poly(vinylchloride)	7.78	1.30
Polystyrene	6.58	0.950
Poly(isoprene)	5.99	0.743
Poly(tetrafluoro-ethylene)	3.80	0.333
Mica (brown)	—	1.98
Mica (green)	—	2.14

Hamaker constants ($\times 10^{+20}$/J

Across air (or vacuum)
Organic materials
4-8 $\times 10^{-20}$ J
Inorganic materials bit
Larger
The *effective* Hamaker
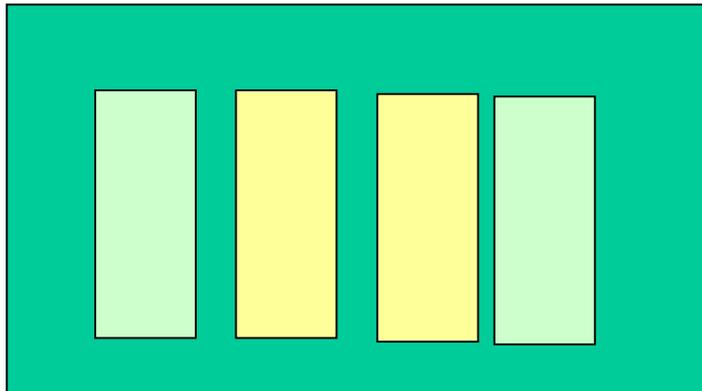constant in water is
much smaller

Exercise: why is the *spread* in the
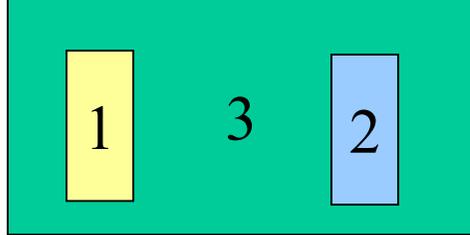Hamaker constant small?

10

Medium effect
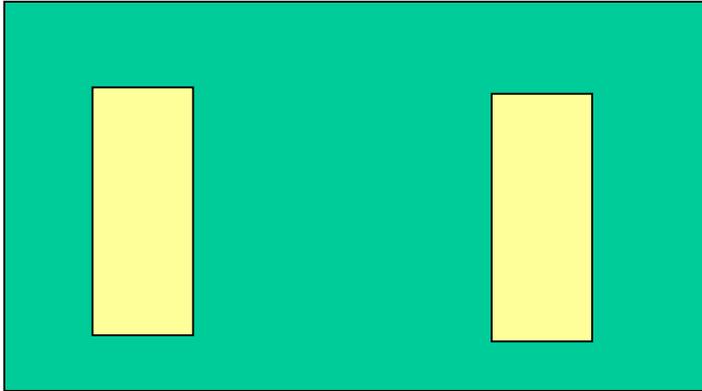
When the two yellow bodies
approach, solvent is displaced
The net interaction is the sum
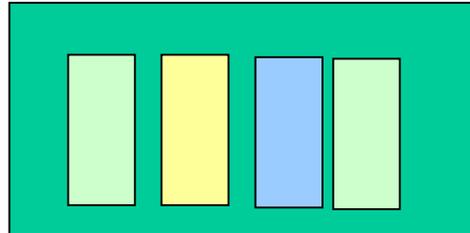of favourable and unfavourable
contributions:
- favourable, because
the two yellow bodies are closer
- unfavourable, because the two
solvent bodies are further apart

Hence, the *effective* vdW interaction
is reduced

Effective Hamaker constant

A_{132} effective Hamaker constant for interaction between colloids 1 and 2 in medium 3

$$A_{132} = A_{12} + A_{33} - A_{13} - A_{32}$$

$$A_{131} = A_{11} + A_{33} - A_{13} - A_{13}$$

$$A_{ij} \sim \alpha_i \alpha_j \rightarrow A_{ij} \approx \sqrt{A_{ii} A_{jj}}$$

$$A_{131} \approx \left(\sqrt{A_{11}} - \sqrt{A_{33}} \right)^2 > 0 \qquad \text{Like particles always attract}$$

$$A_{132} \approx \left(\sqrt{A_{11}} - \sqrt{A_{33}} \right) \left(\sqrt{A_{22}} - \sqrt{A_{33}} \right) \text{ any sign}$$

Unlike particles may repel

How big are the interactions?

$$A_H = 5 \times 10^{-20} \text{ J}$$

$$A = 10 \text{ cm}^2 = 0.001 \text{ m}^2$$

$$h = 0.5 \text{ nm} = 0.5 \times 10^{-9} \text{ m}$$

$$V = -\frac{1.0 \times 10^{-3} \times 5 \times 10^{-20}}{12\pi} \frac{1}{(0.5 \times 10^{-9})^2} = 5.3052 \times 10^{-6} \text{ J}$$

$$F = -\frac{dV}{dh} = 2\frac{1.0 \times 10^{-3} \times 5 \times 10^{-20}}{12\pi} \frac{1}{(0.5 \times 10^{-9})^3} = 21221 \text{ N}$$

The energies are small, but the forces are big!

Van der Waals glue?? You can hang from the ceiling, with one hand...

You need very close contact over a larger area to make this work!

How big are the interactions?

Experiment: bring your hands together,
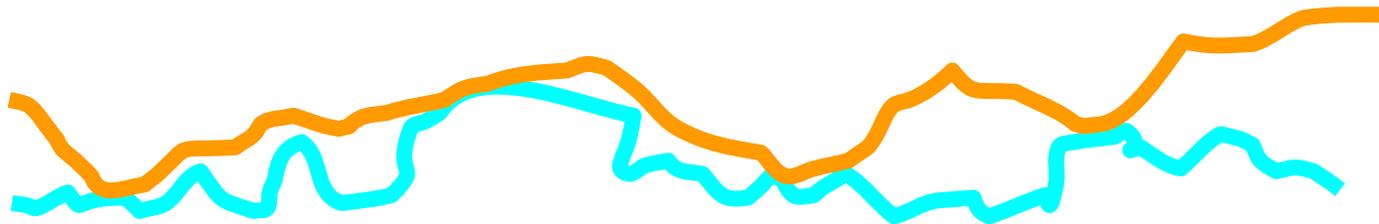is it difficult to pull them apart agin?
NO
According to the theory, when in close contact the hand surfaces
are separated by 0.5 nm , you would need a force of more than 20000 N
(more than 2000 kg) to pull them apart again (based on baby hand 10 cm^2)
Something is wrong?
Yes
What is very wrong, is to assume the average distance
 is constant and (very) small...the surfaces are (very) rough
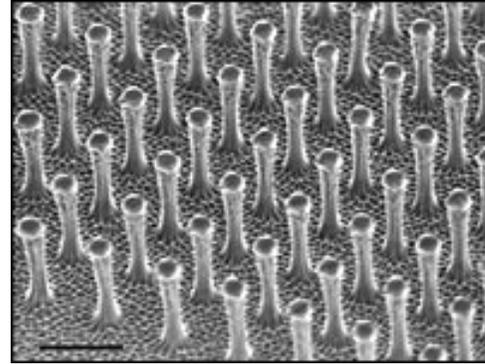
We are not spiderman!

Enter the lizard

How big are the interactions?

Juvenile Tokay Gecko (*Gekko gecko*)
Photo by: Greg Christenson ©2002
Female Tokay (*Gekko gecko*) warning call
recorded by: Greg Christenson ©2000

Professor Andre Geim and colleagues
Synthetic hairs

Gekko glue
Spiderman
weighs 40 grams

The trick of the gekko: increase area of close contact

The toos branch off in branched tiny hairs

How big are the interactions?

On a colloidal scale, we compare the interactions with kT

$$
\begin{aligned}
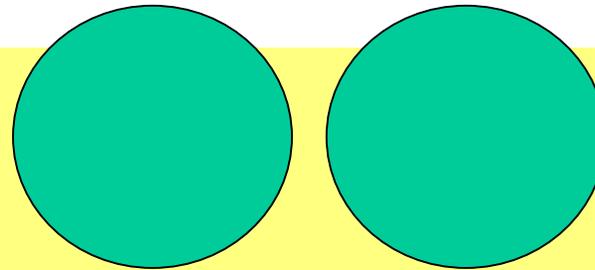A_H &= 5 \times 10^{-20}\text{J} \\
R &= 500 \text{ nm} \\
h &= 0.5 \text{ nm} \\
V &= -A_H \frac{4\pi R^2}{48\pi R}\frac{1}{h} = -\frac{5 \times 10^{-20}}{12}\frac{500 \times 10^{-9}}{0.5 \times 10^{-9}} = 4.1667 \times 10^{-18}\text{J} \\
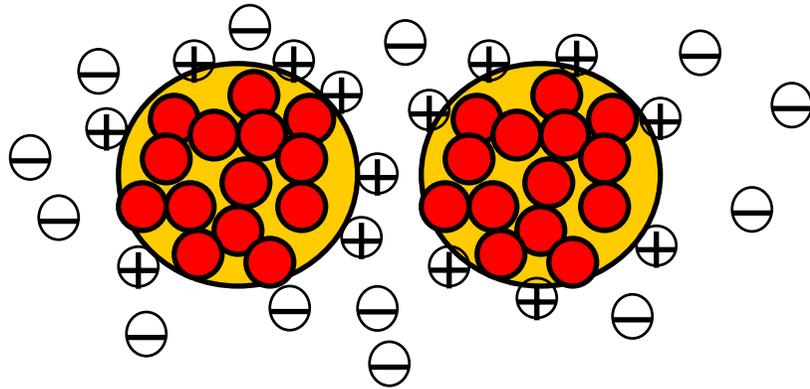\text{at 300 K, kT} &= 1.38 \times 10^{-23} \times 300 = 4.14 \times 10^{-21} \text{ J} \\
V &= \frac{4.1667 \times 10^{-18}}{4.14 \times 10^{-21}} = 1006.4 \text{ kT}
\end{aligned}
$$

This is (much) more than the energy stored
in a covalent bond!

Surface interactions: electrostatics

Ions are bound to the surface
counter-ions gather around in a diffuse cloud
Co-ions are expelled from the surface region
The surface + cloud is the diffuse double layer

Intermezzo: ions

Electrostatic interactions between ions in a dielectric medium (Atkins section10.2)

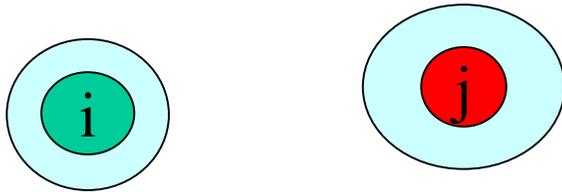$$\nabla^2 \psi = -\frac{\rho}{\epsilon} \quad \text{Poisson equation}$$

$$\psi_i(\mathbf{r}) = \frac{q_i}{4\pi\epsilon|\mathbf{r}_i - \mathbf{r}|}$$

$$\epsilon = \epsilon_r\epsilon_0 \quad \text{water } \epsilon_r \approx 80$$

$$V(|\mathbf{r}_i - \mathbf{r}_j|) = \psi_i(\mathbf{r}_i)q_j = \frac{q_i q_j}{4\pi\epsilon|\mathbf{r}_i - \mathbf{r}_j|}$$

Intermezzo: ions

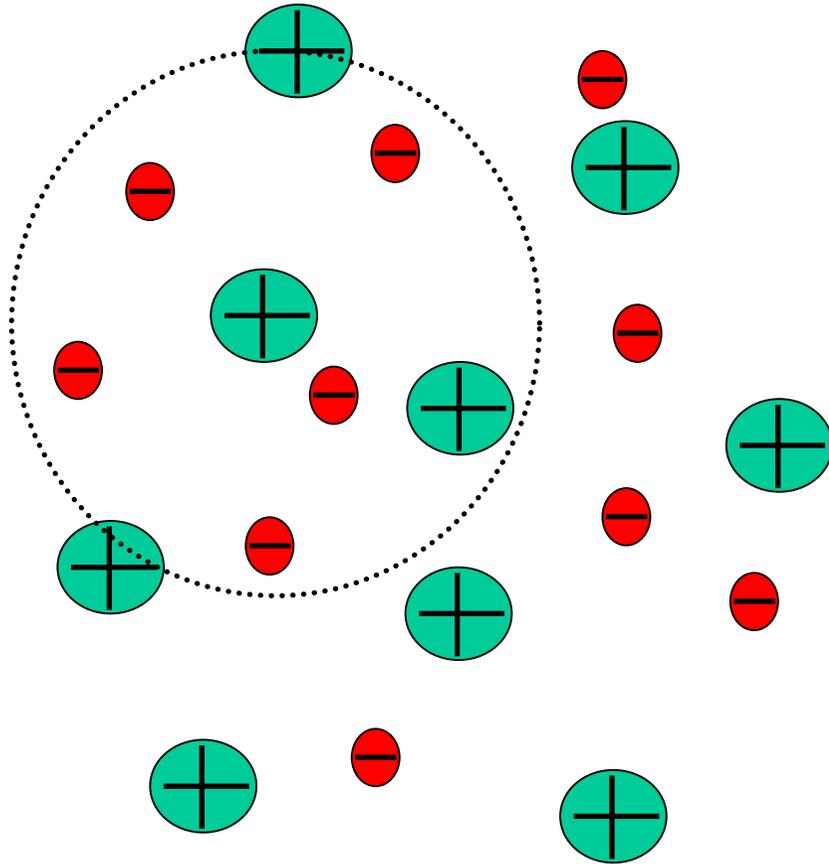Electrostatic interactions in salt solution

i   j   Effect of hydration

Each ion is surrounded by a hydration layer: the ions will not approach closer than this layer

Intermezzo: ions

Electrostatic interactions in salt solution

Co-ions are expelled
Counter-ions are attracted

Intermezzo:Debije-Hückel theorie ions (Atkins, justification 10.2)

$$\nabla^2 \psi = -\frac{\rho}{\epsilon}$$

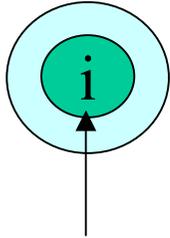$$\rho = ec[e^{-e\psi/kT} - e^{e\psi/kT}] \approx -\frac{2e^2c}{kT}\psi \quad \text{c in molecules/m}^3$$

$$\frac{1}{r^2}\frac{d}{dr}(r^2\frac{d}{dr}\psi) = \frac{2ec}{\epsilon kT}\psi$$

$$\psi_i(\mathbf{r}) = \frac{q_i}{4\pi\epsilon|\mathbf{r}_i - \mathbf{r}|}e^{-\frac{|\mathbf{r}_i - \mathbf{r}|}{r_D}}$$

$$r_D \equiv (\frac{\epsilon kT}{2ce^2})^{\frac{1}{2}} \quad \text{Debije Length}$$

$$\kappa \equiv \frac{1}{r_D} \quad \text{reciprocal double layer thickness}$$
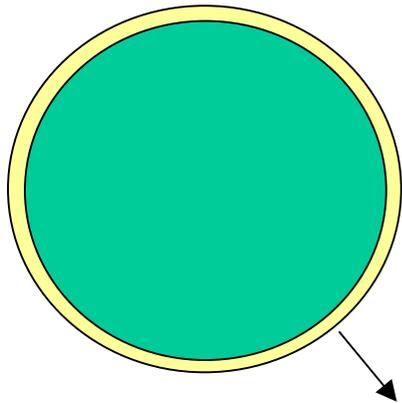
Intermezzo: ions effect size of sphere

The ions cannot approach closer
than the hydration layer

In the case of hydrated ions.
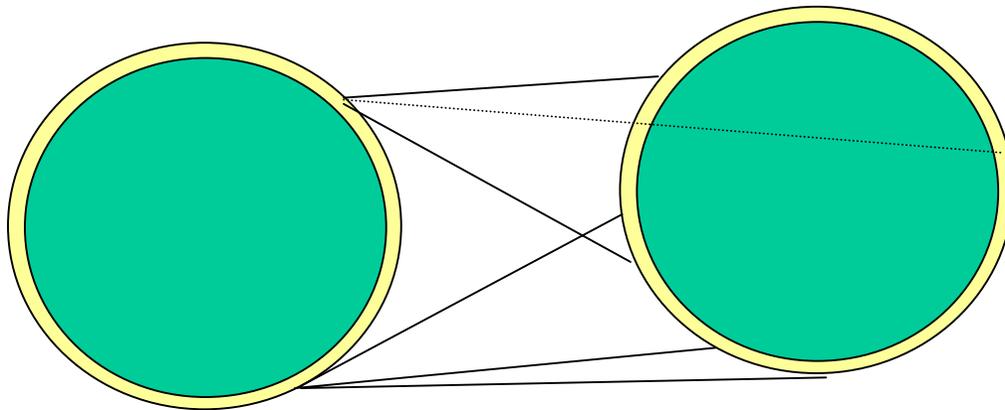the charge is located in the middle of the sphere

Back to colloids: *surface* charge

In the usual case, the charges on
a colloidal particle are located on the *surface*

σ charge density per m^2 on colloid surface

Eelectrostatic interaction colloids

Now, we have to calculate the interaction between
each ion bound to the surface, and integrate…
In the general case: not so easy!
Derjaguin-Landau-Verweij-Overbeek
Solve Poisson-Bolztmann equation for potentials, from
potentials calculate free energy…

Surface of half-body (plate)

Solve Poisson Boltzmann equation directly in 1D

$$\nabla^2 \psi = -\frac{\rho}{e}$$

$$\frac{d^2\psi}{dz^2} = -\frac{e}{\epsilon}c[e^{-e\psi/kT} - e^{e\psi/kT}] \quad \text{Poisson-Boltzmann}$$

$$e\psi < kT$$

$$\frac{d^2\psi}{dz^2} = \frac{2e^2c}{\epsilon kT}\psi = \frac{\psi}{r_D^2}$$

$$\psi = Ae^{-z/r_D}$$

$$\psi(0) = \psi_0 = A$$

$$\psi = \psi_0 e^{-z/r_D} = \psi_0 e^{-\kappa z}$$

z

Surface potential and surface charge

κ^{-1}

$\psi(z)$

ψ_0

z

Debije length
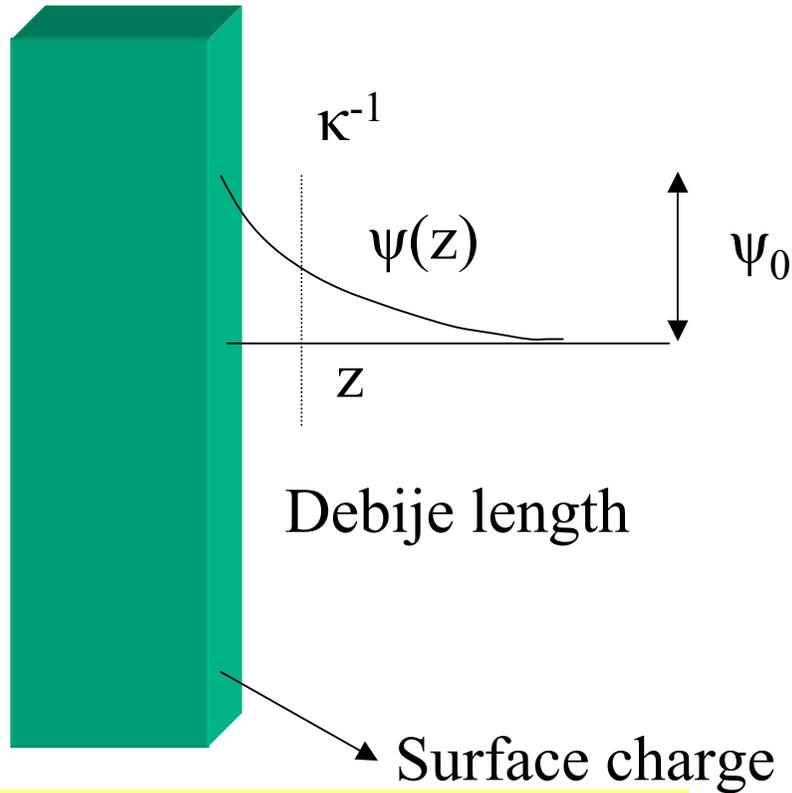
Surface charge

$\sigma = \dfrac{Q}{A}$ surface charge/area
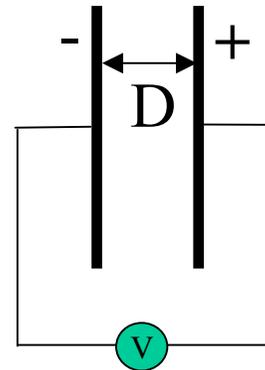
Exercise: derive DL capacitor
relation from potential profile

Capacitor relation

$$\psi_0 = \frac{\sigma}{\epsilon\kappa}$$

$$\psi_0 = Q\frac{r_D}{A\epsilon}$$

$$\frac{Q}{\psi_0} = \frac{A\epsilon}{r_D} \quad \text{double layer capacitance}$$

Compare with capacitor
in electronic circuit

- $\quad$ +

D

$$\frac{Q}{V} = \frac{A\epsilon}{D}$$

27

Properties electrostatic interactions

The important lessons:
1. electrostatic interactions in salt solution rapidly die out at distances larger than the Debije length
2. The decay is roughly exponential e^{-r/r_D}

$$1 \text{ M } 1\text{-}1\text{electrolyte} \quad : \quad r_D \approx 0.3 \text{ nm}$$

$$0.1 \text{ M} \quad : \quad r_D \approx 1 \text{ nm}$$

at physiological conditions, the shielding at 5 nm is $e^{-5} = 0.0067$

Shortcomings DL model

In practice, the simple diffuse layer model works reasonably well in the solution phase, but it is not so good for the surface region.
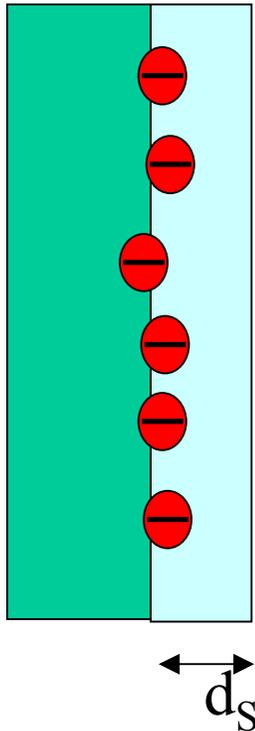
- the distribution of surface charges is uneven on the size scale of the ions themselves (depends on synthesis)
- the surface ions are hydrated

In the Stern layer model, a region of thickness d_S is excluded from mobile ions

d_S

Charge stabilisation

When two charged colloids approach, the surface bound charges will repel each other, and hence the colloids will be pushed apart
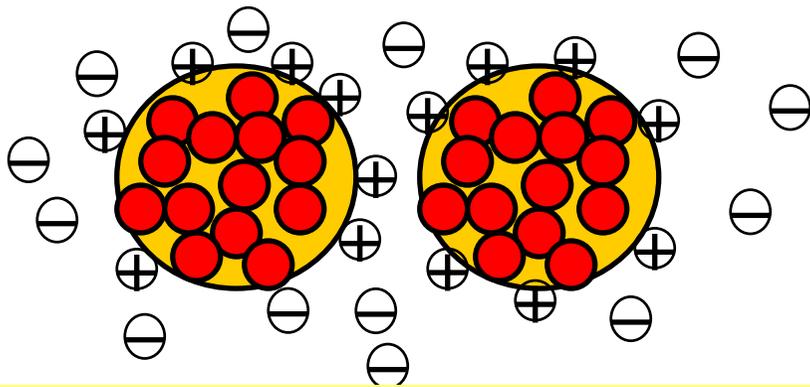
The electrostatic interaction needs to include the diffuse layer
Not so easy!
Derjaguin-Landau-Verweij-Overbeek

$$\frac{V(h)}{A} = 16kTc\tanh^2\frac{e\psi_0}{4kT}\frac{e^{-\kappa h}}{\kappa} \quad \text{plate}$$

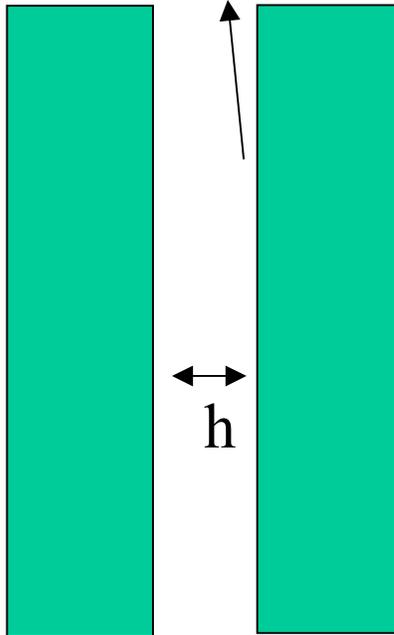$$\frac{V(h)}{A} = 16kTc\tanh^2\frac{e\psi_0}{4kT}\frac{e^{-\kappa h}}{R\kappa^2} \quad \text{sphere}$$

In both cases:

$$V \sim e^{-\kappa h}$$

How big is the repulsion? numerical example

Surface charge
1 ion / 100 nm²

Two plates
Area 10^4 nm²

When the surface potential is low:
(exercise: derive yourself)

$$\frac{V}{A} = \frac{2\sigma^2}{\kappa\epsilon} e^{-\kappa h}$$

h

$$\sigma = 0.01 \text{ e/nm}^2 = 0.01 \times \frac{1.602177 \times 10^{-19}}{10^{-18}} = 0.0016 \text{ Cm}^{-2}$$

$$\epsilon = 80 \times 8.85410 \times 10^{-12} = 7.0 \times 10^{-10} \text{J}^{-1}\text{C}^2\text{m}^{-1}$$

$$h = 0.5 \text{ nm}$$

$$0.1 \text{ M} \rightarrow c = \frac{0.1 \times 6.02214 \times 10^{23}}{10^{-6}} \text{ m}^{-3}$$

$$\kappa^{-1} = 1 \text{ nm}$$

$$\kappa = 1 \text{ nm}^{-1} = 1 \times 10^9 \text{ m}^{-1}$$

$$V = 10^4 \times 10^{-18} \times \frac{2 \times 0.0016^2}{1 \times 10^9 \times 7.0 \times 10^{-10}} e^{-1 \times 10^9 \times 0.5 \times 10^{-9}} = 4.4 \times 10^{-20} \text{ J}$$

$$V = \frac{4.4 \times 10^{-20}}{4.14 \times 10^{-21}} = 10.6 \text{ kT at } 300 \text{ K} \longrightarrow \text{Big! (big enough)?}$$

Exercise: calculate repulsion for $\sigma = 0.1$ e/nm²

This concludes file ism04