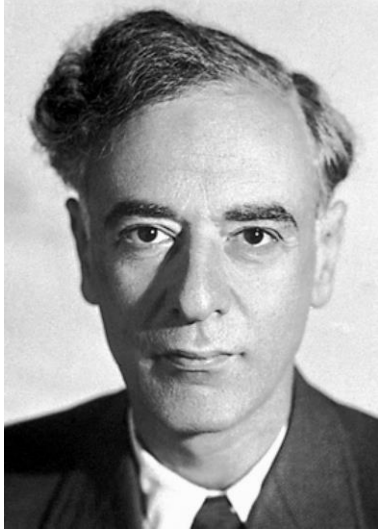
Physical Chemistry of Colloids

Boris Vladimirovich Derjaguin
1902 – 1994
Russian chemist



Lev Davidovich Landau
1908 – 1968
Russian physicist
(Nobel Phys. 1962)

Evert Johannes Willem Verwey
1905 – 1981
Dutch physical chemist

Jan Theodoor Gerard Overbeek
1911 – 2007
Dutch physical chemist

images from: Wikipedia, chg.kncv.nl, ecis-web.eu

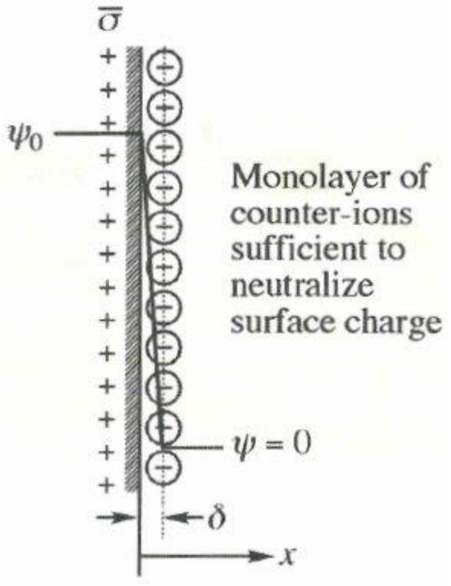
Lecture 8, *May 8, 2019*

Manos Anyfantakis
Physics & Materials Science Research Unit

Previously in ColloidsPhysChem…(I)

Helmholtz model (1879)

- two adjacent monolayers of opposite charge ("molecular capacitor") @ distance δ
- δ: the hydrated radius of the counterions
- all of the potential drop occurs across δ

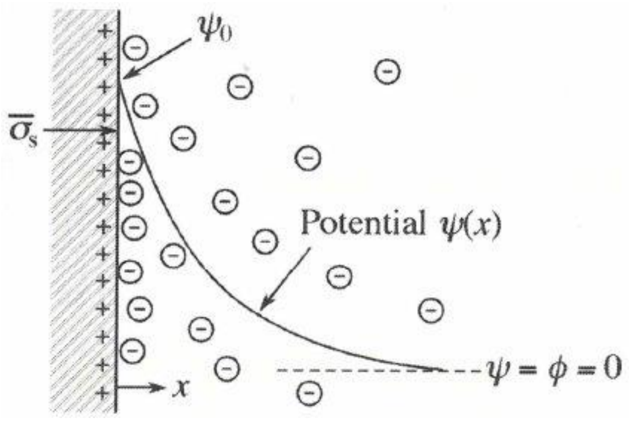


Gouy-Chapman model (1910, 1913)

- counterion layer should be diffuse because of thermal motion → uniform concentration
- equilibrium: balance between orienting effect of surface electric field & diffusion
  → high [counterion] near surface, ↓ with x

assumptions

- *ions point charges (they have no volume)*
- *no specific adsorption of ions*
- *ε_r of medium constant within the double layer*
- *surface charge uniform over the surface*



***linearized* Poisson-Boltzmann eq. (D-H approx.)**

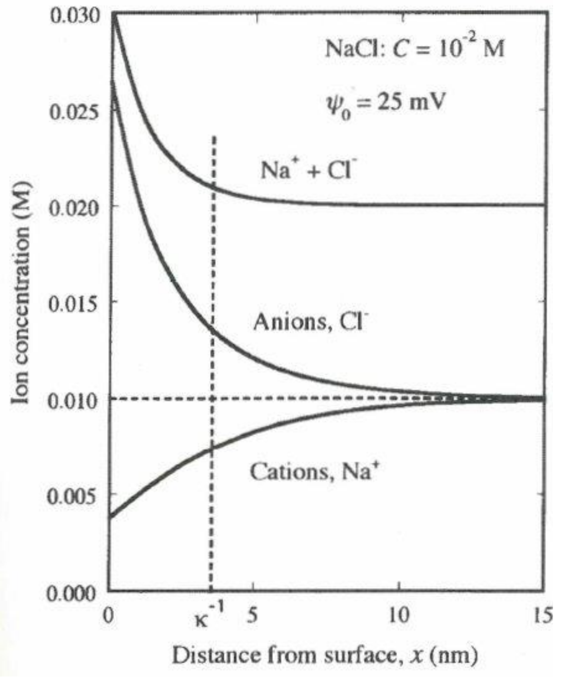
unrealistic for most situations; a good qualitative picture of the Gouy-Chapman diffuse double layer

$$\boxed{\frac{d^2\psi}{dx^2} = \frac{2z^2e^2n_\infty}{\varepsilon_r\varepsilon_0 k_B T}\psi = \kappa^2\psi}$$

$$\boxed{\psi(x) = \psi_0 exp(-\kappa x)}$$

Previously in ColloidsPhysChem…(II)

diffuse part of the double layer: enriched in counterions & depleted in co-ions



Debye screening length κ^{-1}

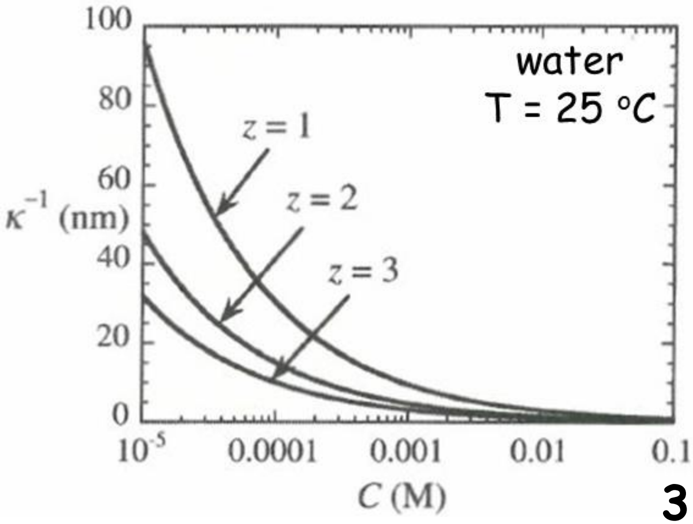
- a measure of thickness of double layer; $\boldsymbol{\kappa}$[=] 1/length

$$\boxed{\kappa^{-1} = \frac{0.304}{|z|\sqrt{C}}}$$

C: salt conc. in mol/L **κ^{-1}** [=] nm *for symmetrical electrolytes*

- property of electrolyte solution & a measure of screening power (length scale over which charge carriers screen-out electric fields)

- κ^{-1} decreases significantly with ion concentration & valence



non-aqueous media (@ 25 °C)

$$\boxed{\kappa^{-1} = \frac{0.0343\sqrt{\varepsilon_r}}{\sqrt{I}} [=]\ nm}$$

I: ionic strength

- lower dielectric constants (ε_r) of organic solvents compared to water (~80) should give thinned double layers, but the much lower [ion] yield double layers more than one order of magnitude thicker

Previously in CollоidsPhysChem…(III)

The Gouy-Chapman model provides a better approximation of reality compared to the Helmholtz model, however its predictions are sometimes unacceptable because:

- assumes that ions are point charges → no physical limits for ions while they approach the surface
- treats all ions (of same valence) as being identical with respect to their adsorption

The Stern model (1924)

- modification of Gouy-Chapman model
- double layer consists of an inner & an outer portion
- ***inner portion:*** monolayer of counterions at a distance δ away from the surface; δ = ion radius
- ***Stern plane:*** the plane @ x=δ; all of charge in Stern layer resides here
- assumption: ions can specifically adsorb onto the Stern layer → potential ψ_0-ψ_δ
- ***outer portion:*** this is a Gouy-Chapman diffuse layer, as described before

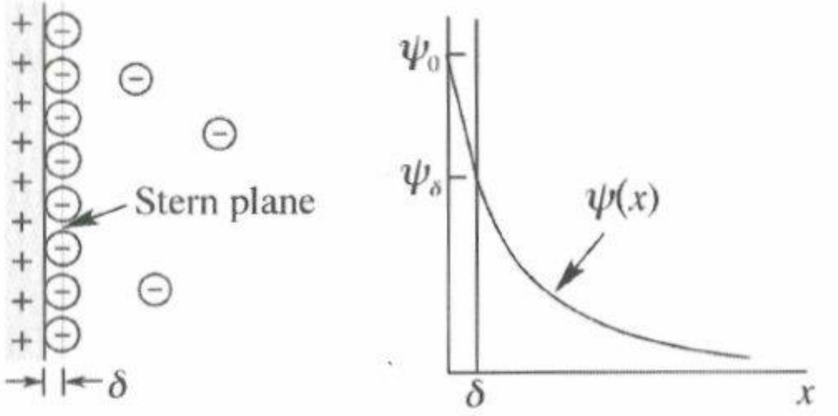


Fig. 6-17: Stern model of the electric double layer.

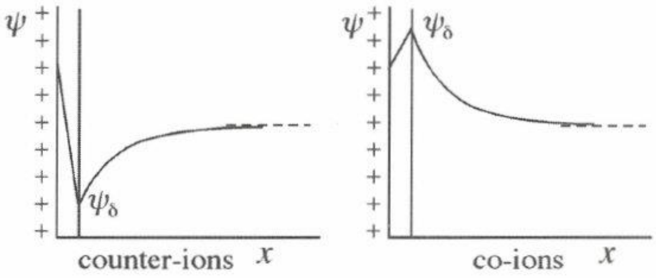


Fig. 6-18: Potential profiles in the case of specific adsorption of counterions (left) and coions (right), in accord with the Stern model.

Previously in ColloidsPhysChem…(IV)

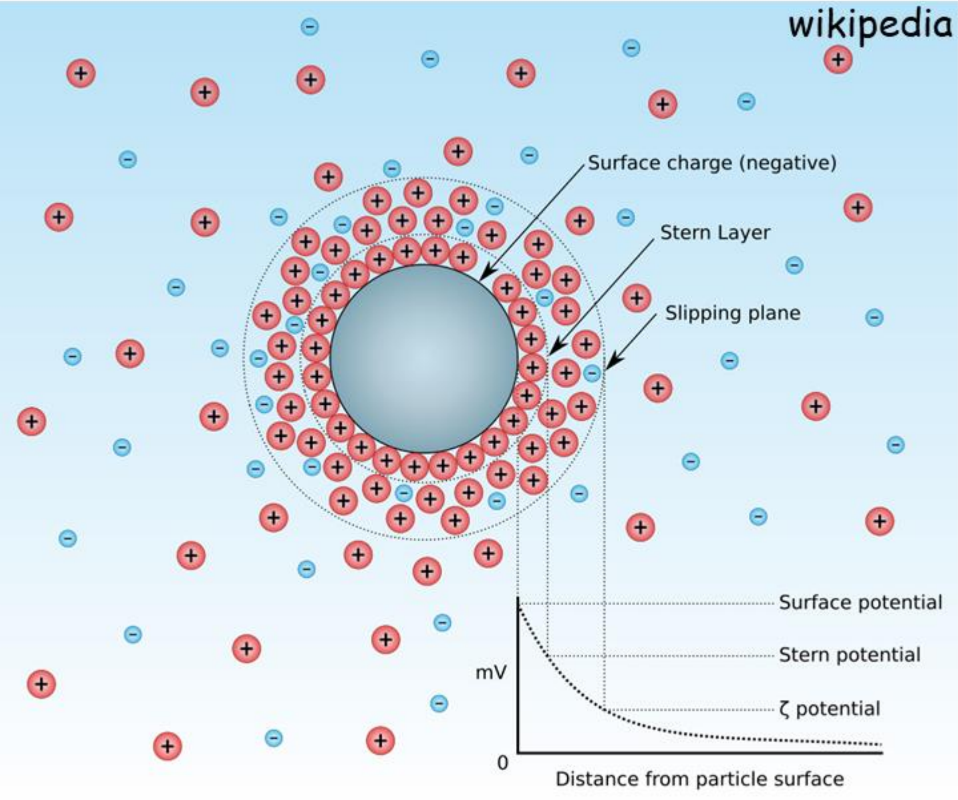
Consider a negatively charged colloid particle dispersed in water

there are three important locations:

- the (physical) particle surface (ψ_0)
- the Stern layer (ψ_δ)
- the slipping plane

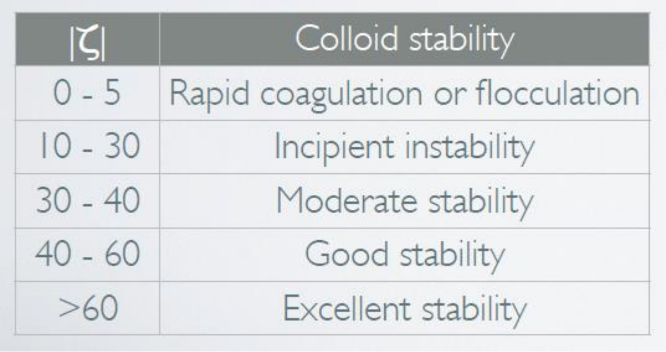
The diffuse layer can move under the influence of tangential stress

Slipping plane
conventionally introduced plane that separates mobile fluid from fluid that is attached to the surface



Zeta (ζ) potential
the electric potential corresponding to the slipping plane, [=] V or mV

- not equal to Stern potential or surface potential (different locations)
- practical for determining stability against aggregation



|ζ|	Colloid stability
0 - 5	Rapid coagulation or flocculation
10 - 30	Incipient instability
30 - 40	Moderate stability
40 - 60	Good stability
>60	Excellent stability

Overview of interactions between colloid particles

colloid particles exert forces on one another when they come close
→ determine if aggregation occurs, its rate & aggregate structure

particles of any type in a fluid medium
-universally subject to long-range, attractive vdW forces
-attraction between particle molecules + influence of medium molecules

Two descriptions of vdW forces: **Hamaker** & **Lifshitz**

Hamaker description (microscopic)
-assumes the pairwise additivity of forces

Lifshitz description (macroscopic)
-quantum electrodynamic theory: treats vdW forces as mutual electromagn. interactions betwwen macroscopic bodies
-electromagn. waves emanate from any body due to collective e^- oscillations & interact with any neighboring body

only vdW → rapid particle aggregation (depends on [particle])

often: interparticle repulsions are also present (e.g. aqueous media with low [salt])

DLVO theory: describes the interplay of vdW & electrostatic forces; basic account of colloidal stability with respect to aggregation (electrocratic colloids)

Hugo Christiaan Hamaker
(1905 – 1993)
Dutch scientist

Evgeny Mikhailovich Lifshitz
(1915-1985)
Soviet Physicist

http://www-history.mcs.st-and.ac.uk

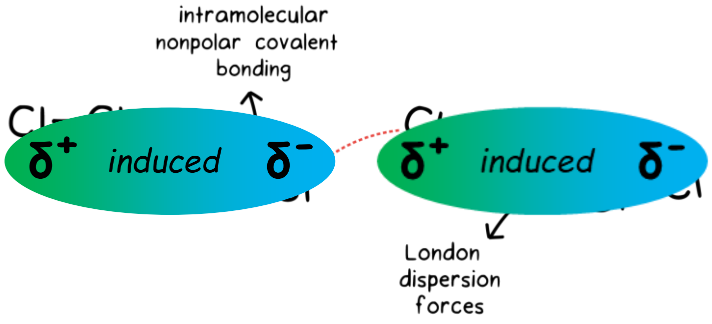
Hamaker description of dispersion interactions

vdW forces consist of electrostatic interactions between i) permanent (Keesom) ii) permanent-induced (Debye) & iii) induced-induced (London) charge distributions

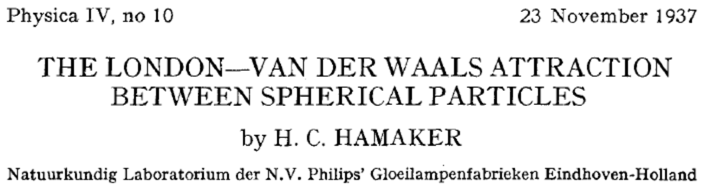
Often: only dipersion forces are considered (*exception*: small polar molecules, e.g. H_2O)

London dispersion forces

- induced dipole – induced dipole
- e⁻ densities in nearby molecules redistribute *via* fluctuations to minimize energy



Hamaker proposed (1937) a simple way to quantify the London type of vdW interactions between two macroscopic objects


Physica IV, no 10 23 November 1937

THE LONDON—VAN DER WAALS ATTRACTION
BETWEEN SPHERICAL PARTICLES

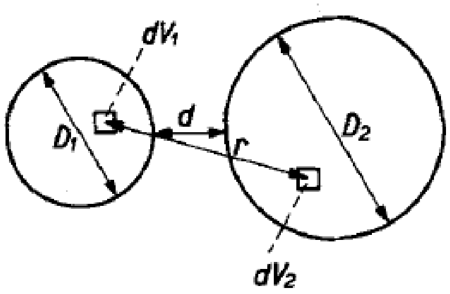
by H. C. HAMAKER

Natuurkundig Laboratorium der N.V. Philips' Gloeilampenfabrieken Eindhoven-Holland

Basic assumption
the interaction between two bodies can be approximated by summing the interactions between every pair of molecules that make up the bodies

$$\Phi = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1(\neq i)}^{N}\Phi^{ij}(r_{ij})$$

gross approximation: interaction of molecule 1 in particle A with molec. 2 in part. B unaffected by all other molec.!



General form of Hamaker description

Interaction potential between colloid particles is calculated using two components:

$$\boxed{\Phi = A \cdot f(geometry)}$$

- a material property, the **Hamaker constant *A***

$$A = \pi^2 \rho_1^2 \rho_2^2 B$$

ρ_1: molecular density of medium 1

B: depends on ground-state E of molecular oscillations (~ to 1st ionization potential & polarizabilities of molecules)

  - ***A*** takes into account the particle material(s) & the separating medium (continuous phase)

- **f (geometry):** geometries of the interacting particles & their **separation**
  - common assumption: separation distance much smaller than particle size

Interaction potential & force can be calculated using tabulated data & formulae

- ***A*** may be computed *ab initio* from molecular parameters
- **f (geometry)** has been calculated for various cases

The geometry component of Hamaker interactions

two atoms (or molecules)

- there is no A (Hamaker description extends the London theory from molecules to macroscopic bodies)
- $\Phi \sim -1/r^6$, short-range attraction

two flat surfaces

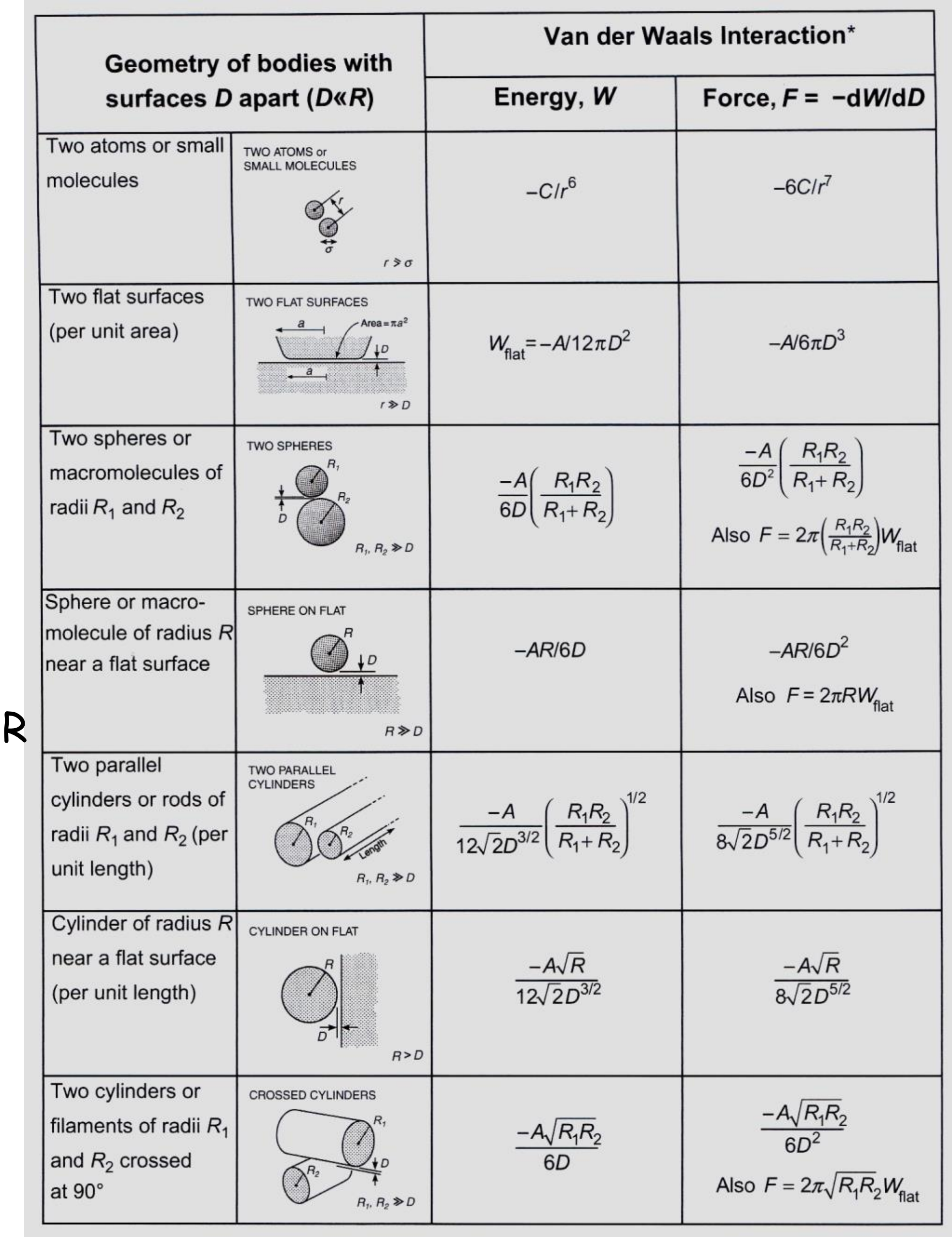
- large contact area, separation $D \ll r$
- $\Phi \sim -1/D^2$, long-range attraction

two spheres of equal radius R

- smaller contact area, separation $D \ll R$
- $\Phi \sim -1/D$, long-range attraction

two cylinders

- Φ depends on cylinder orientation
- Parallel: $\Phi \sim -1/D^{3/2}$; normal: $\Phi \sim -1/D$



Geometry of bodies with surfaces D apart ($D \ll R$)		Van der Waals Interaction*	
		Energy, W	Force, $F = -dW/dD$
Two atoms or small molecules	TWO ATOMS or SMALL MOLECULES r σ $r \gg \sigma$	$-C/r^6$	$-6C/r^7$
Two flat surfaces (per unit area)	TWO FLAT SURFACES a Area $= \pi a^2$ D a $r \gg D$	$W_{\text{flat}} = -A/12\pi D^2$	$-A/6\pi D^3$
Two spheres or macromolecules of radii R_1 and R_2	TWO SPHERES R_1 R_2 D $R_1, R_2 \gg D$	$\dfrac{-A}{6D}\left(\dfrac{R_1R_2}{R_1+R_2}\right)$	$\dfrac{-A}{6D^2}\left(\dfrac{R_1R_2}{R_1+R_2}\right)$ Also $F = 2\pi\left(\frac{R_1R_2}{R_1+R_2}\right)W_{\text{flat}}$
Sphere or macromolecule of radius R near a flat surface	SPHERE ON FLAT R D $R \gg D$	$-AR/6D$	$-AR/6D^2$ Also $F = 2\pi R W_{\text{flat}}$
Two parallel cylinders or rods of radii R_1 and R_2 (per unit length)	TWO PARALLEL CYLINDERS R_1 R_2 Length $R_1, R_2 \gg D$	$\dfrac{-A}{12\sqrt{2}D^{3/2}}\left(\dfrac{R_1R_2}{R_1+R_2}\right)^{1/2}$	$\dfrac{-A}{8\sqrt{2}D^{5/2}}\left(\dfrac{R_1R_2}{R_1+R_2}\right)^{1/2}$
Cylinder of radius R near a flat surface (per unit length)	CYLINDER ON FLAT R D $R > D$	$\dfrac{-A\sqrt{R}}{12\sqrt{2}D^{3/2}}$	$\dfrac{-A\sqrt{R}}{8\sqrt{2}D^{5/2}}$
Two cylinders or filaments of radii R_1 and R_2 crossed at 90°	CROSSED CYLINDERS R_1 R_2 D $R_1, R_2 \gg D$	$\dfrac{-A\sqrt{R_1R_2}}{6D}$	$\dfrac{-A\sqrt{R_1R_2}}{6D^2}$ Also $F = 2\pi\sqrt{R_1R_2}\,W_{\text{flat}}$

from "**Intermolecular and Surface Forces**"
J. N. Israelachvili

The material component of Hamaker interactions (I)

- Hamaker constant ***A*** is a material property (e.g. it depends on structure)

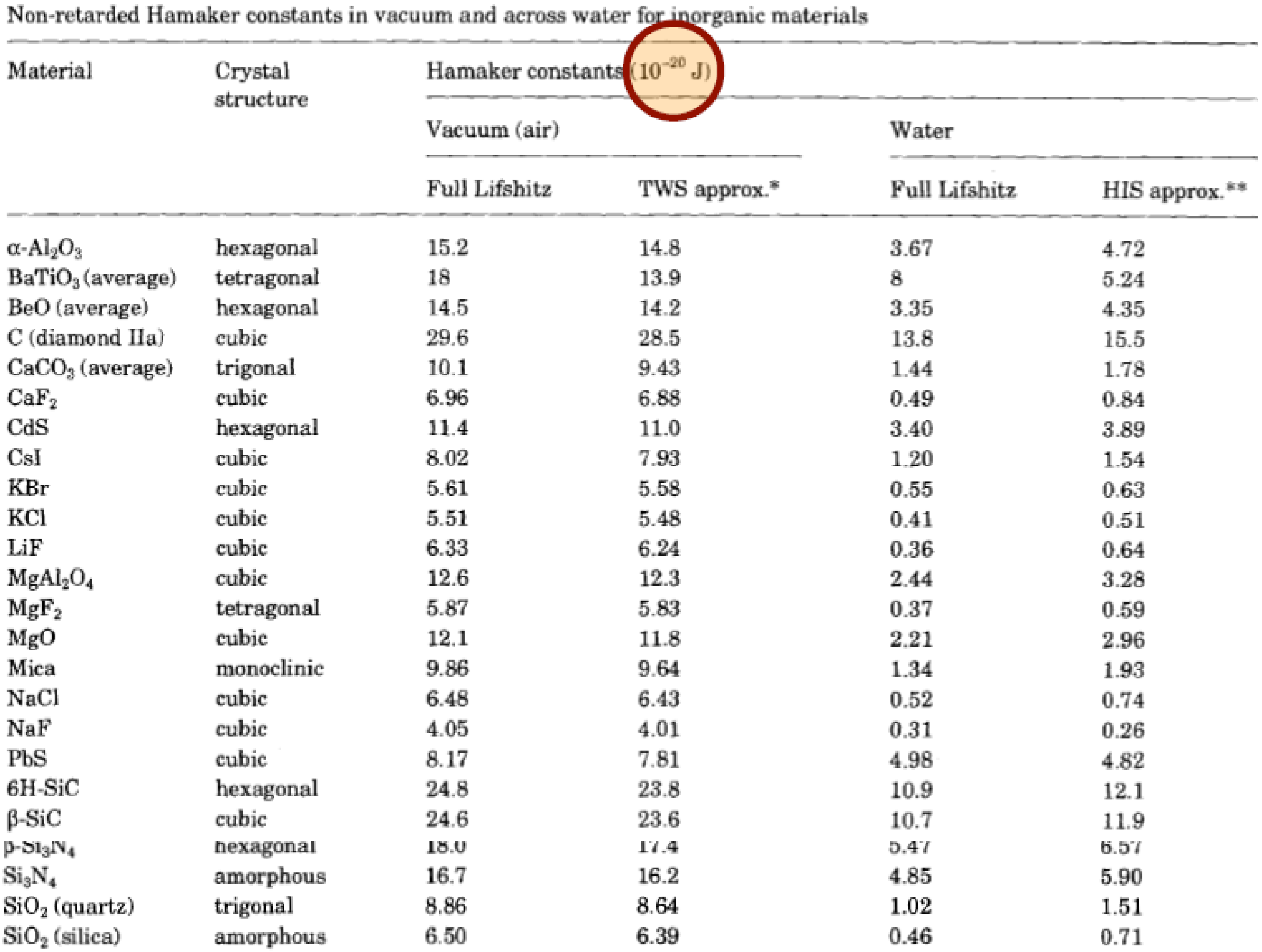
- ***A*** values in-between 10^{-19} & 10^{-20} J

rough guidline

- hydrocarbons: ~ 10^{-20} J
- oxides & halides: ~ 10^{-19} J
- metals: ~ 5 x 10^{-19} J

- ***A*** of a material in vacuum larger than that in water

→ continuous medium important



Non-retarded Hamaker constants in vacuum and across water for inorganic materials

Material	Crystal structure	Hamaker constants (10^{-20} J)			
		Vacuum (air)		Water	
		Full Lifshitz	TWS approx.*	Full Lifshitz	HIS approx.**
α-Al_2O_3	hexagonal	15.2	14.8	3.67	4.72
$BaTiO_3$ (average)	tetragonal	18	13.9	8	5.24
BeO (average)	hexagonal	14.5	14.2	3.35	4.35
C (diamond IIa)	cubic	29.6	28.5	13.8	15.5
$CaCO_3$ (average)	trigonal	10.1	9.43	1.44	1.78
CaF_2	cubic	6.96	6.88	0.49	0.84
CdS	hexagonal	11.4	11.0	3.40	3.89
CsI	cubic	8.02	7.93	1.20	1.54
KBr	cubic	5.61	5.58	0.55	0.63
KCl	cubic	5.51	5.48	0.41	0.51
LiF	cubic	6.33	6.24	0.36	0.64
$MgAl_2O_4$	cubic	12.6	12.3	2.44	3.28
MgF_2	tetragonal	5.87	5.83	0.37	0.59
MgO	cubic	12.1	11.8	2.21	2.96
Mica	monoclinic	9.86	9.64	1.34	1.93
NaCl	cubic	6.48	6.43	0.52	0.74
NaF	cubic	4.05	4.01	0.31	0.26
PbS	cubic	8.17	7.81	4.98	4.82
6H-SiC	hexagonal	24.8	23.8	10.9	12.1
β-SiC	cubic	24.6	23.6	10.7	11.9
β-Si_3N_4	hexagonal	18.0	17.4	5.47	6.57
Si_3N_4	amorphous	16.7	16.2	4.85	5.90
SiO_2 (quartz)	trigonal	8.86	8.64	1.02	1.51
SiO_2 (silica)	amorphous	6.50	6.39	0.46	0.71

Adv. Colloid Interface Sci. **1997**, *70*, 125

The material component of Hamaker interactions (II)

Screening of vdW interactions by the continuous phase can be very important

- Hamaker constants for water suspensions lower by ~ a factor of 10 compared to vacuum
- *extreme case:* objects that are attracted in vacuum may not be attracted in another medium!

approximate way to account for the continuous phase

two particles of material 2 dispersed in a medium of material 1

effective Hamaker constant $$\boxed{A_{212} = \left[\sqrt{A_{11}} - \sqrt{A_{22}}\right]^2}$$

- **A_{212}** always positive regardless of **A_{11}** & **A_{22}** → like particles in solvent always attracted to each other (vdW)
- large difference between *A* of the particles & the solvent → large vdW attraction between the particles

two particles of material 2 & material 3 dispersed in a medium of material 1

effective Hamaker constant $$\boxed{A_{213} = \left(\sqrt{A_{22}} - \sqrt{A_{11}}\right)\left(\sqrt{A_{33}} - \sqrt{A_{11}}\right)}$$

- negative effective *A* (= vdW repulsion) if **A_{11}** in-between **A_{22}** & **A_{33}**

Coffee break

gameinformer.com

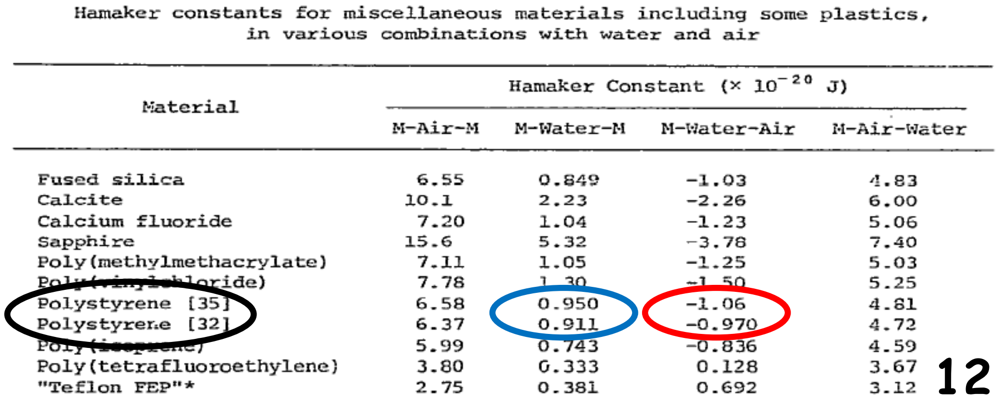
ign.com

For Mario, swimming & diving is not the same…
what about (interacting) colloidal particles?

two polystyrene colloid particles in water
→ **attractive vdW force**

polystyrene particle & air-water interface
→ **repulsive vdW force**

Adv. Colloid Interface Sci. **1980**, *14*, 3



Hamaker constants for miscellaneous materials including some plastics, in various combinations with water and air

Material	Hamaker Constant ($\times 10^{-20}$ J)			
	M-Air-M	M-Water-M	M-Water-Air	M-Air-Water
Fused silica	6.55	0.849	−1.03	4.83
Calcite	10.1	2.23	−2.26	6.00
Calcium fluoride	7.20	1.04	−1.23	5.06
Sapphire	15.6	5.32	−3.78	7.40
Poly(methylmethacrylate)	7.11	1.05	−1.25	5.03
Poly(vinylchloride)	7.78	1.30	−1.50	5.25
Polystyrene [35]	6.58	0.950	−1.06	4.81
Polystyrene [32]	6.37	0.911	−0.970	4.72
Poly(isoprene)	5.99	0.743	−0.836	4.59
Poly(tetrafluoroethylene)	3.80	0.333	0.128	3.67
"Teflon FEP"*	2.75	0.381	0.692	3.12

The effect of retardation

assumption for computing London interactions between molecules

e^- cloud oscillations in one molecule synchronous with oscillations in a neighbouring molecule with which it is interacting (true for small separations)

Retardation

as molecules get further apart, the finite time required for wave propagation becomes significant (generally it appears for distances > 5 nm)

- for large distances, the interactions decrease substantially & $\Phi \sim -1/r^7$ (instead of $-1/r^6$)
- corrections (taking into account retardation) developed for various geometries of interacting bodies

example: interaction of a pair of semi-infinite half-spaces (distance D)

$$\Phi = -\frac{A}{12\pi D^2}$$

uncorrected interaction potential

$$f(D) = \left(\frac{1}{1 + 0.0532D}\right)$$

correction factor

Retardation effects must be considered to avoid vdW over-estimations

corrected expressions suggest that long-range vdW interactions between spheres:

- *drop by 35% at a separation of 5 nm*
- *drop by 70% @ a separation of 20 nm*

The Lifshitz (macroscopic) approach

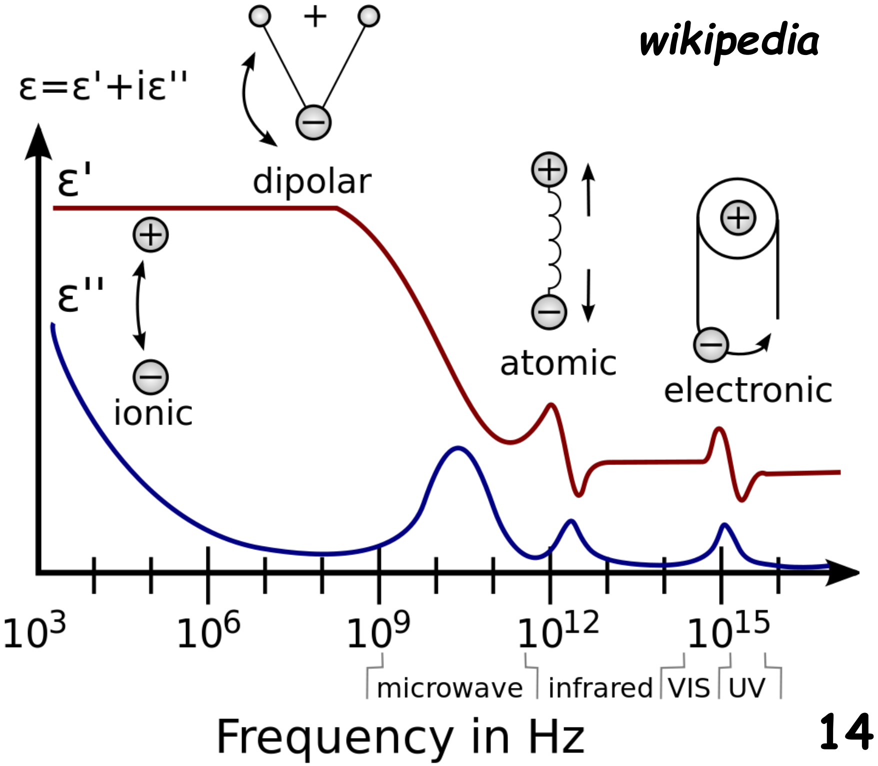
Hamaker's approach assumes that each molecule pair interacts independent of other molecules → neglection of multi-body effects

- good approximation for gaseous systems & often for condensed phases with vaccuum/dilute gas as the intervening medium
- poor for condensed phase systems interacting in a condensed phase medium

Lifshitz's approach

- released the above assumption by treating interacting bodies as continua
- macroscopic body interactions due to fluctuating EM field in gap between bodies
- macrosc. material property reflecting propagation & reception of EM energy: dielectric permittivity ε
- response of a material to an electric field depends on frequency (polarization does not change instanaeously)
- ε': energy storage in material (polarization)
- ε'': absorption of energy → heat (out of phase motion)
- absorption peaks: key data used in Lifshitz's theory to calculate *A*

wikipedia



Key results of Lifshitz's theory

- Interaction strong (high A value) if absorption spectra of particles are similar (always the case if we have only one particle species)
- Interaction weakened (decreased A value) if continuous phase has similar spectral properties to that of particles

Calculation of A for interaction of media (e.g. particles) 1 & 2 accross medium 3

$$A = \frac{3k_BT}{4}\left(\frac{\varepsilon_1-\varepsilon_3}{\varepsilon_1+\varepsilon_3}\right)\left(\frac{\varepsilon_2-\varepsilon_3}{\varepsilon_2+\varepsilon_3}\right)+\frac{3h\nu_e}{8\sqrt{2}}\left[\frac{(n_1^2-n_3^2)(n_2^2-n_3^2)}{\{(n_1^2+n_3^2)(n_2^2+n_3^2)\}^{\frac{1}{2}}\left\{(n_1^2+n_3^2)^{\frac{1}{2}}+(n_2^2+n_3^2)^{\frac{1}{2}}\right\}}\right]$$

ε_i $(i = 1, 2, 3)$: dielectric constants of media 1, 2, 3 **n_i $(i = 1, 2, 3)$:** refractive indices

ν_e: main electronic absorption frequency in the UV (~ 3×10^{15} – 5×10^{15} s^{-1})

h: Planck's constant (= 6.626×10^{-34} J s) **k_B:** Botlzmann's constant (= 1.381×10^{-23} J/K)

- 1st term (zero-freq. contribution): includes Debye & Keesom contributions
- 2nd term: non-retarded dispersion energy contribution
- for two identical bodies (**$\varepsilon_1 = \varepsilon_2$ & $n_1 = n_2$**) → **$A > 0$, vdW atttractive**
- for two different bodies (**$\varepsilon_1 \neq \varepsilon_2$ & $n_1 \neq n_2$**) → **A can be positive or negative**, depending on the medium (3) between them, **vdW attractive or repulsive**

The DLVO theory

The DLVO theory

- after **Derjaguin** & **Landau** (Soviet Union) and **Verwey** & **Overbeek** (Netherlands)
- it is the summing of van der Waals attraction & electrostatic repulsion (plus a short-range steep repulsion)
- desrcibes well interactions between particles in aqueous colloidal dispersions & thus their stability behaviour against aggregation (*electrocratic colloids*)

spheres of equal radii a separated by S_0 (closest approach distance)

attractive vdW potential $\Phi_A = -\frac{Aa}{12S_0}$

repulsive double layer potential

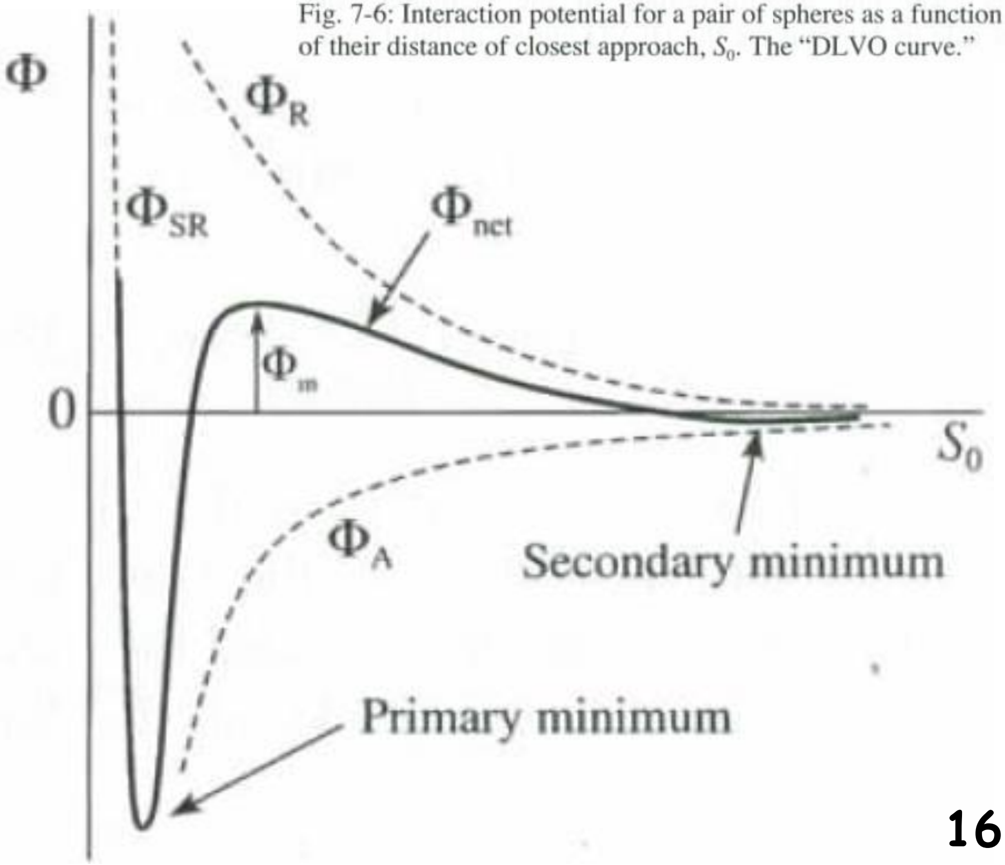
$$\Phi_R = \frac{64\pi a n_\infty k_B T \gamma_\delta^2}{\kappa^2} exp(-\kappa S_0)$$

n_∞: $total\ ion\ concentration$

$\gamma_\delta = tanh\left(\frac{ze\psi_\delta}{4k_BT}\right)$ $\quad \kappa^{-1}$: $Debye\ length$

short-range repulsive potential Φ_{SR}

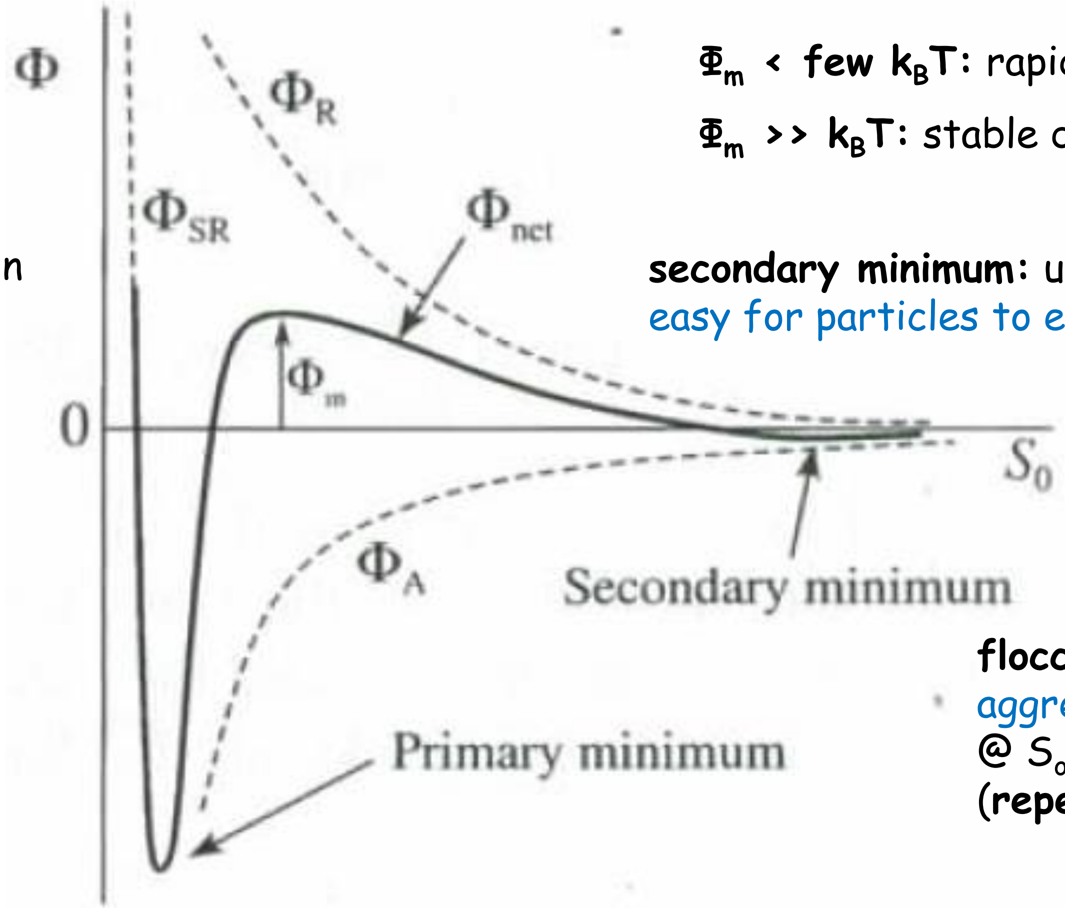
Fig. 7-6: Interaction potential for a pair of spheres as a function of their distance of closest approach, S_0. The "DLVO curve."



The DLVO theory (II)

Brownian motion energy (~k_BT): means for particles to overcome the potential barrier & aggregate

aggregation probability: determined by Φ_m height (→ determines stability against aggregation)



Φ_m **< few k_BT:** rapid aggregation

Φ_m **>> k_BT:** stable dispersion

Φ_m: potential energy barrier to coagulation

secondary minimum: usually pretty shallow, easy for particles to escape once they are in

coagulation: irreversible aggregation of particles @ S_o of primary min.

flocculation: reversible aggregation of particles @ S_o of secondary min. (**repeptization** can occur)

primary minimum: depth determined by short term repulsion (not part of DLVO, could be due to tighly bound hydration layer)

Parameters affecting the DLVO potential (I)

particles of material 2 in a medium 1 (a=100 nm, T= 25 °C, single z-z electrolyte)

$$\frac{\Phi_{net}}{k_B T} = -2.025 \cdot 10^{21} \frac{A_{212}}{S_0} + \frac{1119.8}{z^2} tanh^2\left(\frac{z\psi_\delta}{102.8}\right) exp\left(-3.288z\sqrt{C}S_0\right)$$

$C: electrolyte\ conc.\ [=]\ \mathrm{M} \qquad A_{212}\ [=]\ \mathrm{J} \qquad S_0\ [=]\ \mathrm{nm} \qquad \psi_\delta: Stern\ potential\ [=]\ \mathrm{mV}$

influence of Hamaker constant

- larger A values → lower barriers (Φ_m)
- little control over A; adlayers can be used to modify A, however for large separations their effect is unimportant

influence of ψ_δ

- strongly affects DLVO potential
- ψ_δ controlled by varying surface potential (controlled by ion concentration, i.e. pH)
- often determined by specific adsorption of ions (especially surfactants)
- often ζ-potential used to estimate ψ_δ

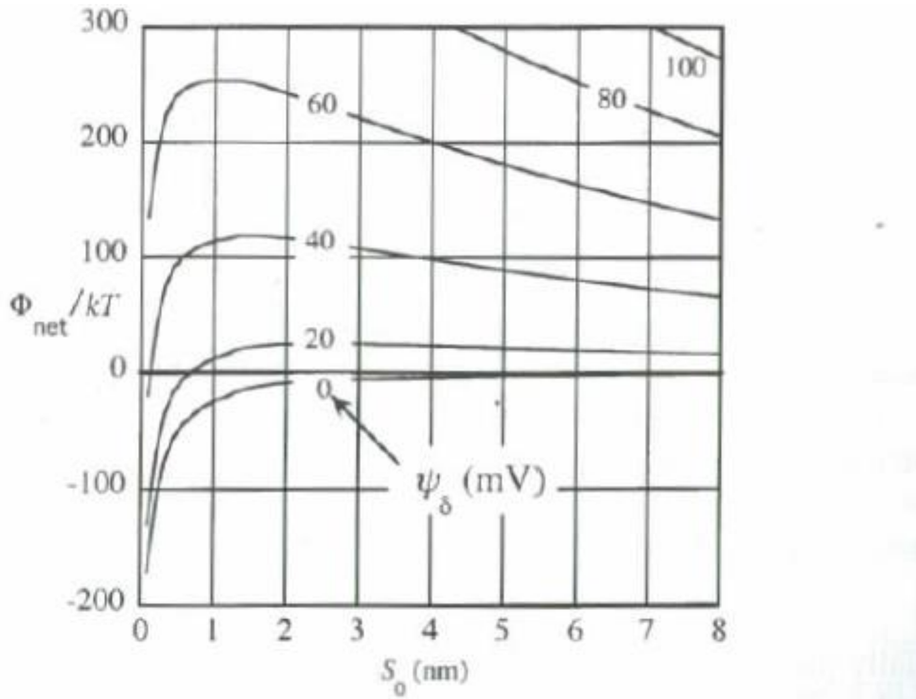


Fig. 7-7: The influence of the Stern potential on the total potential energy of interaction of two spherical particles: a = 100 nm, T = 298 K, $A_{212} = 0.849 \times 10^{-20}$ J, $z = 1$, $C = 1$ mM.

Parameters affecting the DLVO potential (II)

influence of salt addition

- Φ_m decreases strongly with salt conc. ***C*** (compression & collapse of double layer)
- **critical coagulation concentration (CCC)** critical ***C*** (~ 400 mM): Φ_m → 0, rapid aggregation expected
- **coagulation criterion:** $\Phi_m = 0$ req.: $\Phi_{net} = 0$ & $d\Phi_{net} / dS_0 = 0$
- application of the above to analytical expressions of Φ_{net} yields ***CCCs*** ~ 50 - 250 mM for monovalent salts
- for high ψ_δ (> 100 mV), ***CCC*** ~ $1/z^6$, independent of ψ_δ (Schulze-Hardy rule, explained by DLVO)

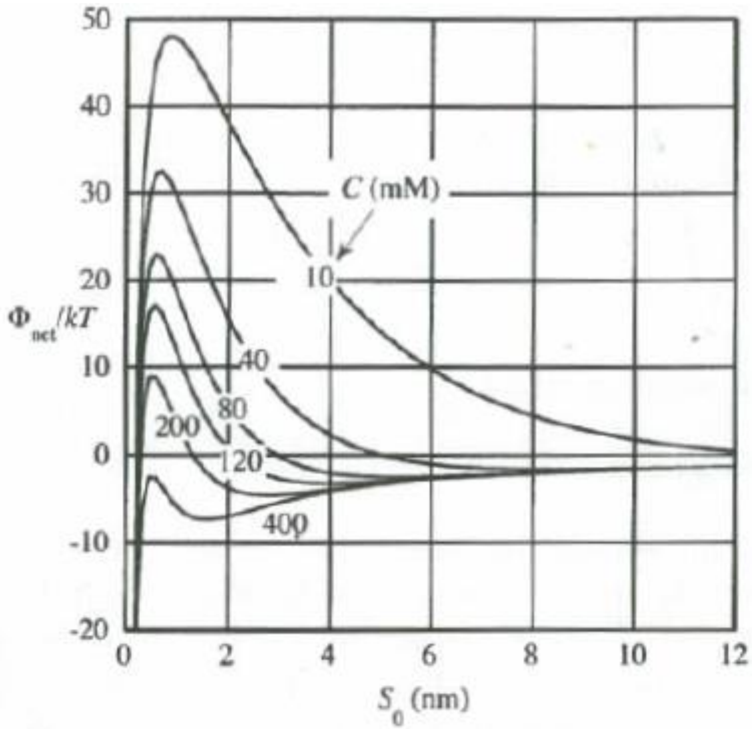


Fig. 7-8: The influence of indifferent electrolyte concentration on the total potential energy of interaction of two spherical particles: $a = 100$ nm, $T = 298$ K, $A_{212} = 0.849 \times 10^{-20}$ J, $z = 1$, $\psi_\delta = 30$ mV.

aggregation jar test to determine CCC

Fig. 7-10: Aggregation jar test series for As_2S_3 sol with 1-1 electrolyte concentrations in mM. The *CCC* appears to lie between 60 and 70 mM. From [Overbeek, J. Th. G., **Colloidal and Surface Chemistry, A Self-Study Subject, Part 2**, Lyophobic Colloids, p. 6.6, MIT, Cambridge, MA (1972).]