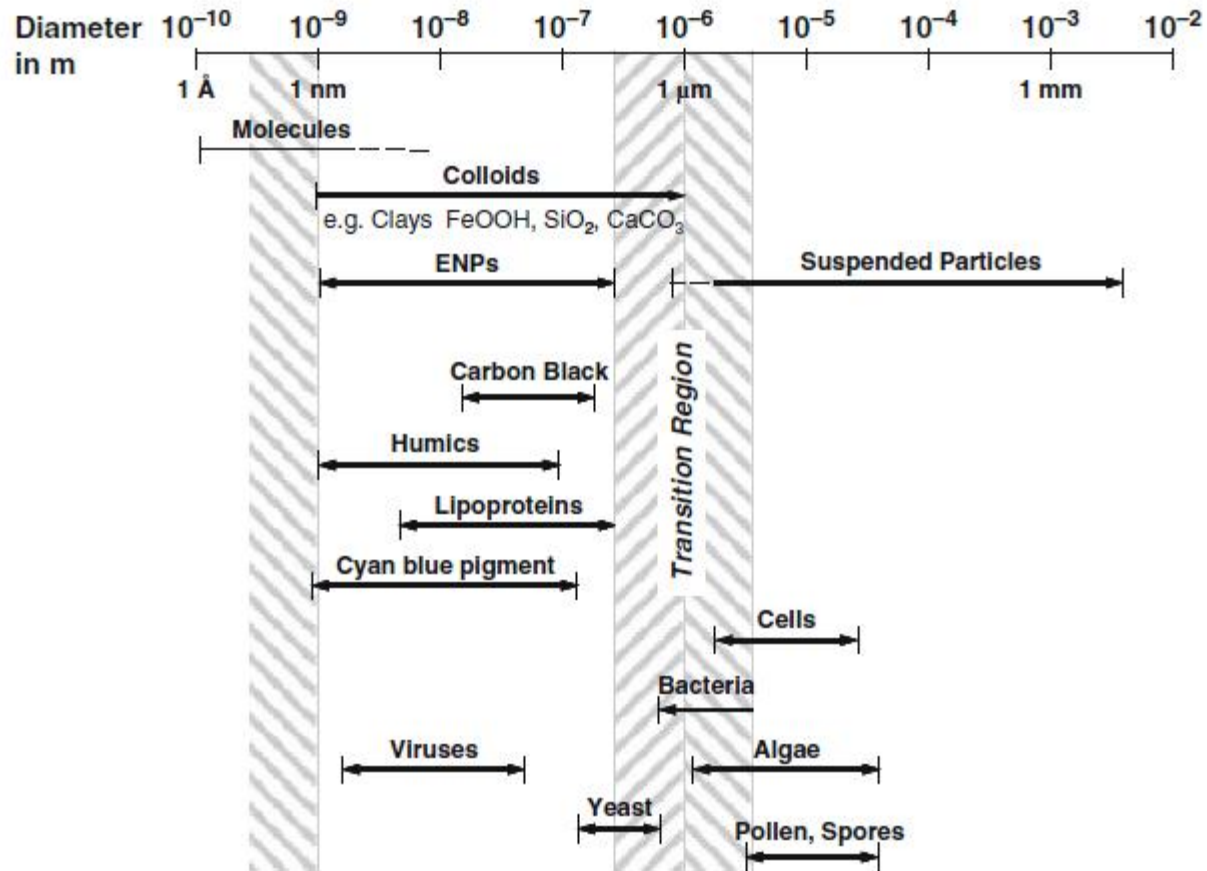


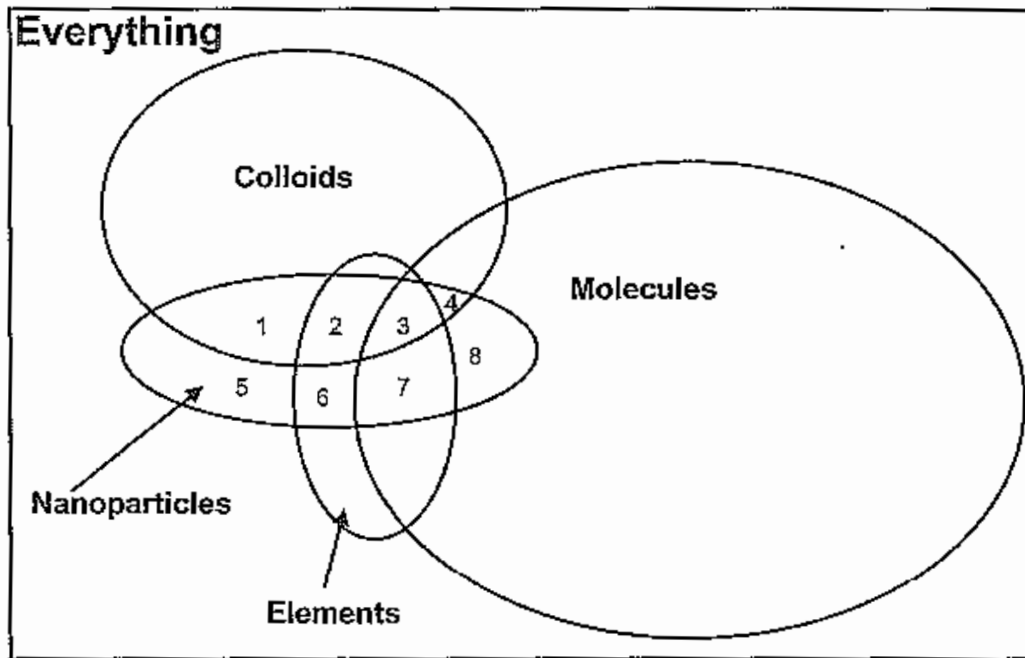
# **VL „Nanopartikel in der Umwelt“ - NP properties**

**morphology, surface area  
colloidal stability  
colloid stabilization**

# Size ranges for ENP and colloids in aqueous systems



# The interrelation of various types of material



- 1: a stable colloid of an inorganic compound (CdS)
- 2: a stable colloid of an element (gold)
- 3: a stable colloid of an element which has some molecular architecture (sulfur)
- 4: a stable colloid of a molecule (polystyrene)
- 5: an aggregate of an inorganic compound
- 6: an aggregate of an element
- 7: an aggregate of an element which has some molecular architecture
- 8: an aggregate of a molecule

**1-4 form stable colloids**

**5-8 are precipitated forms of 1-4**

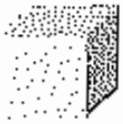
# Morphologies of nanomaterial



**Spherical:** typical in non-crystalline materials and very small crystalline particles



**Tear Drop:** An extension of the spherical morphology.



**Geometric solid:** typical of crystalline materials. May be a range of shapes inc. cubic, tetrahedral, icosahedral, etc.



**Dendritic:** Composed of nanoscale wires the dendrite may be much larger than 100 nm.



**Rod or wire:** May have a range of cross sections including circular, cubic and pentagonal



**Dumbbell:** Formed by the growth of one material only at the ends of a rod of another material



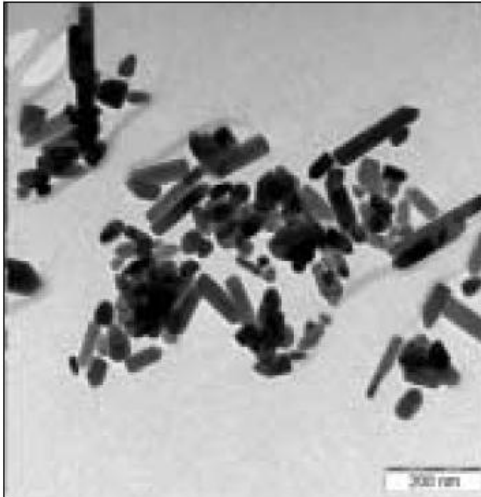
**Discotic:** thin flat plate often wider than 100 nm. May be a range of shapes including hexagonal and irregular



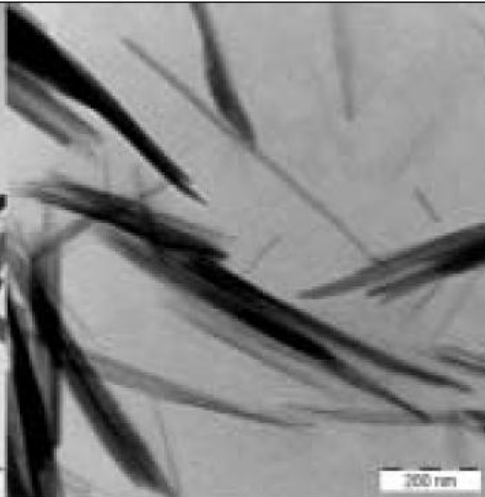
**Tetrapod:** Formed by the growth hexagonal phase rods from a cubic seed crystal

# Morphologies of nanomaterial - examples

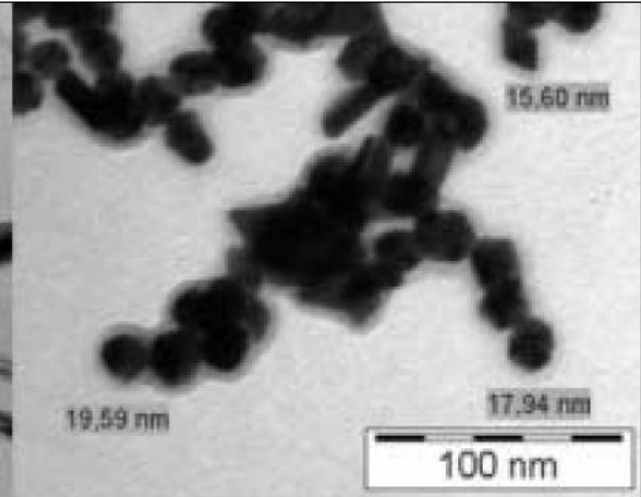
ZnO



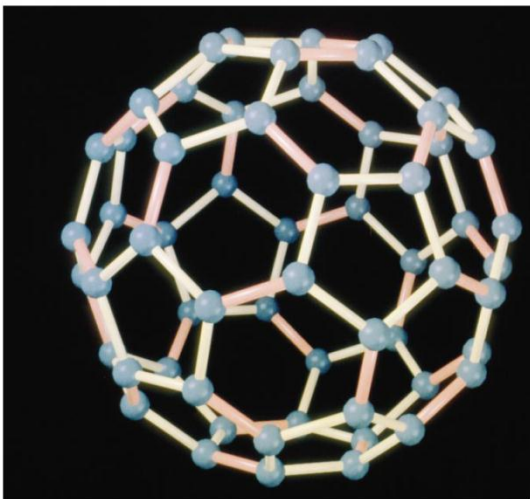
Vanadiumtrioxide



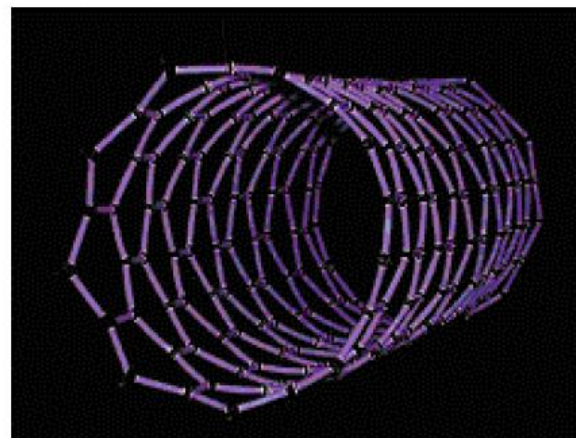
Palladium



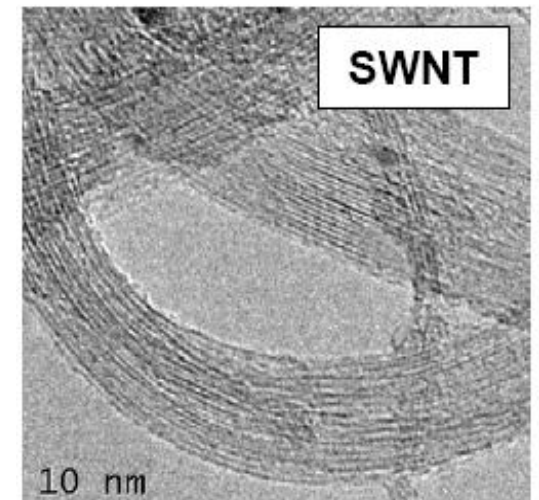
Fullerene



Carbon nanotube



<http://www.nccr-nano.org/ncc>

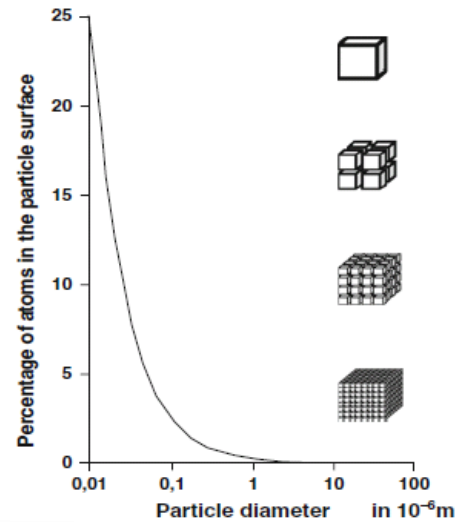


# Surface area (A)

(Frimmel & Niessner)

$$\Delta G = \Delta W = 2\delta^0 A$$

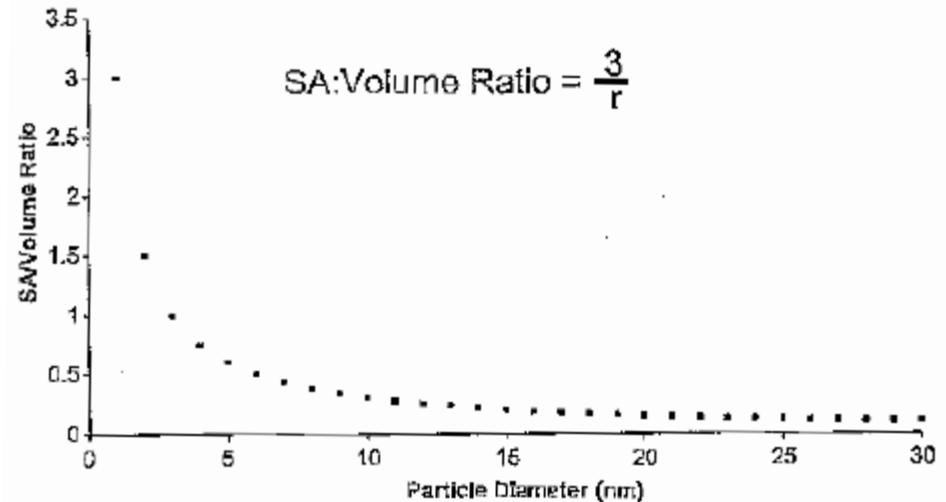
$\Delta G$ : increase of free energy,  
 $\Delta W$ : work needed to separate the pieces reversibly against the forces of attraction,  
 $\delta^0$ : proportionality factor (surface or interfacial tension)



Cube number	Volume	Area
$n=1$	$V$	$A$
$n=8$	$V$	$2A$
$n=64$	$V$	$4A$
$n=512$	$V$	$8A$

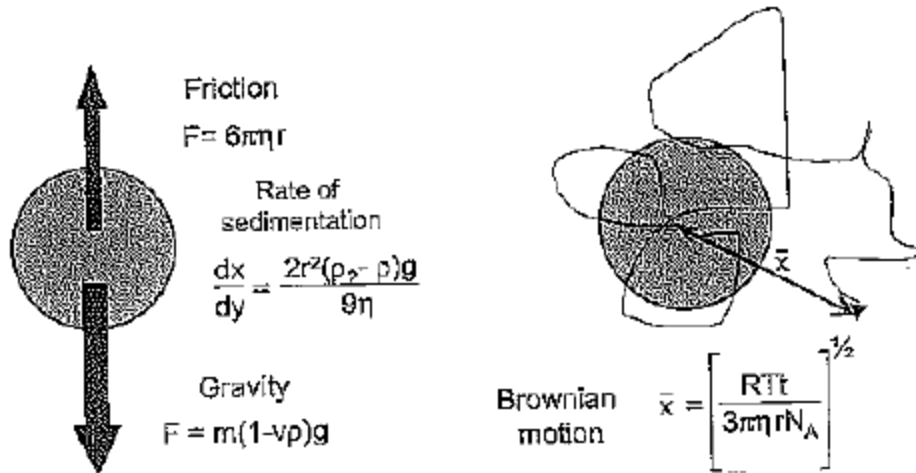
The effect of radius on the surface area (SA) to volume ratio for a constant mass of material

(P. Christian in Lead & Smith)



The fraction of atoms at the surface of NP can be very high: Au-NP  $d=2.5$  nm  $\rightarrow$  53%  
 $d=10$  nm  $\rightarrow$  16%

# Forces acting on suspended particles



Gravity causing sedimentation  
 Friction working against gravity  
 Collision with molecules of medium  
 (Brownian motion)

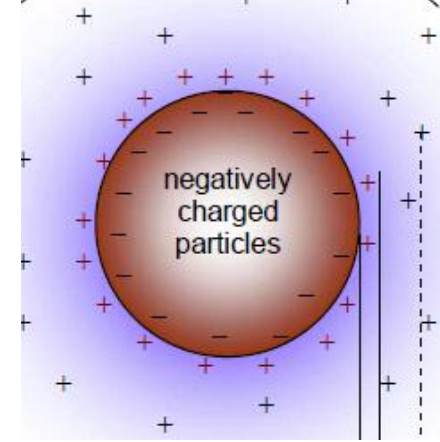
Calculated diffusion rates (mm/h) against sedimentation rates (mm/h) in water at room temp.

Particle diameter (nm)	1	10	100	500
<b>Brownian diffusion</b>	1.8635	0.5893	0.1863	0.0833
Polyethylene (0.96)	$-8.82 \times 10^{-8}$	$-8.82 \times 10^{-6}$	-0.0009	-0.0220
Polystyrene(1.05)	$1.10 \times 10^{-7}$	$1.10 \times 10^{-5}$	0.0011	0.0276
Graphite (2.25)	$2.76 \times 10^{-6}$	0.0003	0.0276	0.6889
Titania anatase (3.84)	$6.26 \times 10^{-6}$	0.0006	0.0626	1.5652
Zinc oxide (5.61)	$1.02 \times 10^{-5}$	0.0010	0.1016	2.5407
Cerium (IV) oxide (7.13)	$1.35 \times 10^{-5}$	0.0014	0.1351	3.3784
Silver (10.5)	$2.09 \times 10^{-5}$	0.0021	0.2094	5.2357
Gold (18.9)	$3.94 \times 10^{-5}$	0.0039	0.3942	9.8541
Osmium (22.5)	$4.74 \times 10^{-5}$	0.0047	0.4735	11.8381

Density in  $\text{g/cm}^3$  in brackets

(P. Christian in Lead & Smith)

# Surface properties of nanoparticle

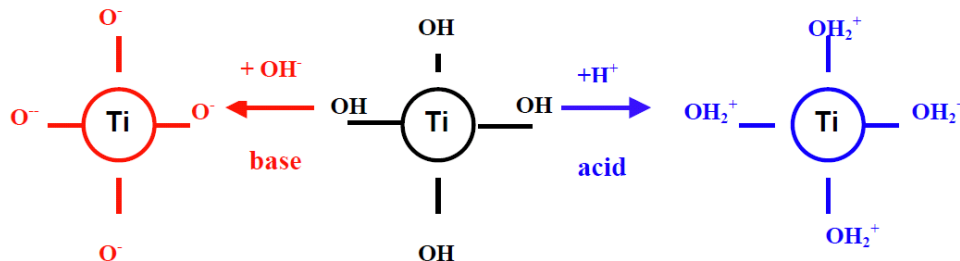


- the surface of suspended nanoparticles is electrically charged (in many cases)
- counter ions are adsorbed onto the surface, more or less to compensate the electrical charges
- the layer of surface charges + the layer of counter ions = electrical double layer

## Origin of surface charges of nanoparticle

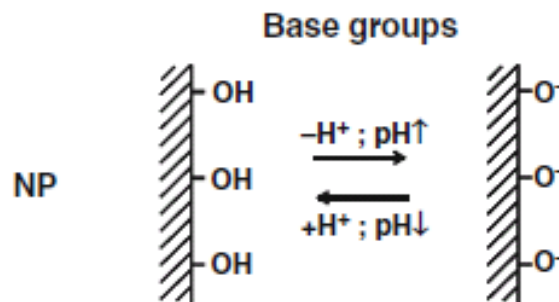
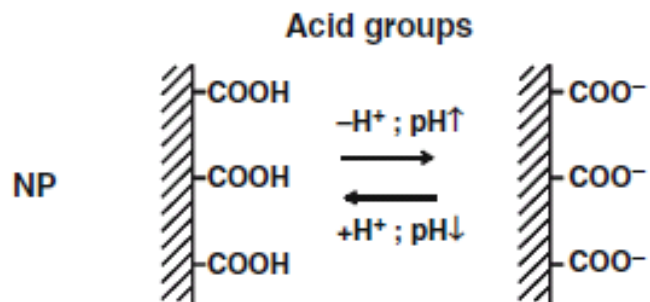
- lattice defects by substituted atoms
- adsorption of ions onto surface of the solid particle
- adsorption of molecules with functional groups which have electrical charges and/or are dissociable
- chemical (e.g. acid / basic) reactions on the surface of the solid particles (e.g. by dissociation)

e.g. acid / basic reactions on surface of solid particles by dissociation ( $\text{TiO}_2$ )

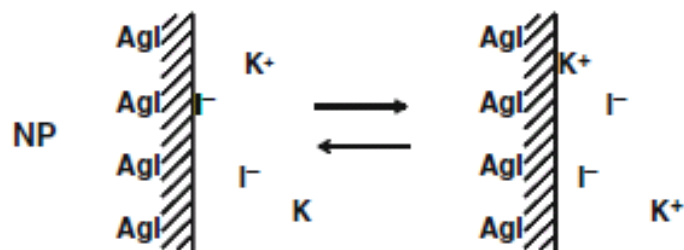




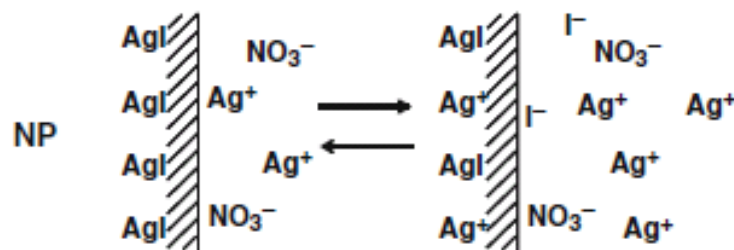
# Surface charges and their generation



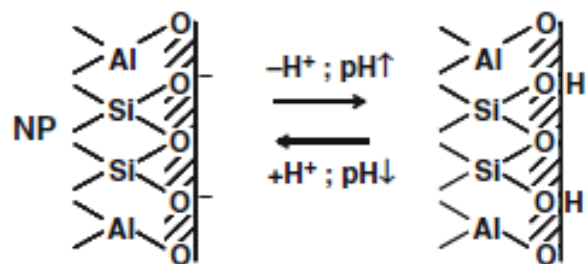
Dissolution of AgI surface in KI solution



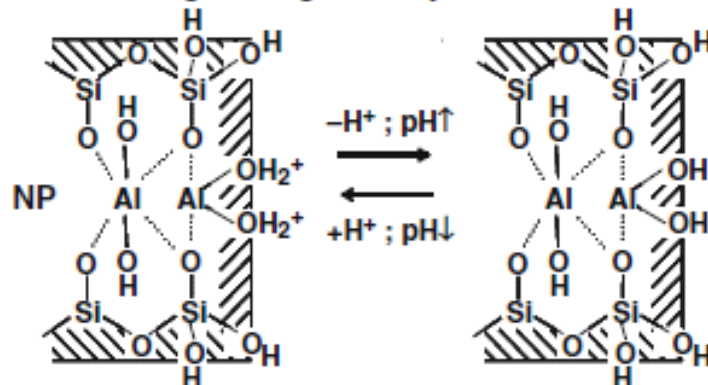
Dissolution of AgI surface in AgNO<sub>3</sub> solution



Isomorphous substitution in clay minerals

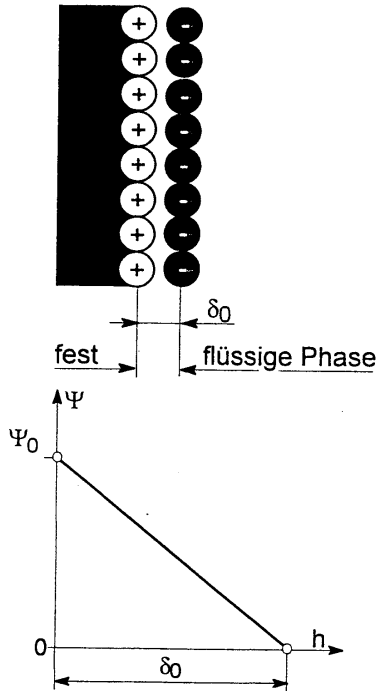


Edge charge of clay minerals

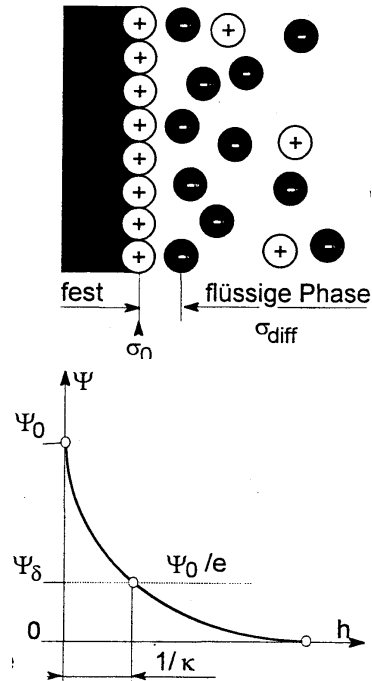


# Electrical double layer models

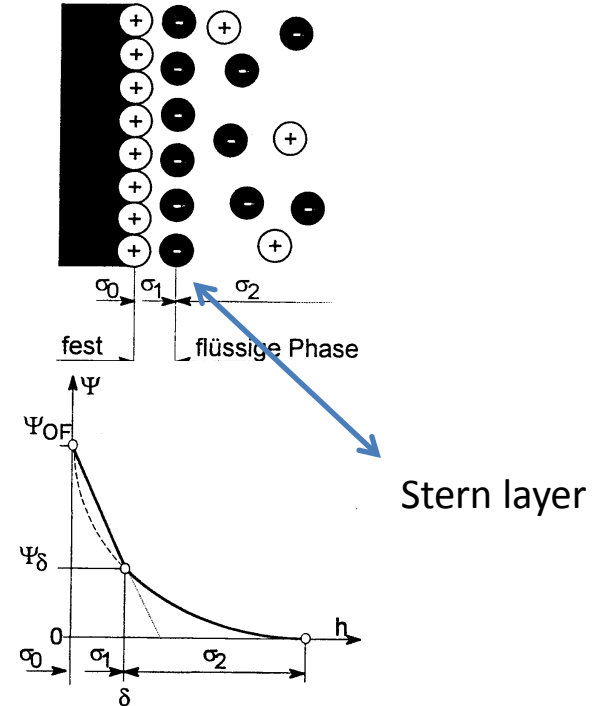
## Helmholtz



## Gouy-Chapman



## Stern



Stern layer

$\Psi$  - surface potential (V),  $\delta$  - Debye-length (nm),  $\kappa$  - Debye-Hückel-parameter:  $\kappa=1/\delta$ ,  $\sigma$  - surface charge ( $C/m^2$ )

the Debye length  $\delta\kappa$  is the thickness of the electrochemical double layer  
 $\delta\kappa$  = decrease of the potential to  $1/e$  of the surface potential

# Electrical double layer models – Debye length

$$\frac{\varphi(r)}{\varphi_s} = \exp\left[-\frac{r}{\delta_\kappa}\right] \quad \text{mit} \quad \delta_\kappa = \sqrt{\frac{\varepsilon_r \varepsilon_0 k T}{e^2 N_A \sum c_i z_i^2}}$$

with  $\varphi_s$  Stern potential

$\varphi$  potential at distance  $r$

$r$  distance  $r$  from the particle surface

$\delta_\kappa$  Debye length

$N_A$  Avogadro constant

$T$  temperature

$\varepsilon_0$  absolute dielectric constant

$\varepsilon_r$  relative dielectric constant

$k$  Boltzmann constant

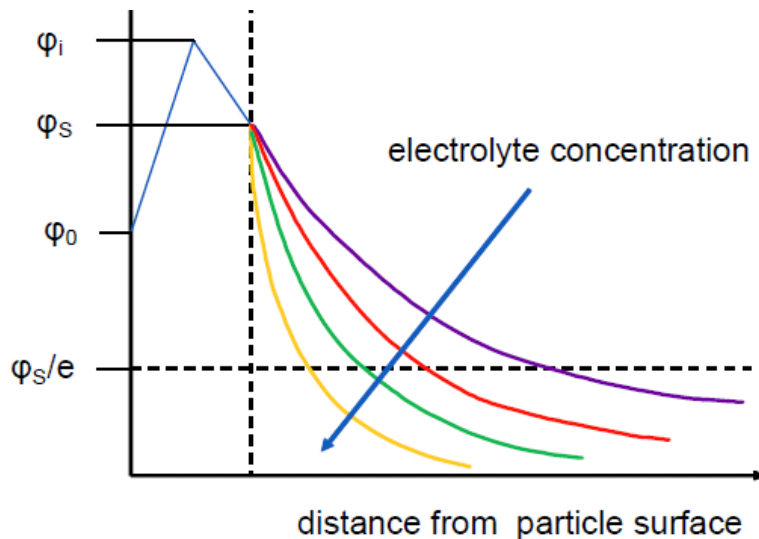
$e$  elementary charge

$c$  concentration of ions

$z$  valence of ions

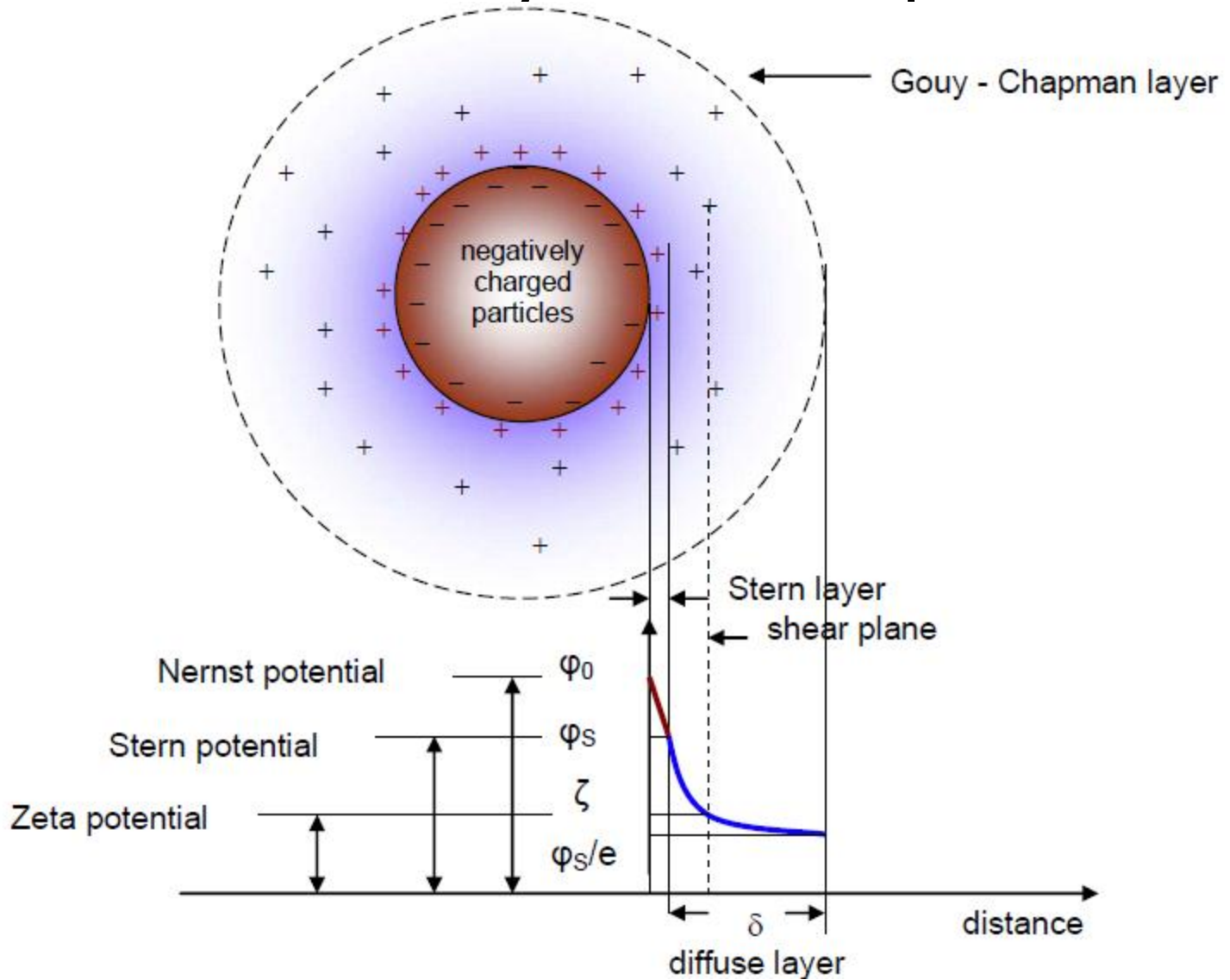
- increasing electrolyte concentration reducing Debye length
- increasing ion valence reducing Debye length
- destabilization of suspension e.g. with addition of  $\text{Fe}^{3+}$  or  $\text{Al}^{3+}$  ions

**compression of diffuse double layer**



$C$ in mol / L <sup>3</sup>	<i>Debye length <math>\delta_\kappa</math> of different types of electrolytes in nm</i>			
	(1,1)	(1,2)	(2,2)	(1,3)
$10^{-1}$	0.96	0.55	0.48	0.39
$10^{-2}$	3.04	1.76	1.52	1.24
$10^{-3}$	9.60	5.55	4.81	3.93
$10^{-4}$	30.40	17.60	15.20	12.40

# Electrical double layer model – zeta potential



zeta potential ( $\zeta$ ) = potential at the shear plane  $\approx$  stern potential

# Zeta potential

A charged particle in motion caused by an electrical field or by diffusion loses a portion of its counter ions of the electrical double layer

Measurement of  $\zeta$  = particle velocity in an electrical field

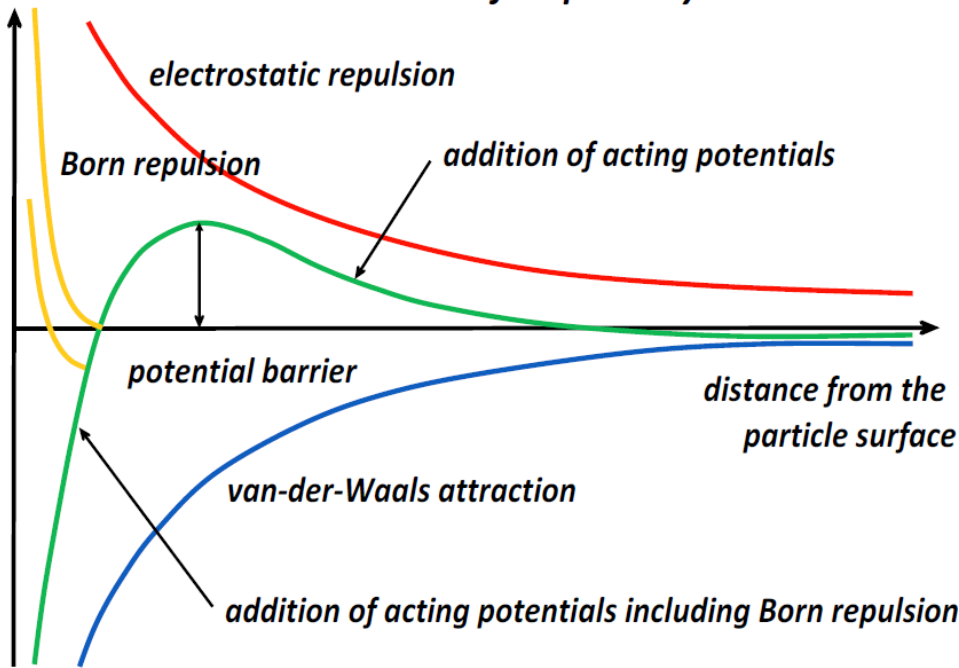
Methods for  $\zeta$  determination = measurement of electrophoretic mobility or streaming potential

Helmholtz – Smoluchowski equation:

$$\zeta = \frac{\vec{v}}{\vec{E}} \cdot \frac{\eta}{\epsilon \cdot \epsilon_0}$$

$\zeta$  zeta - potential  
E electrical intensity  
v particle velocity  
 $\eta$  viscosity  
 $\epsilon \cdot \epsilon_0$  dielectric constant

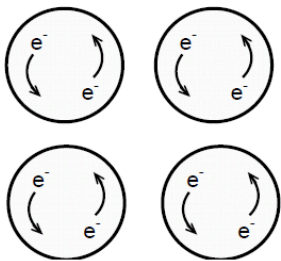
## Stabilisation of disperse systems



repulsive forces = Coulomb's force

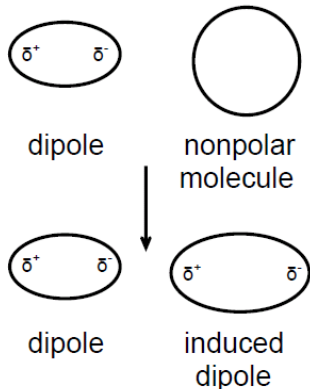
## attractive van der Waals forces

dispersion forces

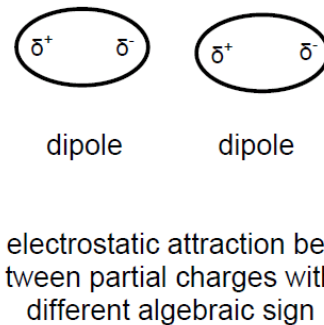


fast electron motions lead to charge fluctuations

inductive forces



dipole - dipole forces

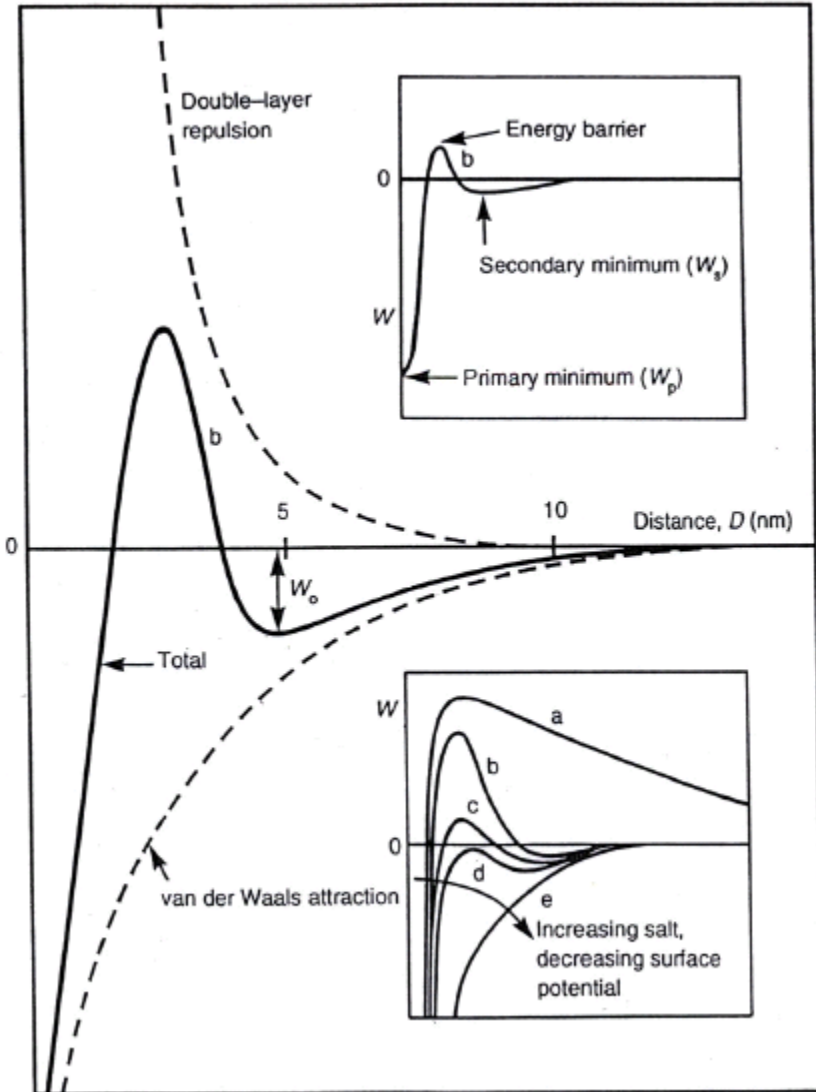


# Interaction energy – distance profiles from DLVO theory

$$V_R = \text{prop} \frac{1}{\sqrt{I}} \tanh[k_1 \Psi d]^2 \exp(-k_2 d / \sqrt{I})$$

$$V_A = -\text{prop} \frac{A}{d^2}$$

$I$  = Ionic strength;  $d$  = distance between the NPs  $A$  = Hamaker-constant



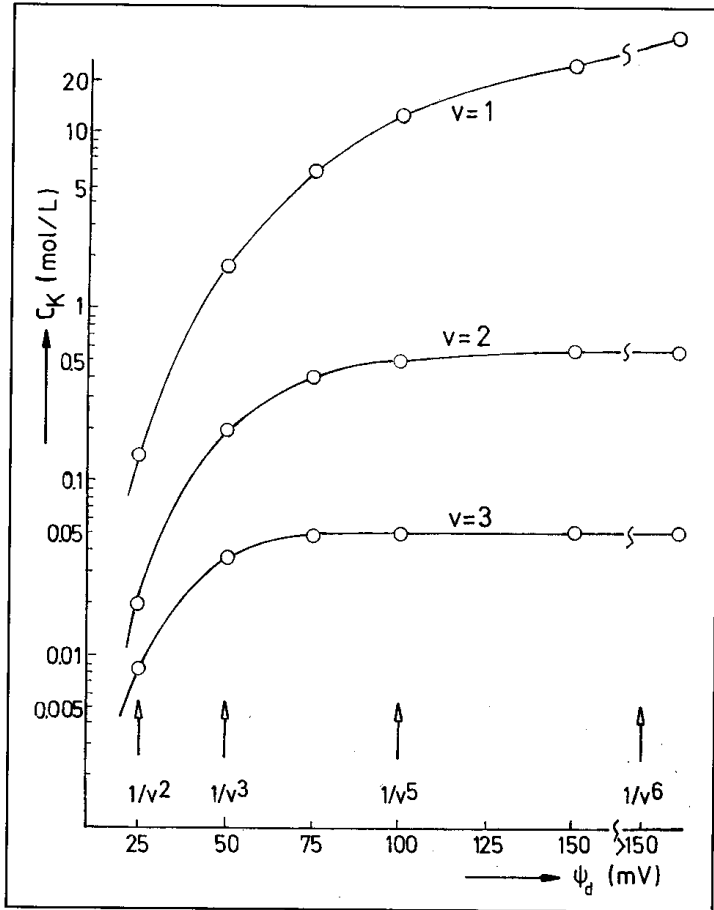
$$V_T = V_A + V_R$$

- a) strong repulsion of surfaces= NP suspension is stable
- b) surfaces come into a stable equilibrium near the second minimum, if deep enough suspension is kinetically stable
- c) surfaces come into the second minimum, slow coagulation of NPs
- d) critical coagulation concentration  $ccc$ : surfaces stay in the second minimum, or coagulate, fast coagulation of NPs
- e) fast coagulation of NPs

# Schulze - Hardy rule

critical coagulation concentration (ccc) is reciprocal proportional to 6th power of ion valence  $z$

$$c(\text{Me}^+) : c(\text{Me}^{2+}) : c(\text{Me}^{3+}) = \left(\frac{1}{1}\right)^6 : \left(\frac{1}{2}\right)^6 : \left(\frac{1}{3}\right)^6$$

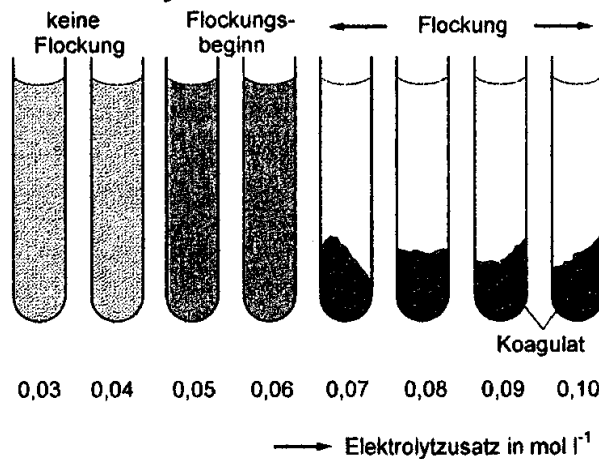
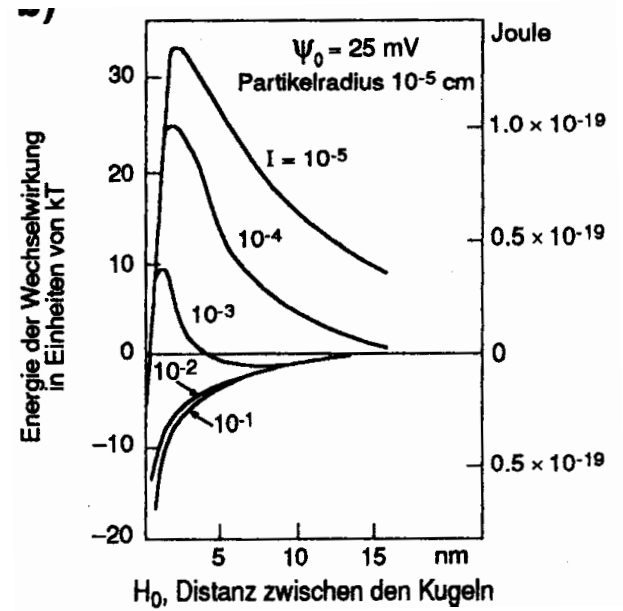
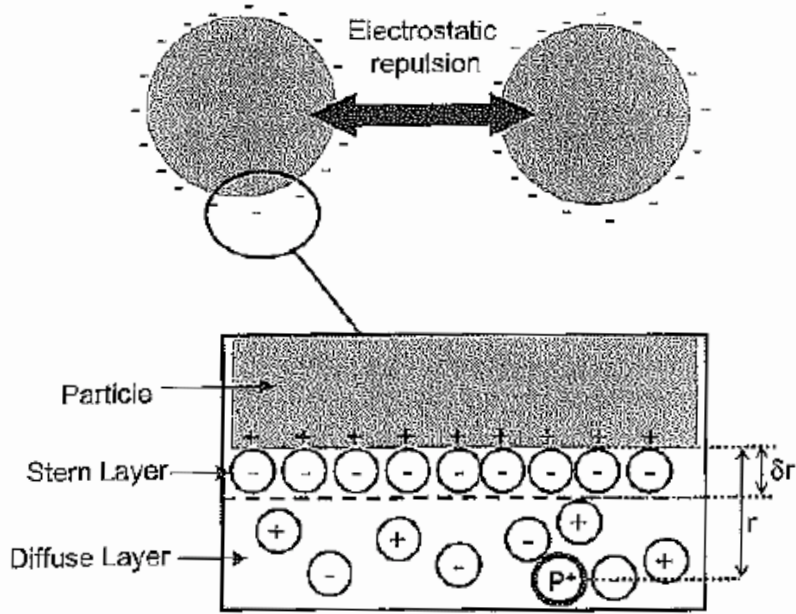


The reciprocal c.c.c of mono-, di- and trivalent ions behave as 1:50:10000;

e.g. for  $\text{Al}^{3+}$  ( $v=3$ ) 1/10000 of  $\text{Na}^+$  ( $v=1$ ) conc. sufficient

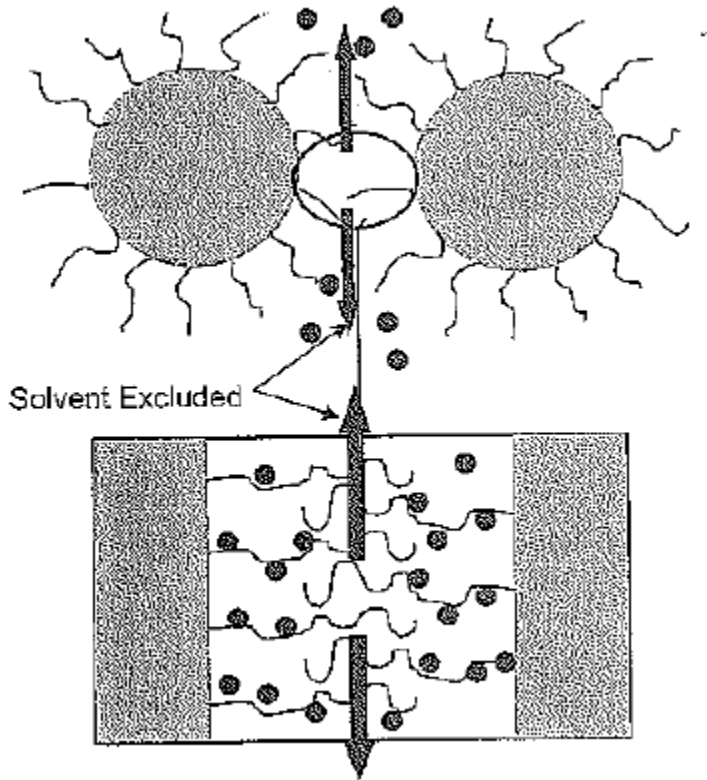


# Electrostatic stabilization of NPs



(P. Christian in Lead & Smith)

# Steric stabilization of NPs

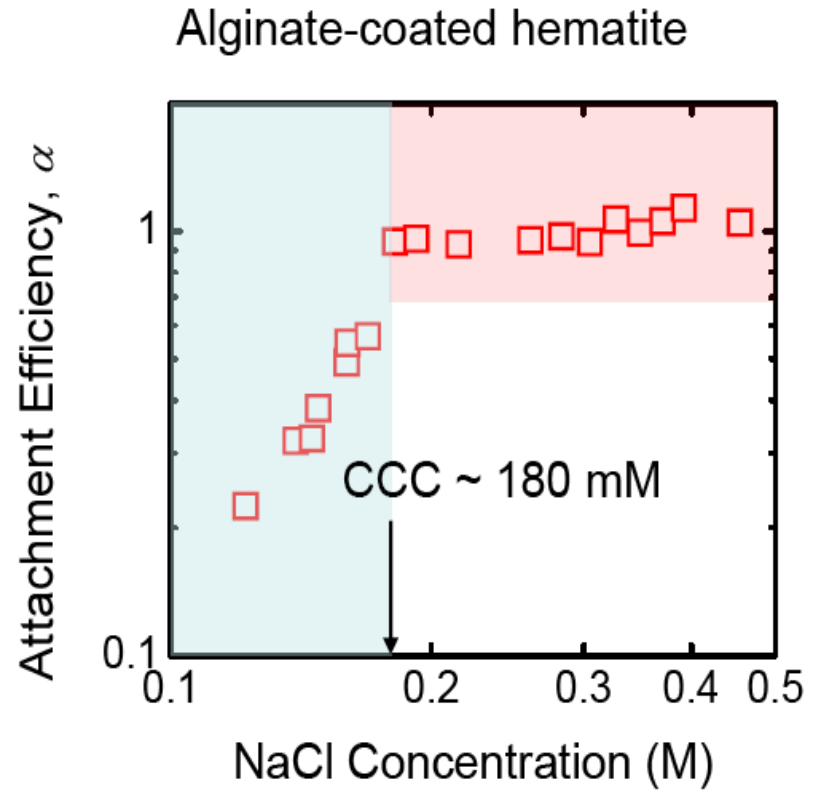
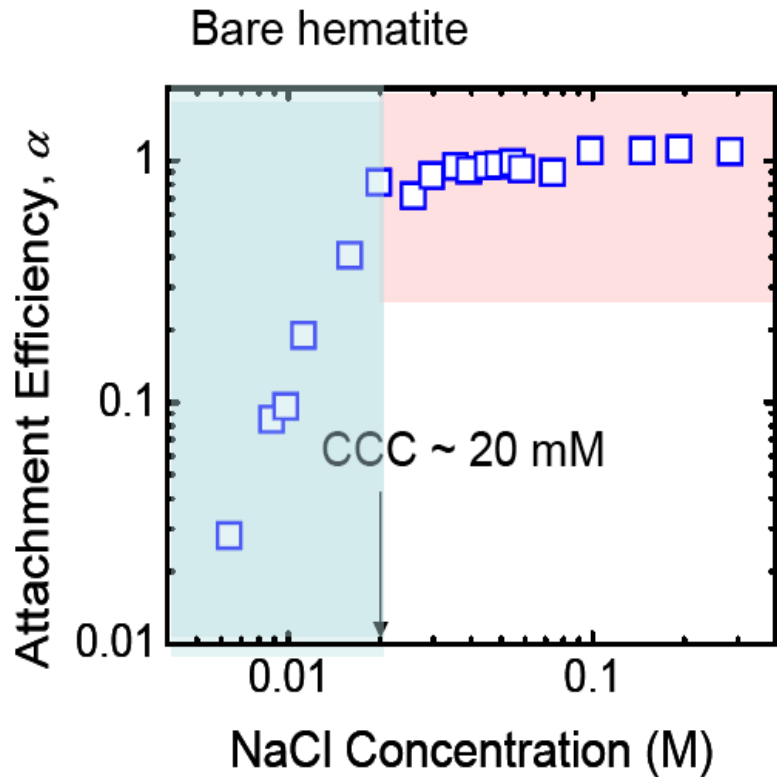


there are polymers on the surface with hydrophilic groups, polymers form short “hairs” towering into the dispersant

stabilisation by entropic effects = numbers of possible configurations would be lowered by coagulation

Stabilization by energetic effects = polymers have in the dispersant a lower energy content than being in contact each other

# Aggregationsverhalten von Hämatit (70 nm) in Ggw. von DOM



CCC (Hämatit)  $\ll$  CCC (Alginat-Hämatit)

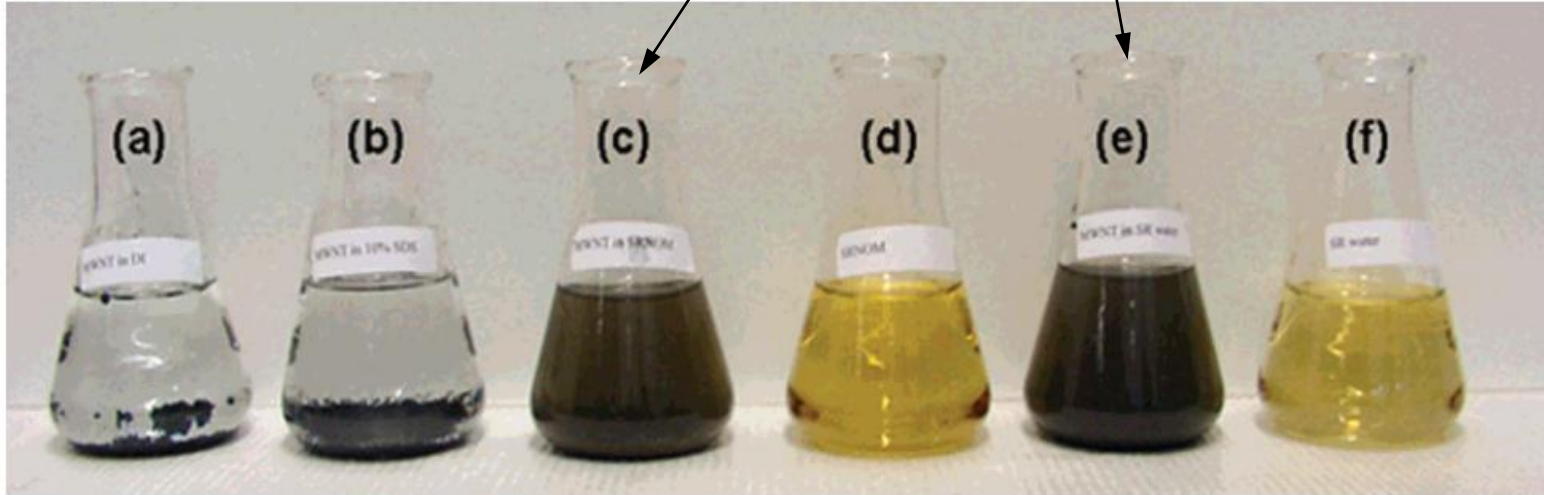
→ Sterische Stabilisierung

Chen et al, ES&T 2006



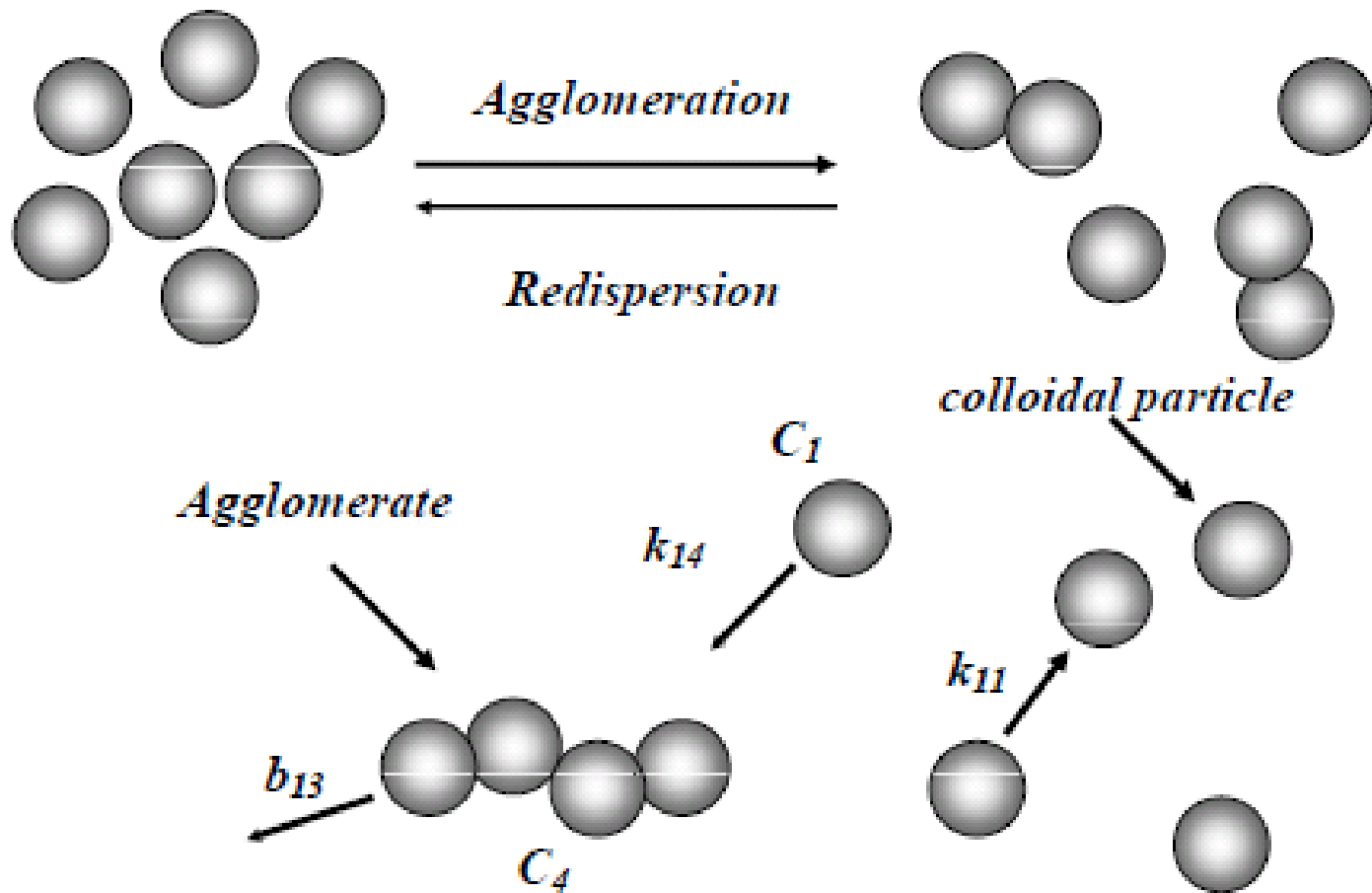
# Aggregationsverhalten von C-Nanoröhrchen in Ggw von DOM

100 mg/l and 500 mg/l Suwannee River organic matter



Die NP Suspensionen bleiben für Monate stabil durch DOM

## Kinetics of particle agglomeration and redispersion



$C_i, C_j, C_k$

Particle concentration of  $i, j, k$  - mers

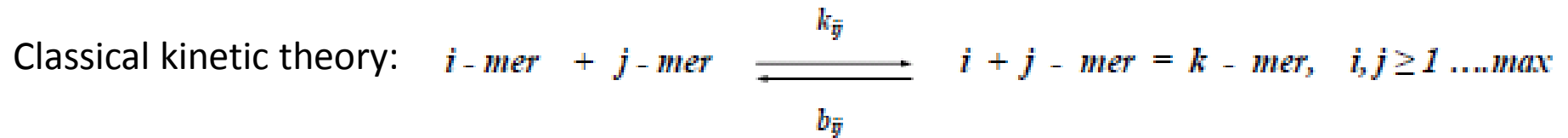
$k_{ij}$

Agglomeration rate constant of  $i$  - mer +  $j$  - mer

$b_{ij}$

Redispersion rate constant of  $k$  - mer to  $i$  - mer +  $j$  - mer

# Population balance model of the particle agglomeration and redispersion



**Agglomeration: Smoluchowski - process**

**Redispersion: reverse Smoluchowski - process**

$$\frac{dC_k}{dt} = \frac{1}{2} \sum_{i=1}^{k-1} (1 + \delta_{i,k-i}) k_{i,k-i} C_i C_{k-i} - C_k \sum_{i=1}^{\text{max}} (1 + \delta_{i,k}) k_{i,k} C_i$$

$$\frac{dC_k}{dt} = -\frac{1}{2} C_k \sum_{i=1}^{k-1} (1 + \delta_{i,k-i}) b_{i,k-i} + \sum_{i=1}^{\text{max}} (1 + \delta_{i,k}) b_{i,k} C_{i+k}$$

with  $\delta_{i,j} = 1$  for  $i=j$  and  $\delta_{i,j} = 0$  for  $i \neq j$

**Smoluchowski - process :**

Increase of k - mers by agglomeration of particles of size i and k - i with  $i = 1, 2 \dots k - 1$   
 Decrease of k - mers by agglomeration with particles of size  $i = 1, 2 \dots \text{max}$

**Reverse Smoluchowski - process :**

Decrease of k - mers by redispersion to particles of size i and k - i with  $i = 1, 2 \dots k - 1$   
 Increase of k - mers by redispersion to particles of size k and  $i = 1, 2 \dots \text{max}$



