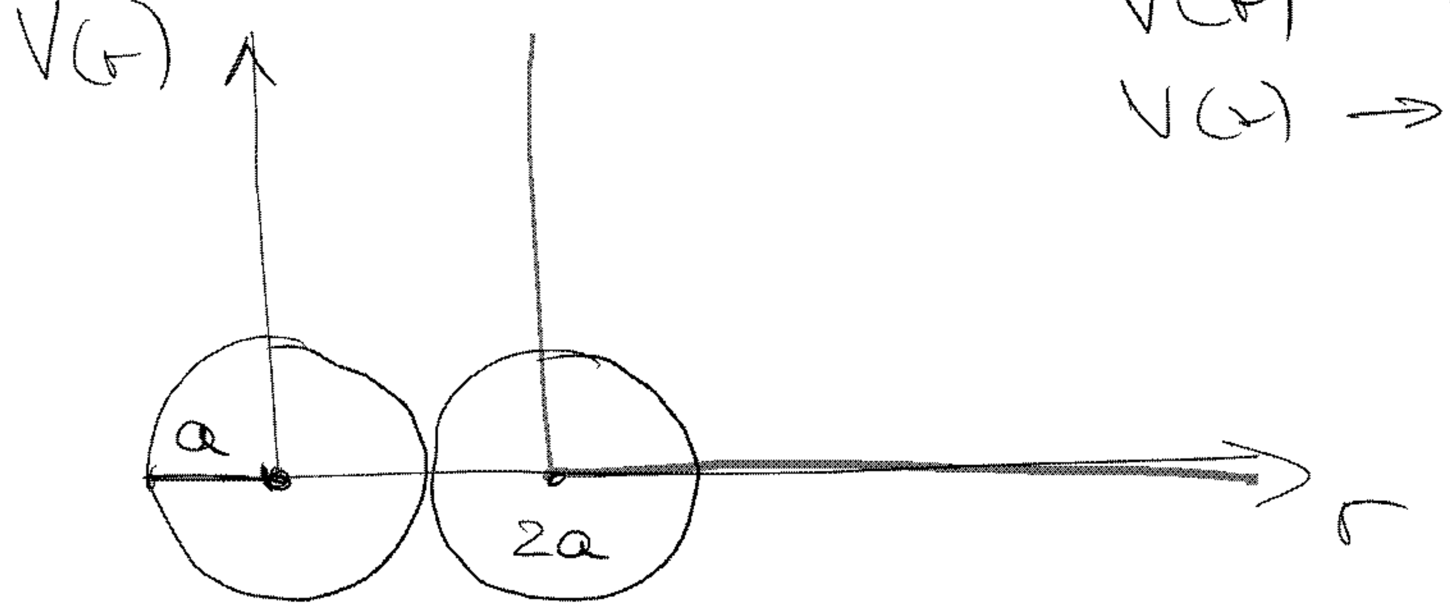
Pair interactions

a) hard-sphere interactions
b) electrostatic interactions
c) van-der-Waals
d) magnetic interactions

a) hard-sphere interactions

$$V(r) = 0 \qquad r > 2a$$
$$V(r) \to \infty \qquad r \le 2a$$



consequences

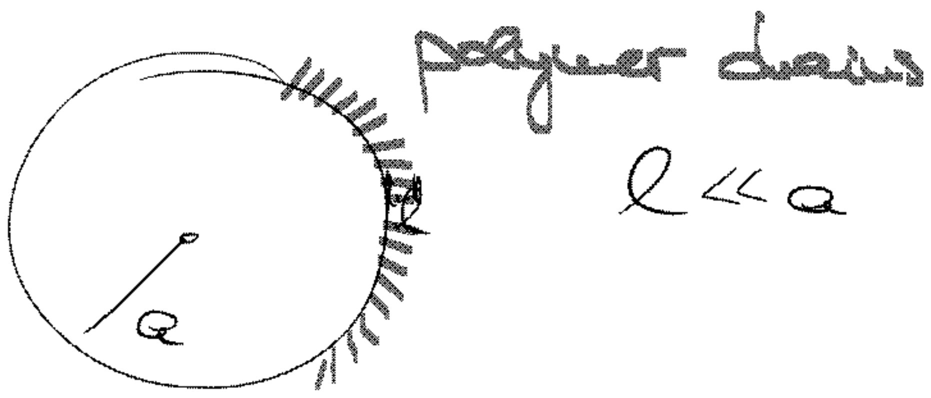
inner energy U = const.

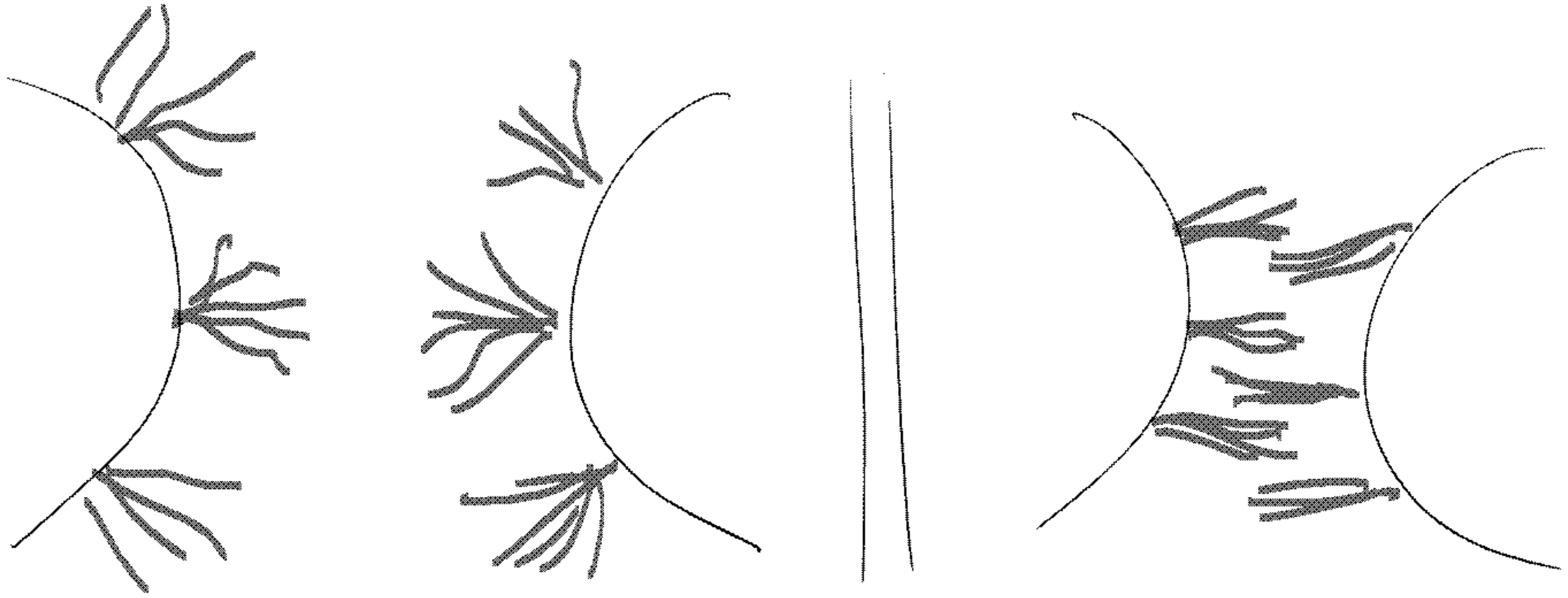
$$F = \cancel{U}_{0} - TS$$

athermic systems

Exp. Realisation

Steric Stabilization





$$\Delta F = -T\underbrace{\Delta S}_{<0} > 0$$

b) electrostatic interaction

most systems in solution are charged (polymers, colloids, ...)

reason: surface chemistry

example: sulfate group on polystyrene surface

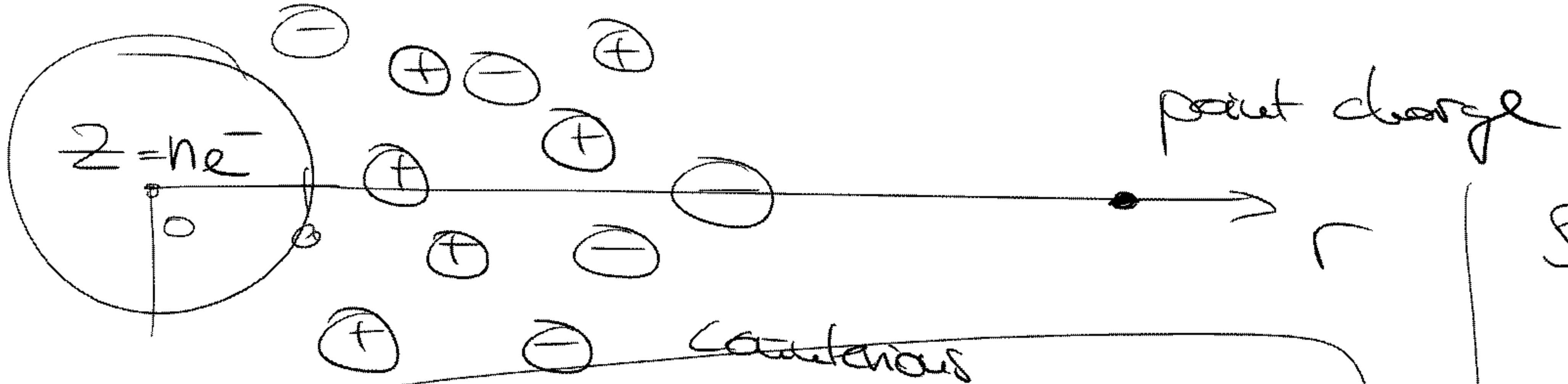
counterion

reaction balance depends pH

the more H^+ in solution (small pH) → the more difficult is dissociation of sulfate groups → surface charge σ of colloids is smaller

pH for which $\sigma = 0$: isoelectric point

Distance dependence of electrostatic potential



$$\Delta \phi(r) = -\frac{4\pi}{\varepsilon} \left(\rho_{el}(r) \right)$$

$r \gg a$: ρ_{el} given by counterions

$$\rho_{el}(r) = \sum_j z_j e \cdot \rho_j$$

j ← type of ions H^+, OH^-

$$\rho_j(r) = \rho_j^0 \exp\left(- \frac{e z_j \phi(r)}{k_B T} \right)$$

→ Poisson-Boltzmann-Equation

$$\Delta\phi(r) = -\frac{4\pi}{\varepsilon}\left(\sum_j z_j e \rho_j^0 \exp\left(-\frac{e z_j \phi(r)}{k_B T}\right)\right)$$

boundary condition $\quad \rho_{el}(r=a) = \sigma = \frac{Z}{4\pi a^2}$

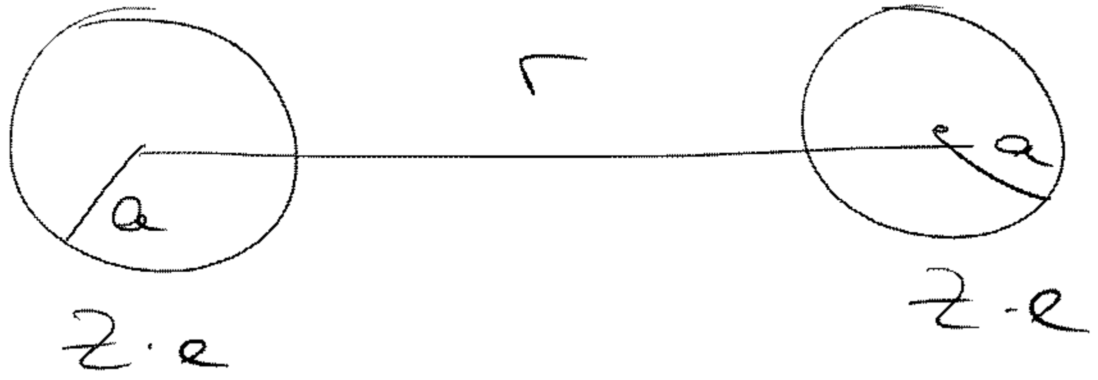
$e z_j \phi(r) \ll k_B T \rightarrow$ linearize

lin. PB-equation : $\Delta\phi(r) = \kappa^2 \phi(r) \qquad r > 2a$

$$\kappa = \sqrt{\frac{4\pi e^2}{\varepsilon k_B T} \sum_j z_j^2 \cdot \rho_j^0} \quad ; \quad \frac{1}{\kappa} = \text{Debye Screening length}$$

$$\phi(r) = \frac{Z \cdot e}{4\pi\varepsilon} \frac{e^{\kappa a}}{(1+\kappa a)} \cdot \frac{e^{-\kappa r}}{r} \qquad \text{(point charge \& colloid)}$$

adding salt $\rightarrow \rho_j^0 \nearrow \rightarrow \kappa^{-1} \searrow$



$$V^{els}(r) = + \frac{(Z \cdot e)^2}{\varepsilon} \left(\frac{e^{\kappa a}}{1 + \kappa a} \right)^2 \cdot \frac{e^{-\kappa r}}{r}$$

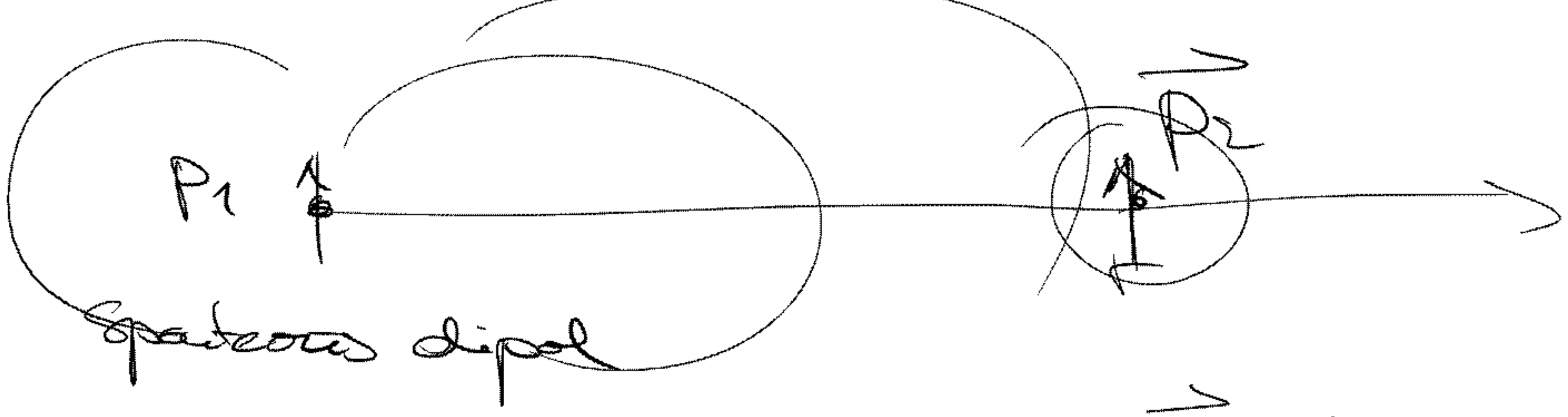
Yukawa - Potential

Screened Coulomb potential

Debye Hückel - potential

c) Van-der-Waals interaction

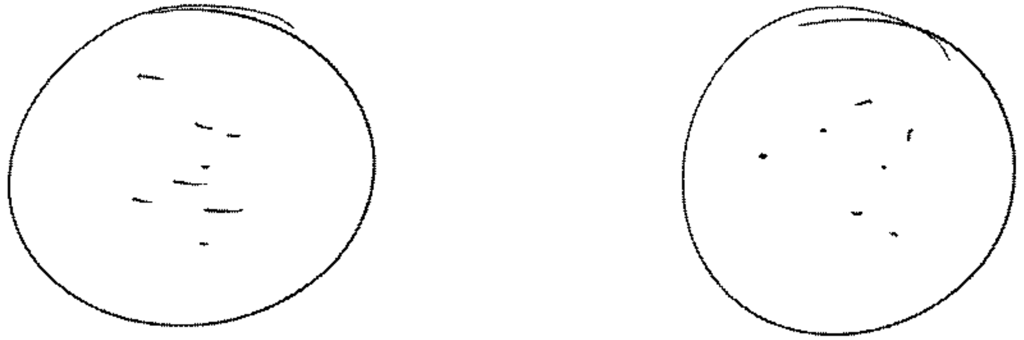
$\Delta x \cdot \Delta p \geq \hbar$



$\vec{p}_1 \rightarrow \vec{E}_1(r)$ $\qquad \vec{E}_1(r) = -\vec{\nabla}\left(\frac{\vec{p}_1 \cdot \vec{r}}{|\vec{r}|^3}\right)$

$\vec{p}_2 \propto \vec{E}_1(r) \propto \frac{1}{r^3}$

$V^{vdW}(r) = -\frac{1}{2}\vec{p}_2\vec{E}_1 = -\frac{C}{r^6}$ (point charges)



vdW between colloids

$V^{vdW}(r) = -\frac{A \, a}{12\,(r-a)}$ — Hamaker constant

Hamaker constant

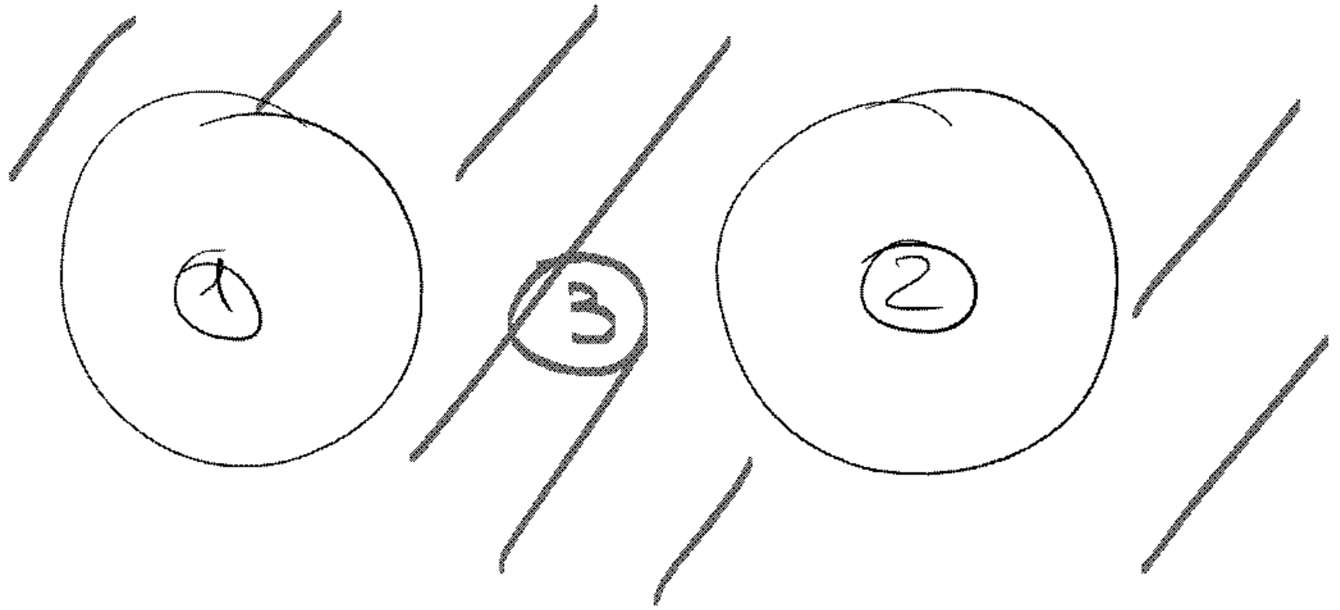
$$A = \pi^2 C \cdot \rho_1 \cdot \rho_2$$

↑ ↑ Densities of the two colloids

$$C \approx 10^{-77}\ J\,m^6$$

Material	$C\ [10^{-79}\ J\,m^6]$	$\rho\ [10^{28}\ m^{-3}]$	$A\ [10^{-19}\ J]$
Hydrocarbon	50	3.3	0.5
H_2O	140	3.3	1.5

A can be also obtained from the index of refraction in the UV



(1) =

$n_1 = n_2$: $A > 0$ (attraction)

$n_1 < n_3 < n_2$: $A < 0$ (repulsive)

$n_1 = n_2 = n_3$ $A = 0$

Superposition of all the above interactions

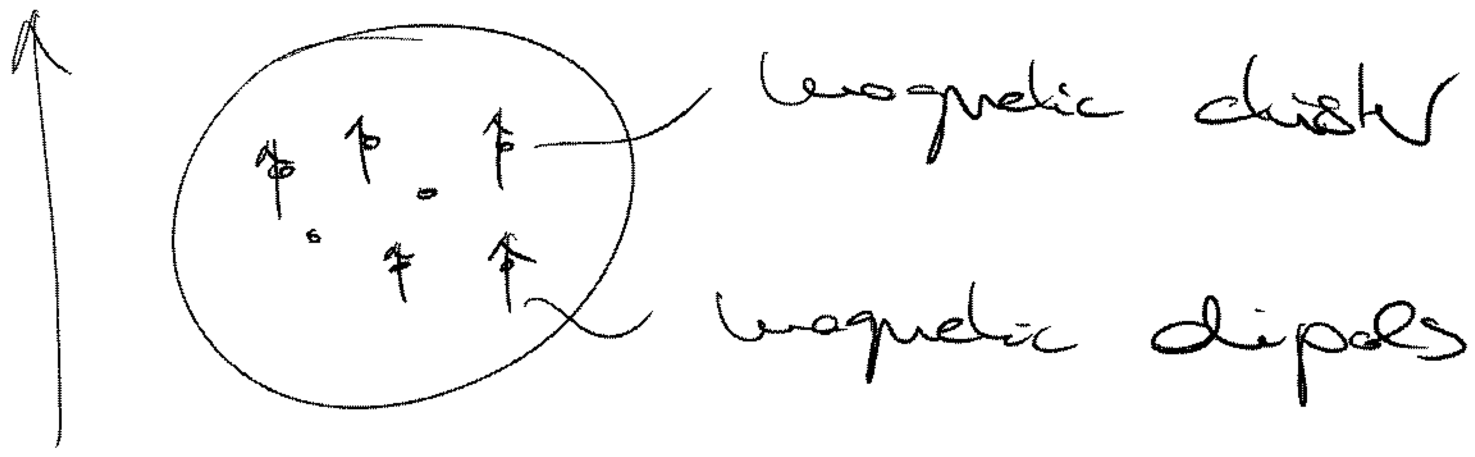
→ DLVO potential (Derjaguin, Landau, Verwey, Oberbeek)

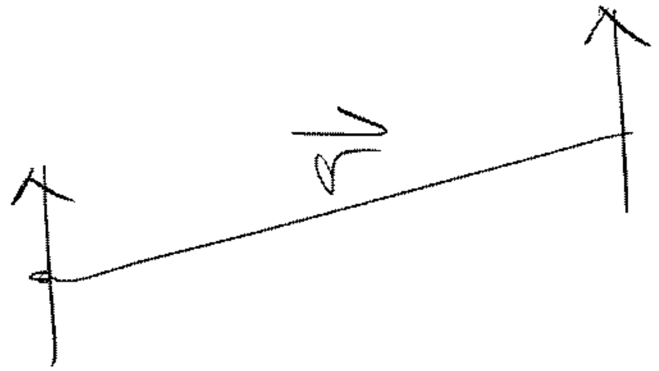
$$V^{DLVO} = V^{HC} + V^{vdW} + V^{els}$$

$$E > 5 k_B T$$

$$p(E) \propto e^{-\frac{E}{k_B T}}$$

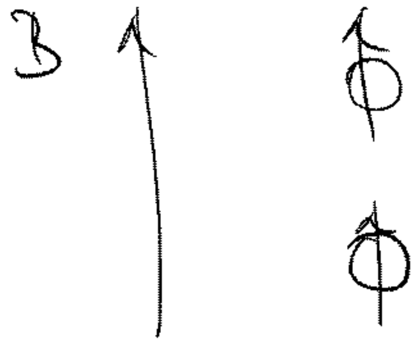
Magnetic interaction





$$V^{magn}(r) = \frac{\mu_0}{4\pi} \frac{\left(r^2 \mu^2 - 3(\vec{r}\vec{\mu})^2\right)}{r^5} \propto \frac{1}{r^3}$$

$$\frac{1}{r^3}$$



$$-\frac{1}{r^3}$$