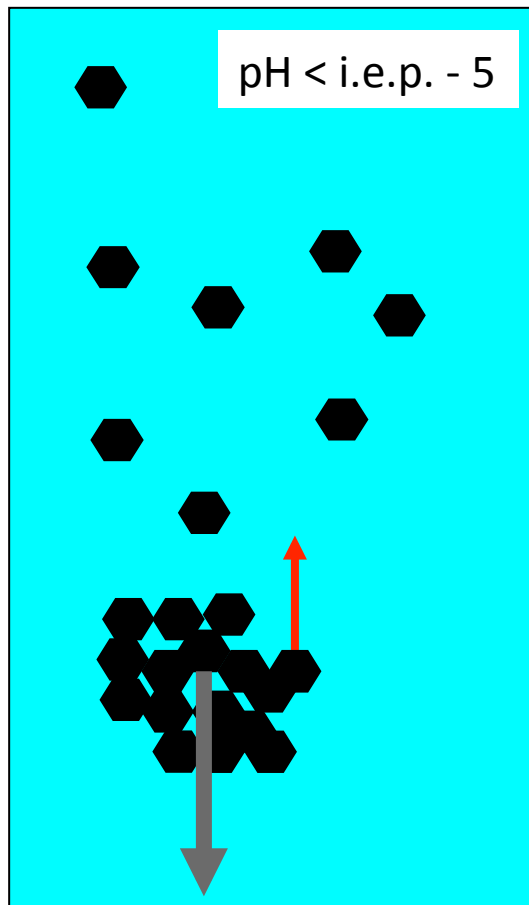


Colloid stability: the reverse problem



Bernard Cabane, Olivier Spalla, Sabine Desset

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Classical colloid stability and evolution

Start with particles in the fully dispersed state.

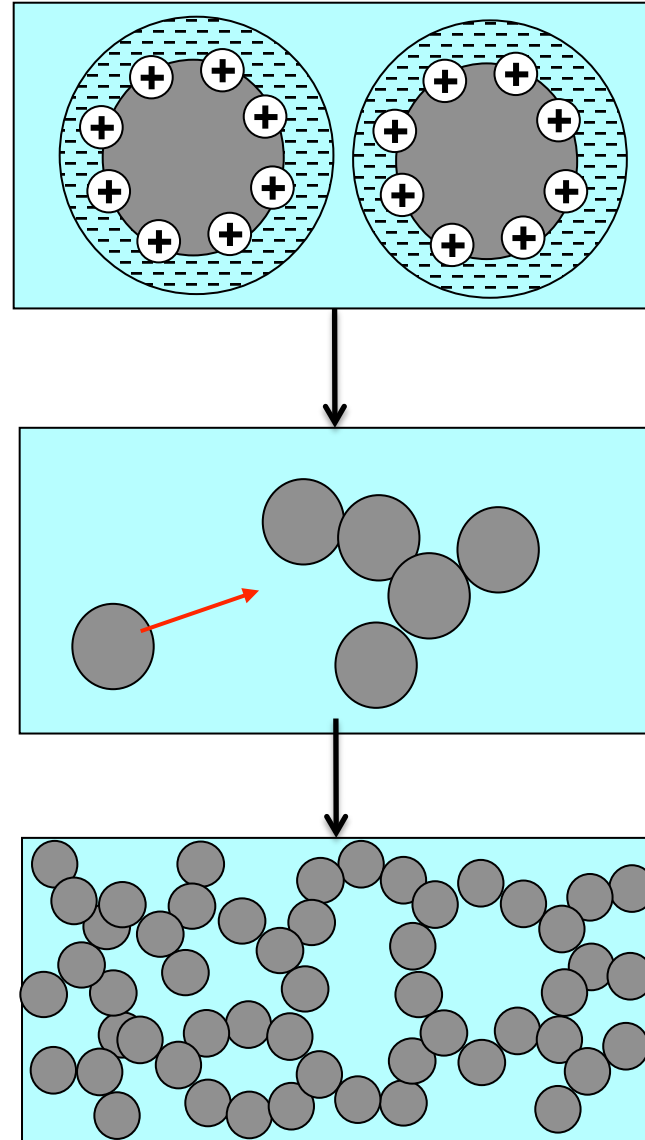
Thermal agitation
Surface forces
(ionic interactions, VdW, hydration)

Aggregation threshold

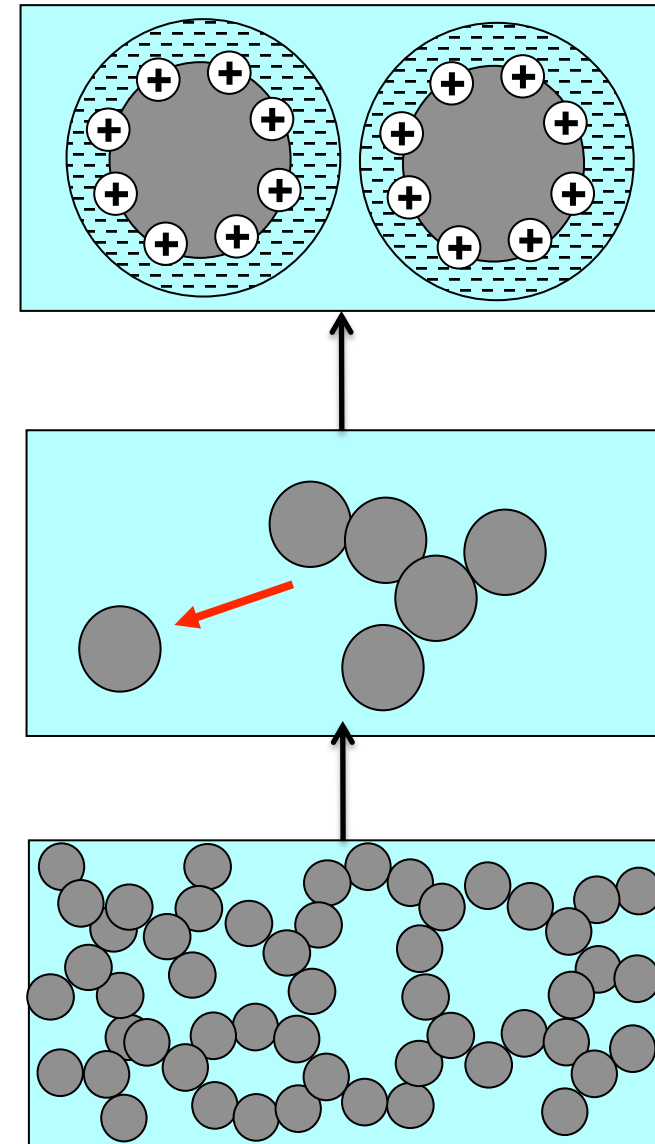
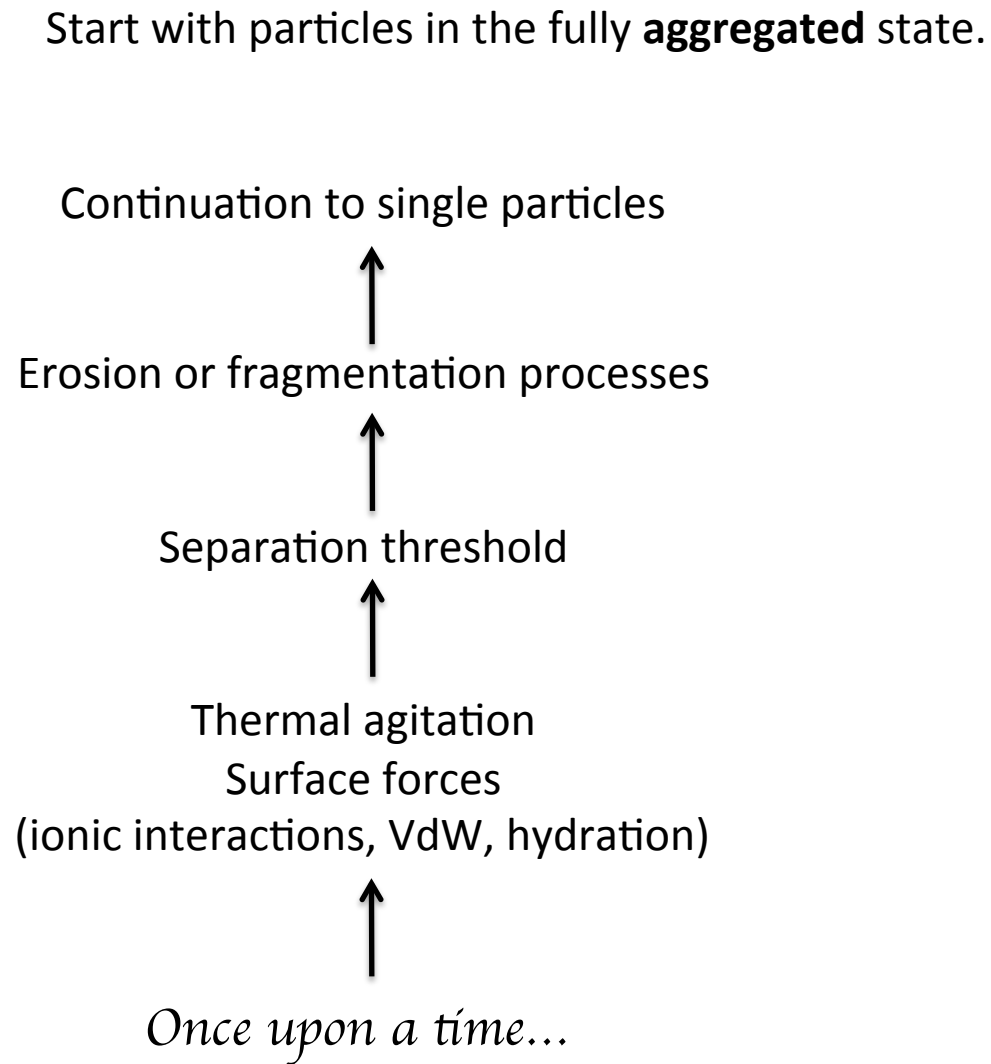
Growth processes

Some reorganization (?)

The end



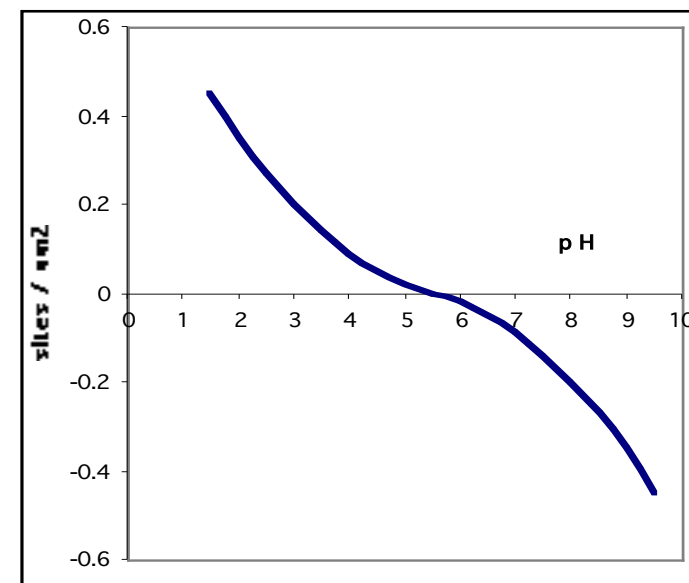
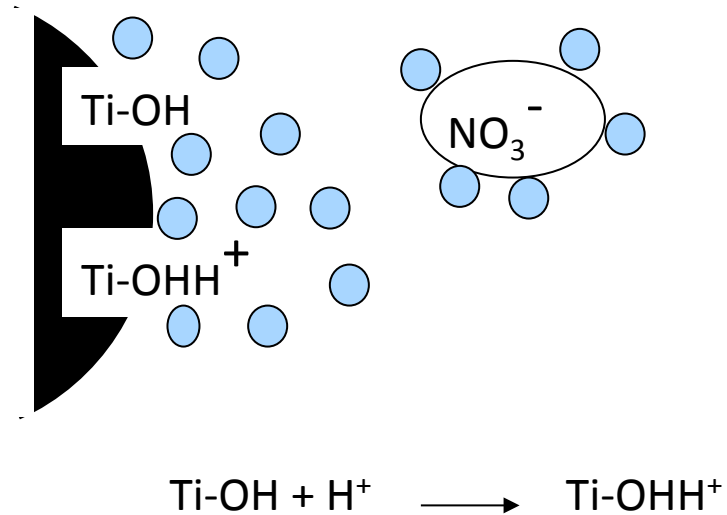
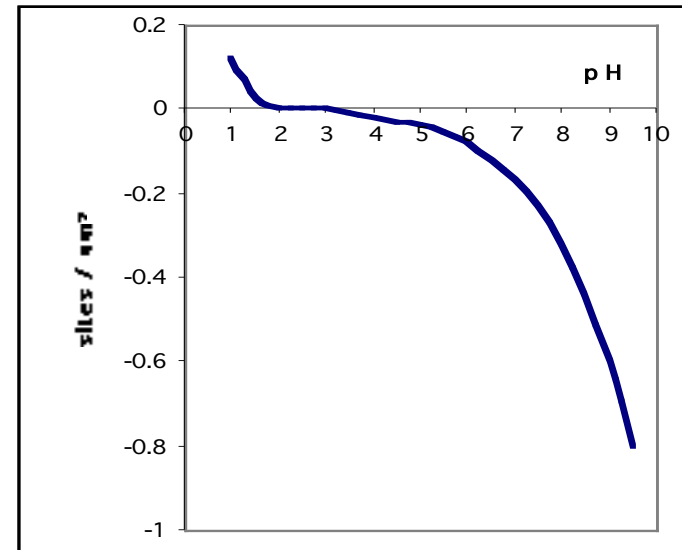
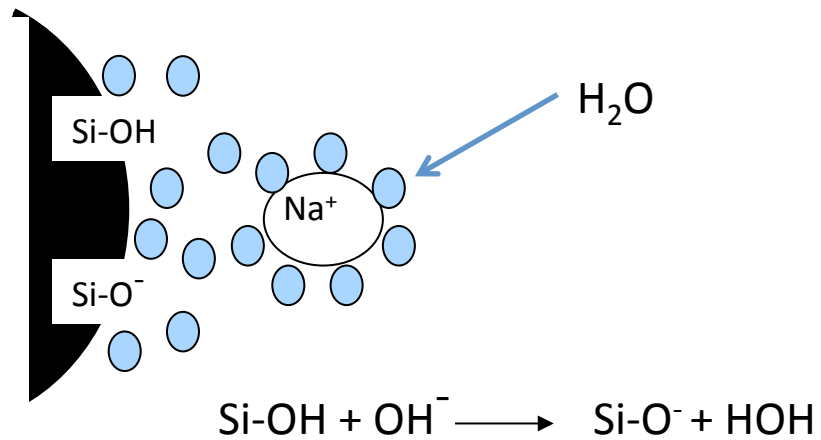
The reverse problem has not been extensively studied



Are the ingredients the same as for the classical colloid stability problem?

Ingredient 1: ionization of surfaces

Ionization through acid-base equilibria of surface sites: nothing new



Ingredient 2: repulsions of counterion layers

Ionization through:

Acid-base equilibria of surface sites

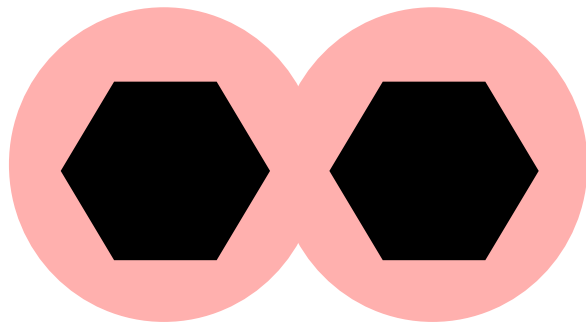
Release of exchangeable ions

Far from the i.e.p.:

Large number of counterions
near the particle surfaces

= « bumpers »

Strong repulsions



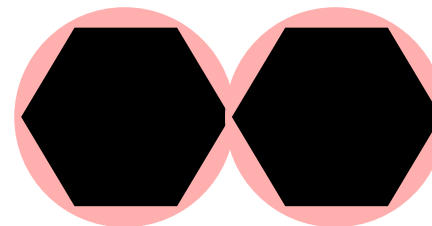
At the i.e.p.:

The surface sites are uncharged
(amphoteric surface)

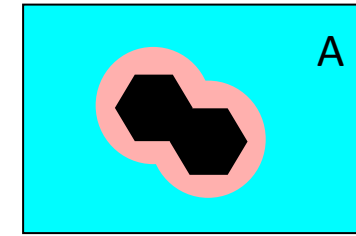
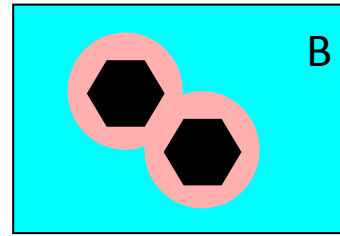
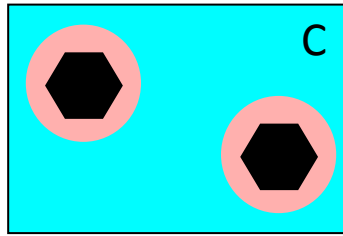
Or there are equal numbers
of + and – sites

Either way the counterions are released
No « bumpers », no repulsions

The particles will aggregate
Through VdW attractions
And chemical reactions



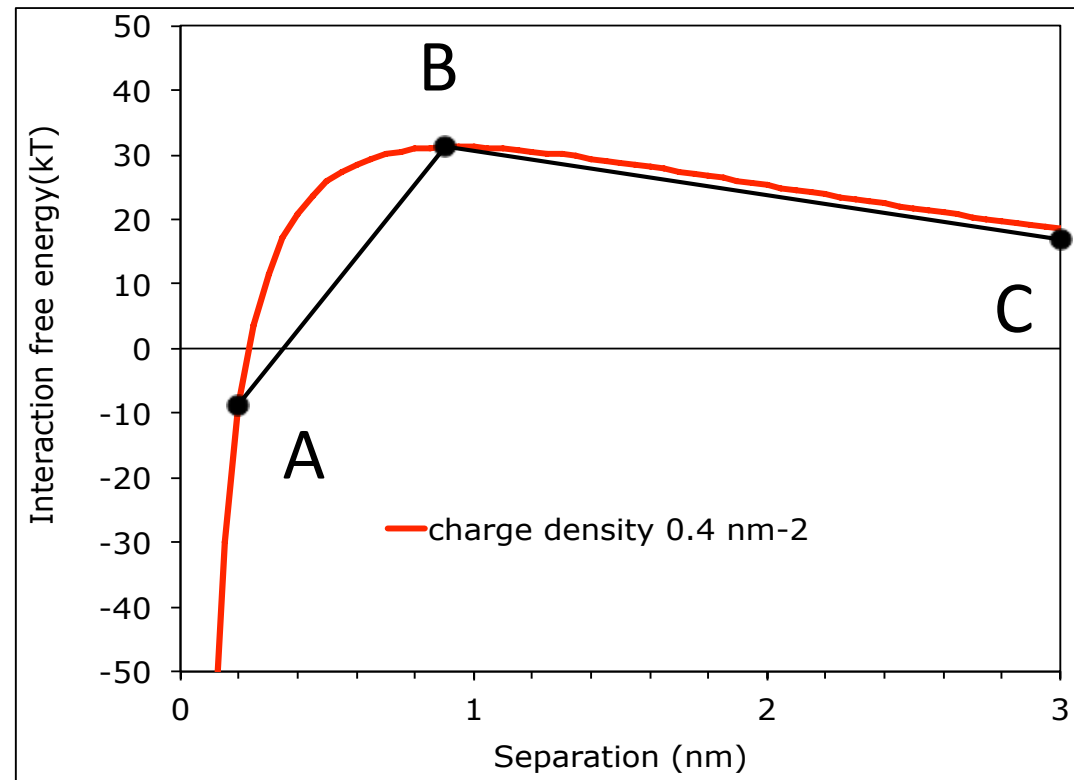
Two colloidal particles



Usual problem: control aggregation **CB** - the key is the potential barrier **B**

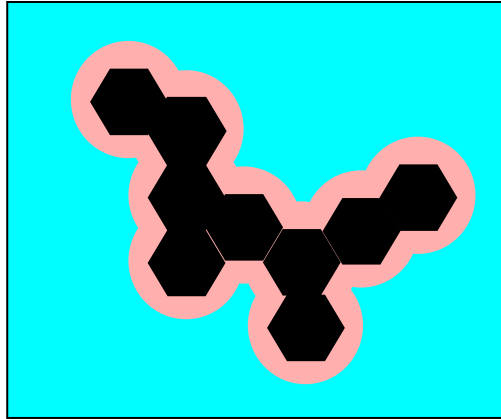
Reverse problem: control separation **AB** - the key is the initial state **A**

For the reverse problem, the initial state, A, is not well known and it depends on how the system was prepared (history)

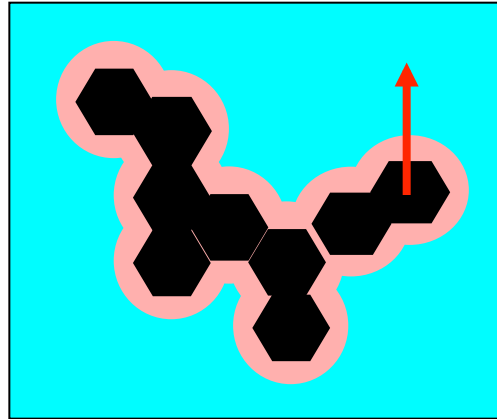


What do we need?

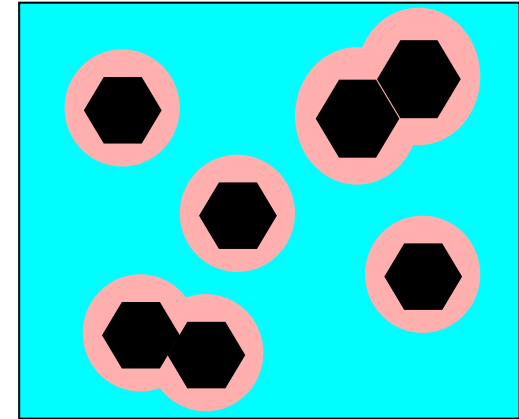
Initial state



Transition state



Final state



We need to know and control the strength of bonds between particles?

We need **protocols** for creating a particular type of surface-surface adhesion

We need to know and control the stresses applied to these bonds?

We need **protocols** for applying a particular type of force to the network

We need to evaluate the rate of success of the redispersion process

We need **protocols** for measuring the fraction of single particles

This talk is going to be about protocols = procedures that make the difference...

Controlling the initial state-1: primary particles

Source of particles: AKP50 alpha-alumina powder

Problem: the particle-particle contacts

were made at high temperature

They are much too strong

Very strong forces are needed to break them

Protocol

High power ultrasound or high shear

→ Erode these aggregates

→ Dispersion of « **primary particles** » in water

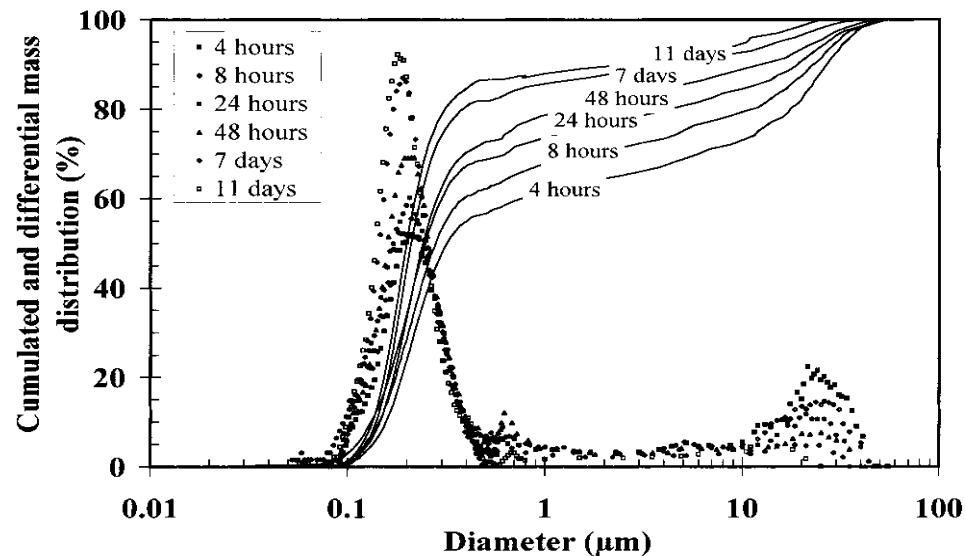
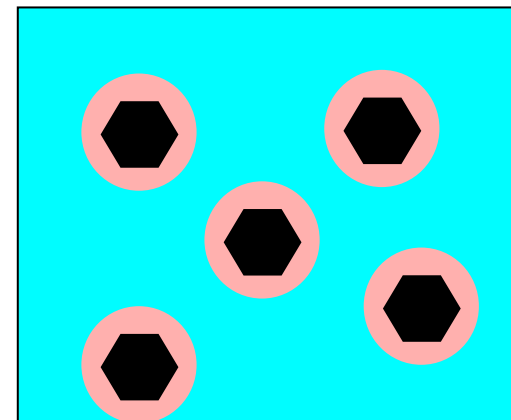
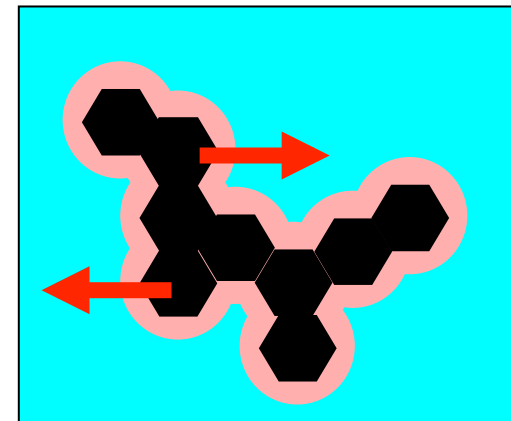
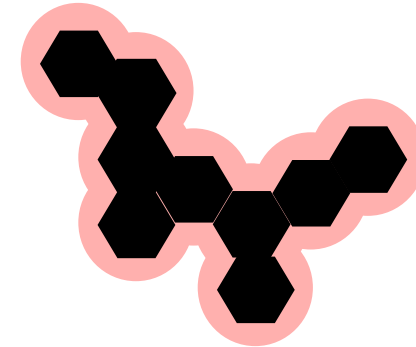
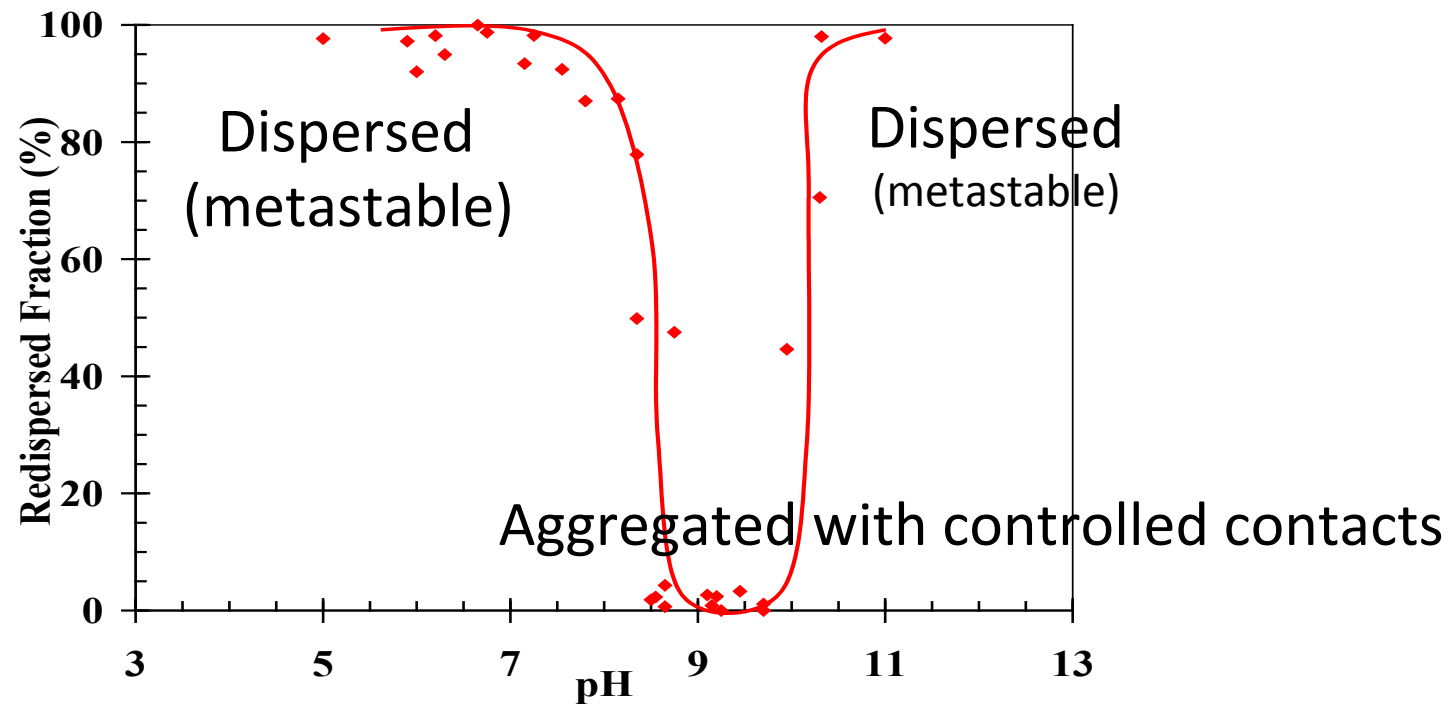
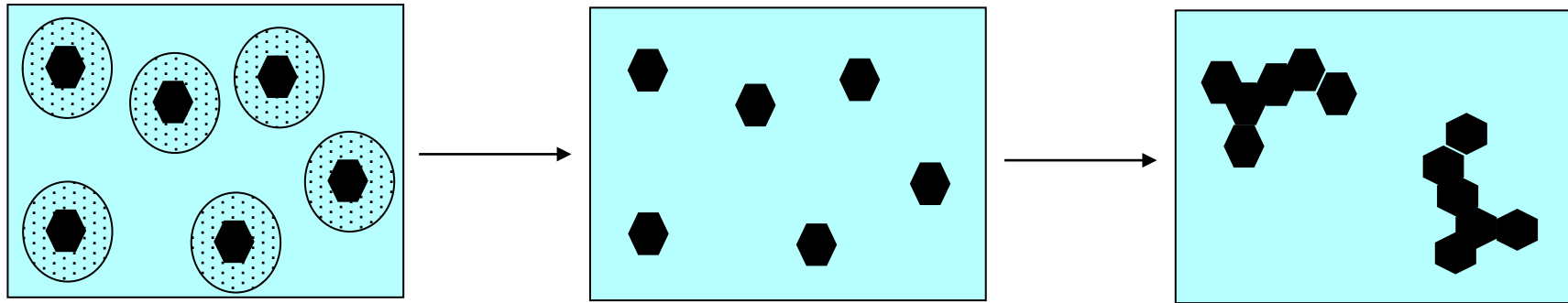


Figure 4. Dispersion kinetics of the raw powder, agitated with a propeller in water at pH5. The vertical axis refers to the cumulated mass (solid lines). The points indicate the mass distribution (derivative of the cumulated mass).

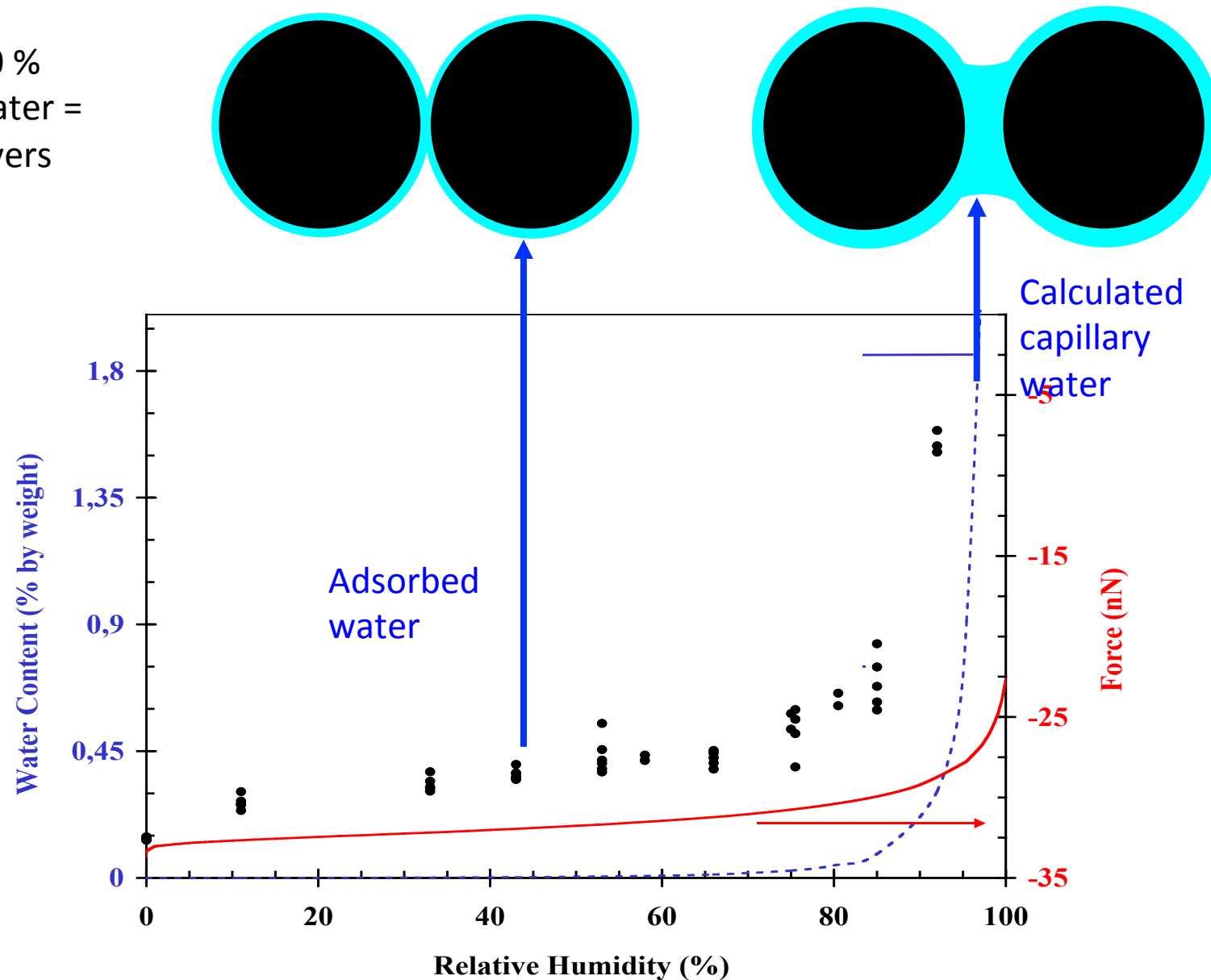


Controlling the initial state-2: wet aggregates



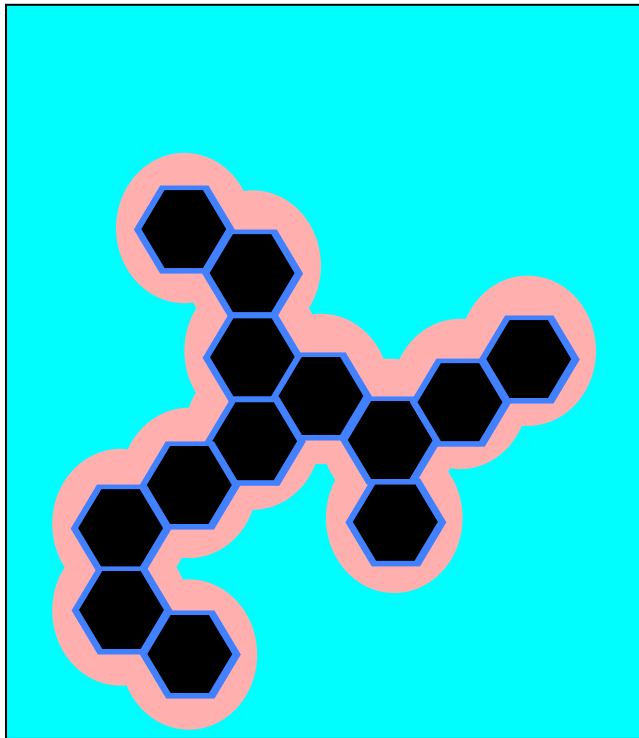
Controlling the initial state-3: dry aggregates

At RH = 50 %
surface water =
3 monolayers



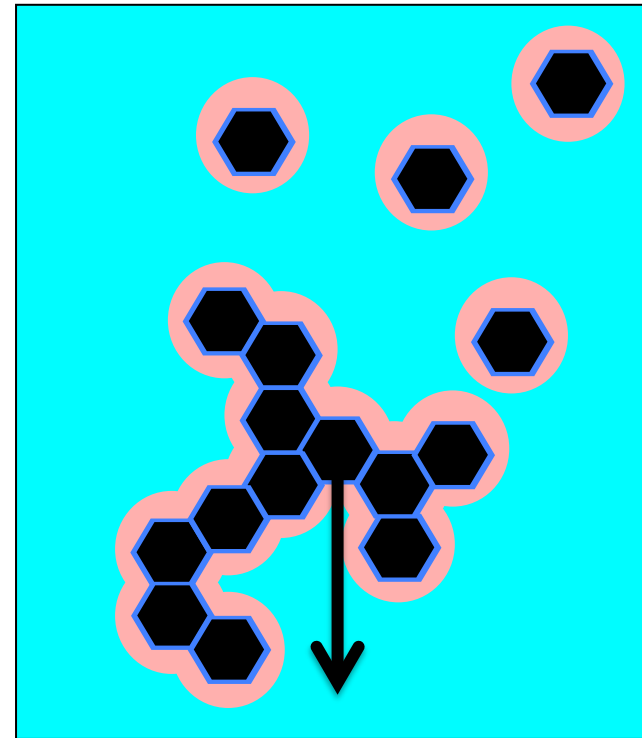
Controlling the transition state

Redispersal at rest



Set pH and salt,
and wait
(chemistry only)

Redispersal through sedimentation

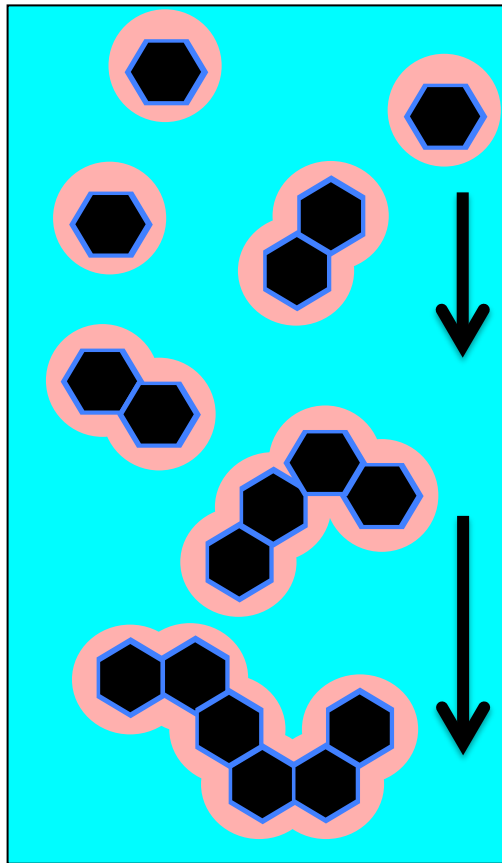


Set pH and keep
tumbling the samples
(chemistry and physics)

Measuring the redispersion in the final state

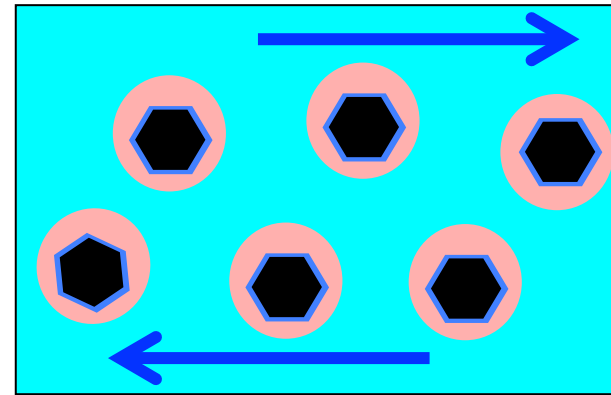
The measurement of aggregate size distributions is too time consuming
Need a quantitative method that is fast and uses small amounts of dispersion

Separation by sedimentation

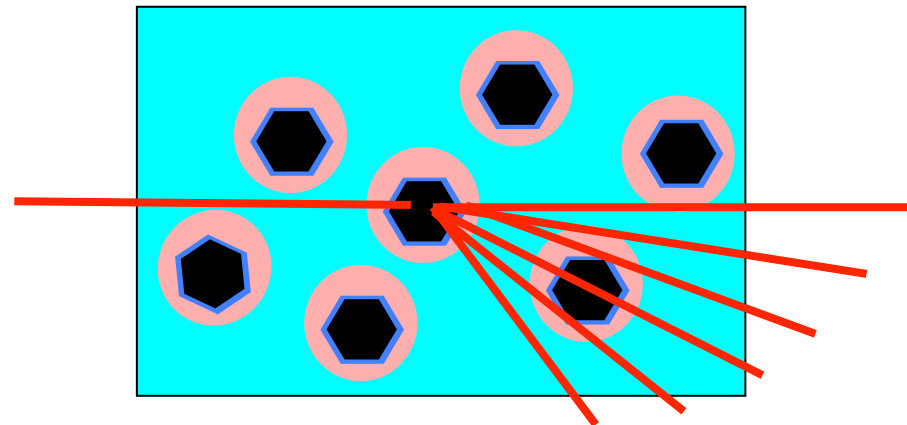


Top layer = single,
doublets, triplets

Ultrasound → break doublets and triplets

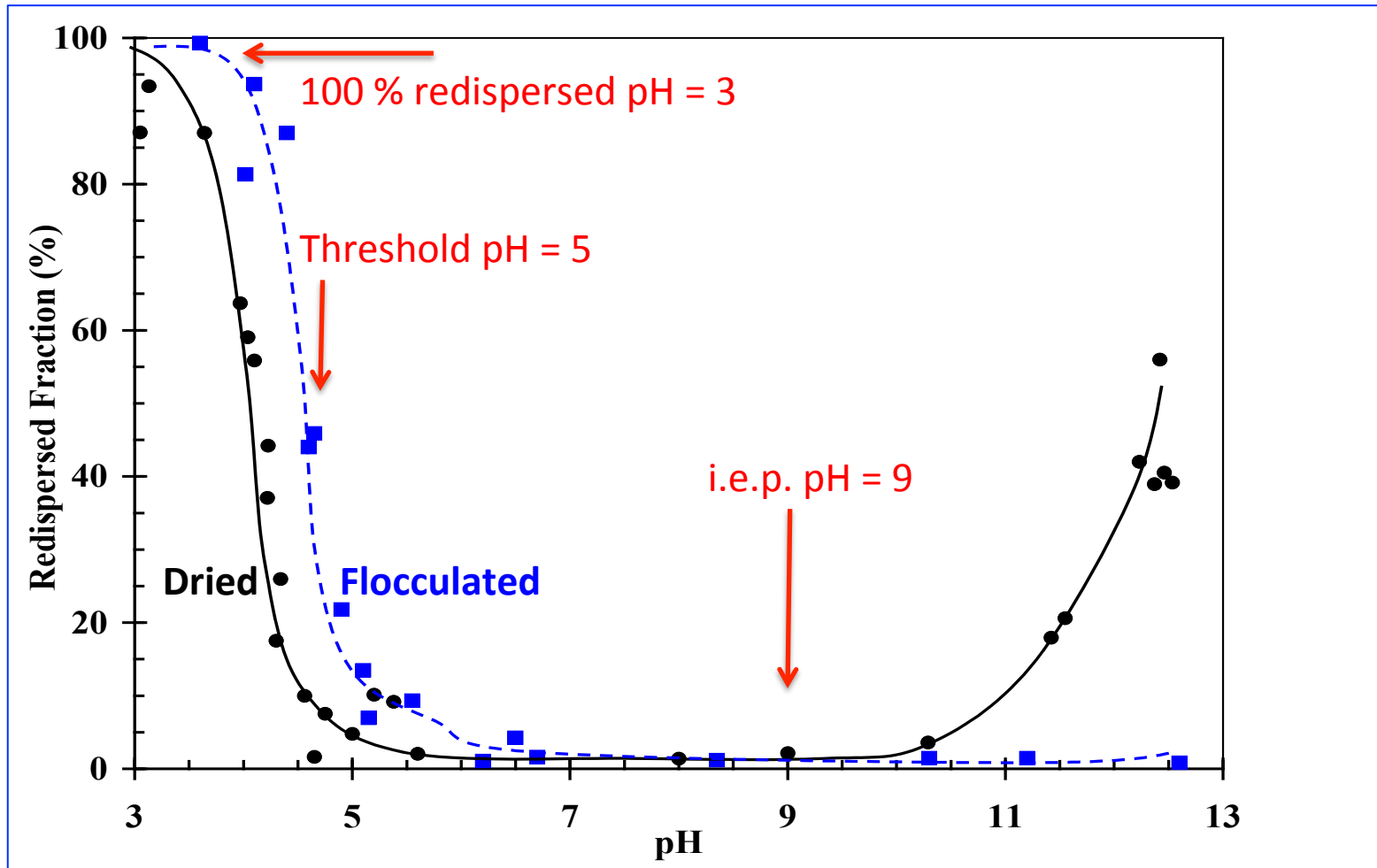


Turbidity → measure the number of particles



Results: redispersion thresholds

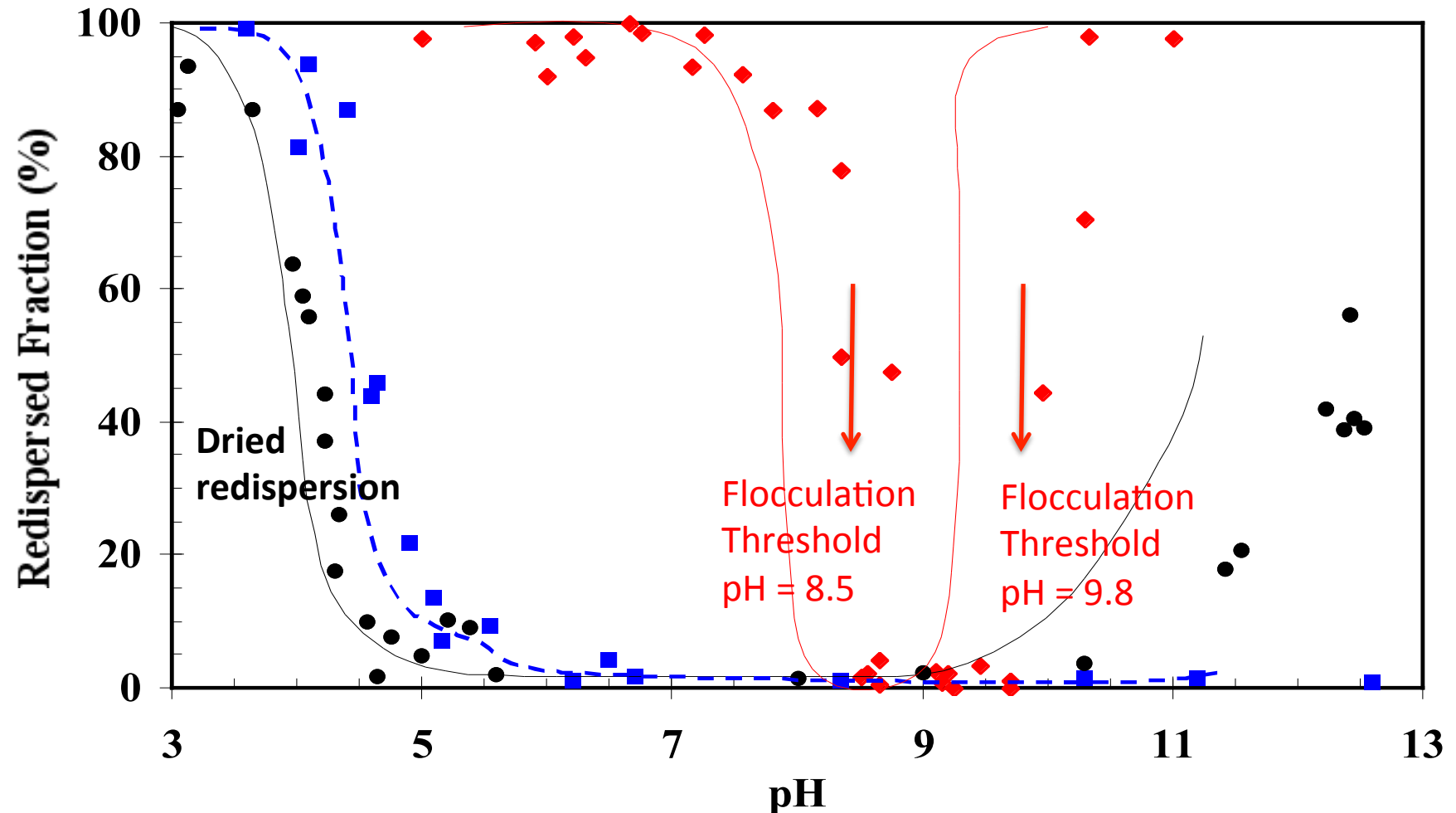
Fraction (%) of redispersed particles in the tumbling protocol, as a function of pH



There is a well-defined threshold for redispersion at low pH (cationic surfaces)
After drying (P2O5) the threshold is at lower pH (need a higher surface charge)
At high pH the phenomena appear different

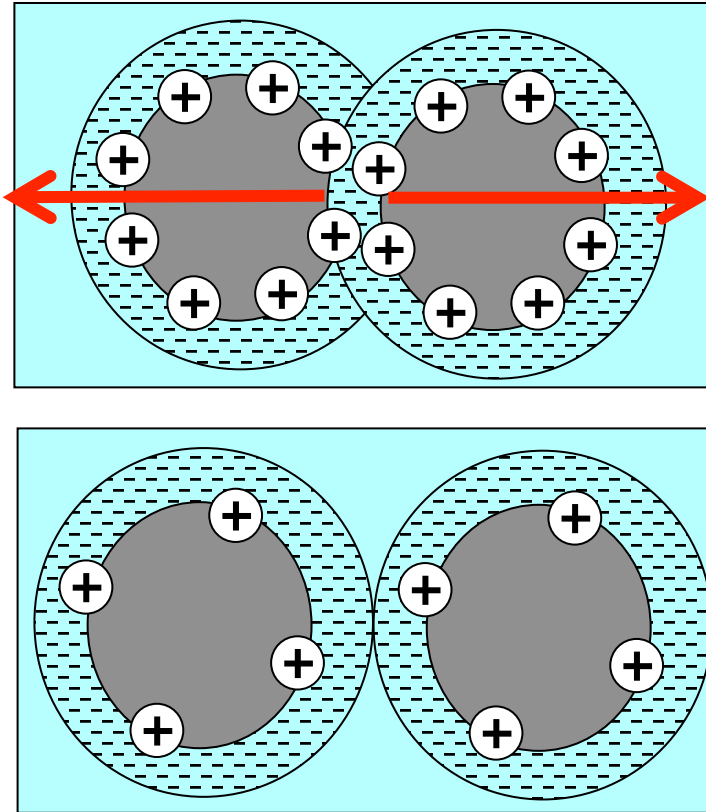
Results: redispersion thresholds

Fraction (%) of redispersed particles in the tumbling protocol, as a function of pH



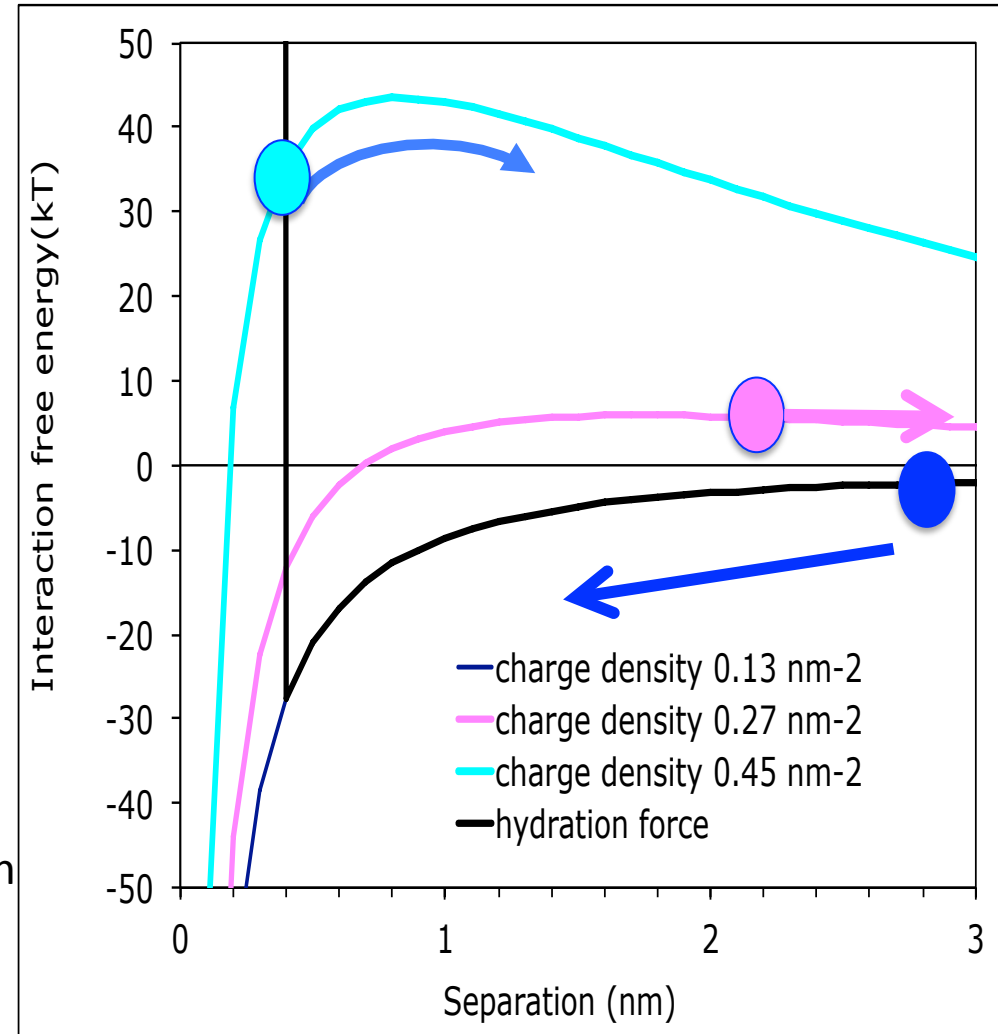
The threshold for redispersion is much further from the I.E.P than that for flocculation = it is a much harder process

Thresholds for aggregation and for redispersion



Charge density $> 0.27 \text{ nm}^{-2}$: no flocculation

Charge density $> 0.5 \text{ nm}^{-2}$: dispersion



→ The redispersion threshold is at a pH much further from the i.e.p.

→ Because the process takes place at much shorter surface-surface separations

Redispersation at rest vs. redispersion by tumbling

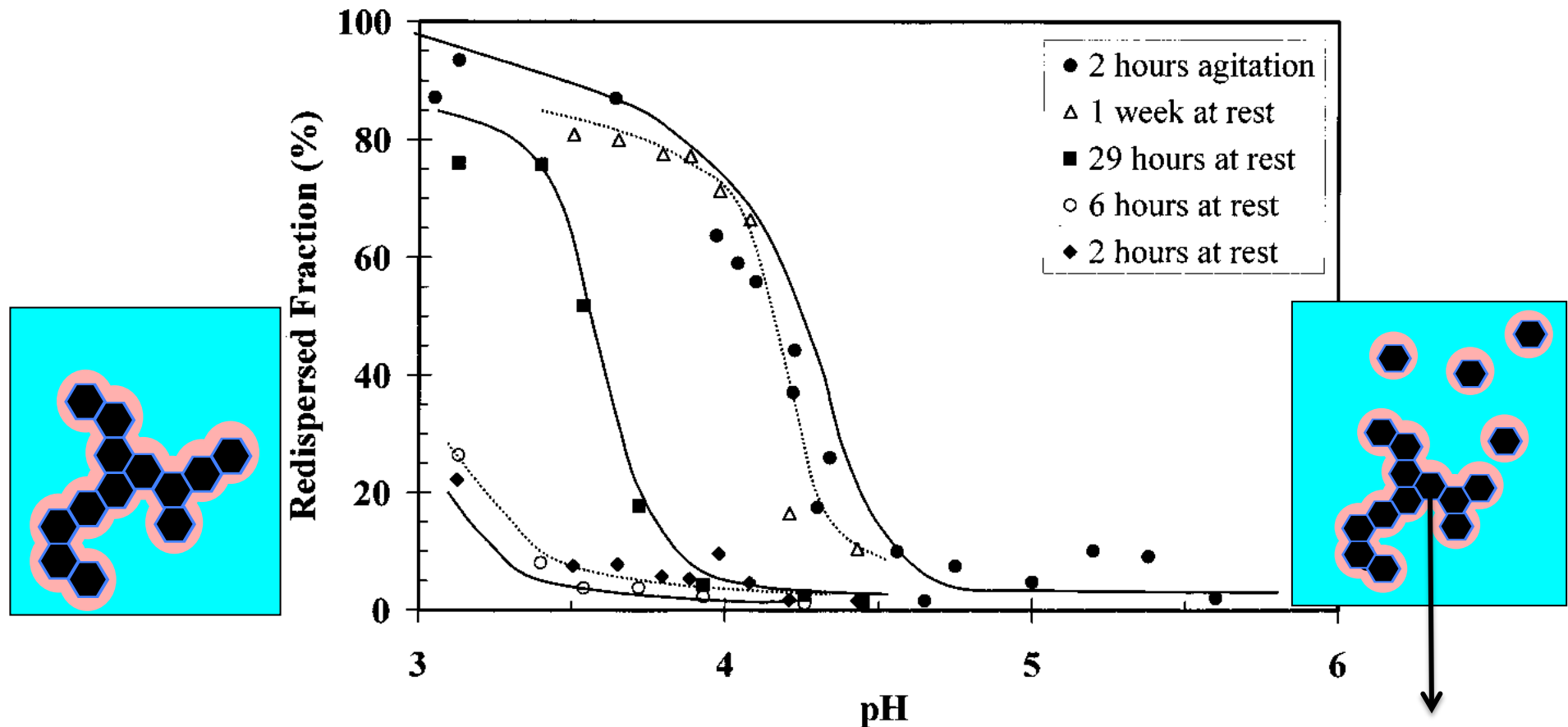


Figure 9. Redispersation kinetics of the powder with dry contacts, at rest. For comparison, the effect of redispersion by 2 h of tumbling is also shown (●).

2 hours tumbling = 1 week at rest

Summary of results – Quantitative interpretation?

There are sharp pH thresholds for the redispersion
On the cationic side, these thresholds are about i.e.p. – 4

The pH thresholds for redispersion at rest and by tumbling
are the same, only the kinetics differ

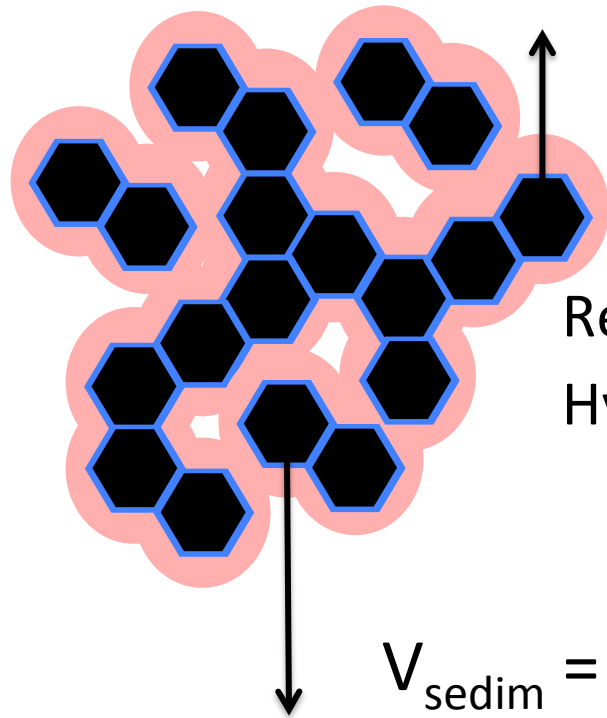
After drying (surfaces closer to each other),
the required pH is more acidic

At each threshold, the fraction of redispersed particles
varies in the same way

Can we make a model that reproduces these features
And predicts the correct kinetics?

What force erodes the aggregates?

Tumbling protocol: the aggregate (radius R) sediments constantly
A particle at its surface (radius r) is eroded by the hydrodynamic force

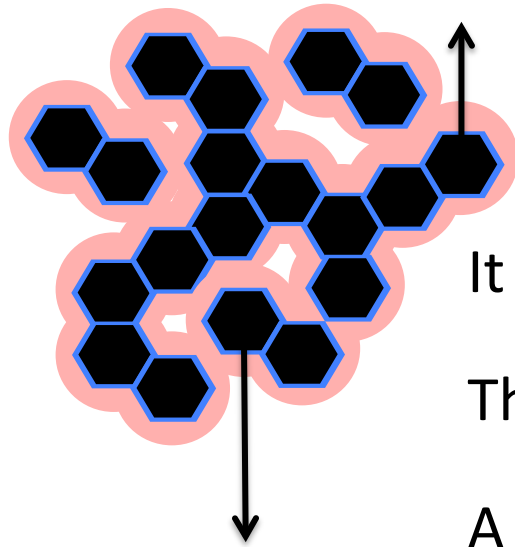


$$\text{Relative fluid velocity } V_r = (r/R) V_{\text{sedim}}$$
$$\text{Hydrodynamic force } F_{\text{hydro}} = 1.7 (6 \pi \eta r V_r)$$

$$V_{\text{sedim}} = (2/9) \Delta \rho R^2 (g/\eta)$$

$$\text{Combine } \rightarrow F_{\text{hydro}} = 1.7 \times (4/3) \times (\pi R \Delta \rho g r^2)$$

Condition for redispersion



The particle at the aggregate surface is submitted to:

$$F_{\text{hydro}} = 1.7 \times (4/3) \times (\pi R \Delta\rho g r^2) = 4.3 \times 10^{-14} \text{ N}$$

It is bound to the aggregate by a contact force F_{contact}

The particle is eroded if:

$$F_{\text{hydro}} = -\gamma F_{\text{contact}}$$

A large aggregate is eroded until a critical radius R_c :

$$R_c = \frac{3(-\gamma F_c)}{1.7 \times 4\pi\Delta\rho g r^2}$$

Condition for redispersion

A large aggregate of radius R is eroded until a critical radius R_c

Initial volume R^3 , final volume R_c^3

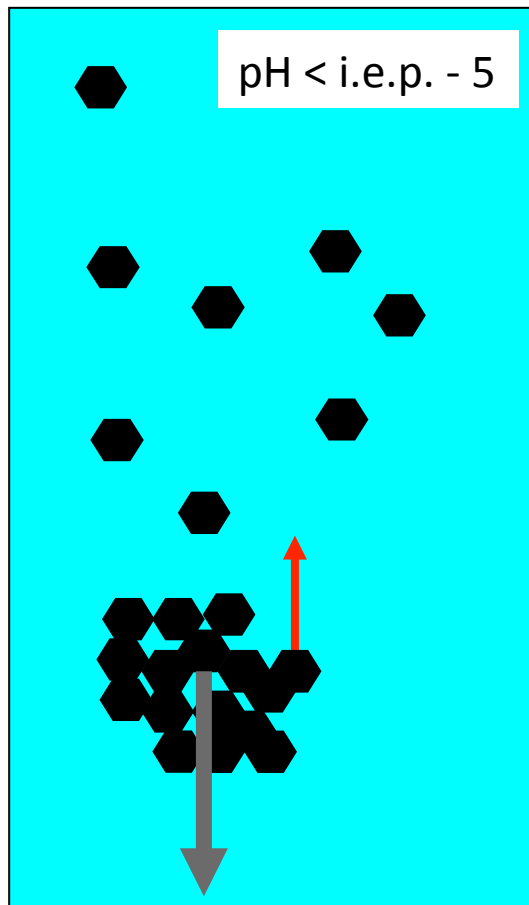
The eroded fraction of the aggregate volume is:

$$FR = 1 - \left(\frac{R_c}{R} \right)^3$$

$$= 1 - \left(\frac{3}{1.7 \times 4\pi\Delta\rho gr^2} \frac{\gamma}{R} (-F_c) \right)^3$$

Hydrodynamic process

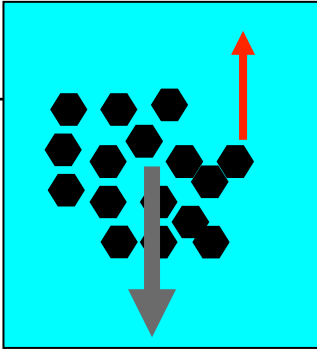
Aggregate cohesion



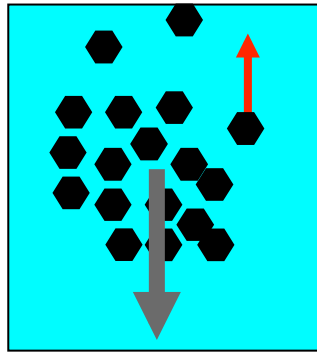
Keep hydrodynamics the same, change pH

→ Eroded fraction = redispersed fraction = FR

Step-like effect of pH on redispersion

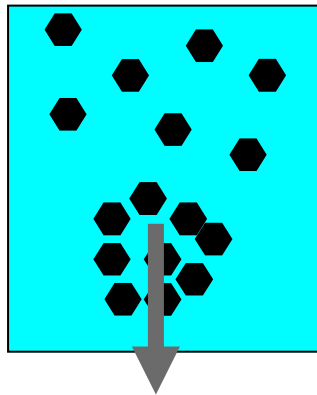


Start at high pH \rightarrow high cohesion,
all aggregates have $R < R_c$, none are eroded



Threshold: R_c = size of largest aggregates
This occurs at a pH such that the contact force is:

$$F_C^* = \frac{1.7 \times 4\pi}{3} \Delta\rho g r^2 \frac{R}{\gamma}$$



Beyond this threshold, any decrease in pH causes
the erosion of a large fraction of the aggregates

This redispersed fraction reaches 100% when the
critical radius reaches the particle radius r

The contact force

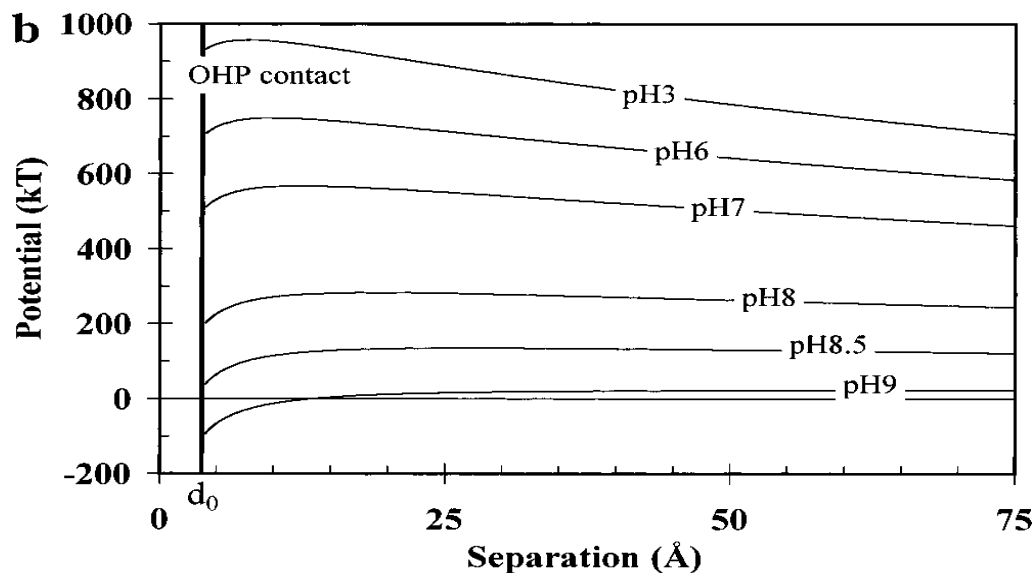
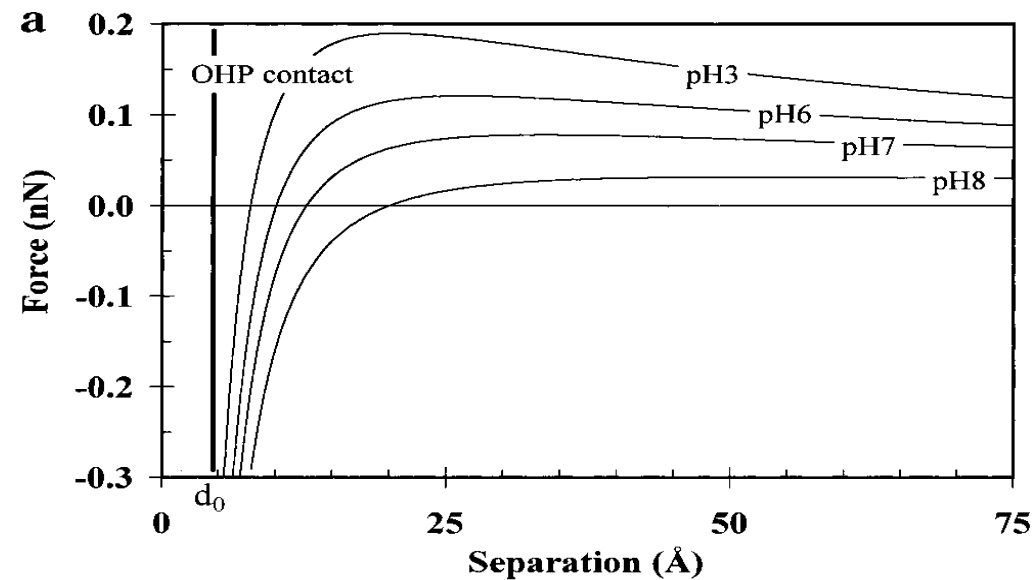


Figure 14. Force and potential of interaction between particles versus pH, calculated with constant charge boundary conditions. Hamaker constant $A = 9kT$, ionic strength $= 5 \times 10^{-5}$ M. The origin of separation corresponds to the solid/solid contact. Accordingly, the separation at which the OHP on each interface are in contact is 4 Å.

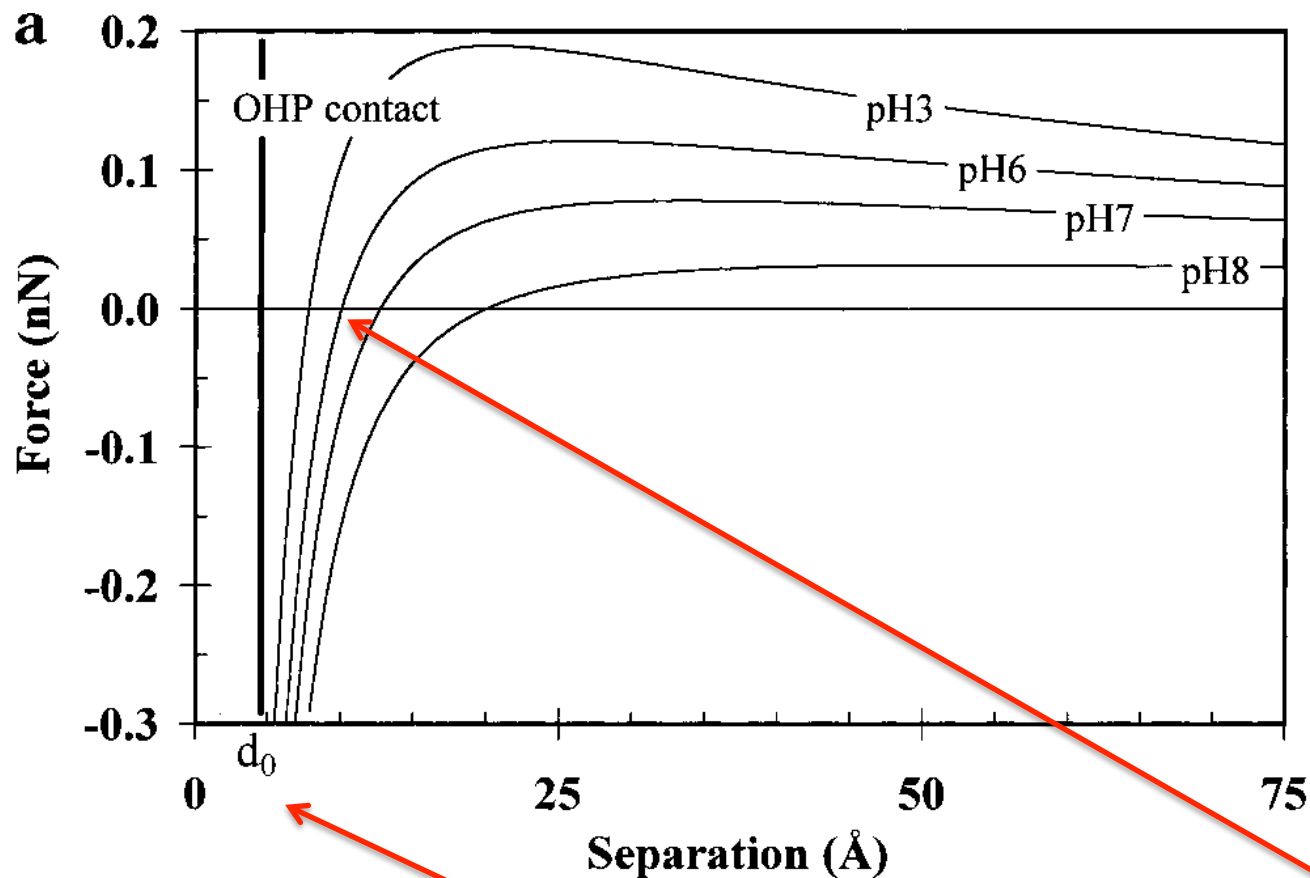
DLVO forces
VdW attractions
+ ionic repulsions

→ Reproduce the
flocculation threshold

But not the redispersion
Threshold:

The contact force is
10000 times too strong

Without hydration forces, the contact force is too strong



Minimal separation is $d_0 = 4 \text{ Å}$,
Adhesive force $F_{\text{contact}} \approx -1 \times 10^{-9} \text{ N}$
But threshold at $F_{\text{hydro}} = 4 \times 10^{-14} \text{ N}$

Minimal separation is $d_0 = 8 \text{ Å}$,
Set by hydration forces

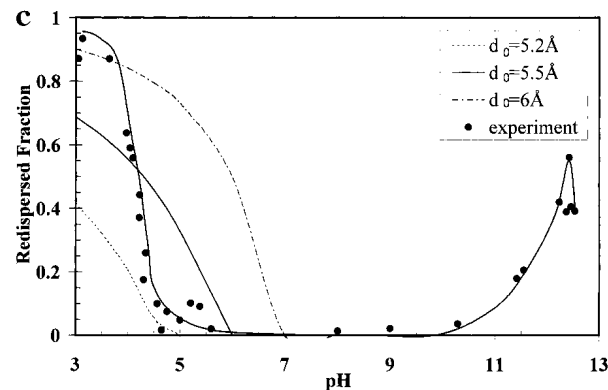
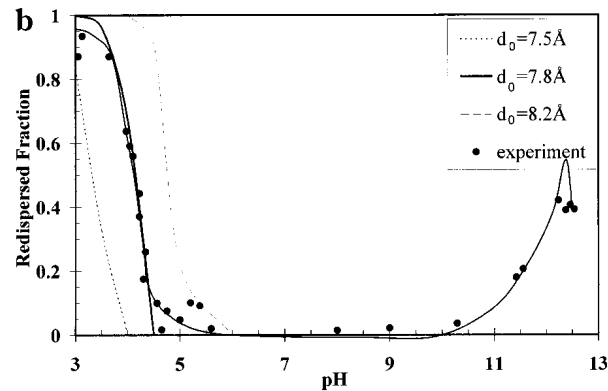
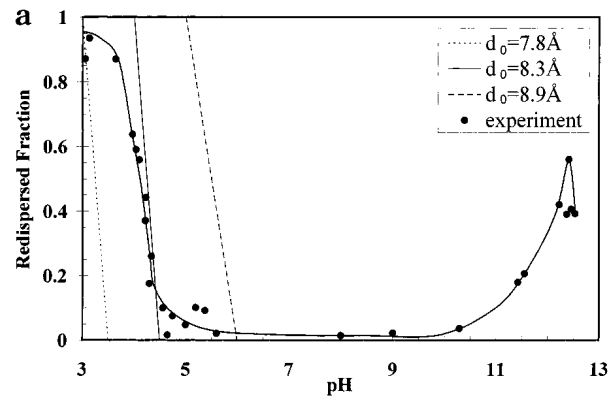


Figure 15. Theoretical redispersion curves obtained for different parameter sets (γ/R , d_0). Constants used: $A = 9kT$, $r = 75$ nm, salt $= 5 \times 10^{-5}$ M. The points are the experimental results for the powders with dry contacts. The γ/R values are, respectively, (a) 2 m^{-1} , (b) 20 m^{-1} , (c) 200 m^{-1} .

Predicted and measured redispersion

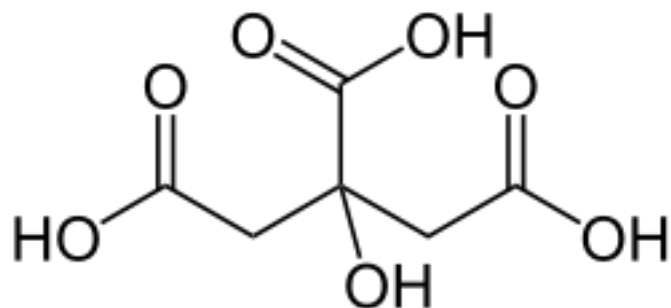
Inefficient hydrodynamics $\gamma/R = 2 \text{ m}^{-1}$
 Need to postulate a strong hydration $d_0 = 8.3 \text{ Å}$
 Even so, the exp results are poorly reproduced

Efficient hydrodynamics $\gamma/R = 20 \text{ m}^{-1}$
 Need to postulate a hydration $d_0 = 7.8 \text{ Å}$
 The exp results are well reproduced

Super-efficient hydrodynamics $\gamma/R = 200 \text{ m}^{-1}$
 Need to postulate a hydration $d_0 = 5.5 \text{ Å}$
 The exp results are not reproduced

We determine:
 The efficiency of hydrodynamic erosion
 The strength of surface-surface adhesion

Surfaces with adsorbed carboxylic acids



Citric acid

At neutral to high pH:
 $\text{C}(\text{CH}_2 \text{COO}^-)_2 (\text{COO}^-)\text{OH}$
Binds to alumina surfaces
Changes the surface charge

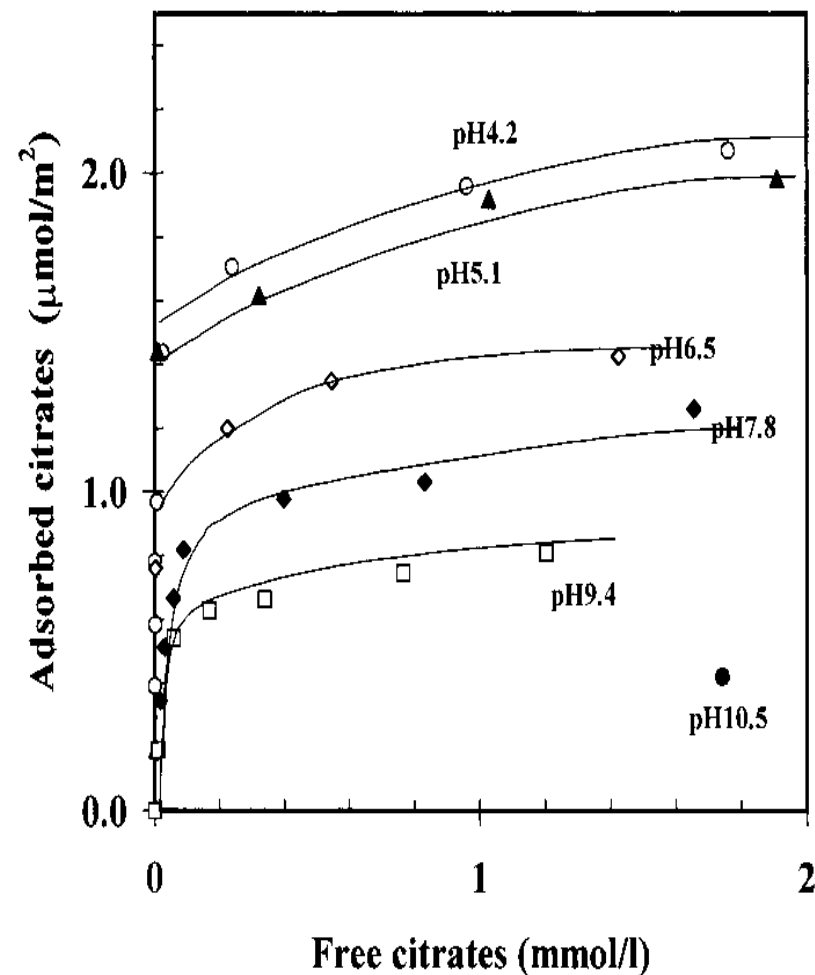
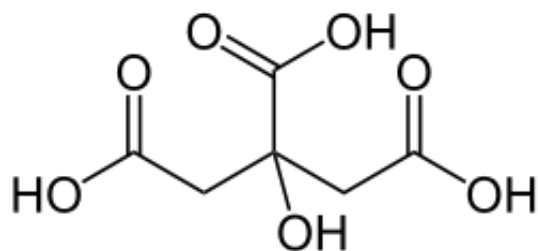


Figure 2. Equilibrium adsorption isotherms of citric acid onto alumina for different pH values.

Surfaces with adsorbed carboxylic acids



At high amounts of adsorbed citrate negatively charged particles can remain dispersed at neutral pH

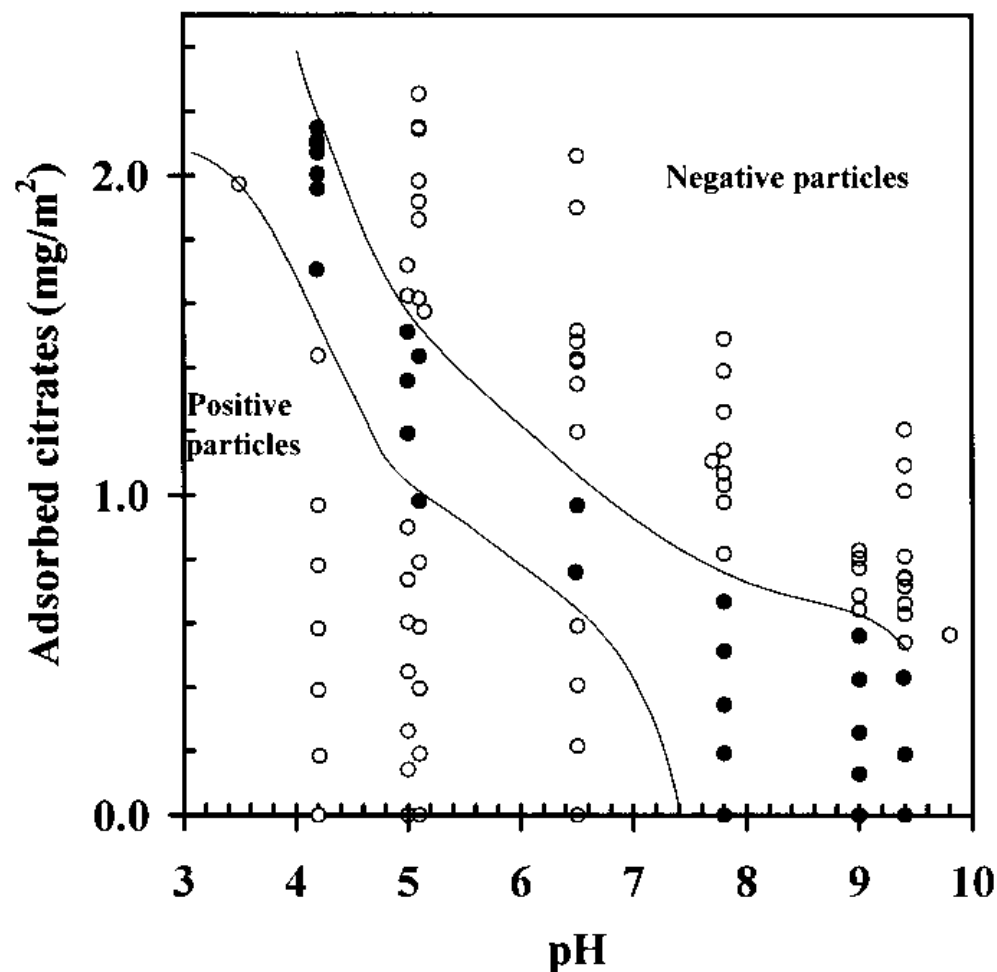
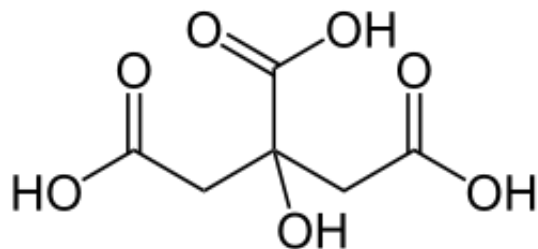


Figure 6. Stability diagram versus pH and adsorbed amount of citric acid: ○, stable dispersion; ●, flocculated suspension.

Surfaces with adsorbed carboxylic acids



At high amounts of adsorbed citrate negatively charged particles can be redispersed at basic pH = i.e.p. + 5

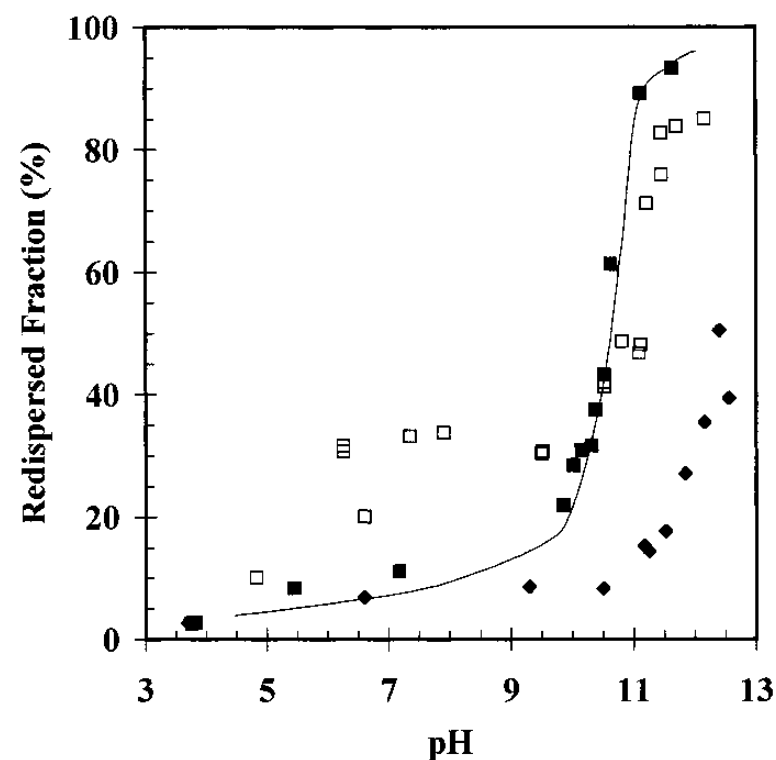
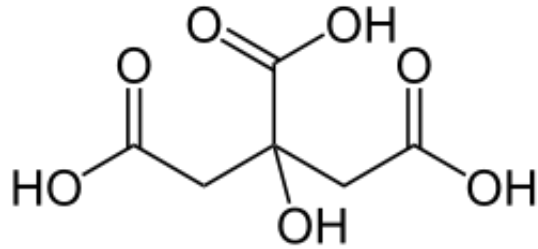


Figure 11. Redispersion in a citric acid solution (0.2 mM) of the alumina powder dried in the presence of ligands with P_2O_5 . The corresponding surface coverage during drying are (◆) no citric acid, (■) citric acid dried at pH 9 ($0.6 \mu\text{mol}/\text{m}^2$), and (□) citric acid dried at pH 5 ($1.5 \mu\text{mol}/\text{m}^2$).

Surfaces with adsorbed carboxylic acids



Surfaces that are at a larger separation can be separated with smaller ionic repulsions

Or:

Surfaces that carry a higher charge can be separated from a shorter minimal separation.

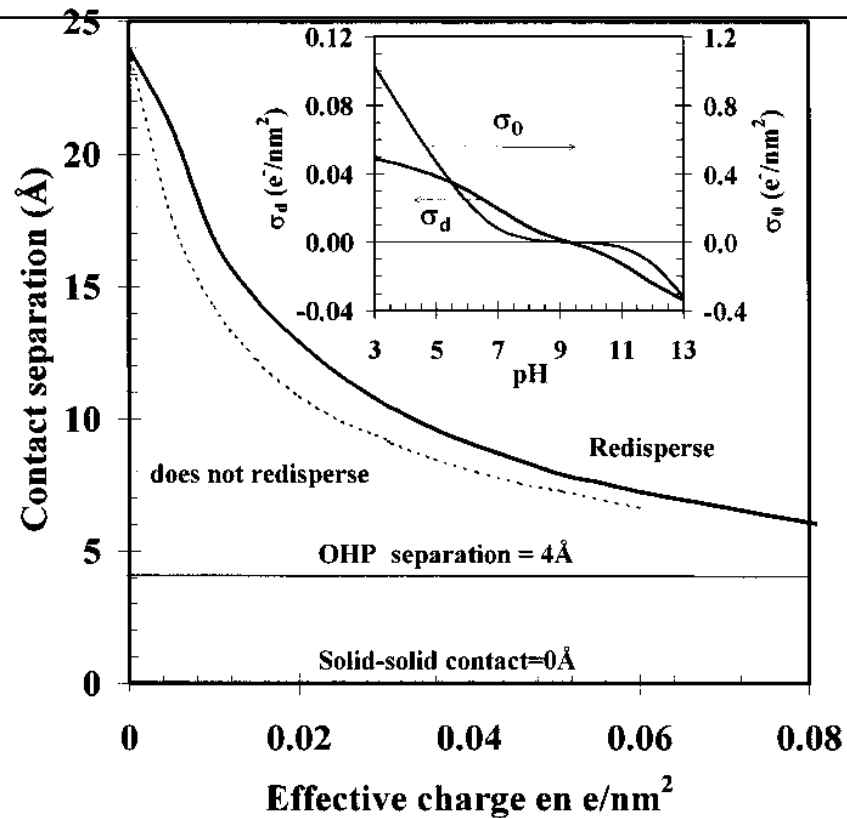


Figure 14. Redisperison limits of alumina powders in the axis effective charge distance of contact separation d_0 . The diameter of the particle is 150 nm, and the Hamaker constant is equal to 9 kT. The two lines report for two different ionic forces the distances d_0 for which, for the given effective charge, the contact force is equal to -0.041 nN, which was shown to be the force threshold for redispersion in the preceding paper: (continuous line) $I = 1$ mM; (dashed line) $I = 0.05$ mM. The insert shows the variation of the structural and effective surface charge for bare alumina particles (extracted from ref 4).

Redisperison of particles with adsorbed polycarboxylates

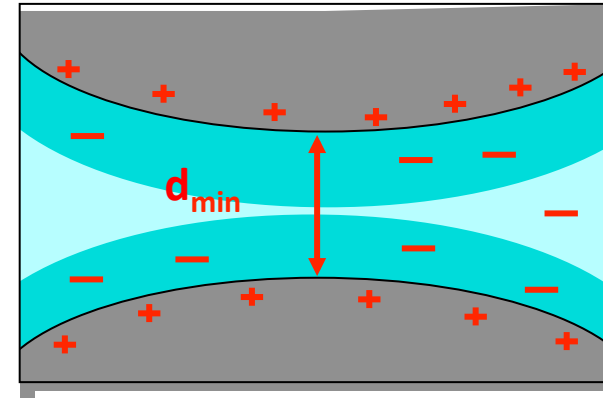
Bare surfaces:

Threshold for redispersion at pH =5

Calculate repulsions, attraction

Calculate d_{\min} = range of hydration forces

$$\rightarrow d_{\min} = 8 \text{ \AA}$$



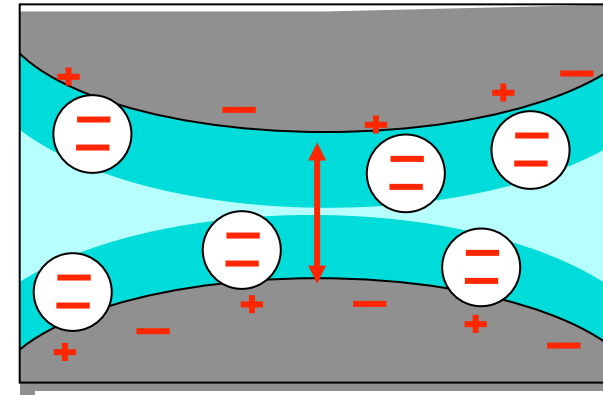
Surfaces with adsorbed molecules (sp

Threshold for redispersion at pH =10

Calculate repulsions, attraction

Calculate d_{\min} = range of hydration for

$$\rightarrow d_{\min} = 8 \text{ \AA}$$



Maintain larger separations \rightarrow “spontaneous” redispersion at neutral pH?

Conclusions

With very tight protocols (and very cheap experiments), the efficiency of redispersion processes can be measured accurately

Alumina particles can be dispersed in water, aggregated, dried and redispersed in water through the application of very weak forces or even no forces at all.

The efficiency of redispersion is related to the minimal separation of surfaces
Even particles that been dried have retained one water layer on their surfaces

The redispersion occurs when repulsive forces (ionic + hydration) overcome VdW attractions

Spontaneous dispersion has the same thresholds as redispersion by slow shear, but much slower kinetics

Adsorbed molecules (polyions) may change the range of pH for redispersion