Introduction to Colloids or ‘What did the Romans know about them?’

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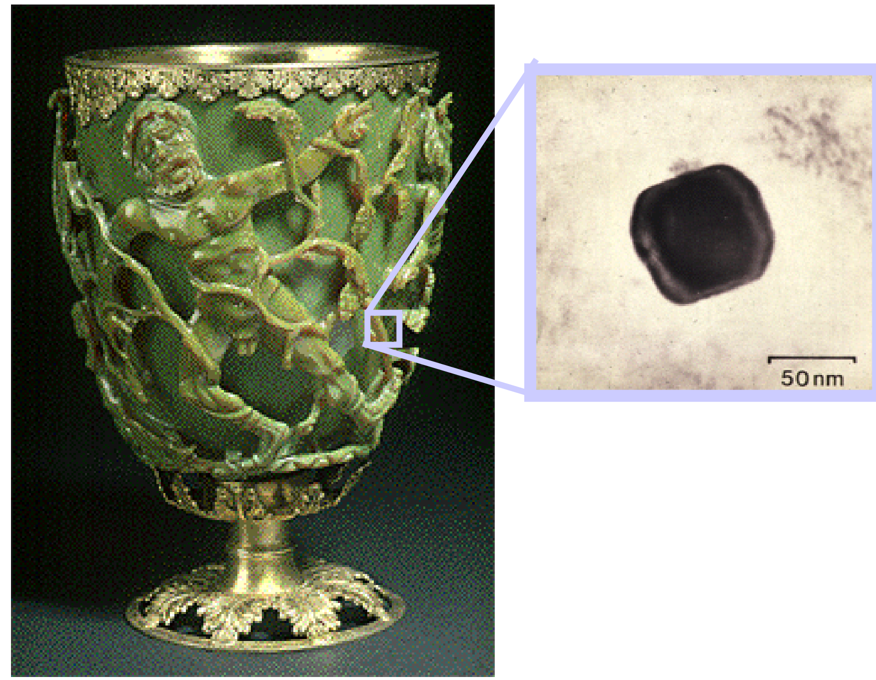
What did the Romans really know about Colloids?

in reflection

in transmission



Lycurgus Cup

The secret: colloidal gold

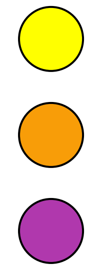
But what are colloids?

Simple liquids:

Argon

Krypton

CH_4, SF_6, CCl_4, …



$\langle R \rangle \sim 1$ Å

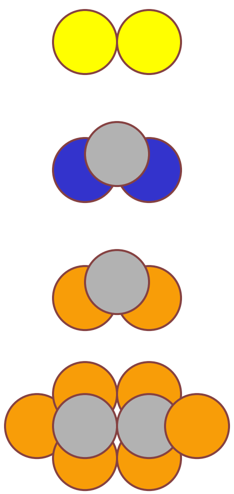
Less simple liquids:

N_2

CO_2

CS_2

C_2H_6, …



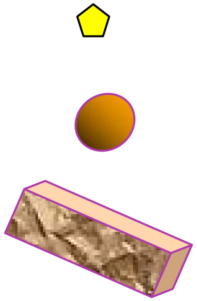
But what are colloids?

Heavy “liquids”:

Sand grains

Pebbles

Bricks, …

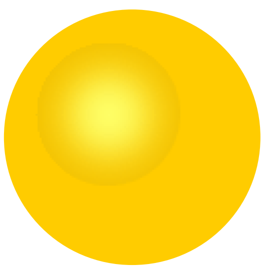


<R> > 1 mm

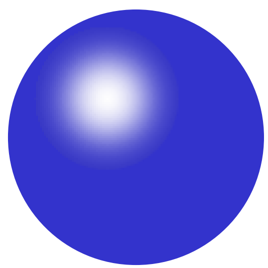
But what are colloids?

1860's: Thomas Graham defined that any object of size between **nm** and **μm** are colloids.

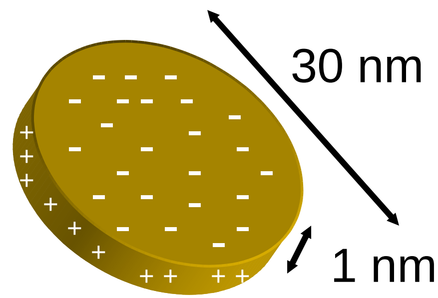
- They cannot be separated by filtration or gravity alone!



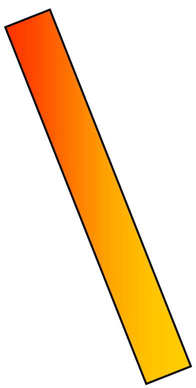
glass (silica)



plastic (PMMA)



clay (Laponite)



Virus (TMV)

T. Graham "On the Properties of Silicic Acid and Other Analogous Colloidal Substances", *J. Chem. Soc. London*, 1864, 17, 318-323.

What distinguishes colloids from atoms?

Is it only the size?

1nm - 1μm

Distinction between small molecules and colloids:

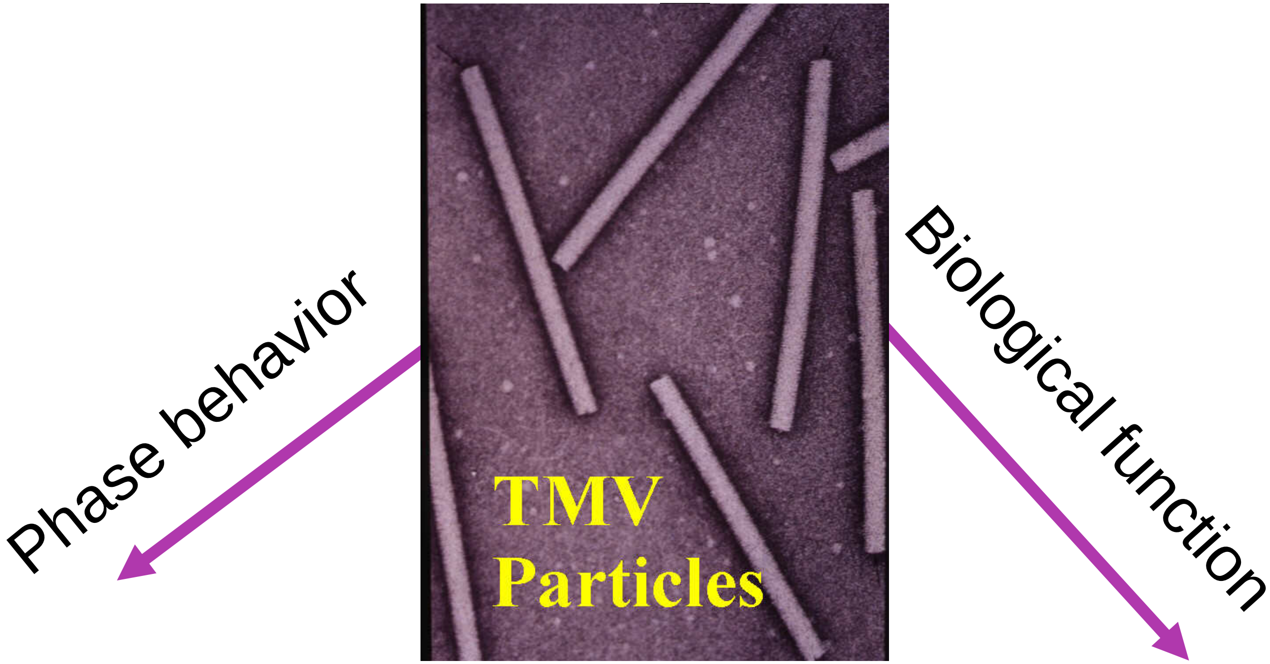
To understand the behavior of colloids we do **NOT** need to know their structure in atomic detail.

Consequences:

What distinguishes colloids from atoms?

Molecules may behave like colloids in **SOME** respects, but not in others…

Example: TMV (tabaco mosaic virus)



Colloid

Only overall shape, charge and flexibility matter

Not a colloid…

Precise sequence matters…

Question: Is a pebble a colloid?

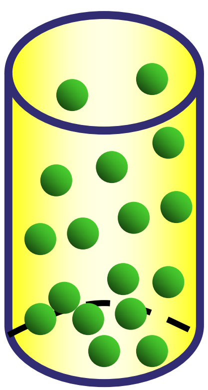
Colloids can be described by statistical mechanics:

Relevant energies $\boldsymbol{O}(k_B T)$

Example: barometric height distribution

$$P(h) = P_0 \exp(-mgh/k_B T)$$

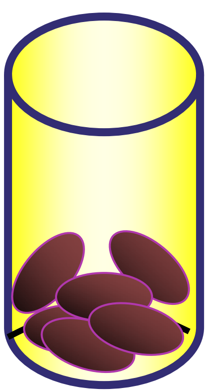
colloids



$$<h> = k_B T$$

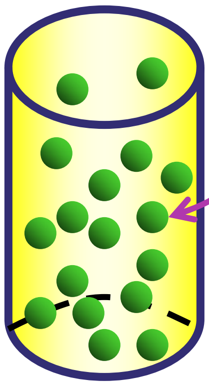
Should be larger than particle size.

pebbles



Colloids must be between pebbles and colloids

For colloids:



$\langle h \rangle = k_B T/mg = k_B T/(4\pi/3\ \Delta\rho\ R^3\ g)$

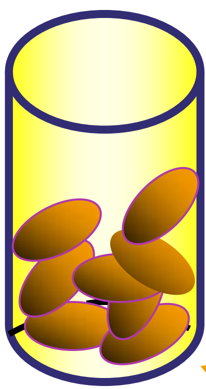
Must be of order R.

$$k_B T/(4\pi/3\ \Delta\rho\ R^3\ g) = R$$

$$k_B T/(4\pi/3\ \Delta\rho\ g) = R^4$$

$$\Rightarrow 2R = \sigma \approx 1\mu$$

on earth…

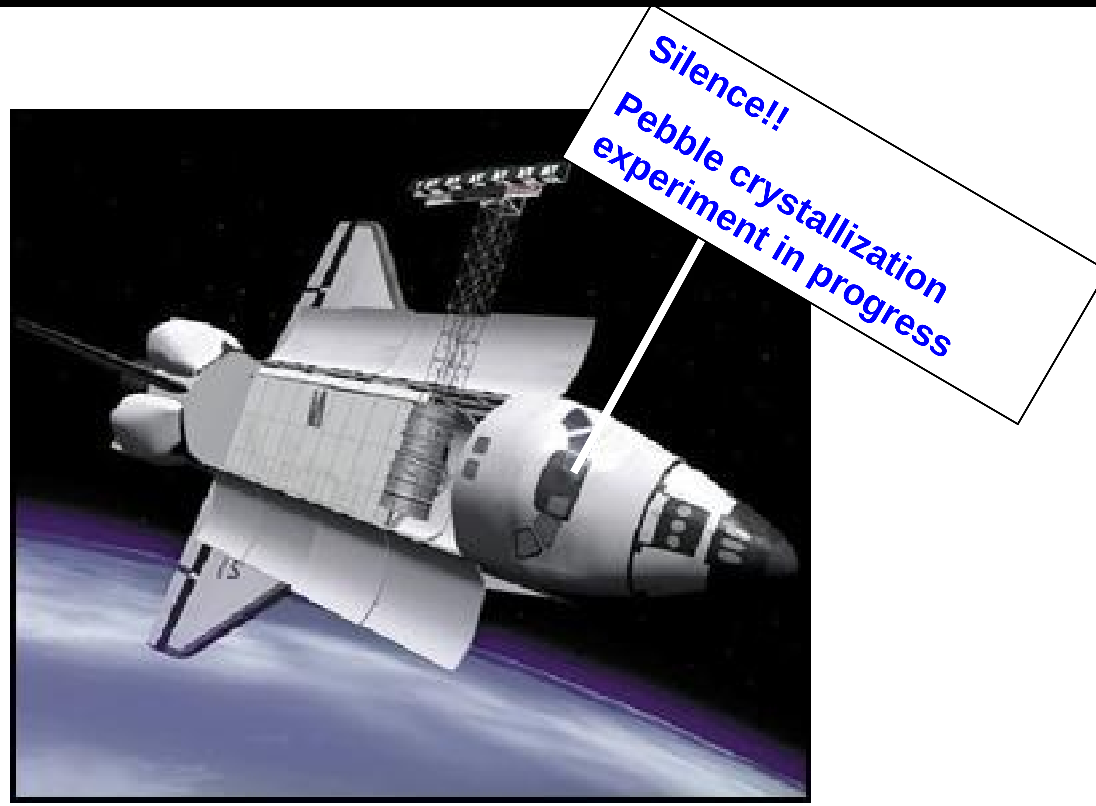


For pebbles (e.g. 50 g)

$\langle h \rangle = k_B T/\mathrm{mg} = 10^{-18}$ cm

on earth…

Does a pebble behave like a colloid in space?



To explore possible structures, the colloids must diffuse at least their own radius during an experiment:

$$2Dt_{exp} = R^2$$,but $$D = \frac{kT}{6\pi\eta R}$$

Therefore:

Colloids must be between pebbles and colloids

Therefore:

$t_{exp} \approx 3\pi\eta R^3/kT$

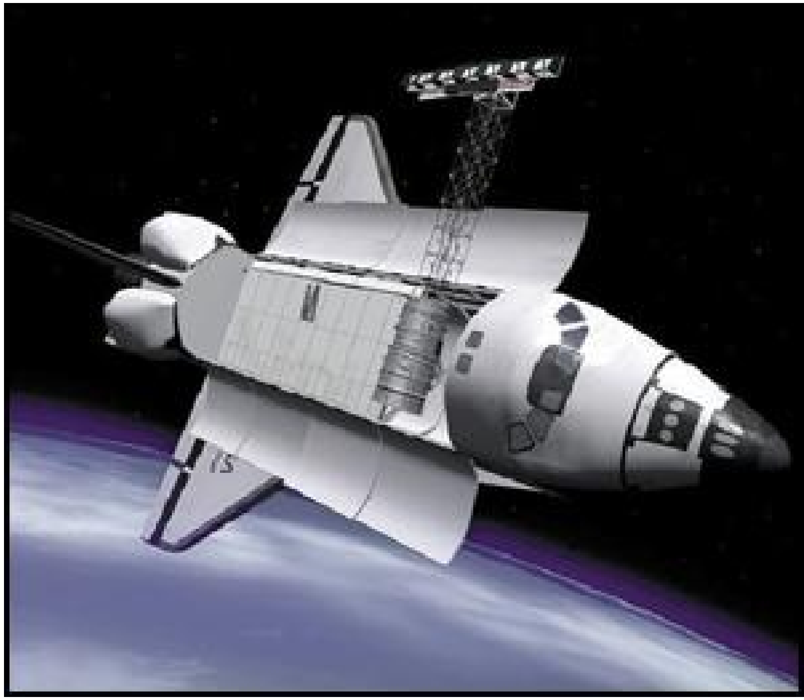
For 1 μm colloids in water:

$t_{exp} \approx 1$ sec

But

For 1 cm pebbles in water:

$t_{exp} \approx 10^{12}$ sec !!!

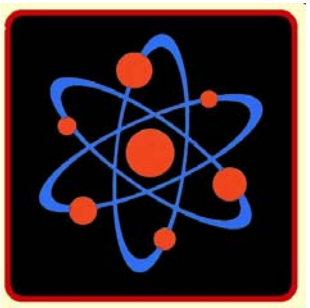


Colloids must be between pebbles and colloids

Hence, the physics of colloids is …

… obviously different to pebbles …

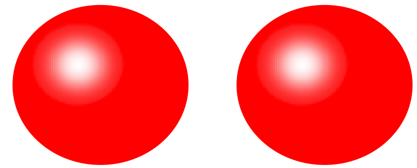
… but also different to atoms,



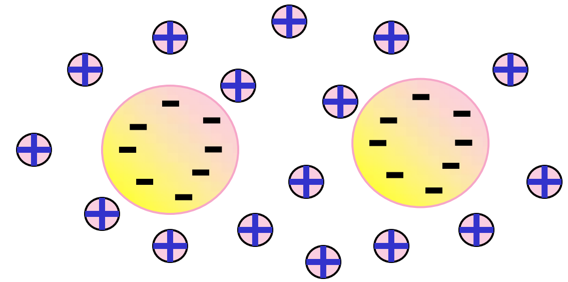
because of the interactions between them…

Interactions Between Colloids

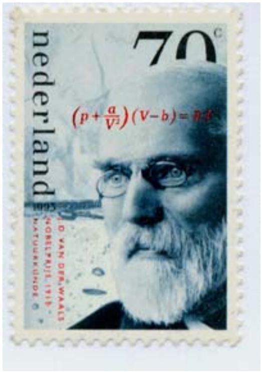
1) "hard core" repulsion



2) Coulomb interactions



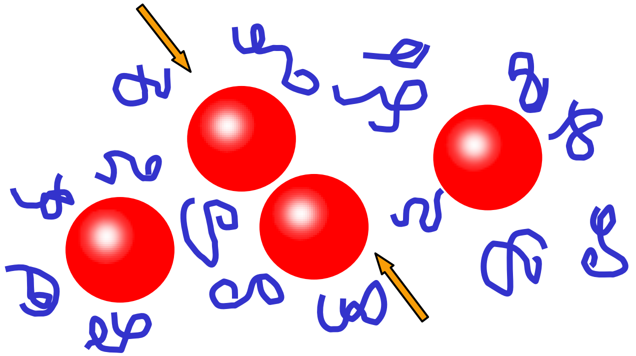
3) Van der Waals interactions



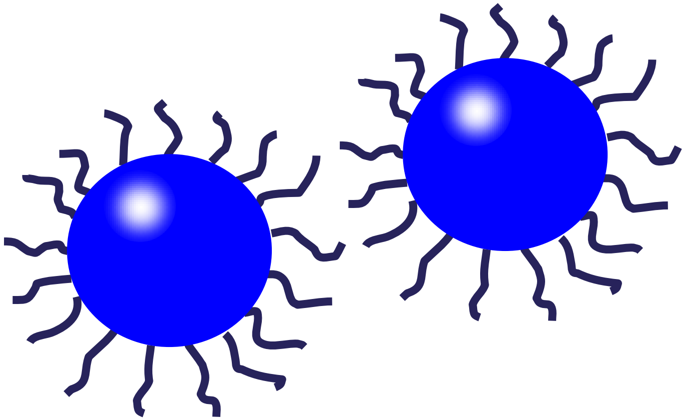
Interactions between colloids

Forces between colloids

4) Depletion attraction

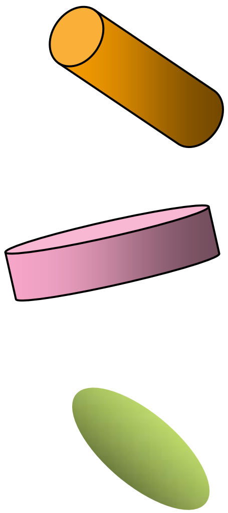


5) Steric stabilization



1) Hard sphere repulsion

Colloids have a shape.



(this is not obvious.

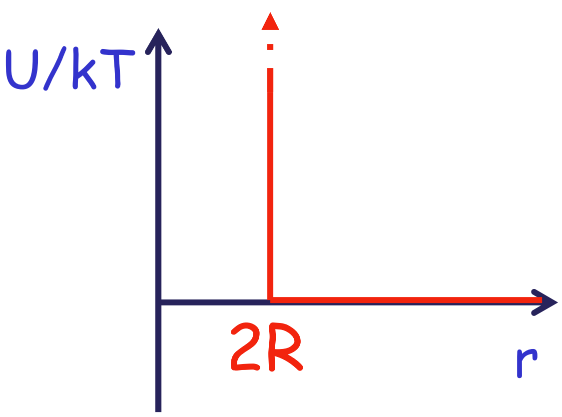
small molecules usually do not have a shape.)

Why do colloids have a shape?

a) **They are fairly solid.**

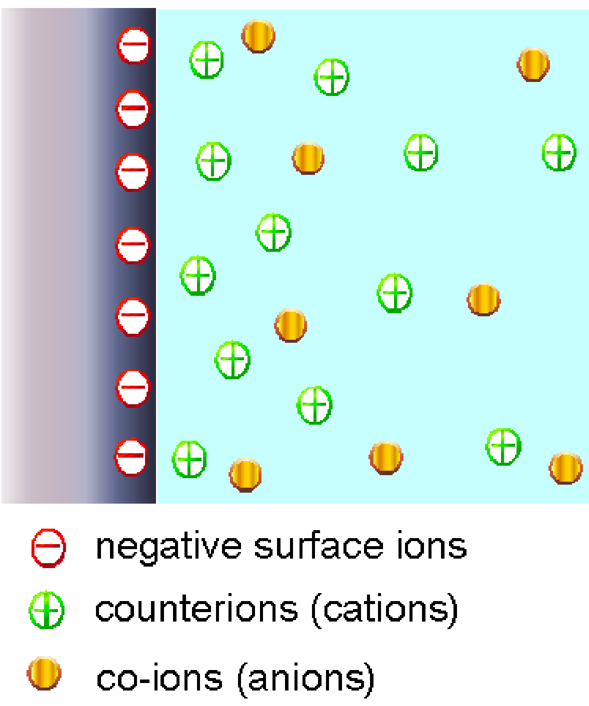
b) **They cannot interpenetrate.**

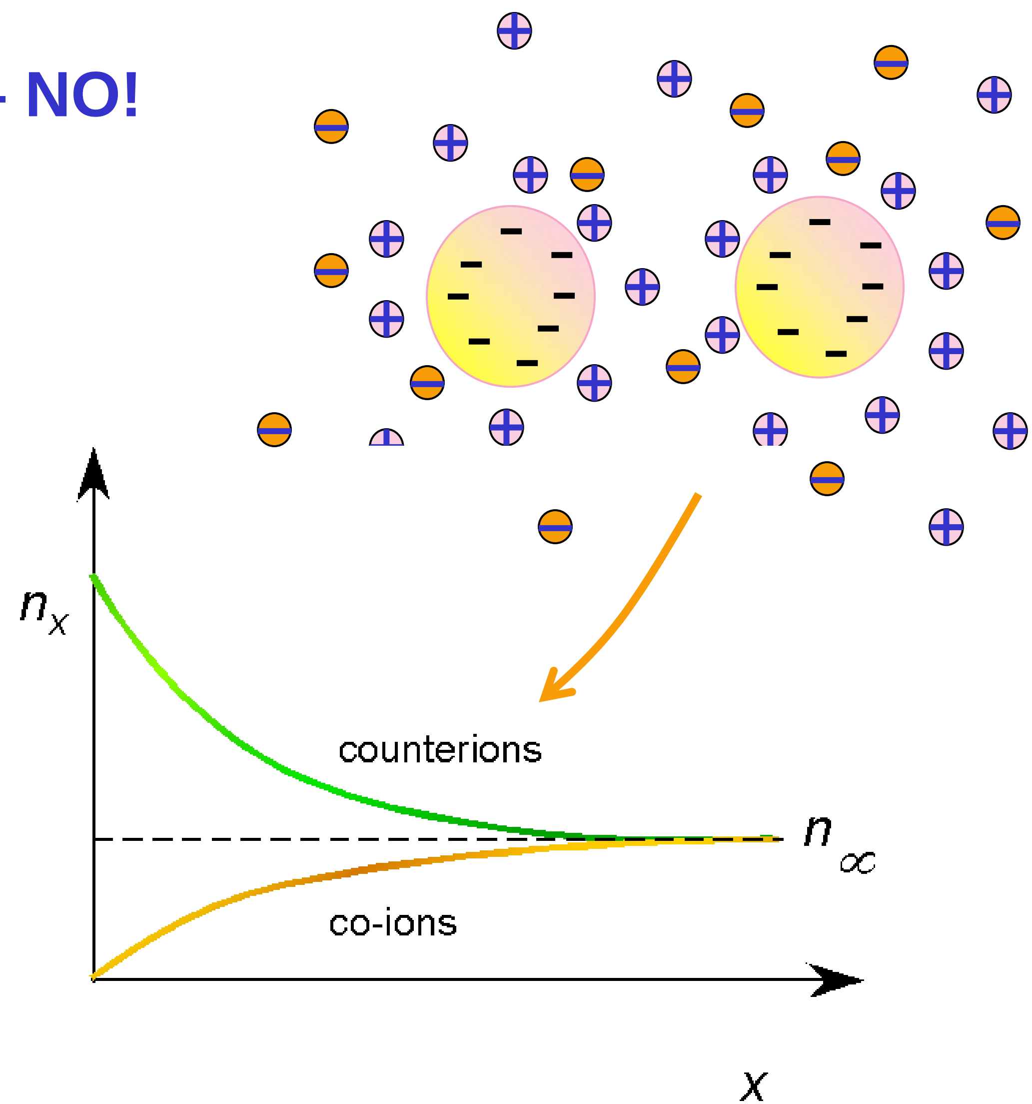
- **Pauli**
- **short-ranged Coulomb repulsion**
- **“steric” stabilization**



2) Coulomb interactions

Straightforward? – NO!

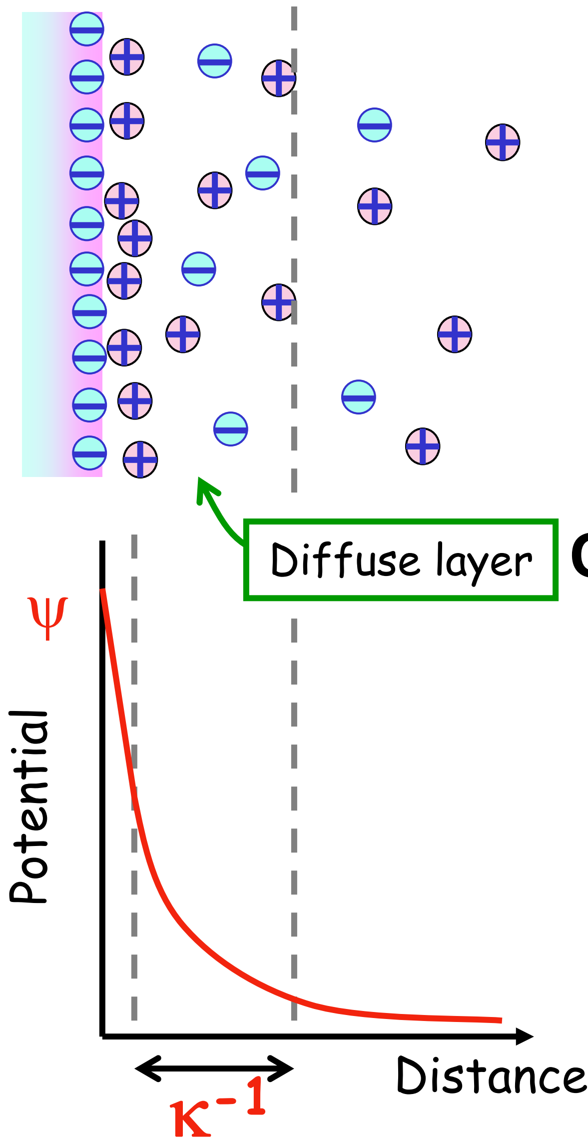




2) Coulomb interactions

The Electric Double-Layer:

with Debye screening length



$$\kappa^{-1} = \sqrt{\frac{4\pi}{\epsilon kT}\sum_i \rho_i q_i^2}$$

ε = dielectric const.

Colloid-Colloid pair interactions:

Yukawa pot.

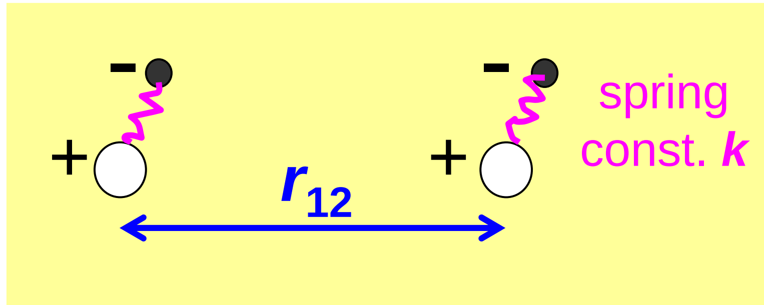
$$U(r) = \left(\frac{Qe^{\kappa R}}{1+\kappa R}\right)^2 \frac{e^{-\kappa r}}{\epsilon r}$$

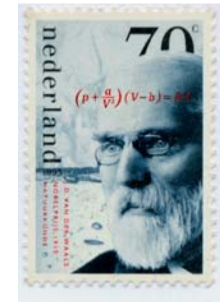
purely repulsive & long ranged & solvent mediated

- Essential for stability of cells.
- Responsible for swelling of clays.

3) Van der Waals or dispersion forces

Atoms:

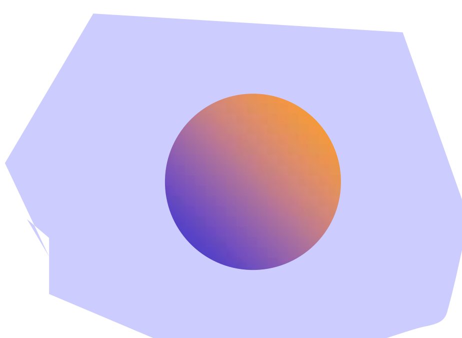




$$U_{disp} \approx -\frac{3\alpha_1\alpha_2 h\sqrt{\nu_1\nu_2}}{4\pi r_{12}^6} \equiv -\frac{C_{disp}}{r_{12}^6}$$

Addition of 1 colloid:

Change in dispersion interaction!

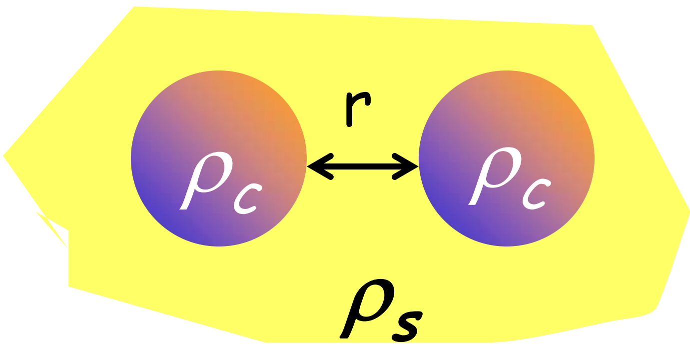


$$\Delta U_{disp} \approx -\rho_s\alpha_s(\underbrace{\rho_c\alpha_c - \rho_s\alpha_s})$$

Replaces solvent by colloid

3) Van der Waals or dispersion forces

2 colloids in solution:

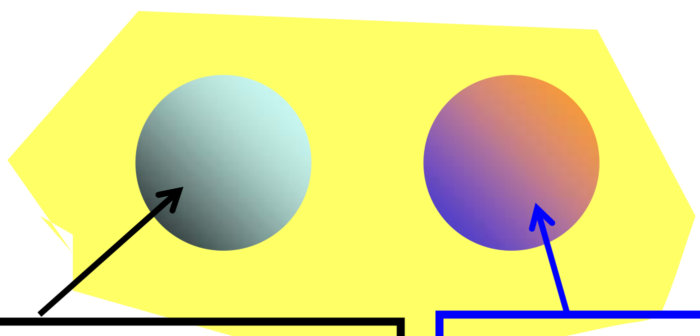


Interaction

$$\Delta U_{disp} \approx -(\rho_c\alpha_c - \rho_s\alpha_s)^2$$

attractive

However: can be repulsive for **2 different** colloids



$(\rho_c\alpha_c)_{\mathbf{1}} < (\rho_s\alpha_s)$

$(\rho_c\alpha_c)_{\mathbf{2}} > (\rho_s\alpha_s)$

→ **repulsive**

3) Van der Waals or dispersion forces

Special case: $\rho_C \alpha_C = \rho_S \alpha_S$

$\Rightarrow$ **No dispersion forces.**

Recall: Clausius-Mosotti $\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} \rho\alpha$

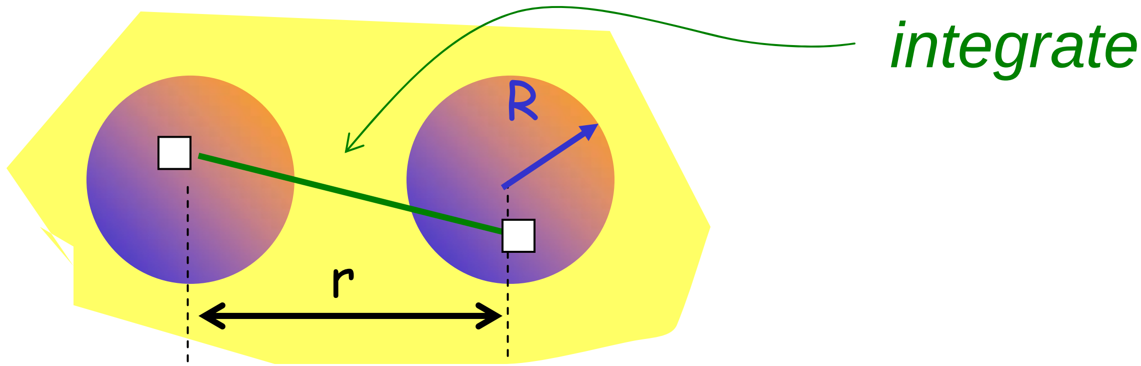
Hence $\rho_c \alpha_c = \rho_s \alpha_s$ implies $\boldsymbol{n_c = n_s}$

"refractive index matching"

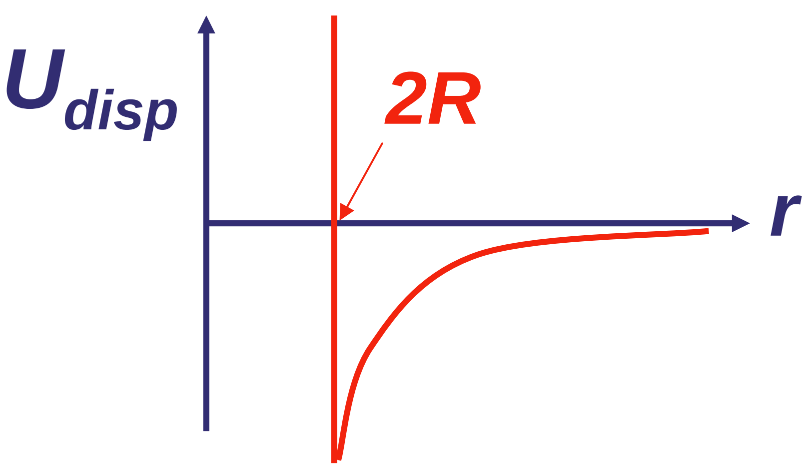
Essential in light scattering and confocal microscopy experiments.

3) Van der Waals or Dispersion forces

How does U_{disp} depend on r ?



$$U_{disp}(r) \approx -\frac{A}{6}\left(\frac{2R^2}{r^2-4R^2}+\frac{2R^2}{r^2}+\ln\left(\frac{r^2-4R^2}{r^2}\right)\right)$$



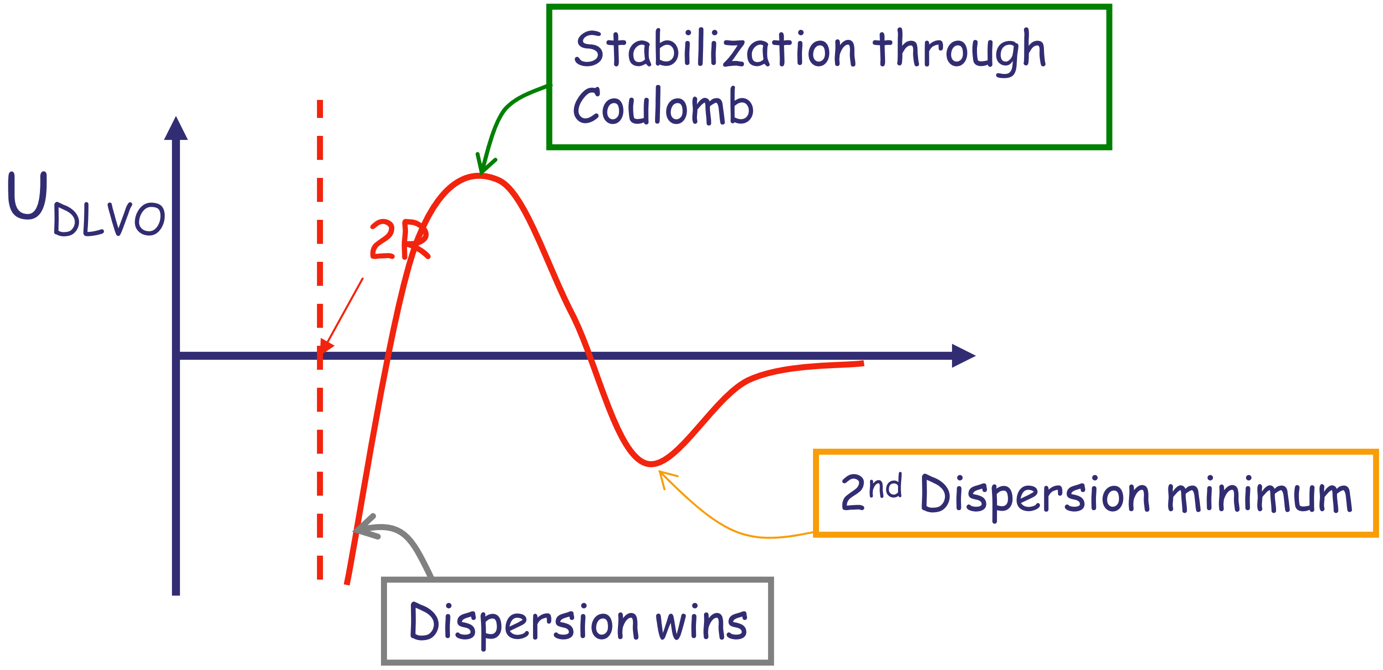
A = "Hamaker constant"

$\leftrightarrow (\rho_c\alpha_c - \rho_s\alpha_s)^2$

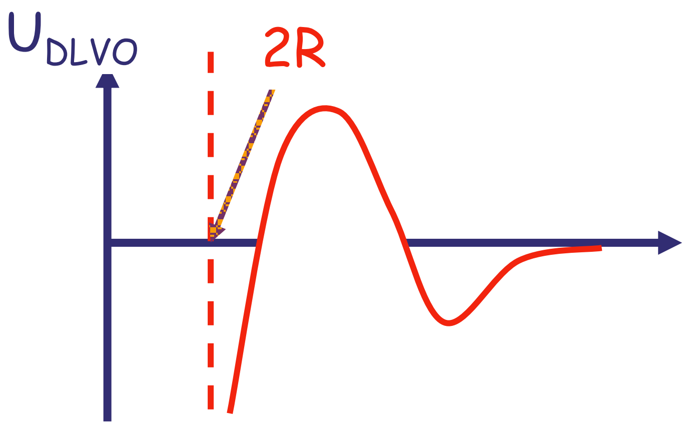
DLVO forces

(Derjagin, Landau, Verweij & Overbeek)

$$U(r) = \left(\frac{Qe^{\kappa R}}{1+\kappa R}\right)^2 \frac{e^{-\kappa r}}{\epsilon r} - \frac{A}{6}\left(\frac{2R^2}{r^2-4R^2} + \frac{2R^2}{r} + \ln\left(\frac{r^2-4R^2}{r^2}\right)\right)$$



DLVO forces



If:

Coulomb barrier >> *kT*

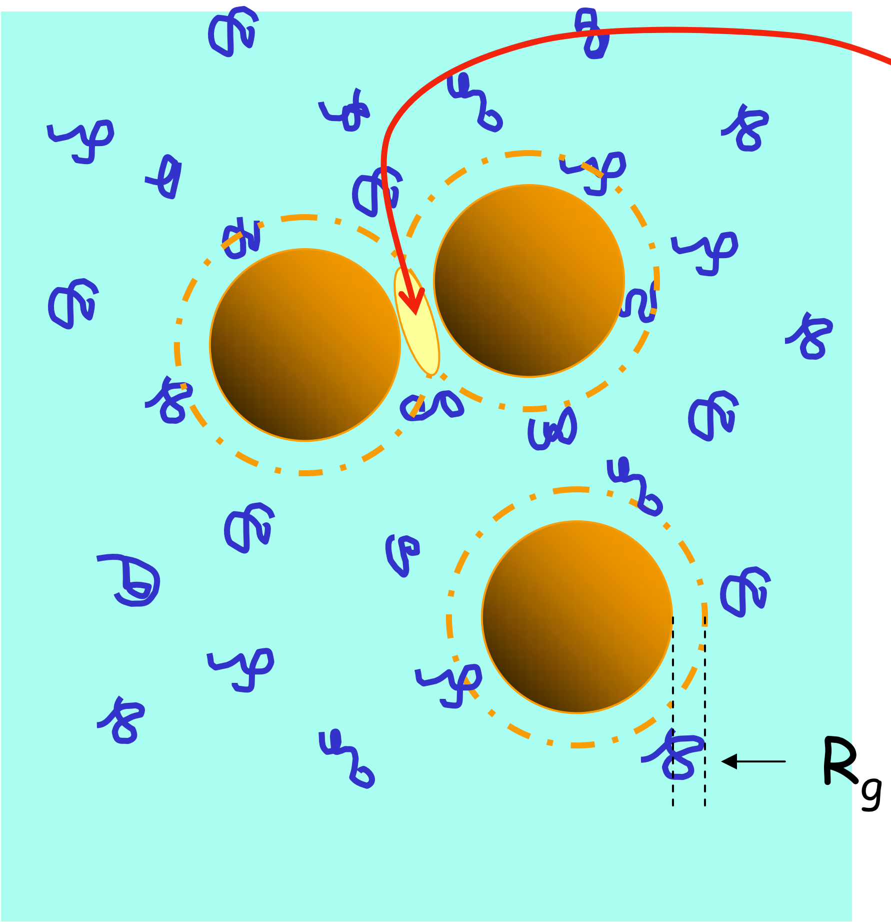
→ (meta)stable system!

<u>Otherwise:</u> Irreversible Aggregation

4) Depletion interactions

Consider:

- Colloid with pure hard-core repulsion
- Dispersed in solution
- Containing non-adsorbing polymers



1) Inside vol. $\Delta V \Rightarrow$ no polymer (Entropy loss!)

2) Osmotic pressure (purely repulsive)

3) Results in attraction

In Summary:

Colloids are like giant atoms,

BUT:

1. **We can control their interactions,**
2. **And their size (distribution),**
3. **And their shape.**

In Summary:

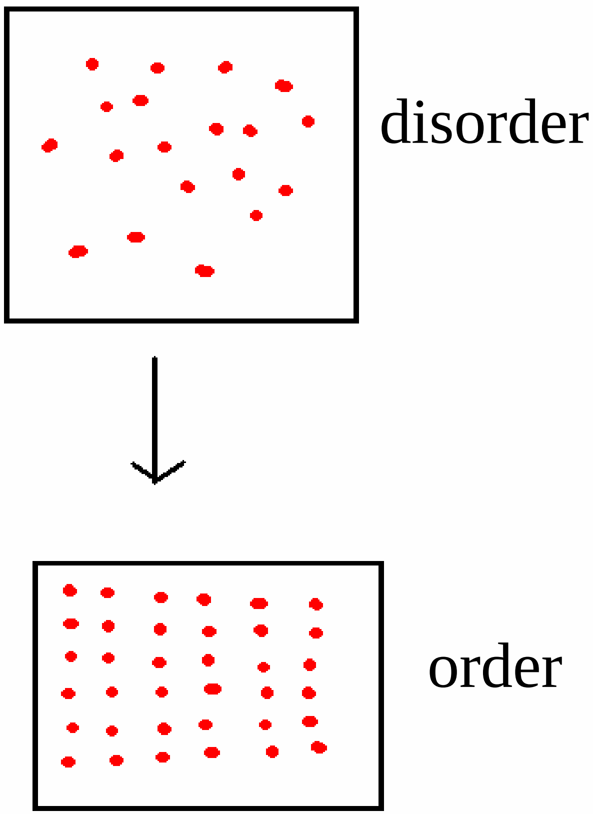
Interesting properties of Colloids.

Phase diagram different from atoms or small molecules.

Colloidal crystallization?

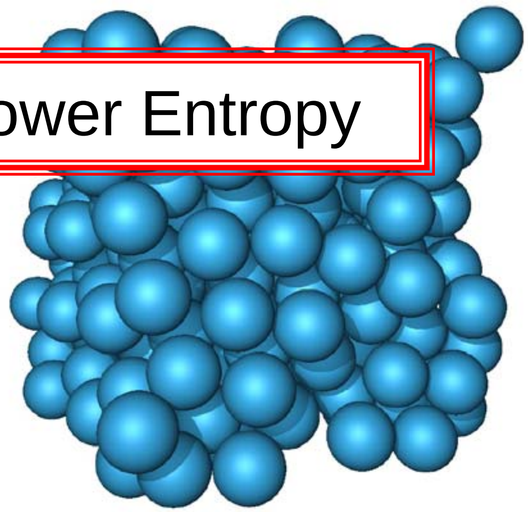
Hard colloids form entropic crystals.

The "intuitive" version of the Second Law of Thermodynamics

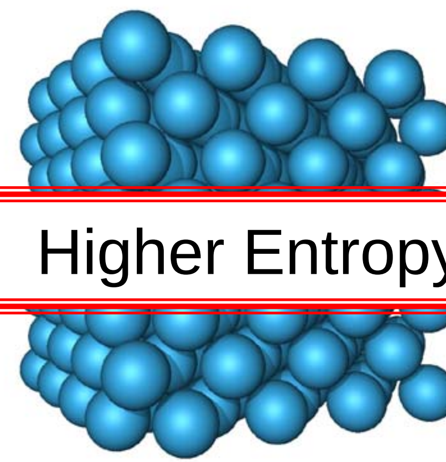


Maxwell Demon

Hard-sphere liquid



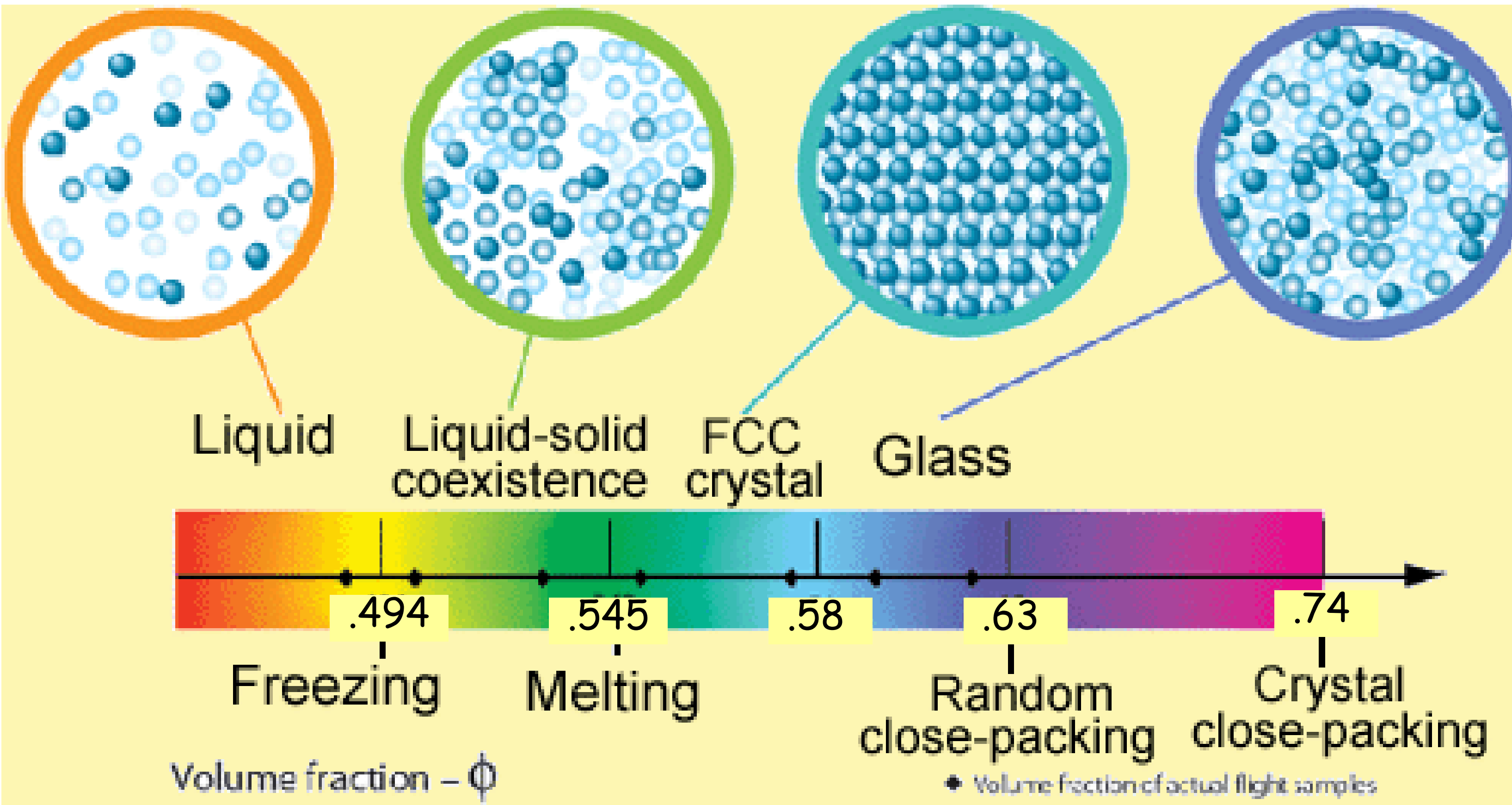
Hard-sphere freezing is driven by entropy !



Entropic hard-sphere crystals

This stuff **REALLY EXIST**

(Ottewill, Vrij, Pusey, Van Megen,….)



Pusey and van Megen, *Nature* **320** 340 (1986)

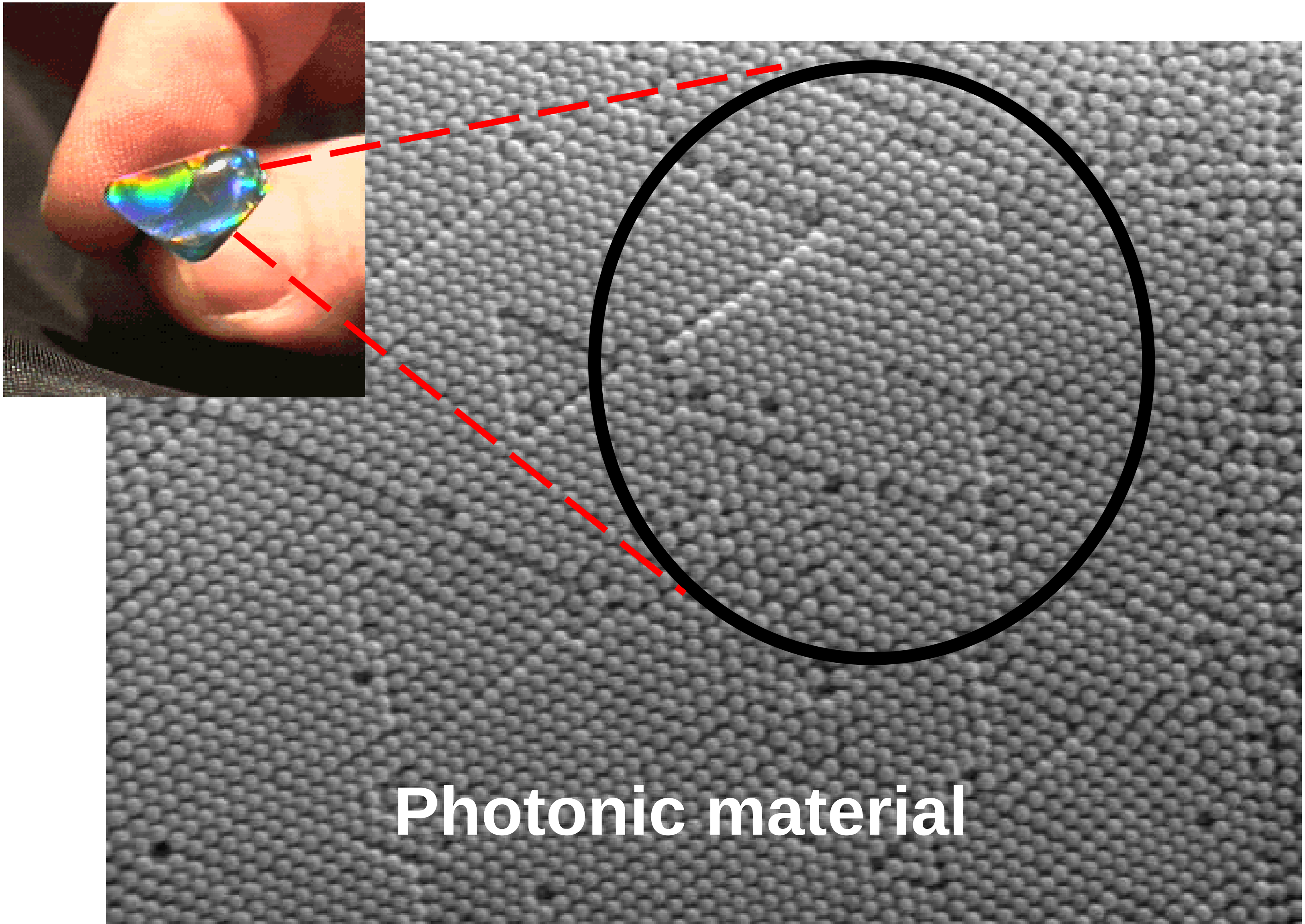
Entropic hard-sphere crystals

← **Volume fraction**

Entropic hard-sphere crystals

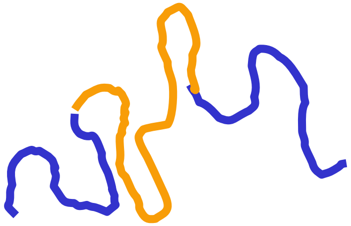
Pusey and van Megen *Nature* 320 340 (1986)

Hard-sphere crystals



Almost hard spheres

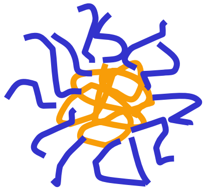
symmetric triblock copolymer Pluronic F68



ethylene oxide ⇒ EO = $-(CH_2-CH_2-O)-_{n=78}$

propylene oxide ⇒ PO = $-(CH_2-CH_2-O)-_{m=30}$ (with CH_3 side group on the second carbon)

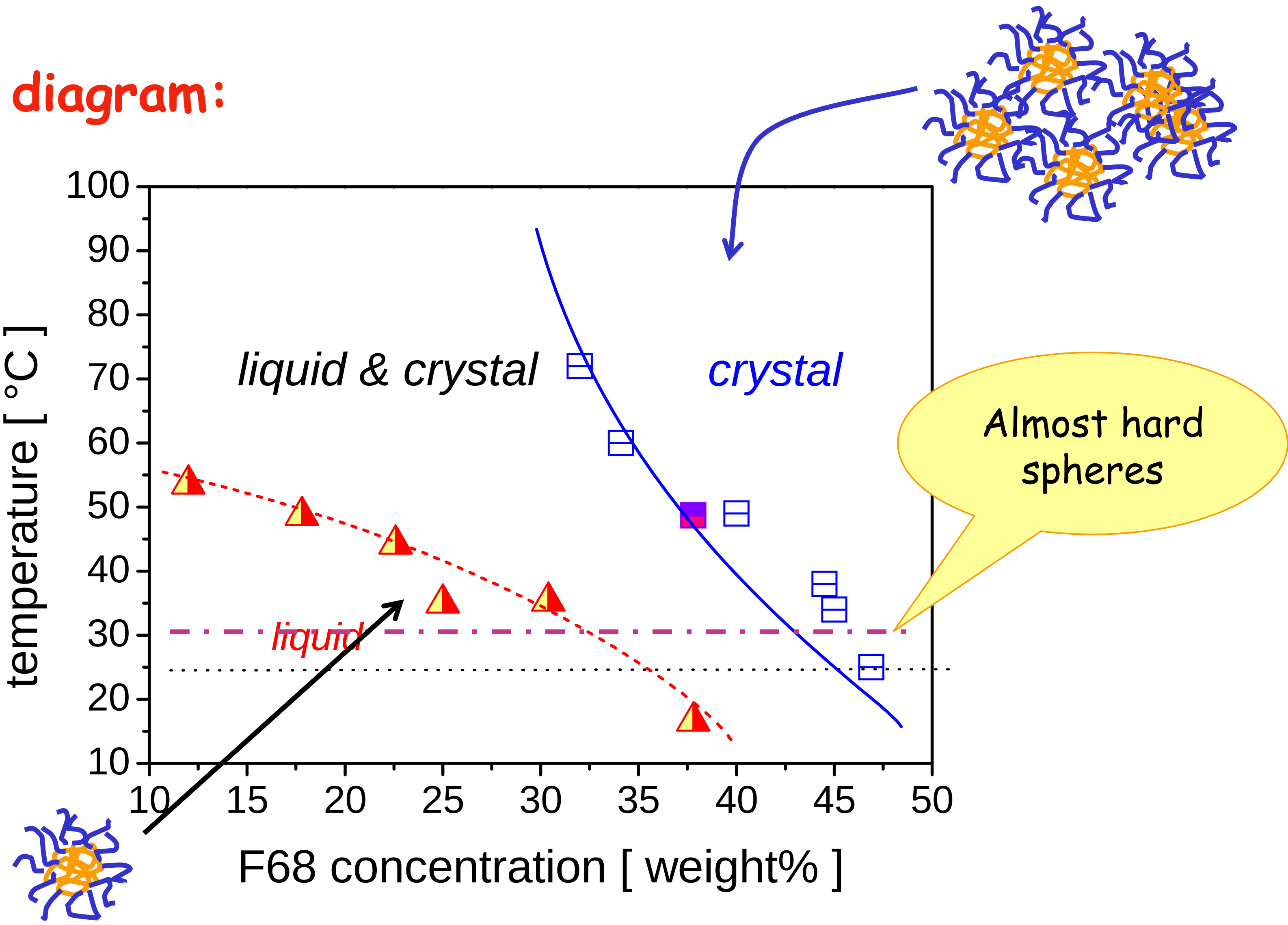
In water: formation of micelles …



… because water becomes a bad solvent for **PEO upon heating.**

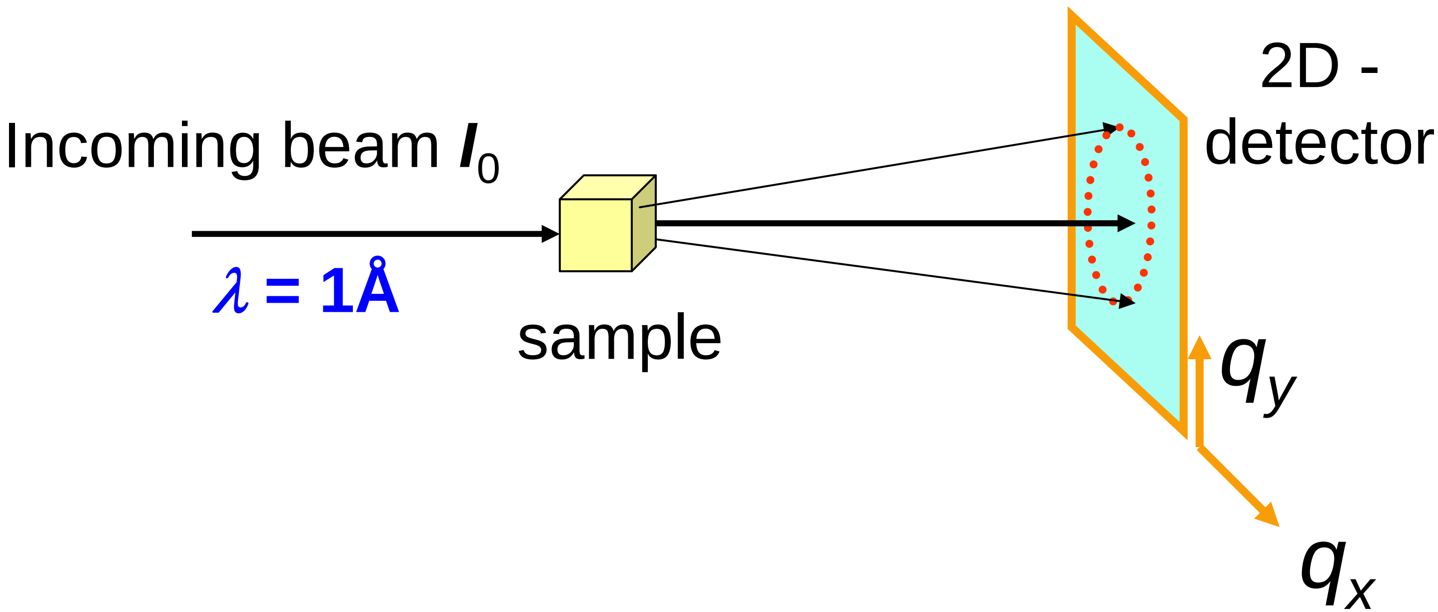
Almost hard spheres

Phase diagram:



Almost hard spheres

Small-Angle X-ray Scattering - SAXS

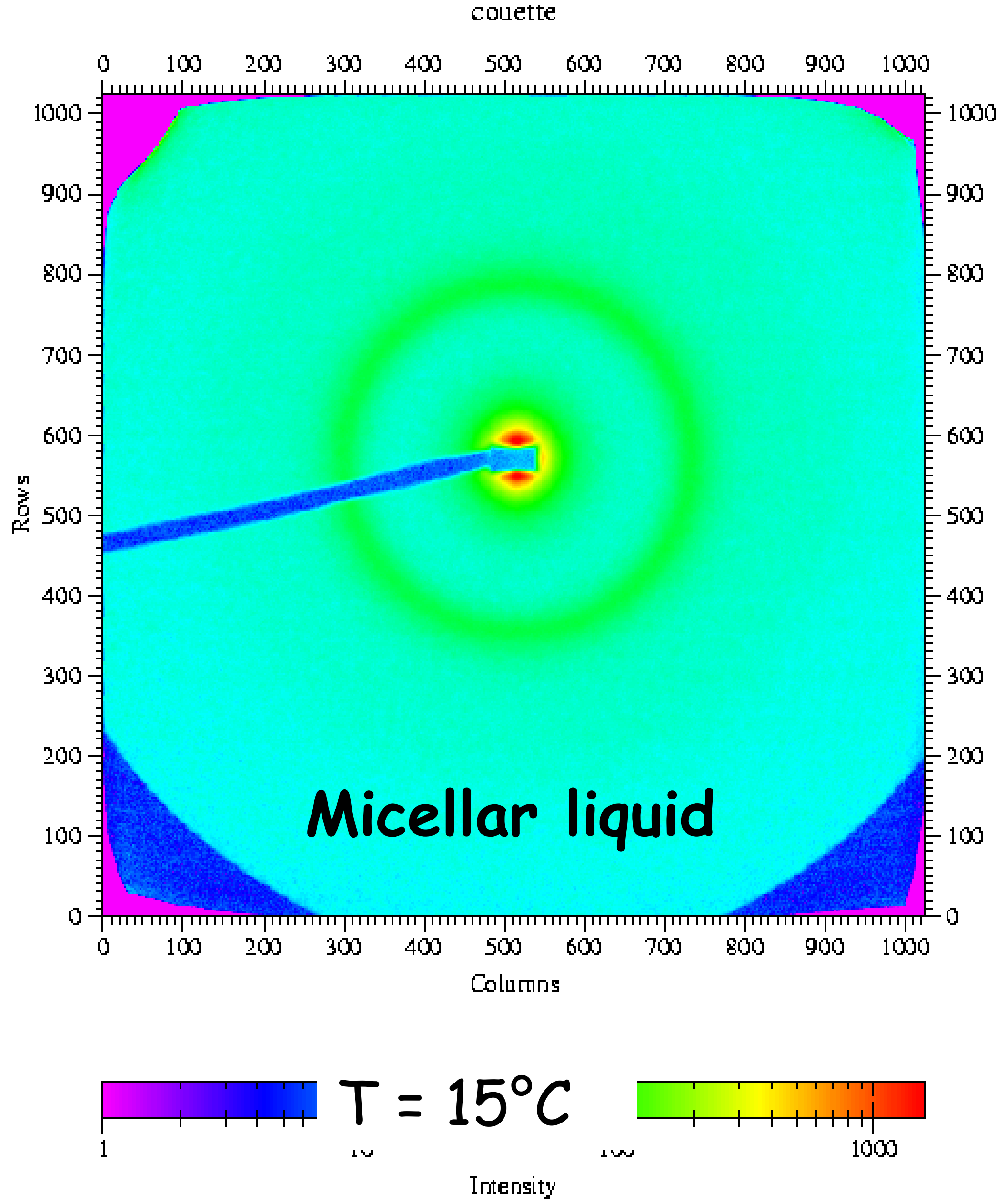


sample – detector separation = **4 m**

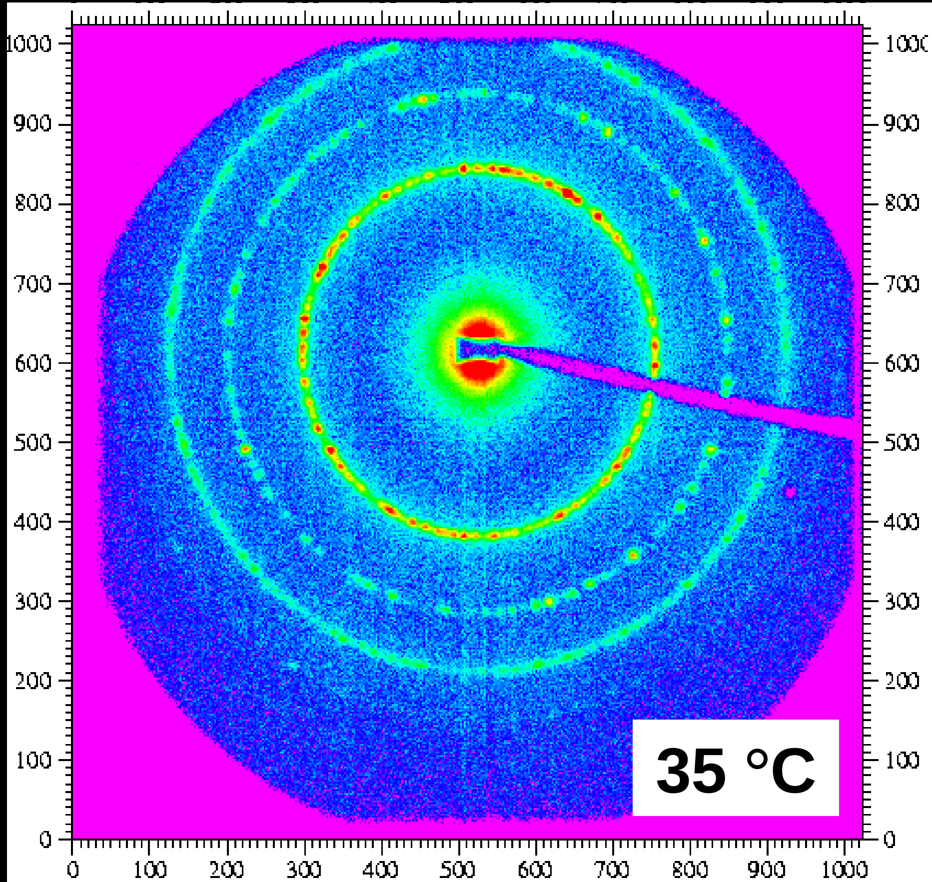
sampling range $\approx$ **0.01 – 0.12 Å^{-1}**

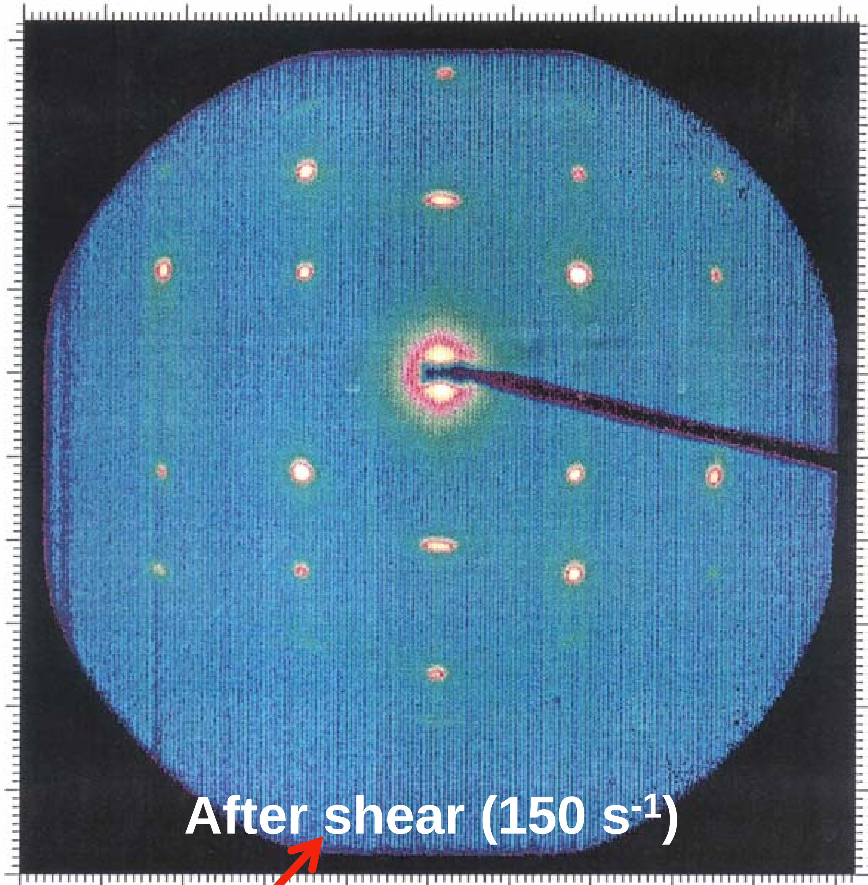
$\Leftrightarrow$ **50 – 600 Å**

Almost hard spheres



Almost hard sphere crystal





bcc - structure

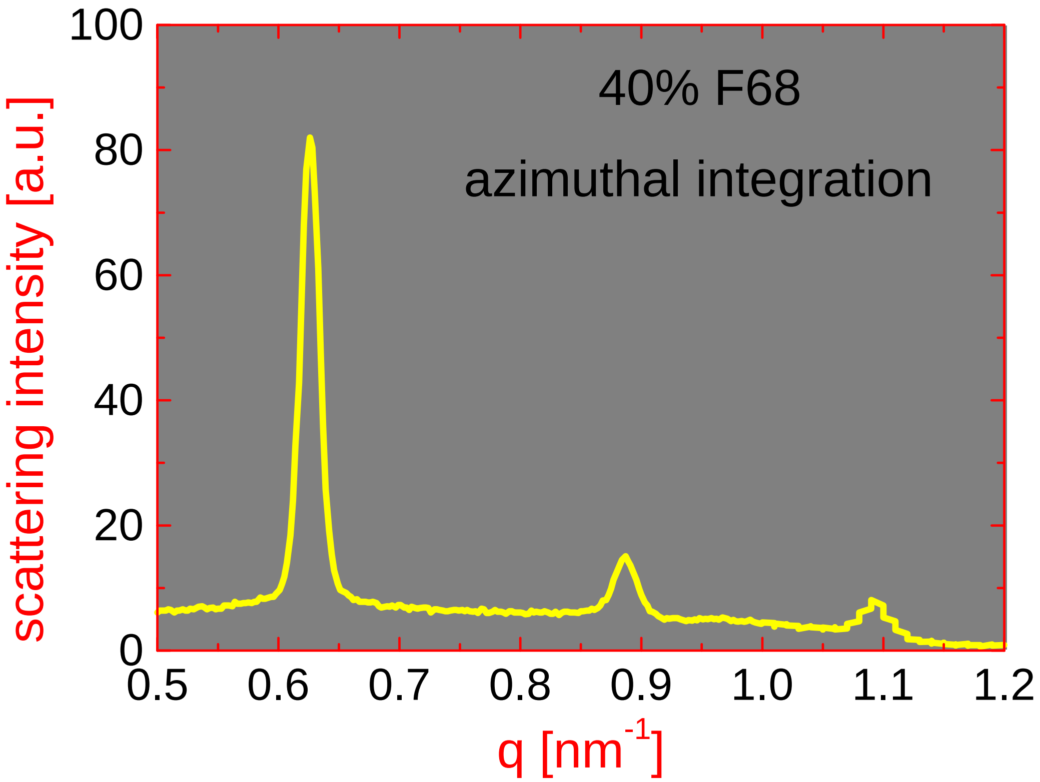
$$\frac{q_i}{q_0} = 1 : \sqrt{3} : \sqrt{4} : \sqrt{5} : \sqrt{6} : \ldots$$

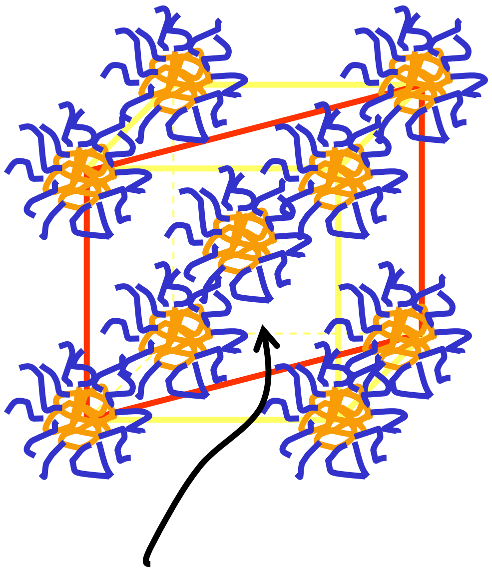
E. Eiser, F. Molino, G. Porte and O. Diat, *Phys. Rev. E* 61, 6759-6764 (2000).

Almost Hard Spheres

⇒ Polymeric micelles behave almost like hard spheres, …

… but with a weak long-ranged attraction.

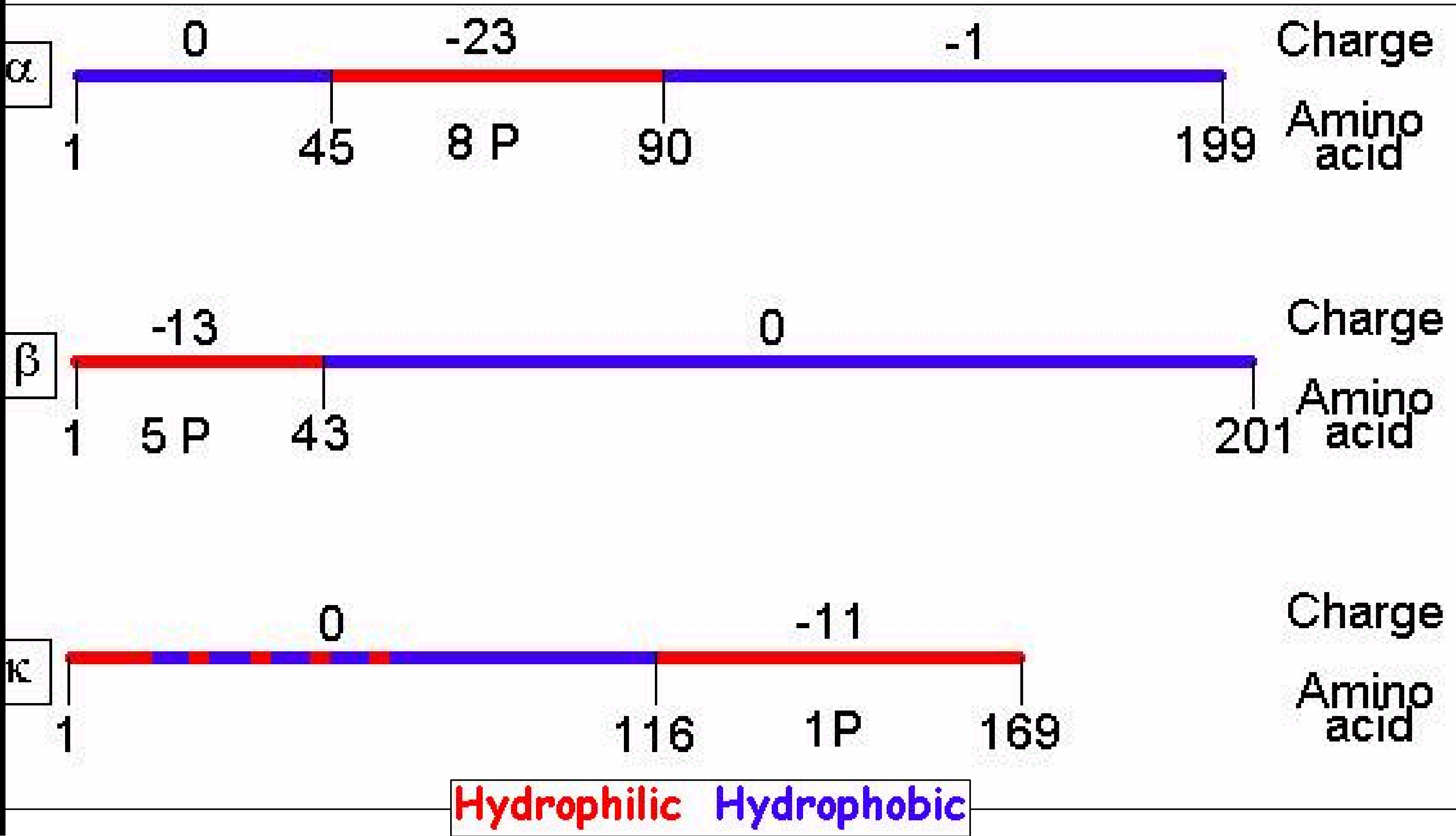




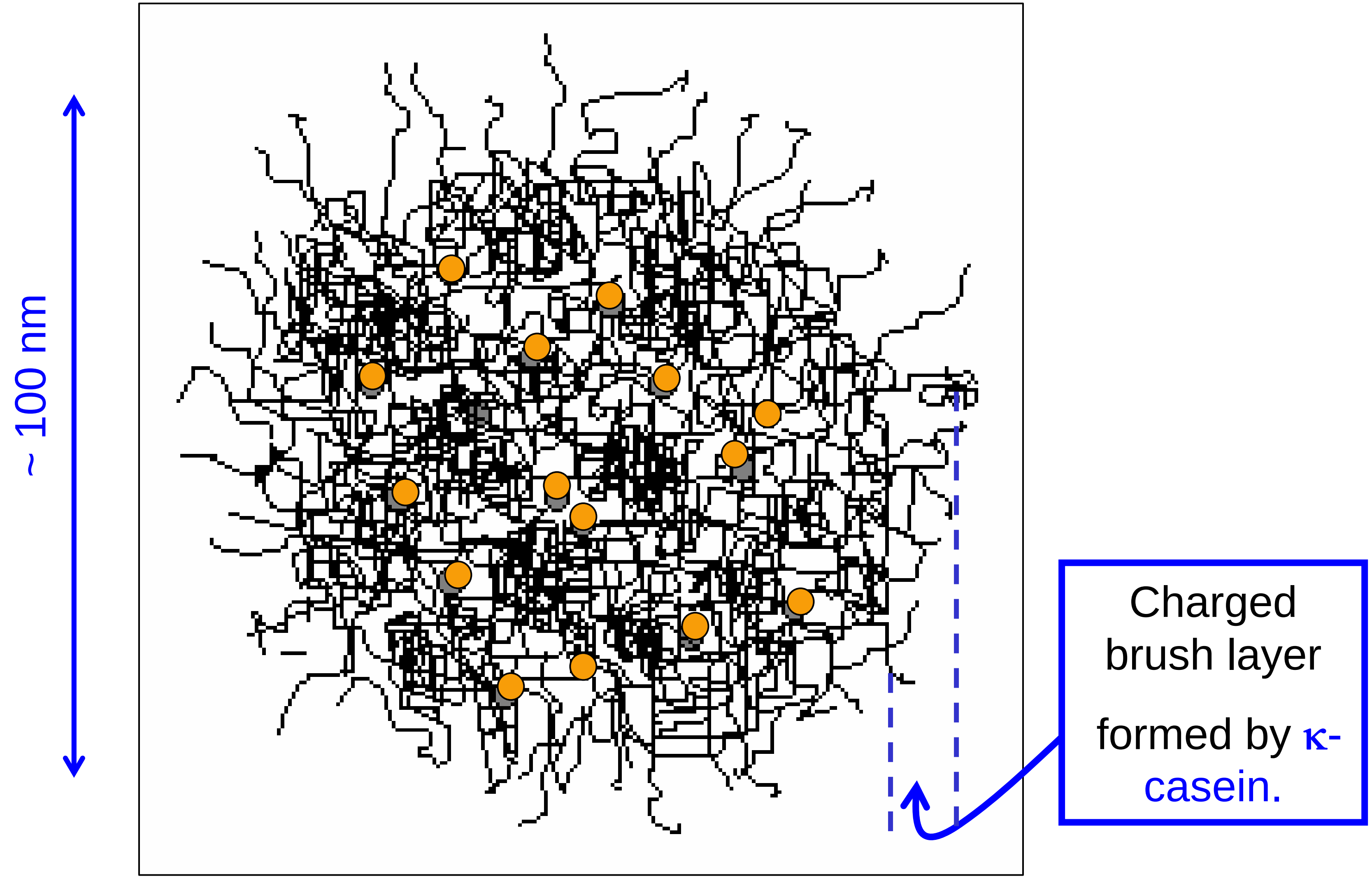
E. Eiser, F. Molino, G. Porte, *Eur. Phys. J. E* 2, 39-46 (2000).
E. Eiser, F. Molino, G. Porte and X. Pithon, *Rheol. Acta* 39, 201-208 (2000).

DLVO + steric interactions

Example: Milk contains mainly the proteins **α-, β-** & **κ-casein**



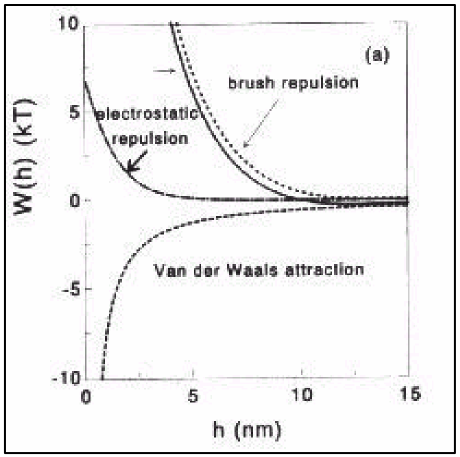
DLVO + steric interactions



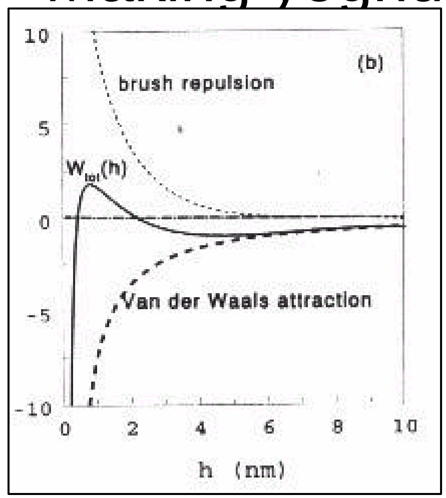
R. Tuinier and C.G. de Kruif, J. Chem. Phys. 1999 / 110 / 9296

Stability of milk, yogurth & cheese

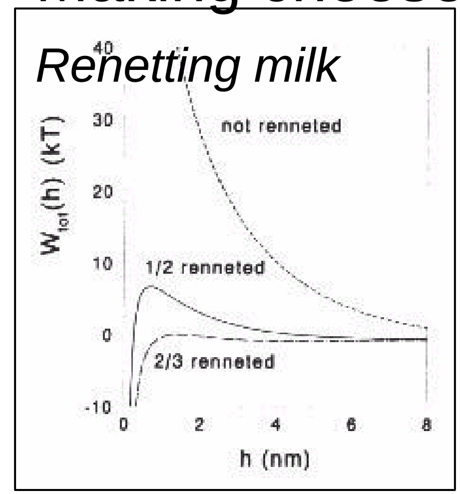
Milk

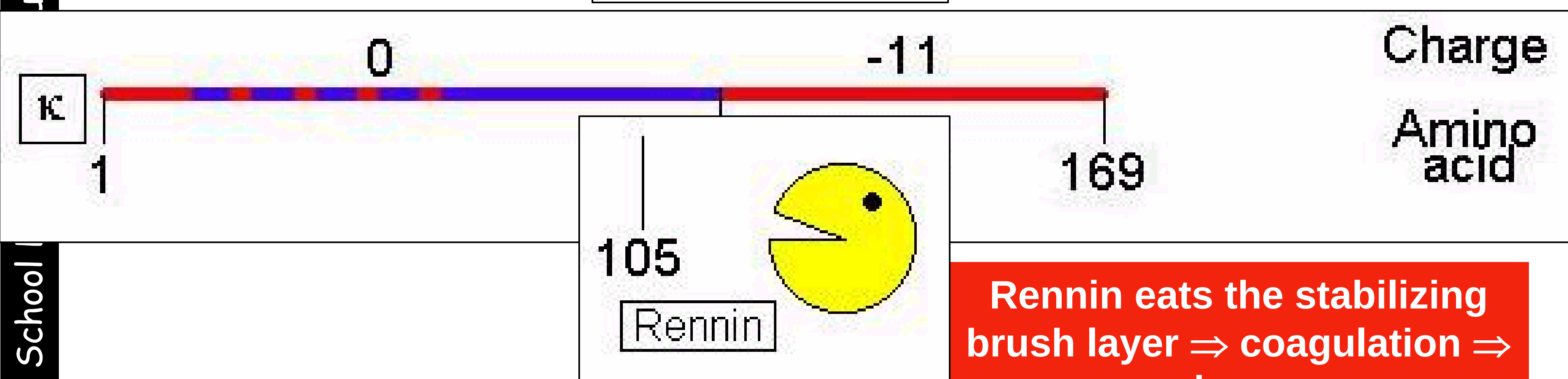


Making yoghurt



Making cheese





Rennin eats the stabilizing brush layer ⇒ coagulation ⇒ cheese

R. Tuinier and C.G. de Kruif, *1999 American Institute of Physics.* [S0021-9606(99)50816-7]

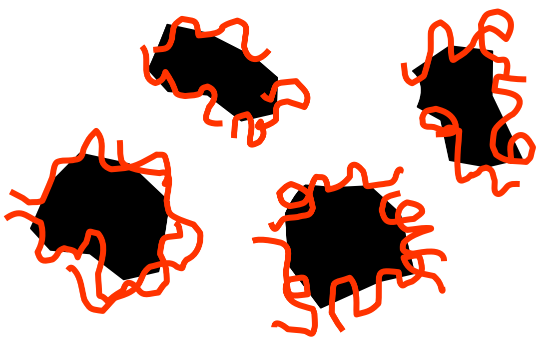
Romans new how to make cheese.

Roman cheese press (some 400 a.d.)

Other colloidal systems

Egyptian ink

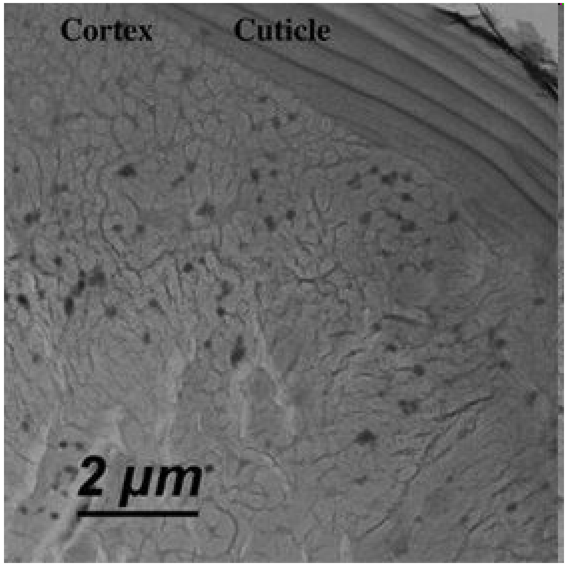
Ink on papyrus dating from about 1200BC containing nanoparticles of soot.



Gum Arabic & carbon black

Cosmetics & hair dye

Galena = PbS colloids



Electron microscopy image of the cross section of dyed hair. Dark spots are lead accumulations.

By: Philippe Walter

*http://www.lsbu.ac.uk/water/hyarabic.html, http://en.wikipedia.org/wiki/Gum_arabic

Conclusion

- Colloids show various phases, e.g. crystals.
- But also new phases that do not exist in atomic/molecular liquids.
- Example: liquid-liquid phase separation that does not exist in simple liquids.
- The reason for these new phases and their physics is …

… interaction potential *U* (r) can be tuned continuously.