Colloids: Phase Behaviour and Self-Assembly

HAN-SUR-LESSE WINTER(SUMMER?)SCHOOL – JUNI 2023

Janne-Mieke Meijer

Soft Matter and Biological Physics, Applied Physics Department & Institute for Complex Molecular Systems

EINDHOVEN UNIVERSITY OF TECHNOLOGY

Outline

Day 1

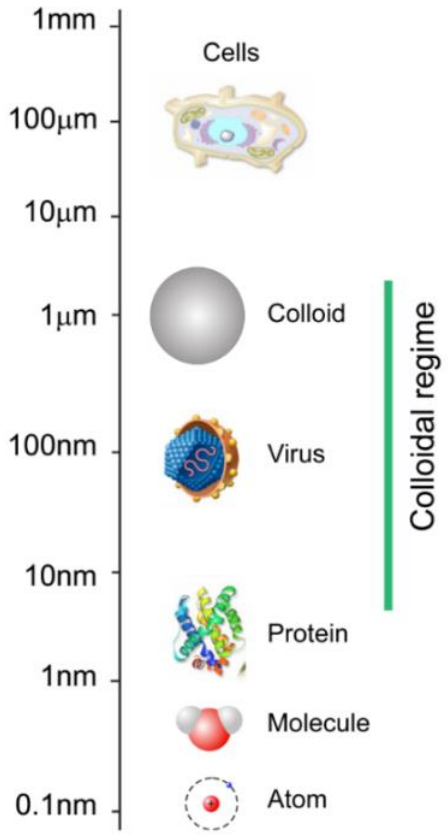
- Colloids basics + historical notes
  - Size, mechanics, systems
- Interactions between colloids
- Characterization of colloid phases
- Phase behaviour of hard spheres

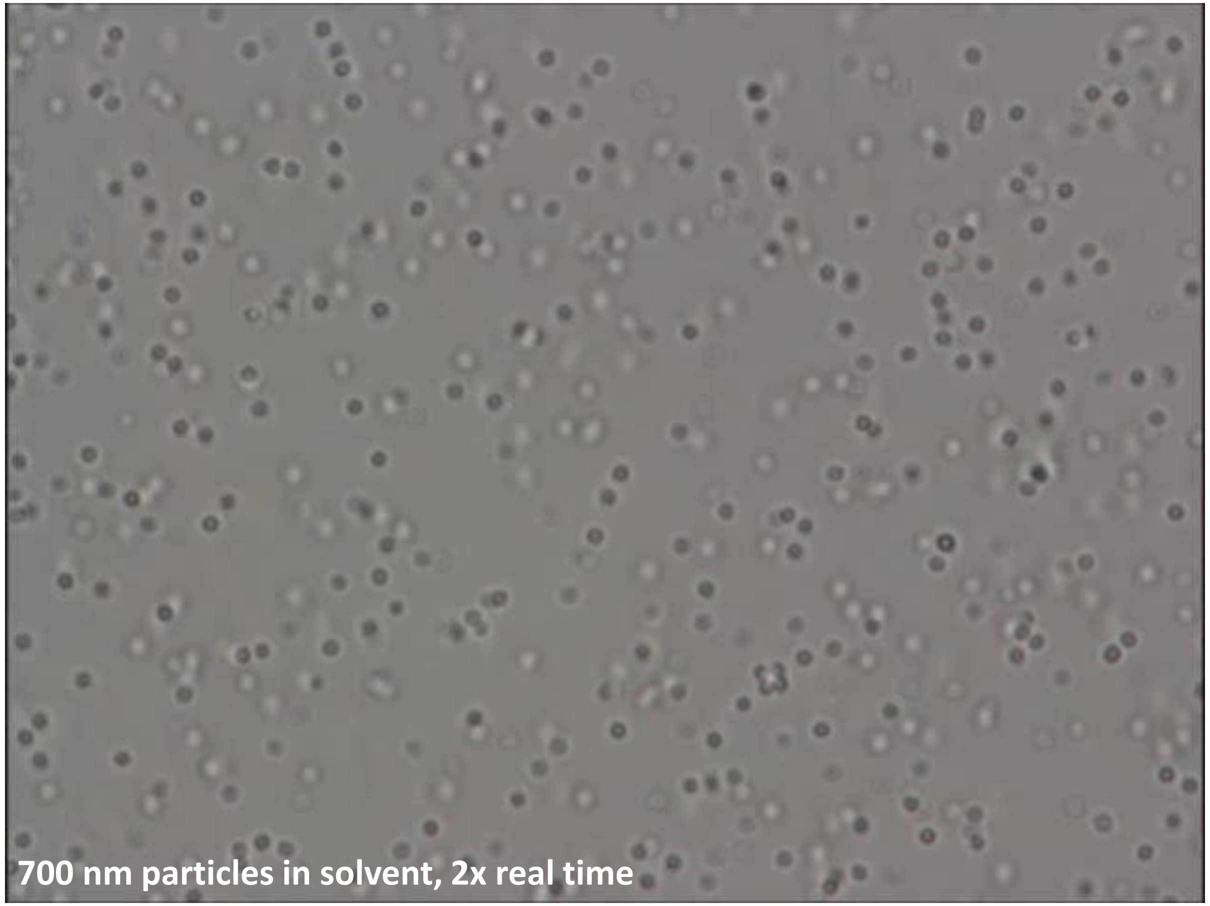
Day 2

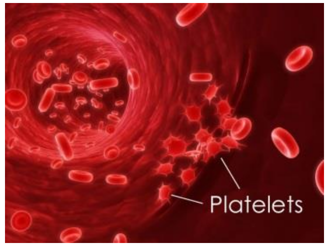
- Phase behaviour of Spheres
  - Repulsive spheres
  - Soft spheres
  - Attractive spheres
- Phase behavior of anisotropic colloids
  - Hard-body interactions
  - Repulsive interactions
  - Attractive interactions

Colloids

- Size range: 1 nm to 1 μm (IUPAC definition)
- Display thermal motion (Brownian motion)




700 nm particles in solvent, 2x real time



Colloids - Classification

- Colloid: ‘Particle’ (solid, liquid, gas) dispersed in a continuous medium (solid, liquid, gas)

Dispersed phase

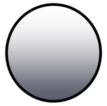
Continuous phase	gas	liquid	solid
gas	✗	**Aerosol** Ex.: hairspray, mist, fog	**Aerosol** Ex.: smoke
liquid	**Foam** Ex.: shaving cream	**Emulsion** Ex.: milk, mayonnaise, vinaigrette	**Sol or dispersion** Ex.: paint, printing ink
solid	**Solid foam** Ex.: insulating foam, carrot, wood	**Solid emulsion** Ex.: ice cream	**Solid dispersion** Ex.: opal

Monodisperse, polydisperse, different shapes

Why are colloidal materials soft?

Soft Materials

Building blocks: Colloids



$a \approx 100$ nm

Interaction energy: $U \approx k_B T$

Yield stress: $\approx$ ***1 Pa***

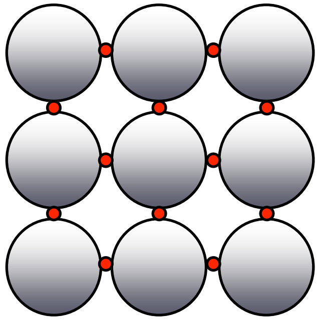
Hard Condensed Matter

Building blocks: Atoms

$a \approx 1$ Å

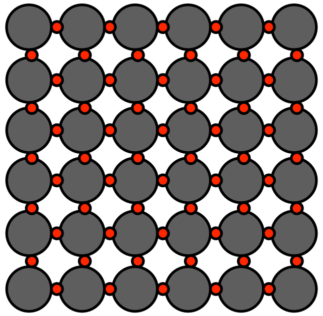
Interaction energy: $U > k_B T$

Yield stress: $>$ ***1 GPa***



Simple estimate for
Shear Modulus, Yield Stress:

Interaction Energy density U / a^3



$\sigma_y \approx k_B T / a^3 \approx 1$ Pa

$\sigma_y > k_B T / a^3 \approx 1$ GPa

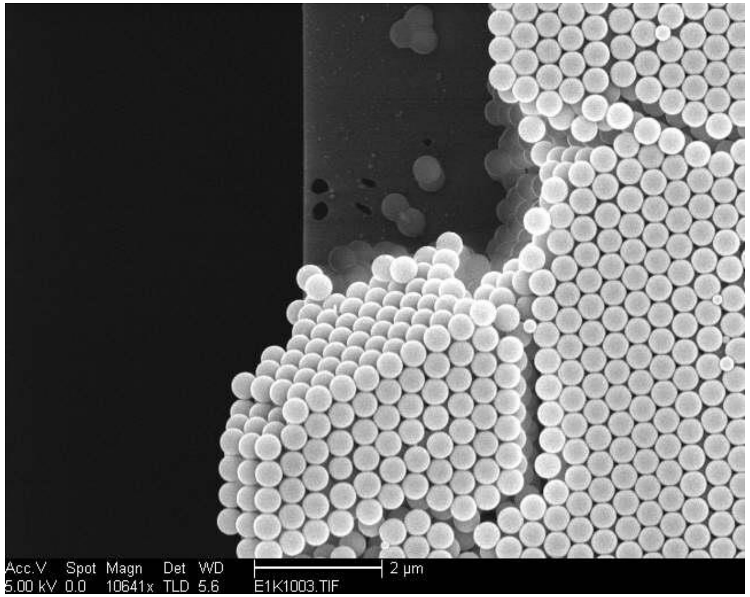
because the objects are big! The energy density is low...

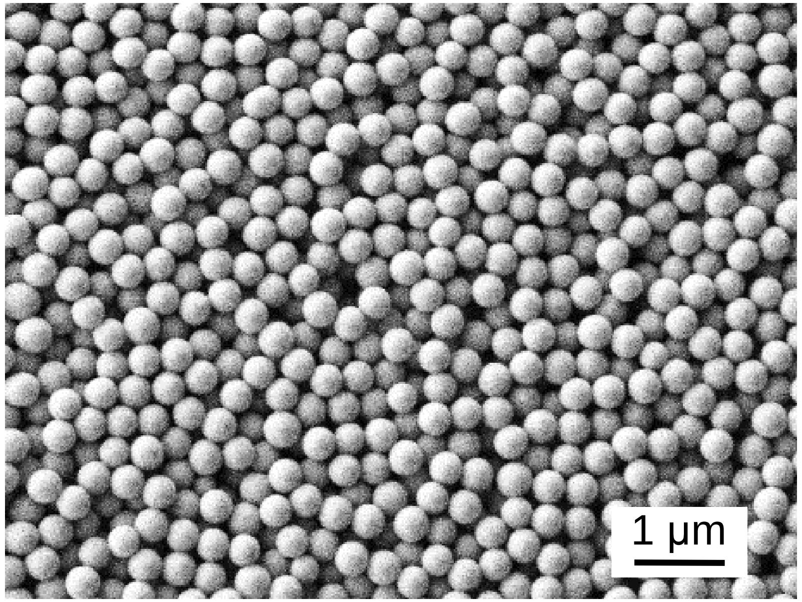
Examples of Colloidal Particles

- Spherical particles of polymers and inorganic materials

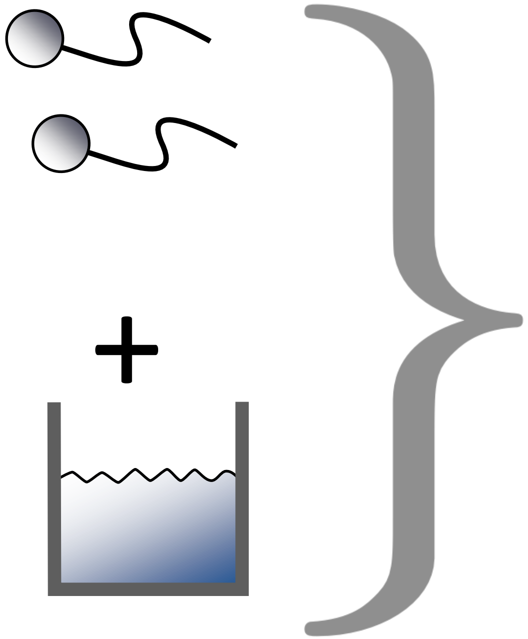
Polystyrene (PS)
Poly methylmethacrylate (PMMA)

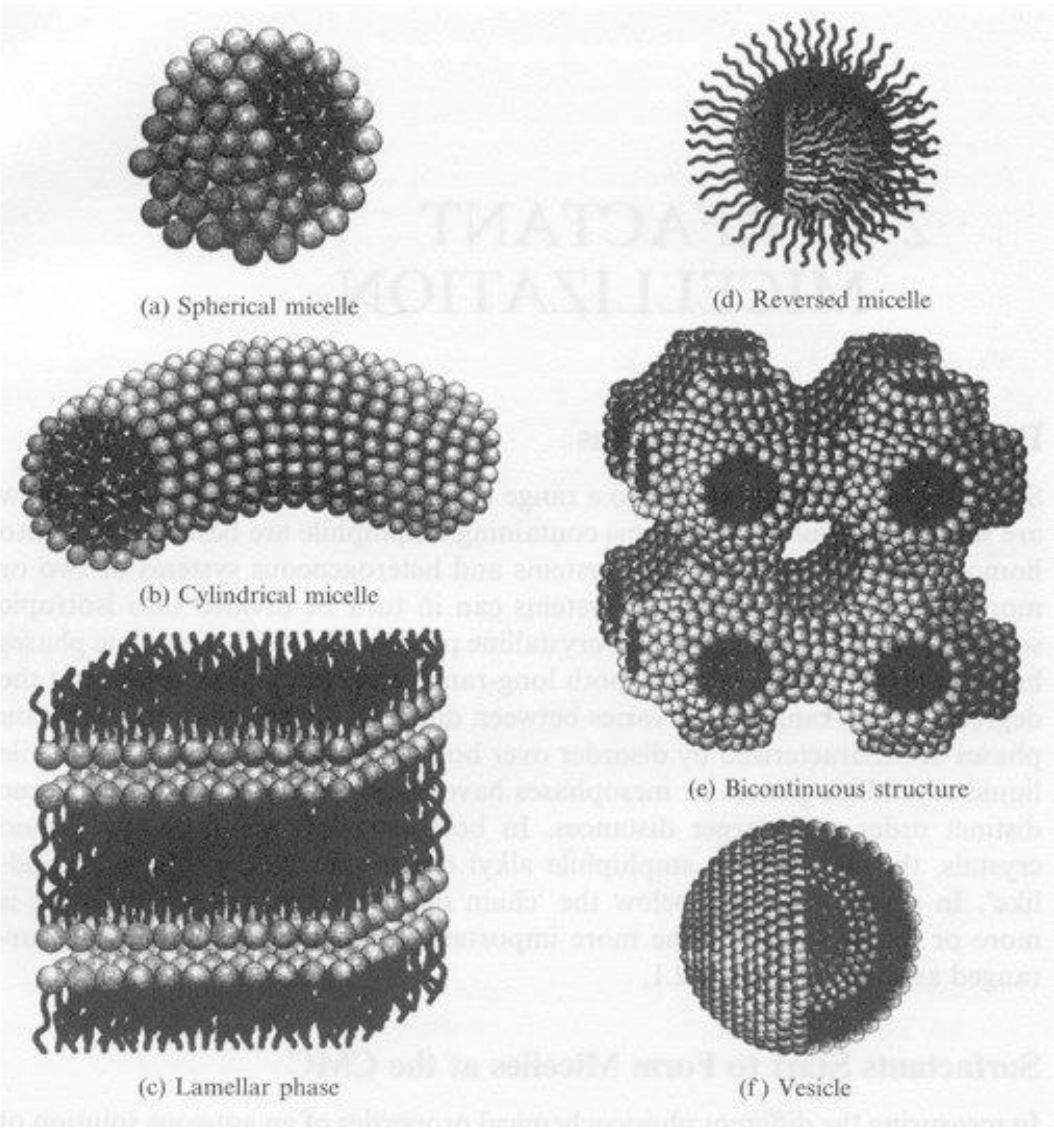
Silica (SiO_2)
Titania (TiO_2)





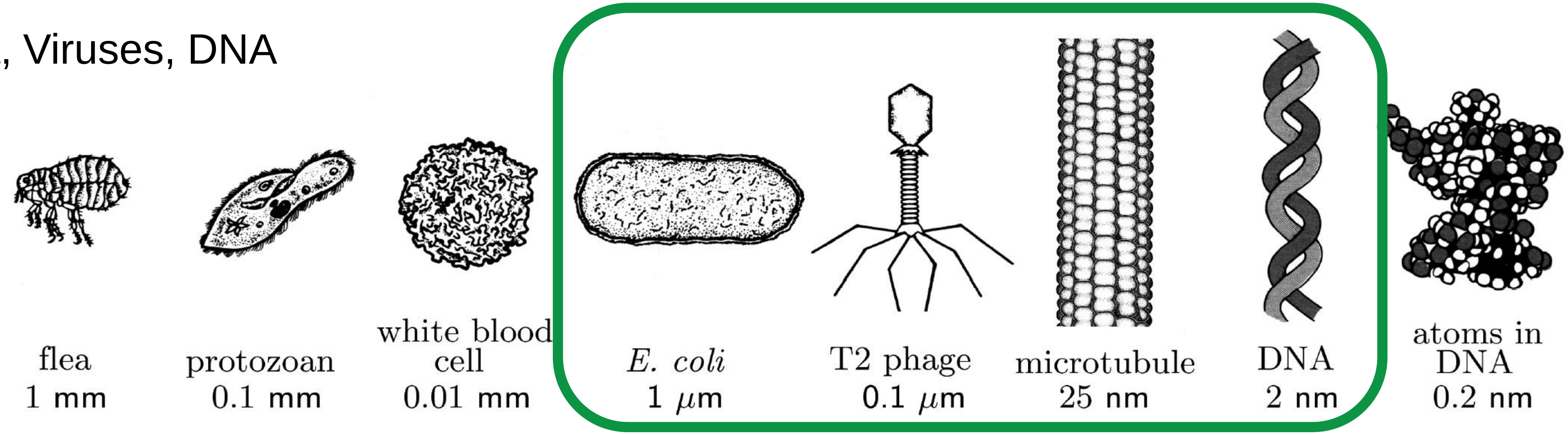
Surfactant systems –> Colloidal

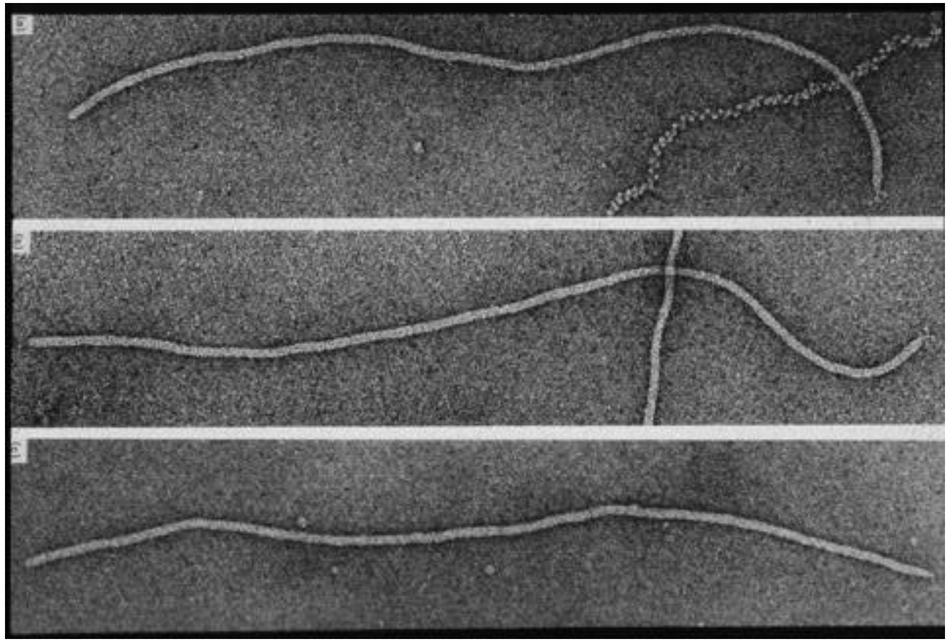




Colloids from Biology

- Bacteria, Viruses, DNA





FD pig virus
Length 900 nm
Diameter ~7nm

Seth Fraden Research Group

TU/e

Why study colloids?

Basic Science

Large, Soft, Slow

→ Can be experimentally studied in detail (often with simple techniques).

Model systems for molecular materials

- Glass formation
- Mechanics vs. Structure
- Phase behavior of soft materials
- Model for polymer melts & glasses
- Instabilities & Structure formation

Applications

Colloids are everywhere!

Cosmetics, detergents, food systems, pharmaceutical formulations, oil recovery, energy applications, functional materials

Colloids have a rich phase behavior!

Self assembly, structure formation

→ Functional materials

Why study colloids?

Analogy between molecular materials and colloidal soft materials

Soft Materials ⟺ Hard Condensed Matter

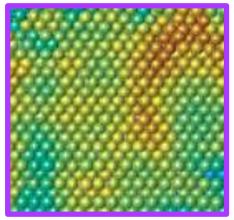
Building blocks: Colloids

$a \approx 100$ nm

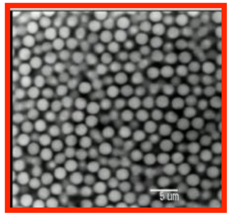
Building blocks: Atoms

$a \approx 1$ Å

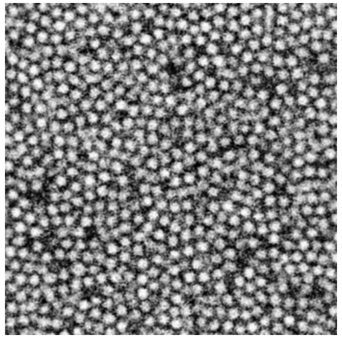
Generic material behaviors displayed in soft matter



Study crystallization



Study glass formation



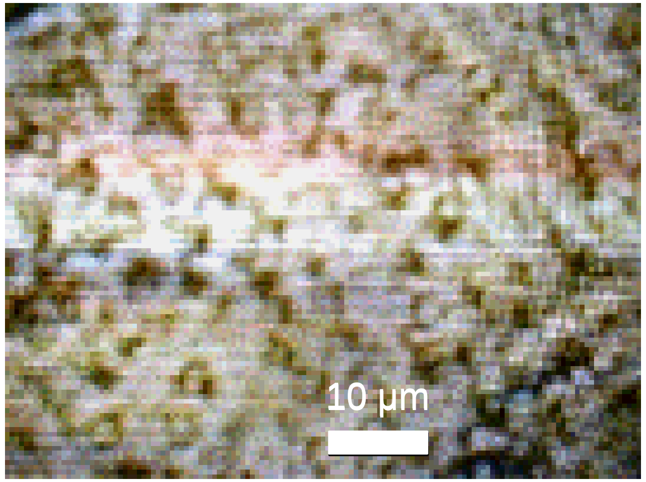
Directly follow structure, dynamics in confocal microscope:

TU/e

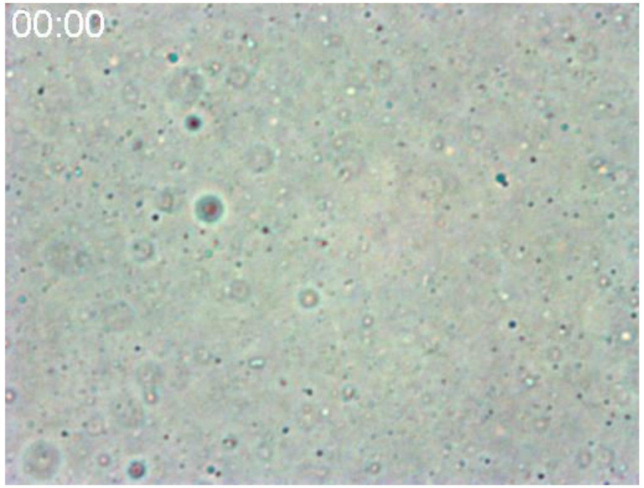
Brownian Motion: a bit of History

- Robert Brown observes Brownian motion of pollen - 1827
- Shows that all microscopic materials possess this motion
- Temperature dependent motion!

Brown's microscope



Fat droplets in milk
observed with Browns microscope
http://www.brianjford.com/wbbrownc.htm

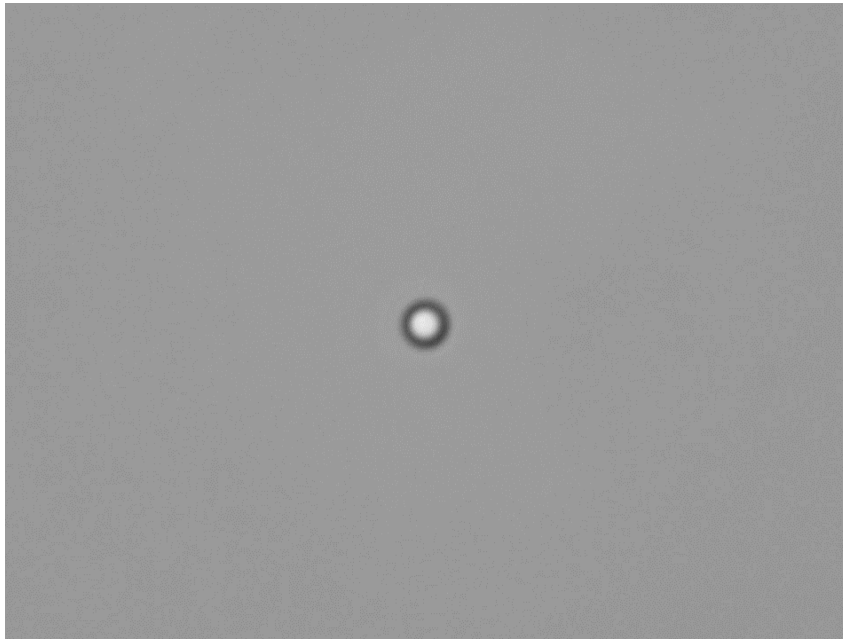


Milk under today's microscope

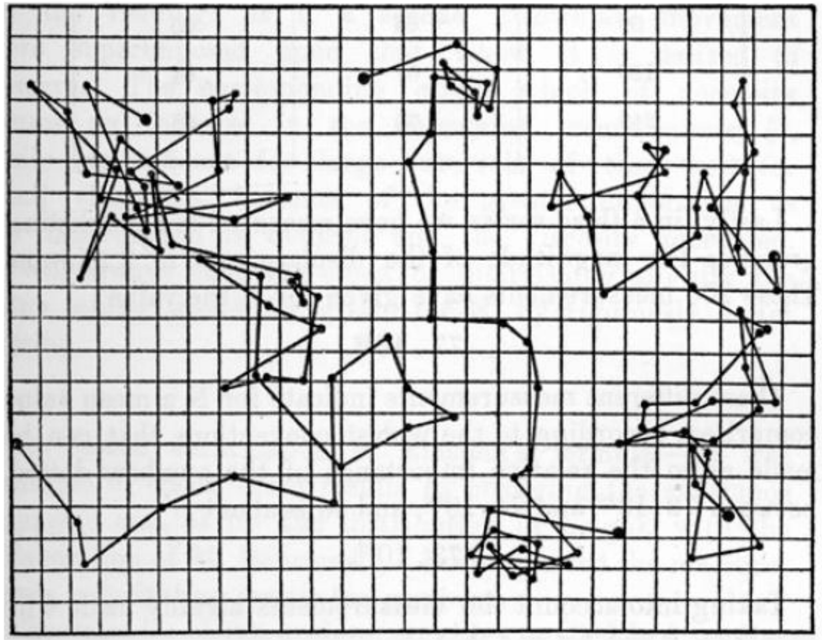
Colloids as Molecules: Einstein & Perrin

- Colloids have a Thermodynamic Temperature
- Brownian Motion explained and measured → N_A

Brownian motion of a single sphere



Positions of 1 µm spheres measured every 30 s



From original 1909 paper Perrin!

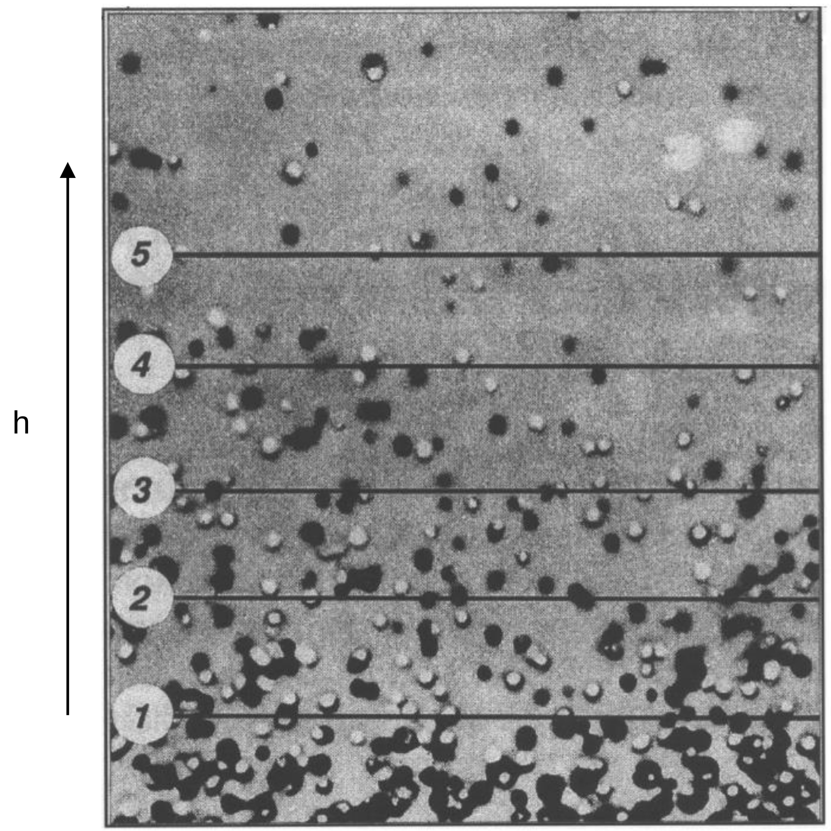
$$D = \frac{kT}{f} = \frac{kT}{6\pi\eta a} \qquad k = \frac{R}{N_A}$$

$$\langle x^2(t)\rangle = 2D_0 t$$

Fluctuation and dissipation

Colloids in External Fields: Perrin

Barometric distribution → Boltzmann distribution



Number of 1 μm spheres at different heights

Particle density

$$\rho = \rho_0 \, e^{-h/l_g}$$

$$l_g = \frac{kT}{m_b g}$$

m_b = buoyant mass

$$k = \frac{R}{N_A}$$

Perrin: $N_{av} = 6.8 \times 10^{23}$

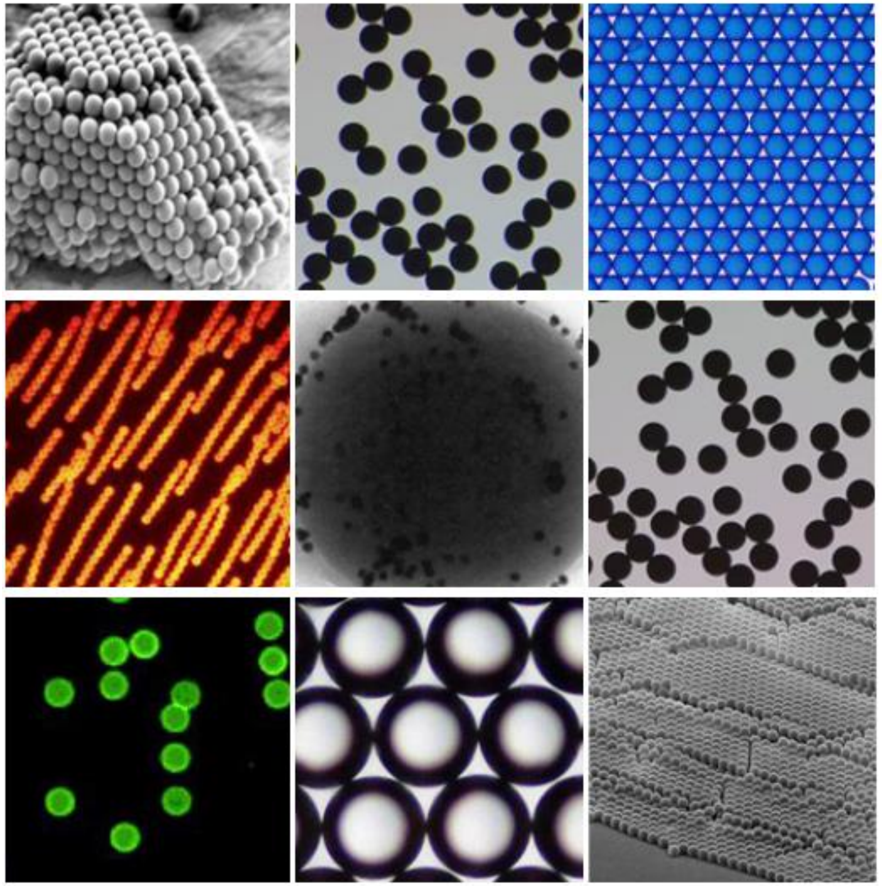
SI unit: $N_{av} = 6.022 \times 10^{23}$

TU/e

Today: Improved synthesis of colloids

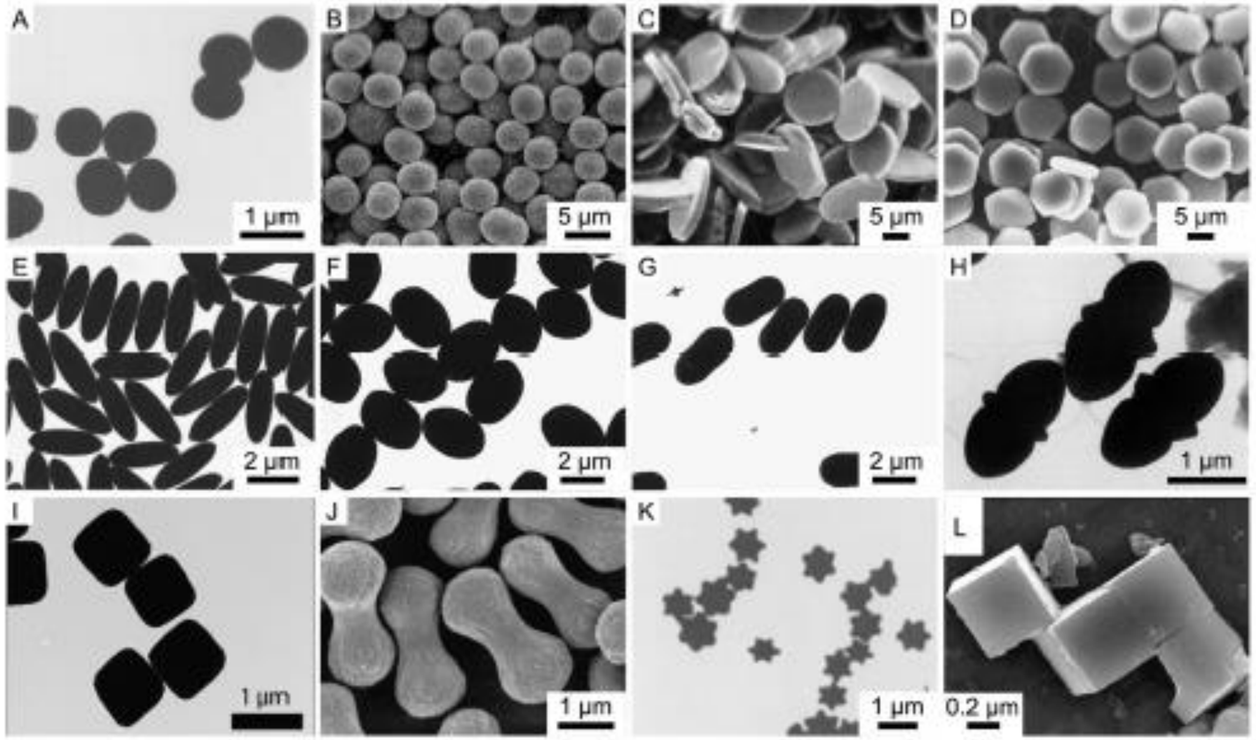
- Last 30 years: advances in colloid synthesis: control over size, shape, composition

Abundance of polymer particles



https://www.microparticles-shop.de

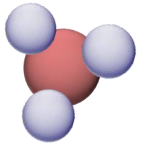
Hematite particles Fe_2O_3



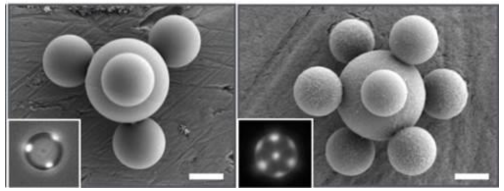
Meijer and Rossi *Soft Matter* (2021)

Today: Improved synthesis of colloids

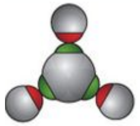
Colloidal molecules

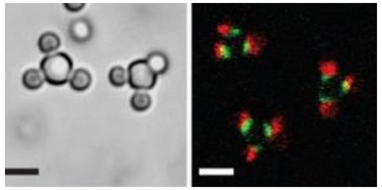


Meester *et al. ACS Nano* (2017)



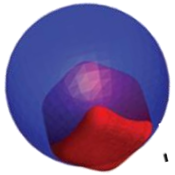
Gong *et al. Nature* (2017)





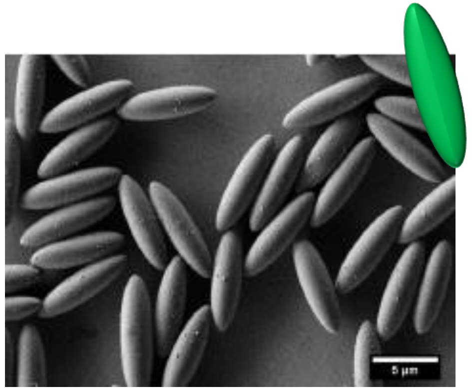
Pine *et al. Nature* (2012)

Dipolar colloids

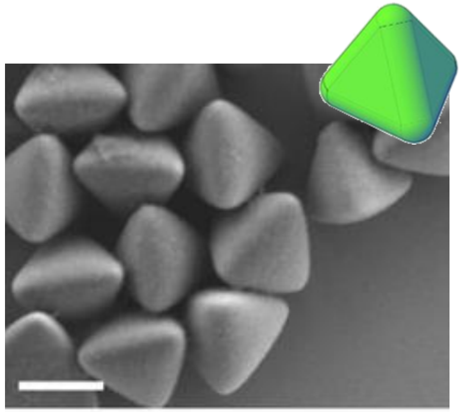


Rossi *et al. JACS* (2012)

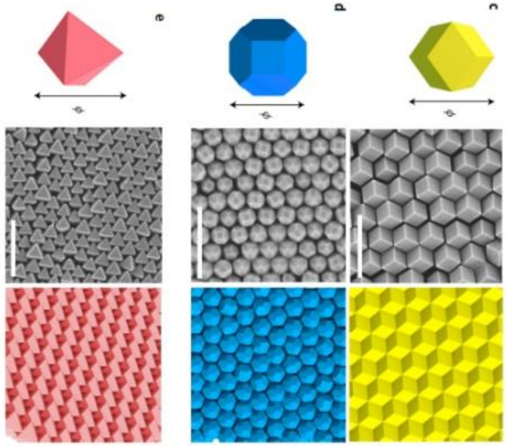
Complex shapes



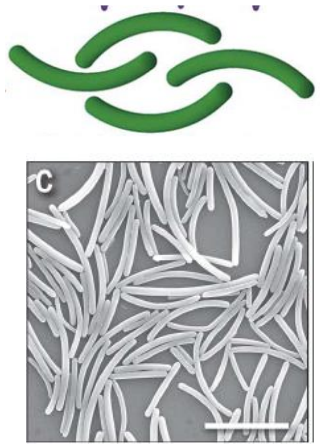
Roller, **Meijer** *et al. PNAS* (2021)



Sacanna *et al. Nature* (2017)



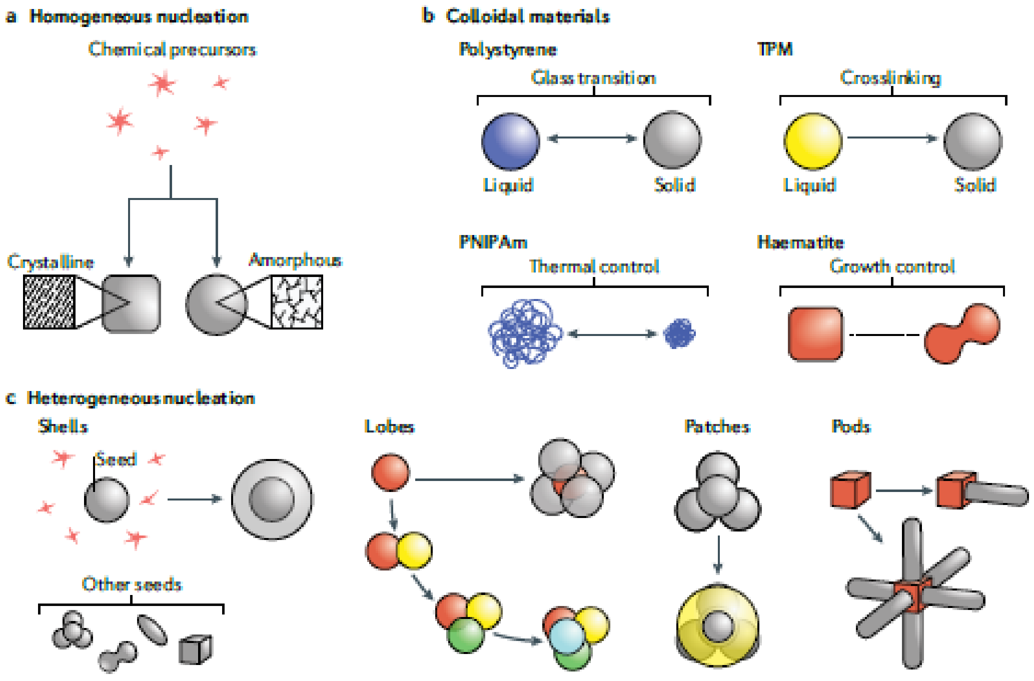
Avci *et al. Nature Mat* (2018)

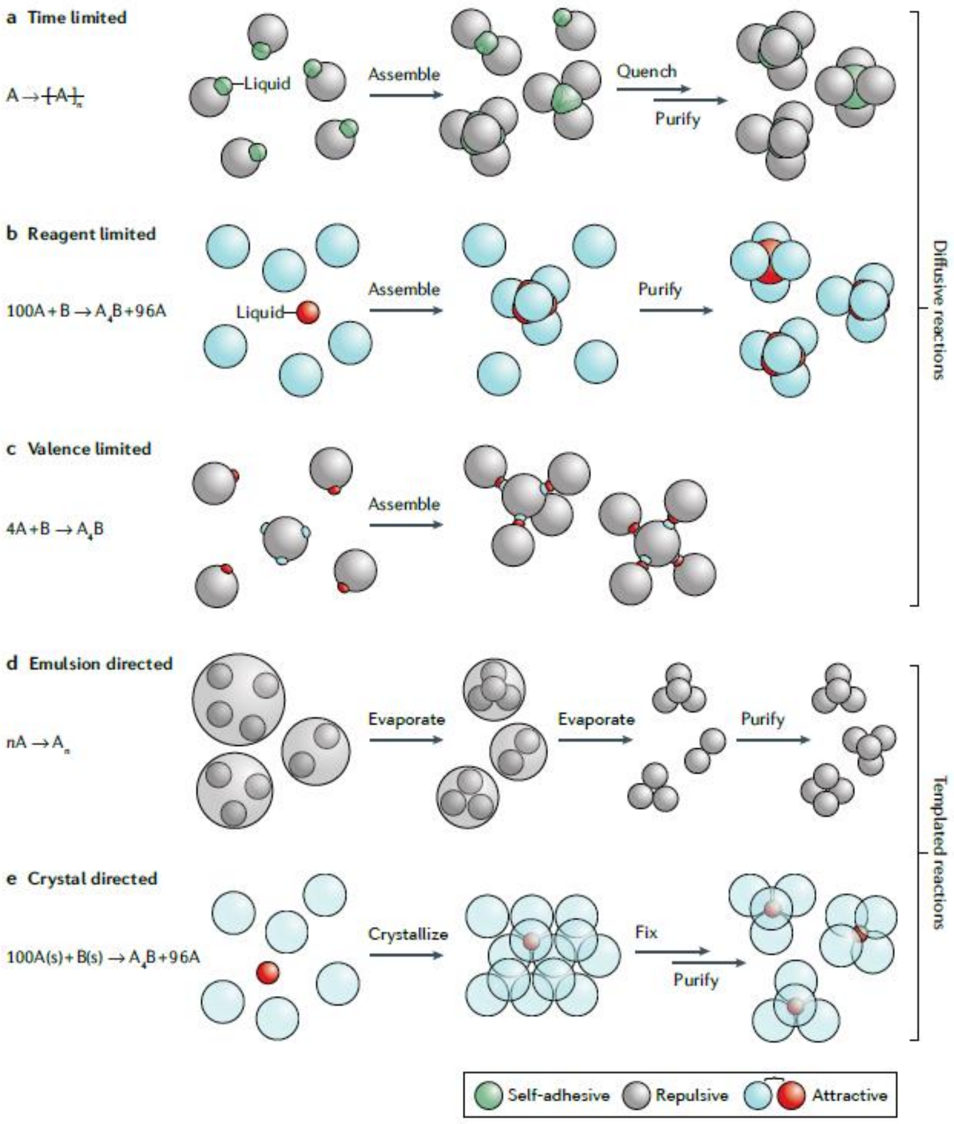


Fernandez *et al. Sciece* (2020)

Total synthesis of colloidal matter

- There are many many more ways to make colloids





Hueckel, Hocky and Sacanna, *Nature Reviews* (2021)

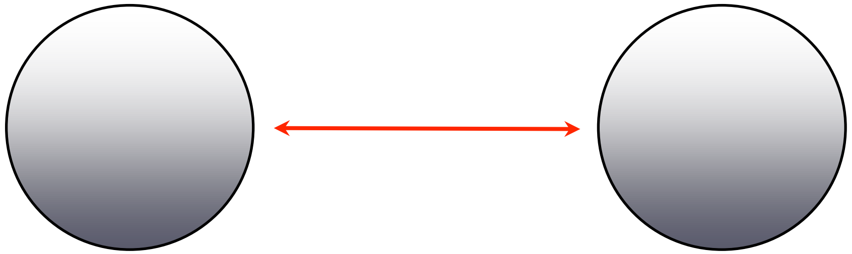
Outline

- Colloids basics + historical notes
  - Size, mechanics, systems
- Interactions between colloids
- Characterization of colloid phases
- Phase behaviour of hard spheres

Interactions between colloids

Wide range of interactions between colloids ..

.. in many ways *more diverse than interactions between atoms & molecules* (covalent, electrostatic, hydrogen bonds)



Attractive Interactions

- van-der-Waals
- (electrostatic)
- Depletion
- Hydrophobic forces

Repulsive Interactions

- Electrostatic
- Steric (brushes)
- Hard repulsion

Can tune strength, range, or even shape for all of these !

TU/e

van-der-Waals attraction

Induced dipole-dipole

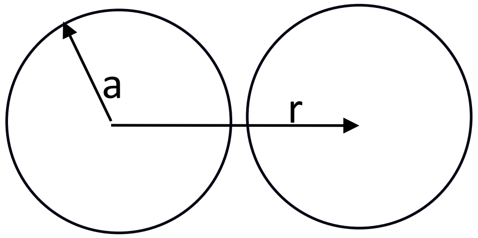
$$E \propto -\frac{\alpha_1 \alpha_2}{r^6}$$

Interaction energy between two molecules with polarizabilities

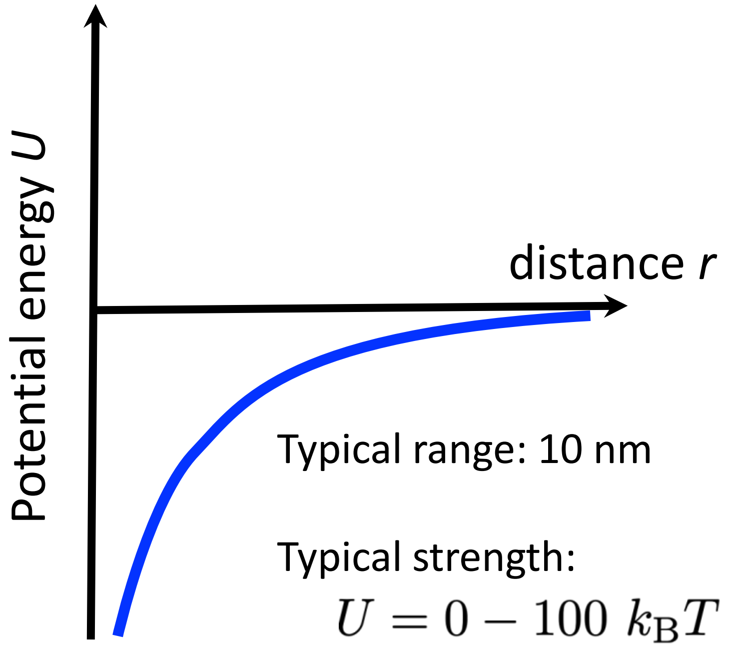
$$\alpha_1, \alpha_2$$

Colloids are not points but spheres... need to integrate over volumes to get interaction:

$$U = \frac{-A}{6}\left[\frac{2a^2}{r^2 - 4a^2} + \frac{2a^2}{r^2} + \ln\left(\frac{r^2 - 4a^2}{r^2}\right)\right]$$



Gases condense; colloids aggregate



Typical range: 10 nm

Typical strength:

$$U = 0 - 100\ k_{\mathrm{B}}T$$

for 1 μm particles..

van-der-Waals attraction

Integrate dipole-dipole interactions over volume of particles

$$E \propto -\frac{\alpha_1 \alpha_2}{r^6}$$

$$U = \frac{-A}{6}\left[\frac{2a^2}{r^2 - 4a^2} + \frac{2a^2}{r^2} + \ln\left(\frac{r^2 - 4a^2}{r^2}\right)\right]$$

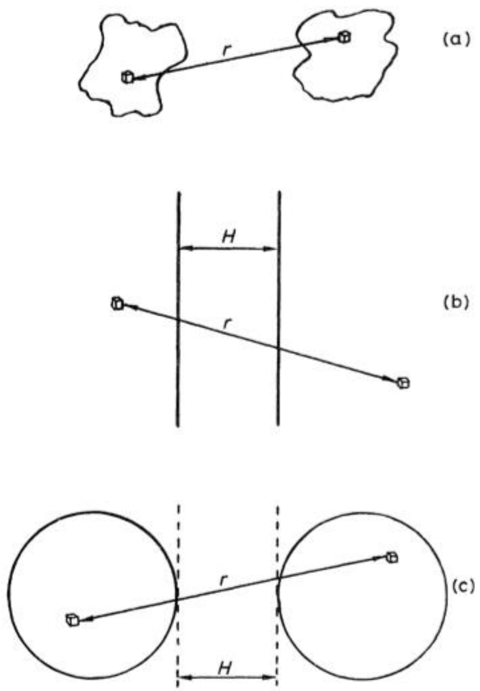


Figure 3.2 *Interaction between elements of volume dV containing qdV molecules, which on summation for all pairs of volume elements gives the total-interaction free energy between the two bodies: (a) particles of arbitrary shape, (b) two parallel semi-infinite plates a distance H apart, (c) two spheres whose surfaces are a distance H apart.*

Depends on particle shape/surface roughness!

TU/e

The Hamaker constant - typical values

	$A_{eff}(0)/10^{-20}$ J		
	Vacuum	Water	
polystyrene	7.9	1.3	
hexadecane	5.4	—	Parsegian & Weiss (1981)
gold	40	30	
silver	50	40	
copper	40	30	
water	4.0	—	
pentane	3.8	0.34	
decane	4.8	0.46	
hexadecane	5.2	0.54	
water	3.7	—	Hough & White (1980)
quartz			
fused	6.5	0.83	
crystalline	8.8	1.70	
fused silica	6.6	0.85	
calcite	10.1	2.23	
calcium fluoride	7.2	1.04	
sapphire	15.6	5.32	
poly(methyl methacrylate)	7.1	1.05	
poly(vinyl chloride)	7.8	1.30	
polyisoprene	6.0	0.74	
poly(tetrafluoroethylene)	3.8	0.33	

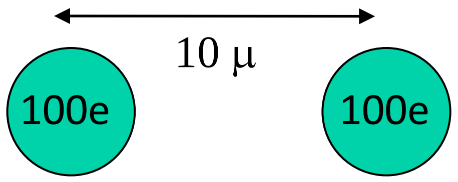
Electrostatic interactions

Bare charges

$$\frac{e^2}{\varepsilon_0 r} = .69 k_B T$$

Single electron charge,
r=1 micron, room temp

$$\frac{Z^2 e^2}{\varepsilon\ r} = 230 k_B T$$

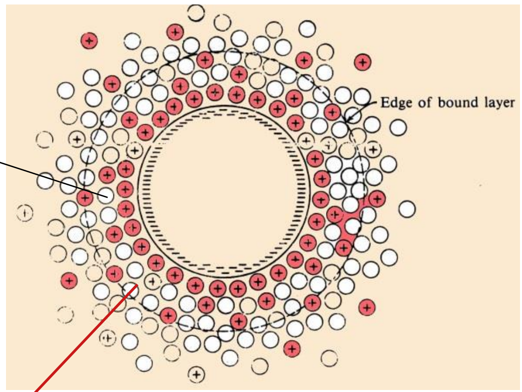


ε=30

(water ε=80, decalin ε=3)

Dissociation of counterions

Gradient in
electric potential ψ



A shell of ions around charged particles is formed.
“screening of the charge”

Electric double layer

$\longleftrightarrow$ κ^{-1}

Double layer thickness
= Debye length

TU/e

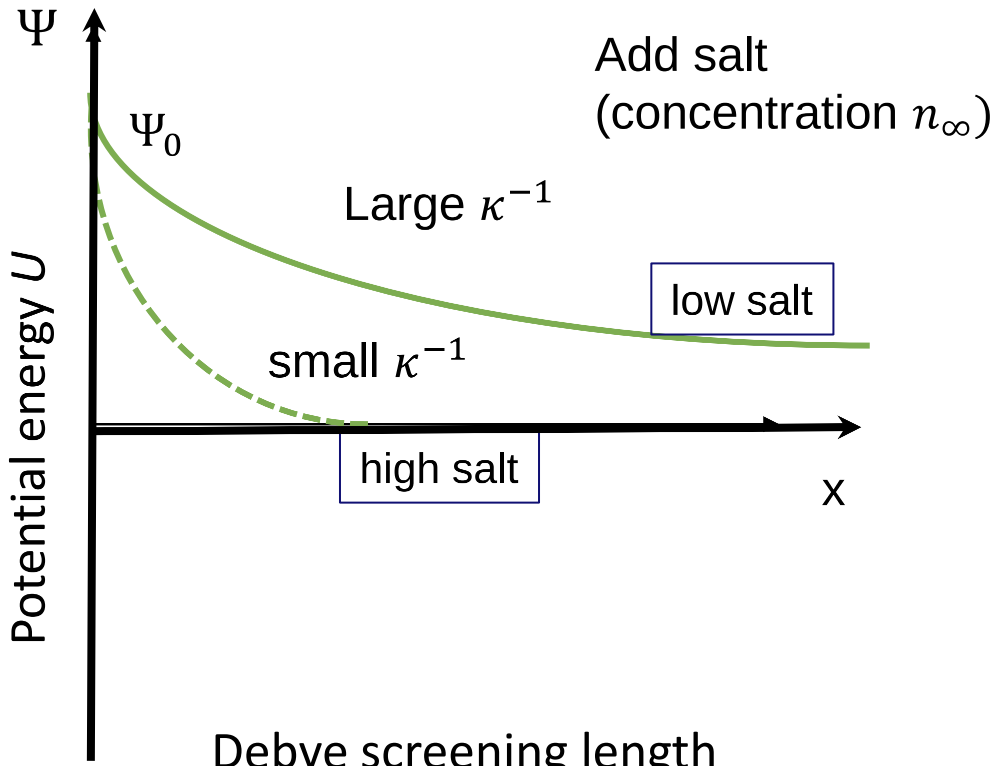
Electrostatic Interactions

Boltzmann – equilibrium distributions ions i

$$n_i = n_{i-bulk}\exp[\frac{-z_i\, e\, \Psi}{kT}]$$

with $\Psi = \Psi_0 \exp(-\kappa\, x)$

Debye-Hückel



Debye screening length

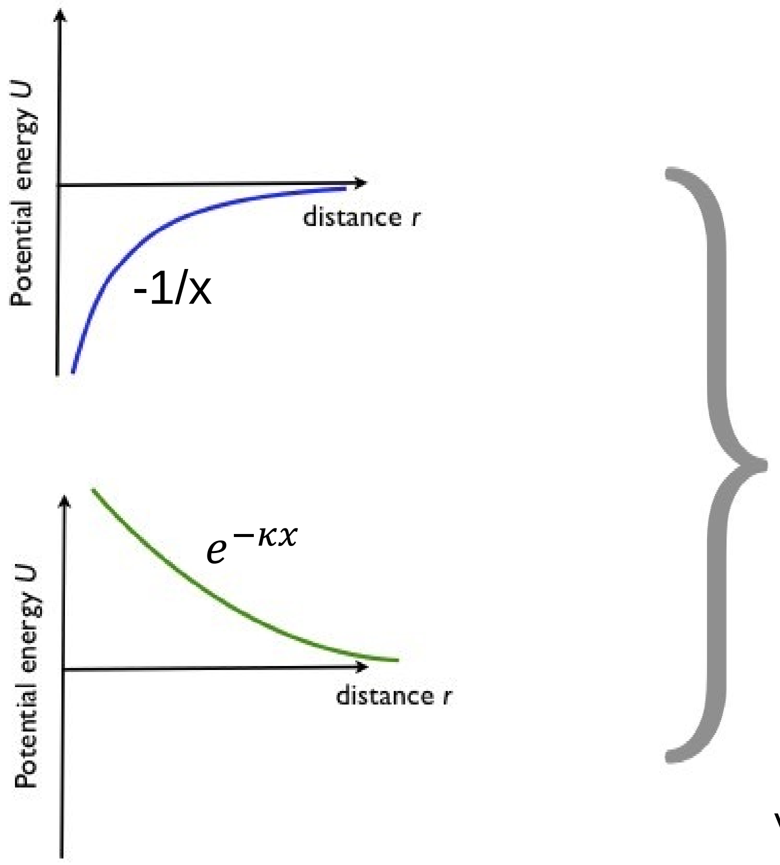
$$\kappa^{-1} = \sqrt{\frac{\varepsilon\varepsilon_0 kT}{2n_\infty z^2 e^2}}$$

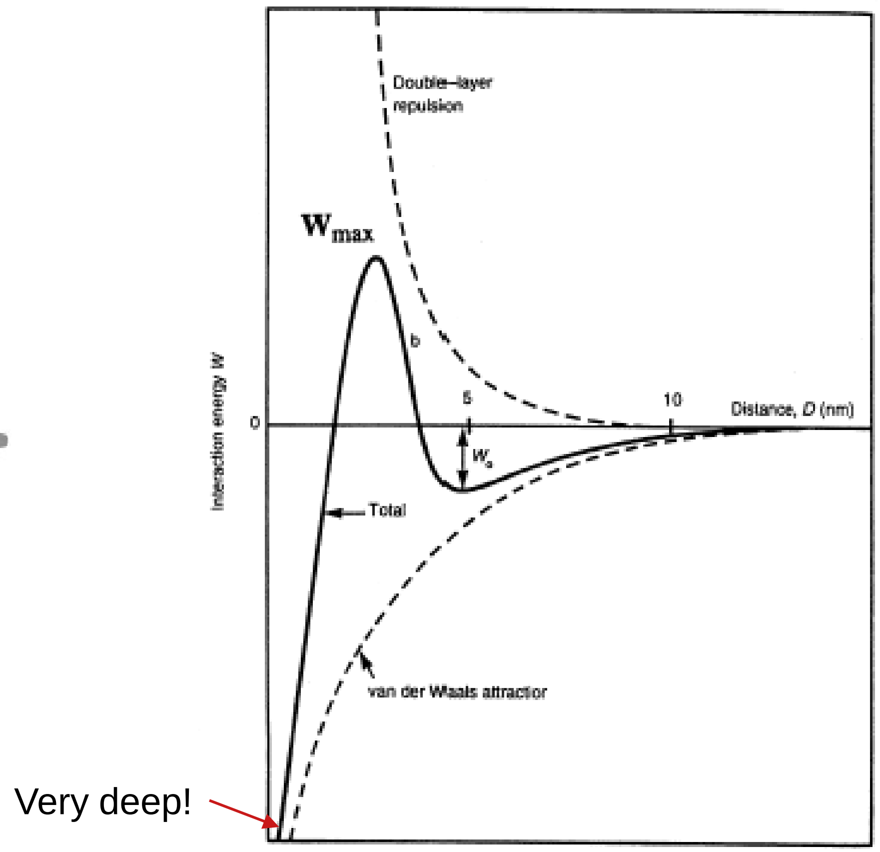
Typical screening length: 1 mM NaCl in water κ^{-1} =10nm

DLVO forces

(named after Derjaguin, Landau, Verwey & Overbeek)

Colloidal stability = balance between attractive van-der-Waals forces and repulsive electrostatic forces



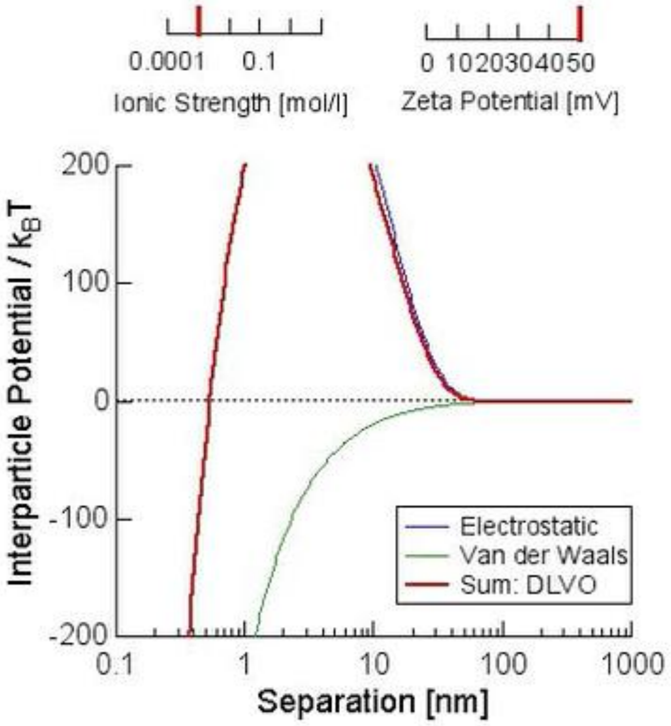


W_{max} protects against:

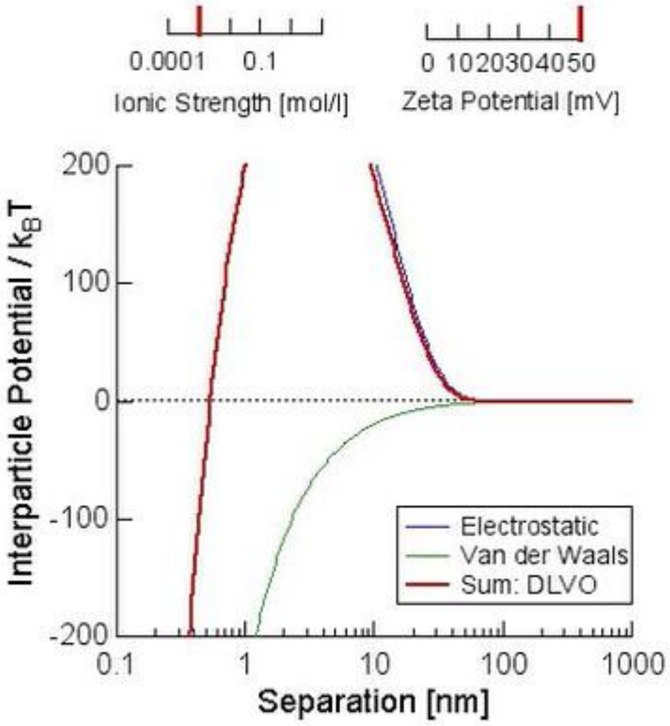
- Aggregation
- Coagulation
- Floculation
- Agglomeration
- gelation

DLVO forces

Changing surface charge (changing pH)



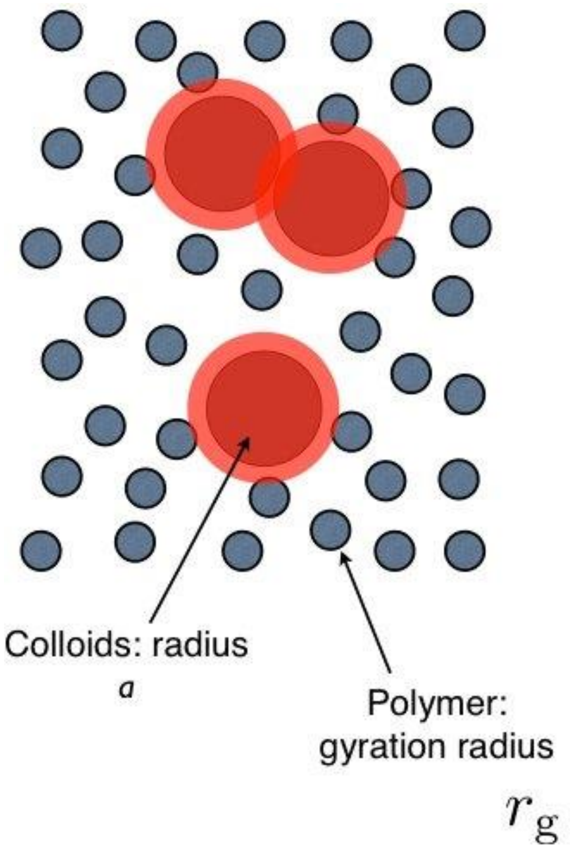
Changing Debye screening (changing ionic concentration)

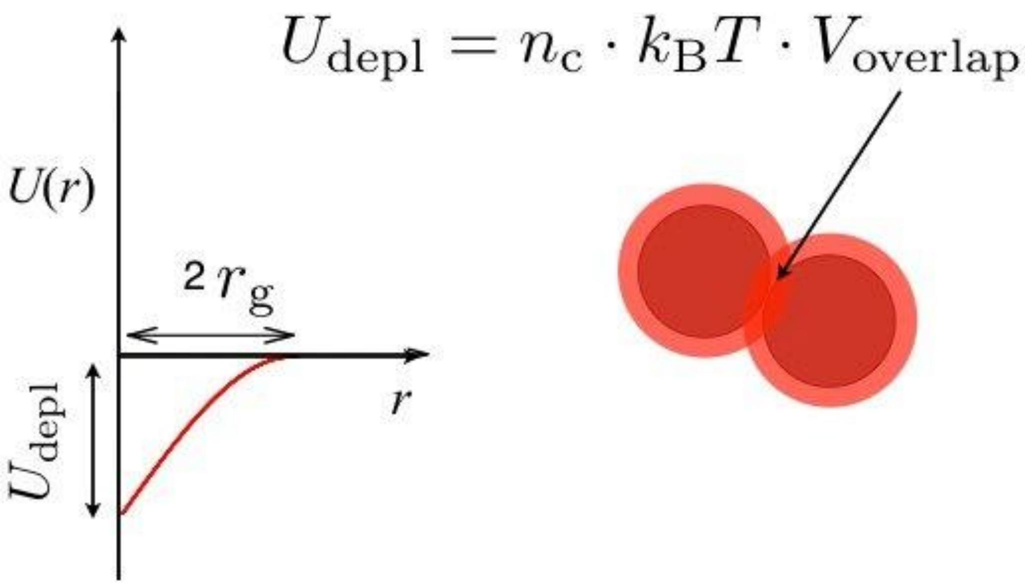


TU/e

Polymers: Depletion interactions

Mixing two sizes of purely repulsive objects together can lead to attractive forces ! ...

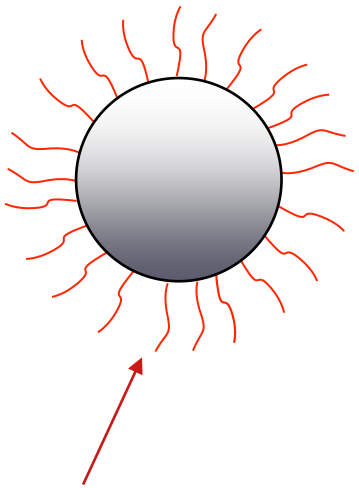




Size r_g sets range
Concentration n_c sets depth

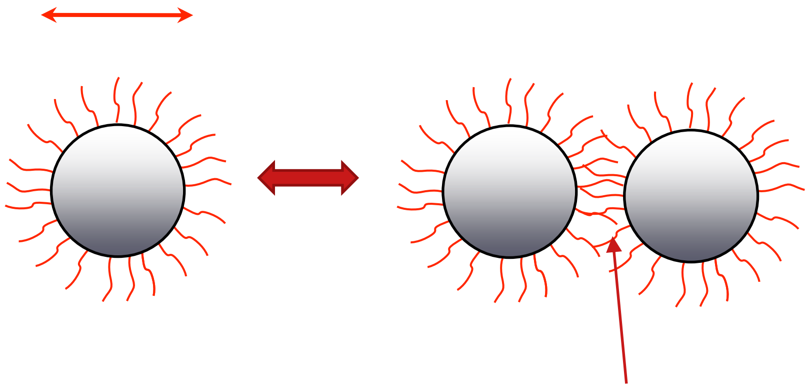
Polymers: Steric interactions

Steric repulsion



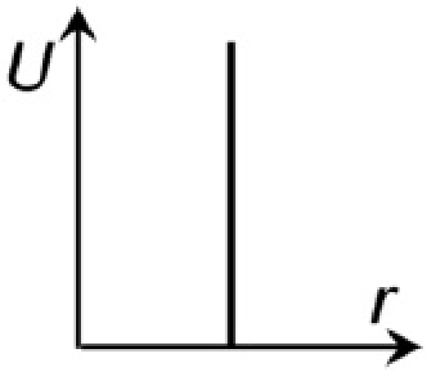
Thin layer of polymer brushes on colloidal particles

Range = 2a



Up on approach
$\Delta S < 0$

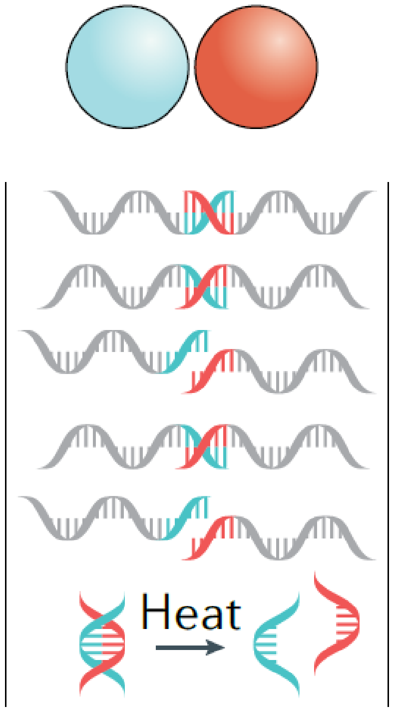
Hard sphere interaction



$$u(r) = \begin{cases} \infty & \text{for } r < 2a \\ 0 & \text{for } r > 2a \end{cases}$$

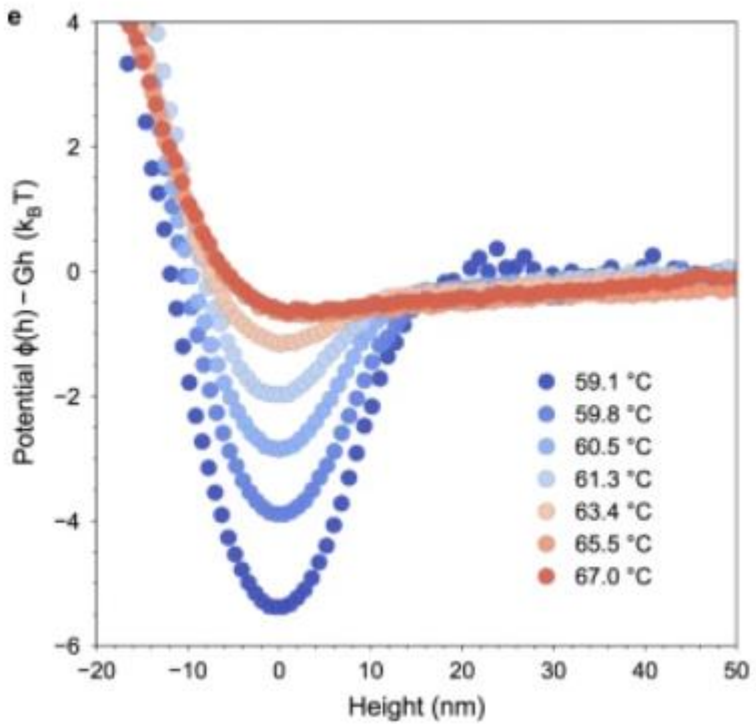
Polymers: DNA interactions – Temperature control

DNA



Hueckel, Hocky and Sacanna *Nature Reviews* (2021)

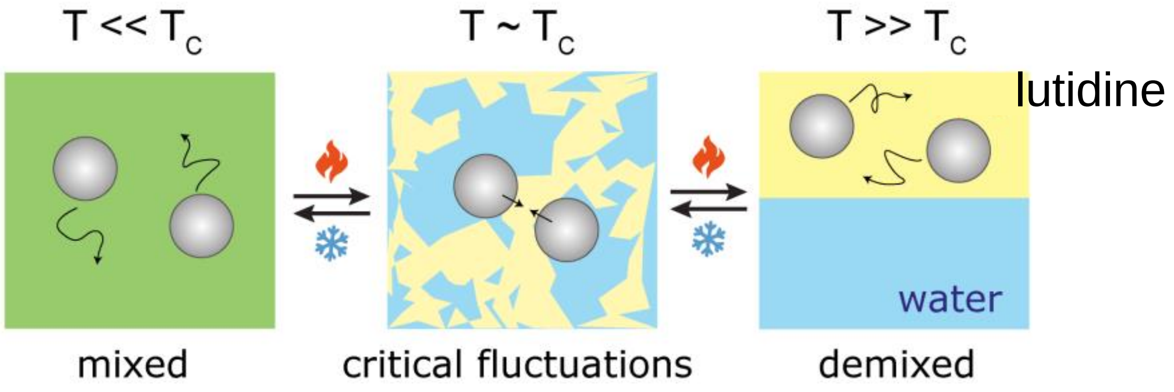
Temperature dependent short-range attraction

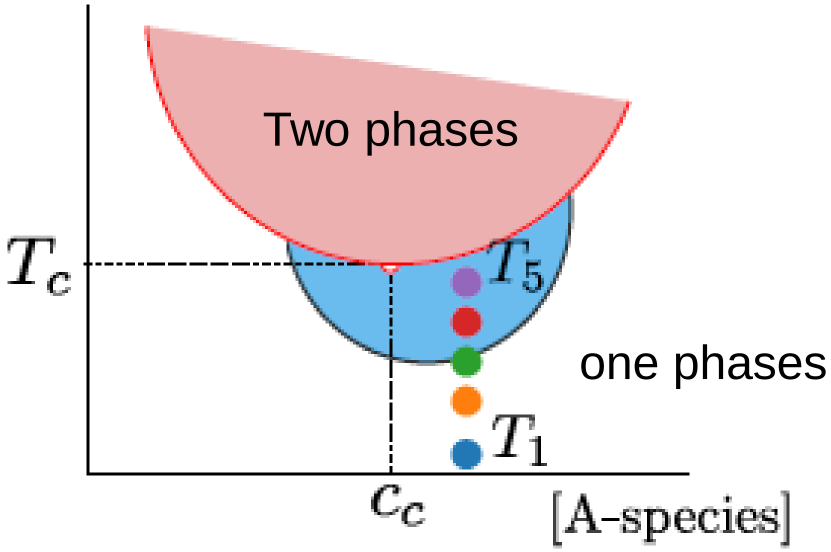


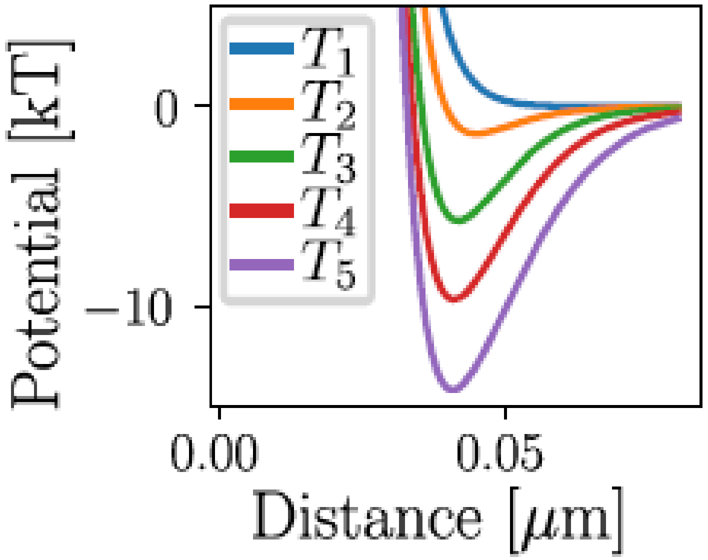
Cui, F., Marbach, S., Zheng, J.A. *et al. Nat Commun* **13**, 2304 (2022).

Critical Casimir Force - Solvent mediated interactions

- In certain solvent mixtures attractive interactions between colloids can be induced upon demixing







Colloidal Interactions

Name	Type	Range	Strength
Van der Waals	Attractive	0.3-10nm	0-100$k_B T$
Electrostatic	Attractive Repulsive	0.3-1000nm	0-1000 $k_B T$
Depletion DNA Critical Casimir	Attractive	10-300nm	0-20 $k_B T$
Brushes	Hard repulsion Soft repulsion Reversible attraction	5-50nm	0-50 $k_B T$

Wide range of interactions, highly tunable !

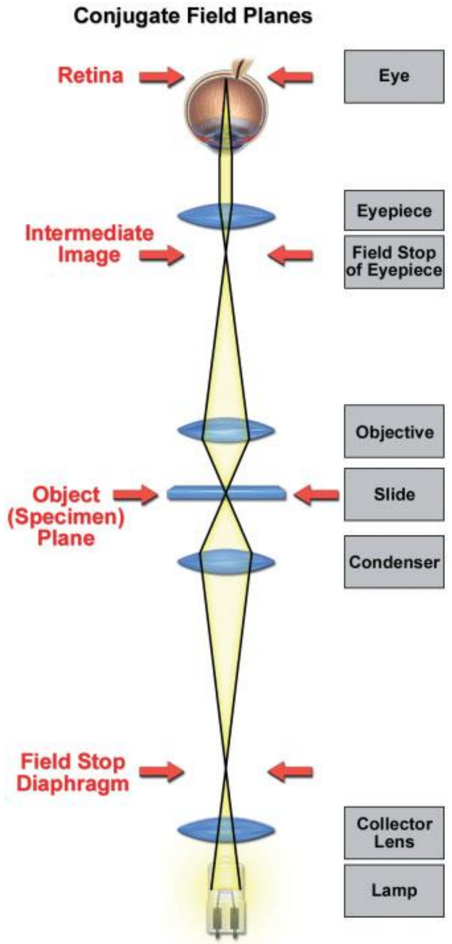
TU/e

Outline

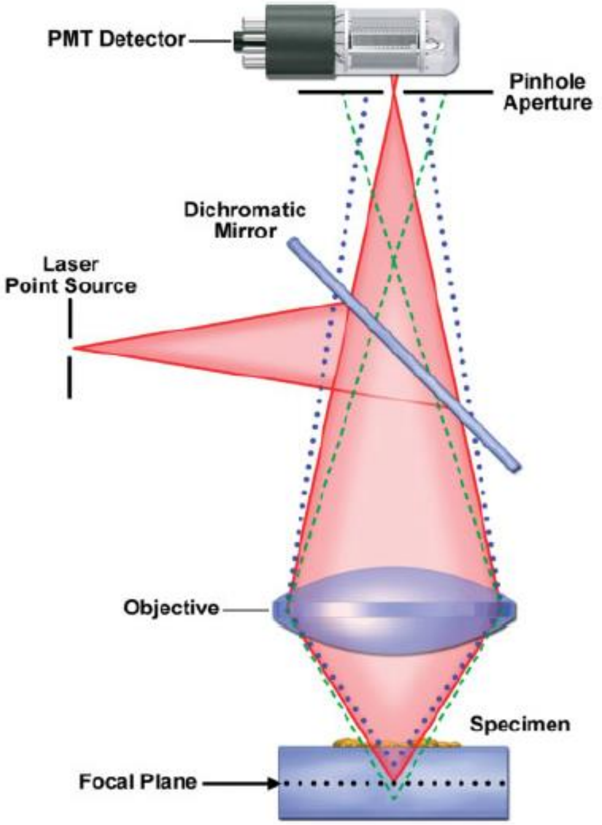
- Colloids basics + historical notes
  - Size, mechanics, systems
- Interactions between colloids
- Characterization of colloid phases
- Phase behaviour of hard spheres

How to investigate Colloids? - Microscopy

- Bright Field Microscopy (1595 – now)
  Mainly 2D imaging



- Confocal Laser Scanning Microscopy (1987)
  Allows 3D imaging

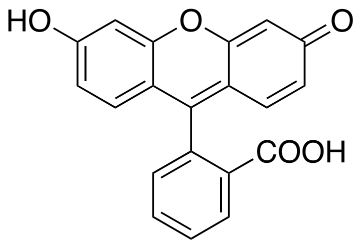


- Super resolution microscopy (beyond diffraction limit)

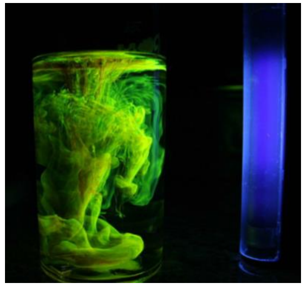
TU/e

Confocal laser scanning microscopy requirements

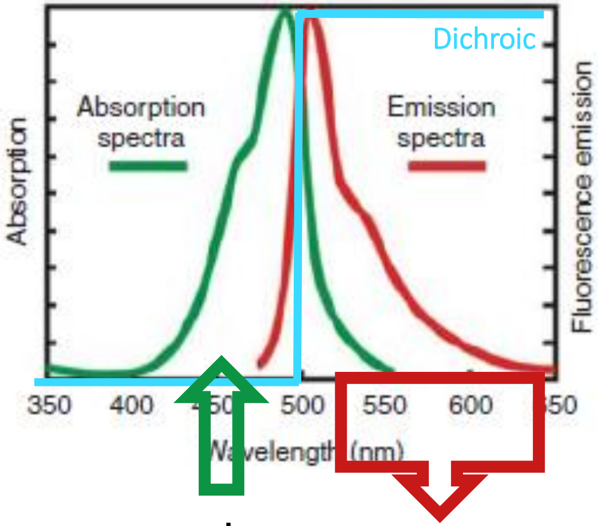
Fluorescent labeling



fluoresceine

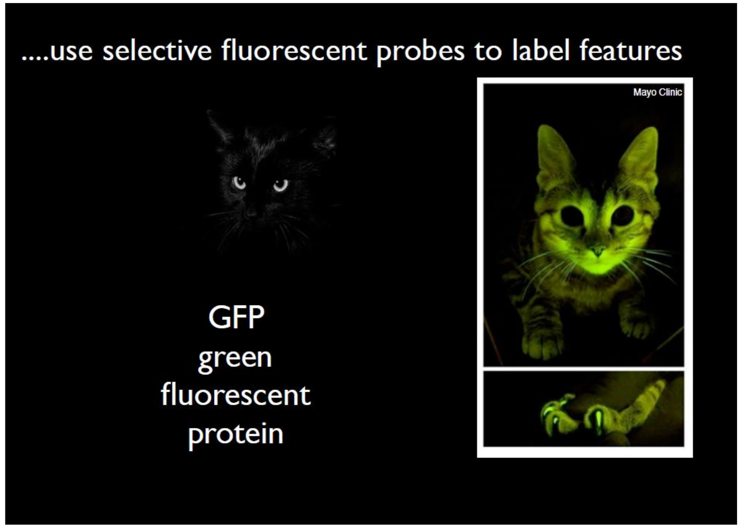


Laser excitation



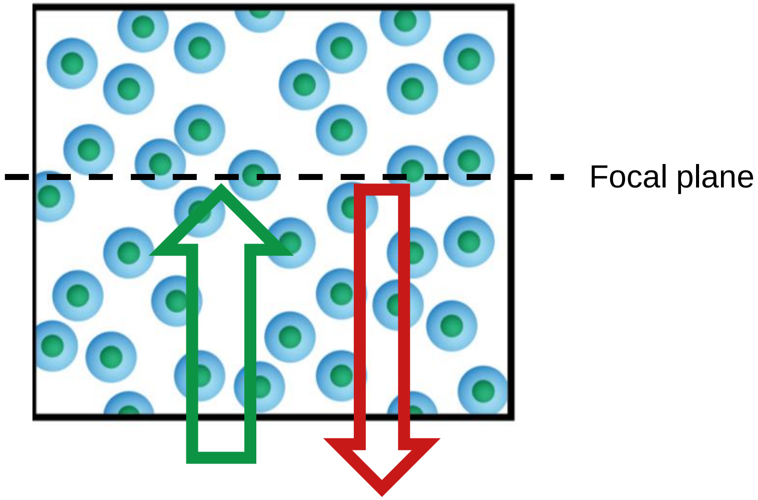
excite

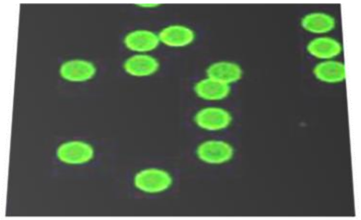
detect



Refractive index matching

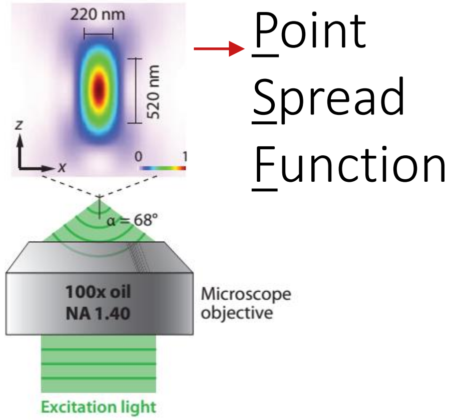
$n_{colloid} = n_{solvent}$



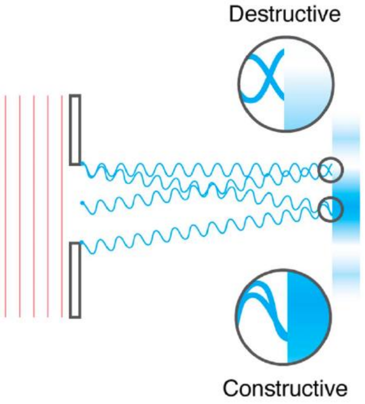


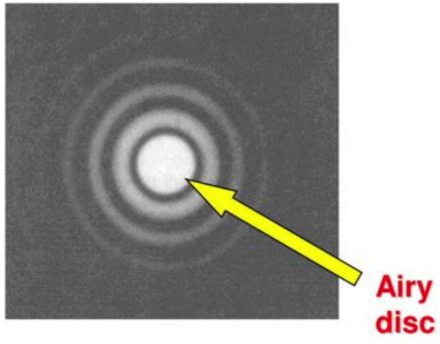
Diffraction limited Imaging

Focusing light



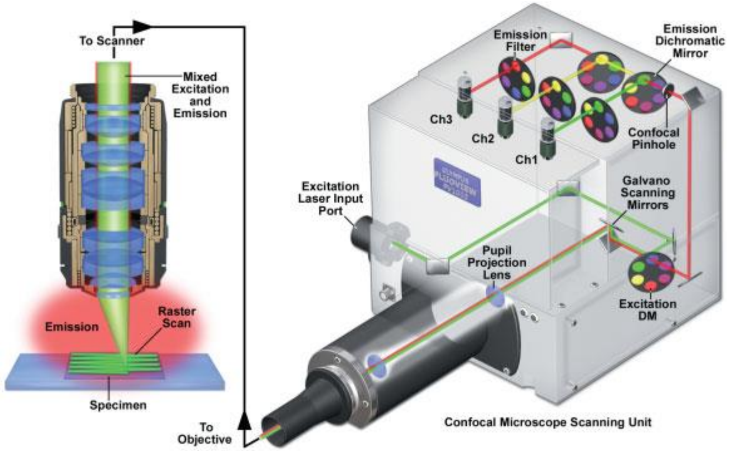
Focusing light is equivalent to diffraction from a circular aperture (light = wave)



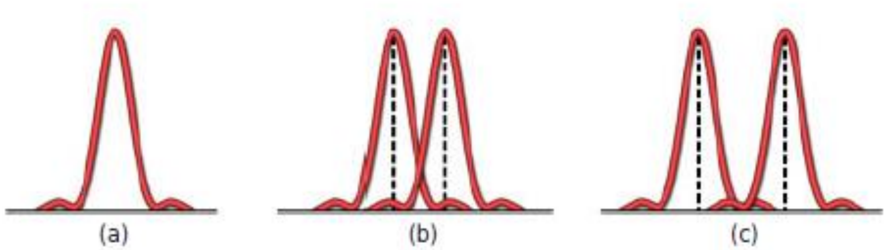


Methods Appl. Fluoresc. 6 (2018) 022003

Laser Scanning of diffraction limited spot



Two points imaged close together can only be distinguished if first minima overlaps with maximum



Abbe criterion:

$$d = \frac{\lambda}{2NA}$$

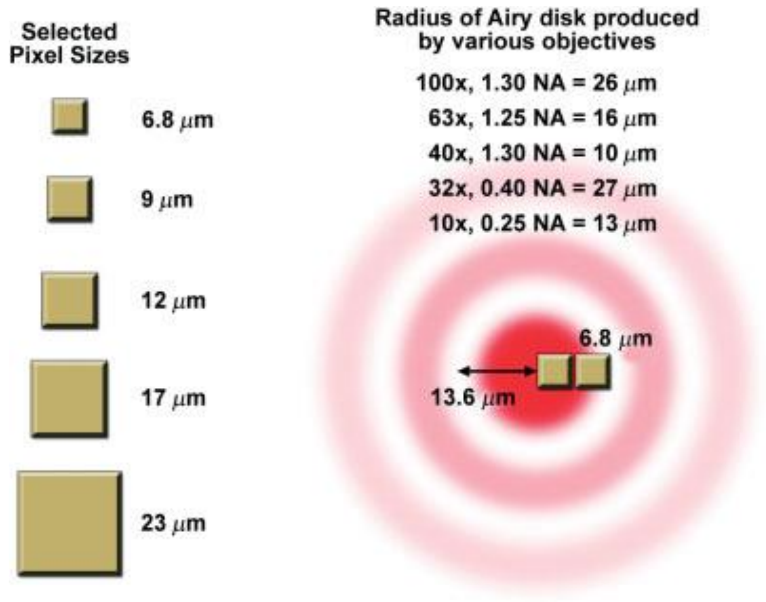
Resolving power of a microscope

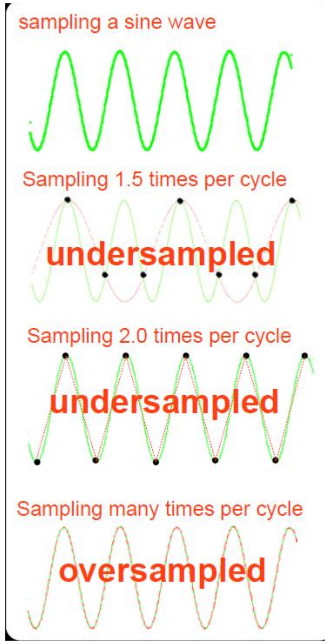
Resolution is determined by numerical aperture

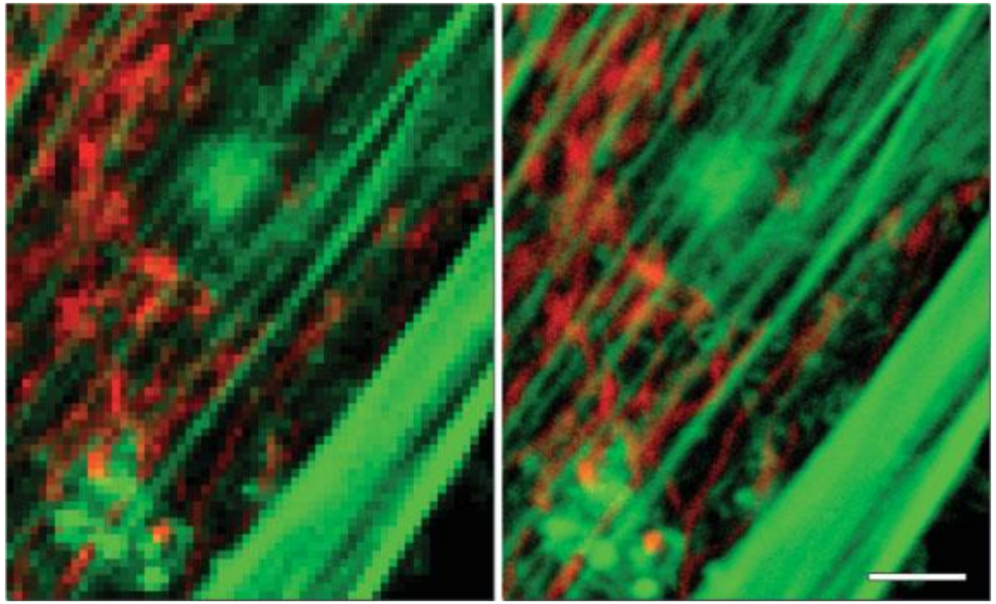
And detector settings

Nyquist theorem: a periodic signal must be sampled at more than twice the highest frequency component of the signal.

Optimum = 2.3 times per cycle





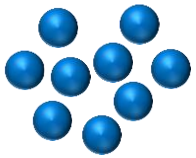


An image in which resolution is only limited by the size of the diffraction spot is called **diffraction limited**

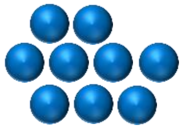
When done well → single particle information in 3D

SINGLE PARTICLE

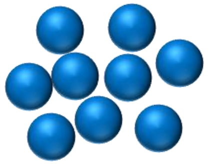
- Spatial resolution
- Dynamics
- Interactions
- Self-assembly



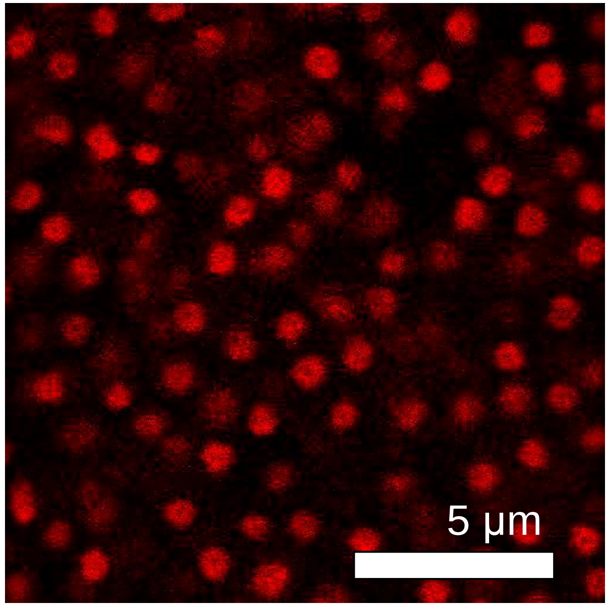
Fluid

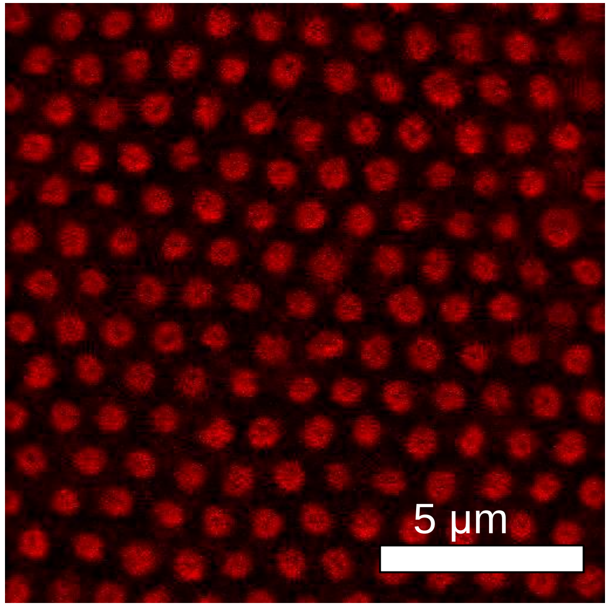


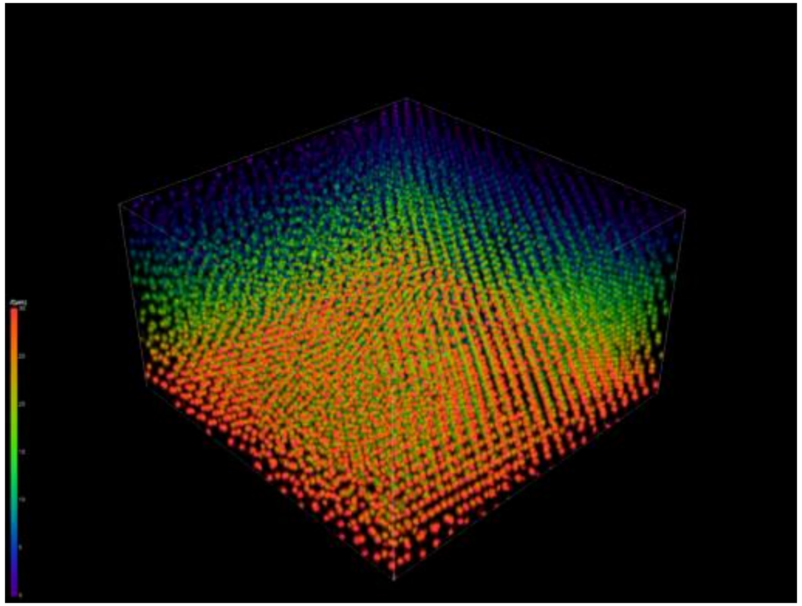
Crystal



Glass





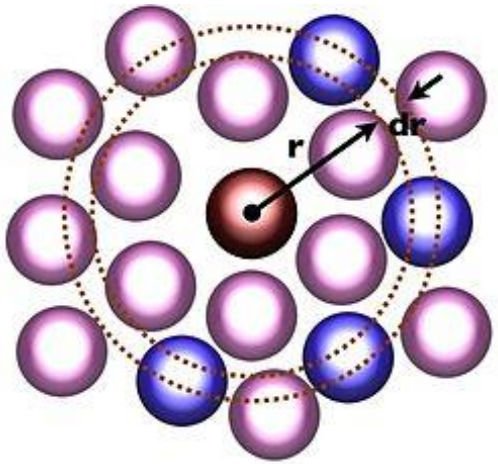


Volume fraction

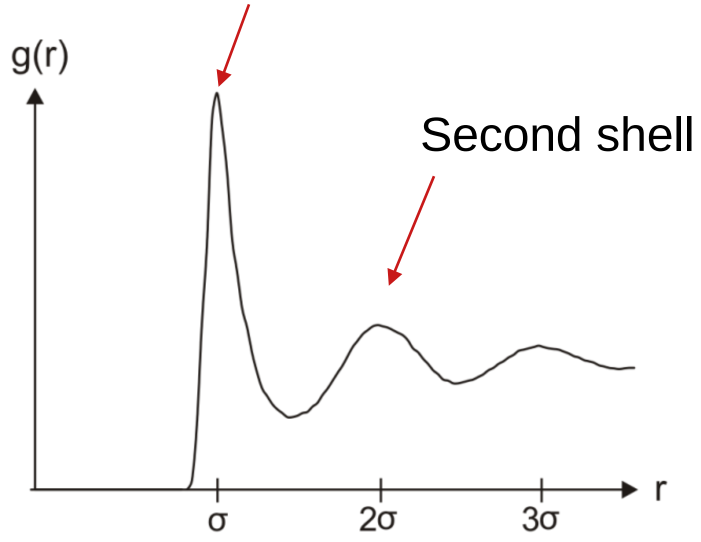
What we can learn? Radial distribution functions

- A.k.a. Pair correlation function
  = probability of finding a particle at a distance *r* from a given particle

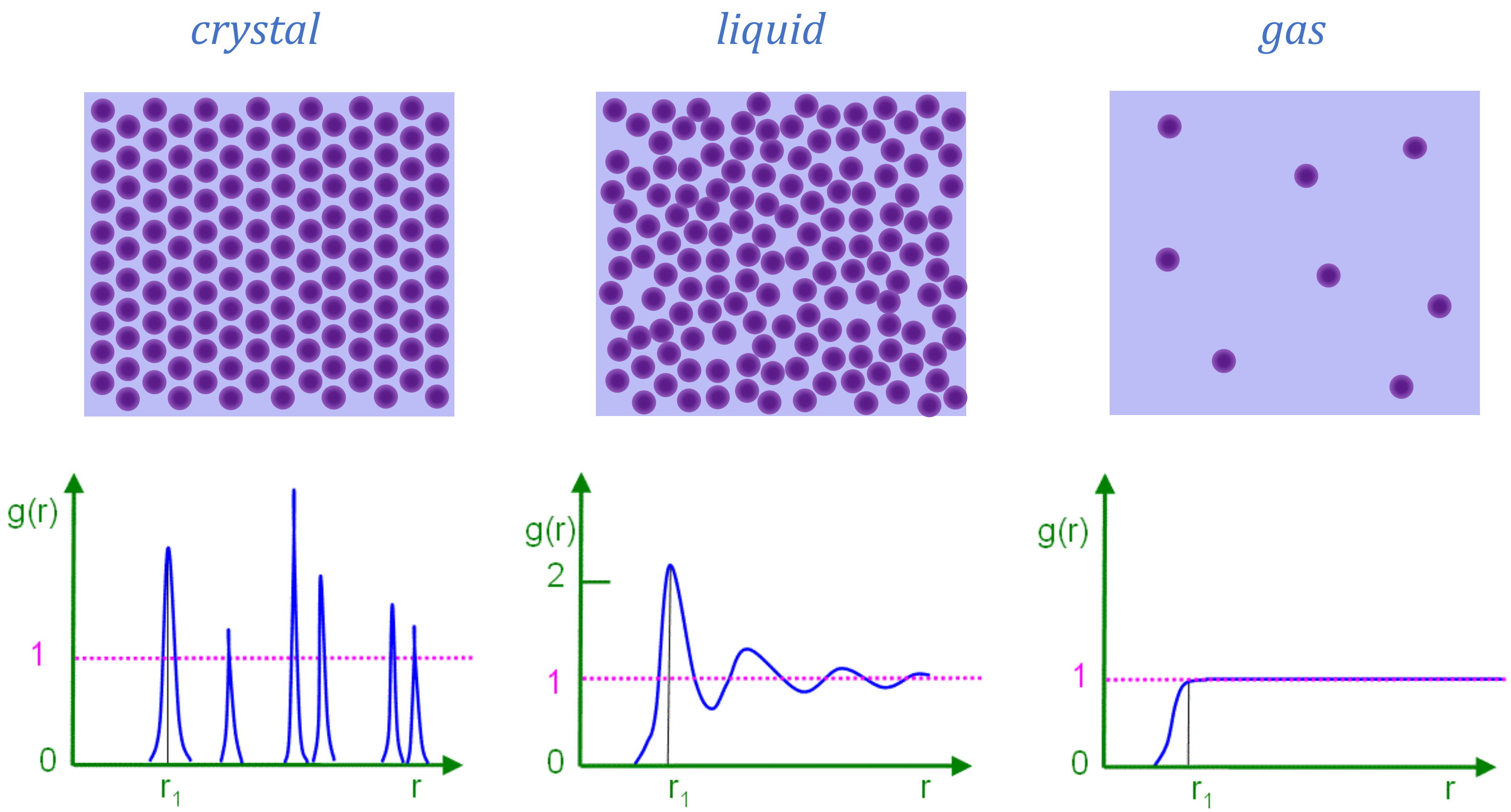
$$g(r) = \frac{1}{\rho^2}\left\langle \sum_i \sum_{j \neq i} \delta(\vec{r_i})\, \delta(\vec{r_j} - \vec{r_i}) \right\rangle$$



position of first peak
= average nearest-
neighbor distance



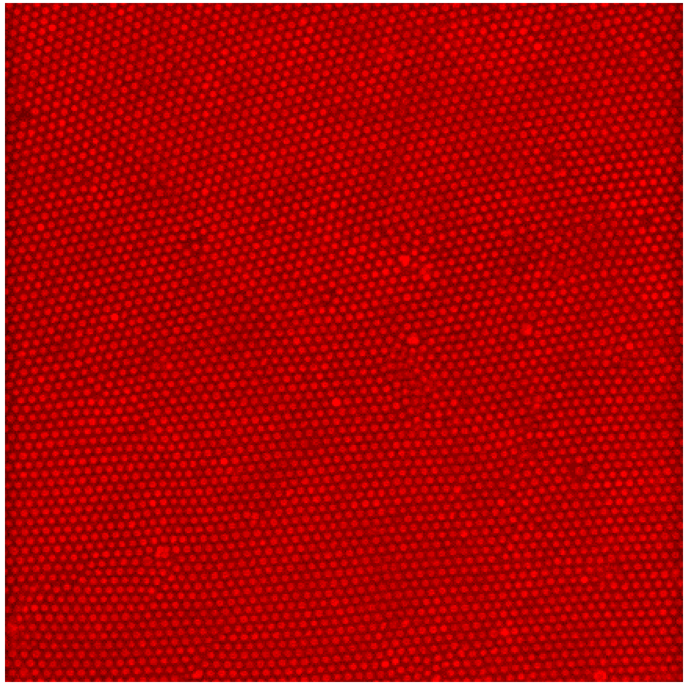
Typical radial distribution functions g(r)

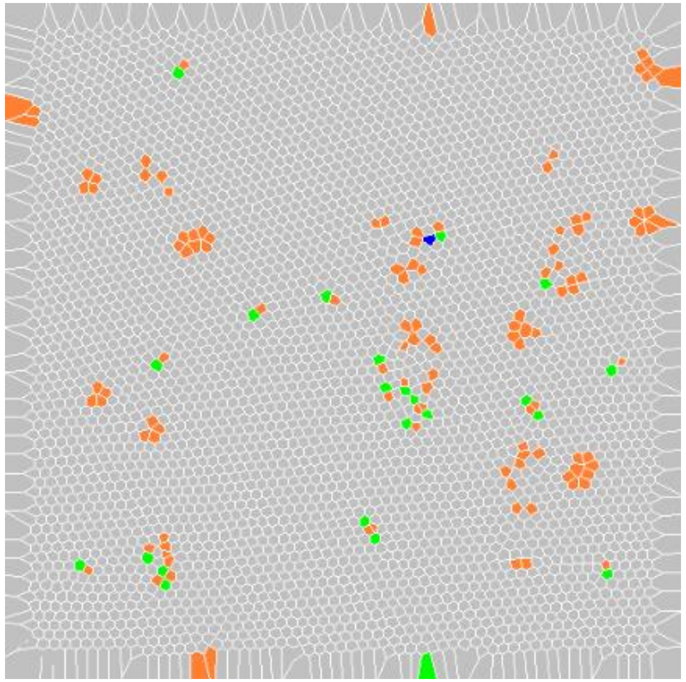


Measuring g(r) gives you direct insight into the (average) structure of a material.

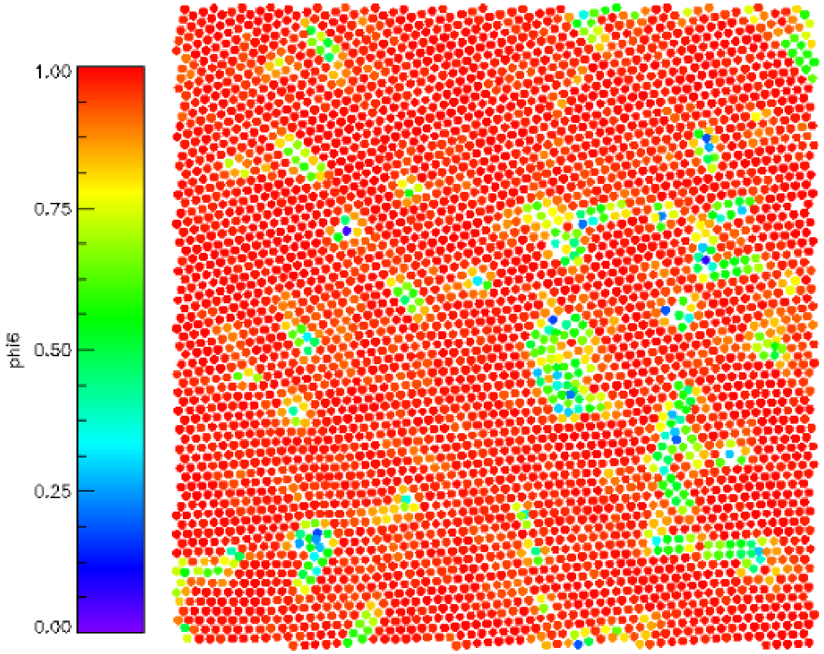
Local Order Parameters

- Particle positional correlations – identify defects





Voronoi construction for neighbors



Bond order parameter Ψ_6

$$\psi_6 = \frac{1}{N}\sum_{i \neq j}^{N} e^{6i\theta(r_{ij})}$$

How to investigate Colloids? - Scattering

Typical Scattering experiment

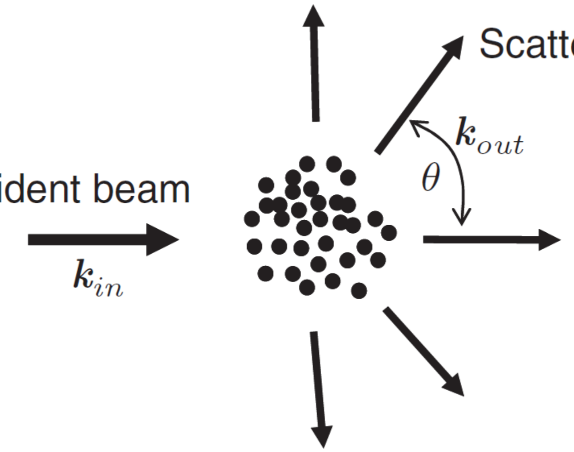
Far-field observation r » R

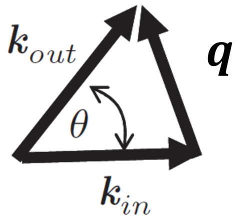
detector

$$I(\theta) = I(\boldsymbol{q})$$

Scattered intensity

λ





Scattering:

$$|\boldsymbol{k}_{in}| = |\boldsymbol{k}_{out}| = \frac{2\pi}{\lambda}$$

Scattering vector:

$$\boldsymbol{q} = \boldsymbol{k}_{in} - \boldsymbol{k}_{out} = \boldsymbol{k}$$

For theorist!

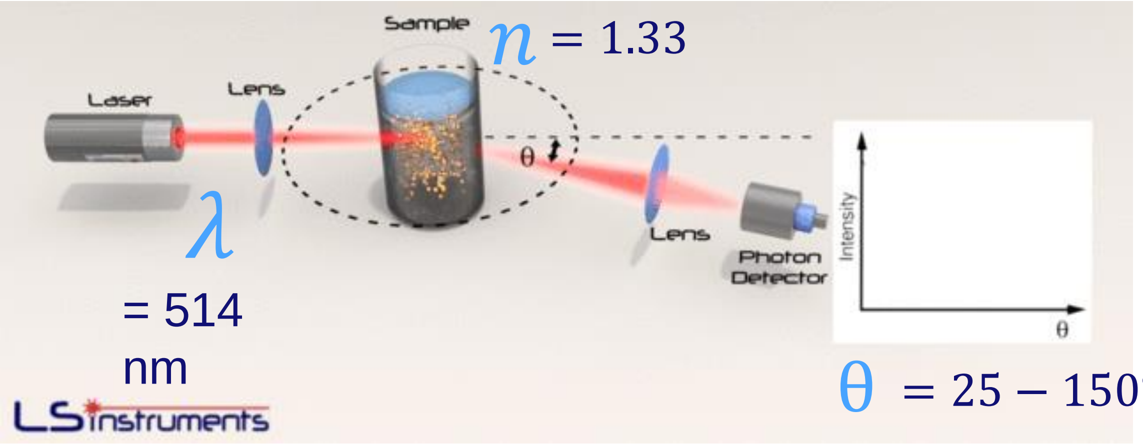
$$|\boldsymbol{q}| = q = \frac{4\pi n}{\lambda}\sin\frac{\theta}{2}$$

Figure: Doi, Soft Matter Physics

TU/e

Static Light Scattering & Small Angle X-ray Scattering

- Typical SLS experiments

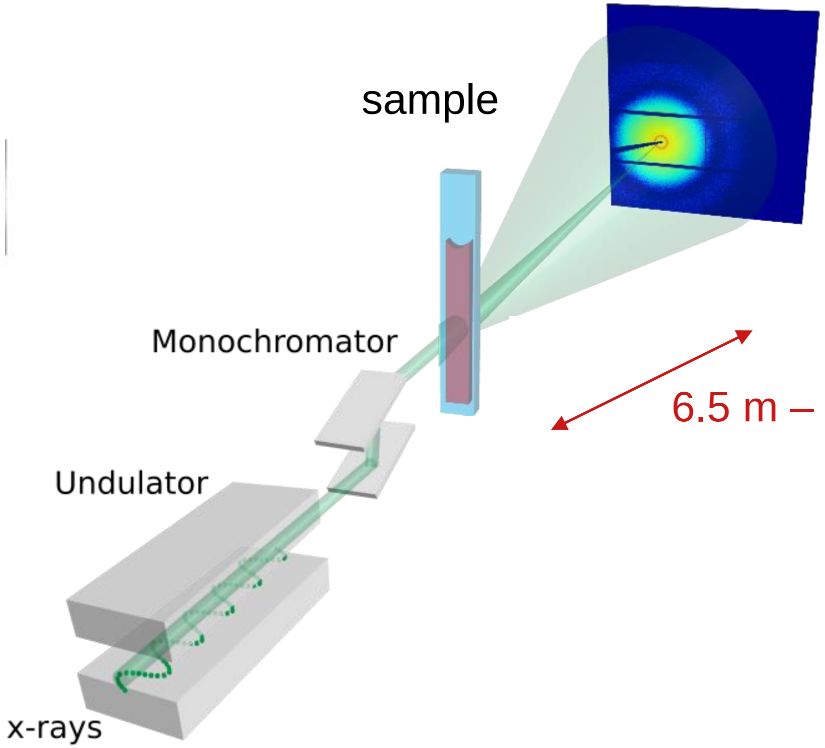


$n = 1.33$

λ = 514 nm

$\theta = 25 - 150°$

- Typical SAXS experiments



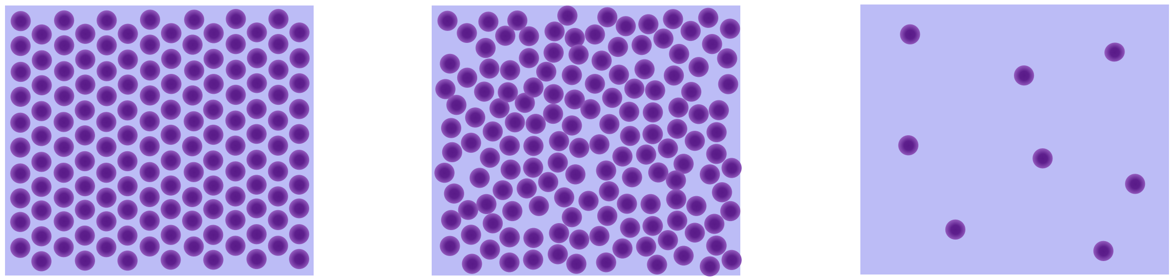
TU/e

What can we learn?

Measured scattering intensity= $I(q) \cong P(q)S(q)$

The form factor $P(\boldsymbol{k})$ contains information about the "form" (=shape) of the particles:

The structure factor $S(\boldsymbol{k})$ contains information about the "structure" (=positions) of the particles:



P(q) - Monodisperse Spherical Colloids

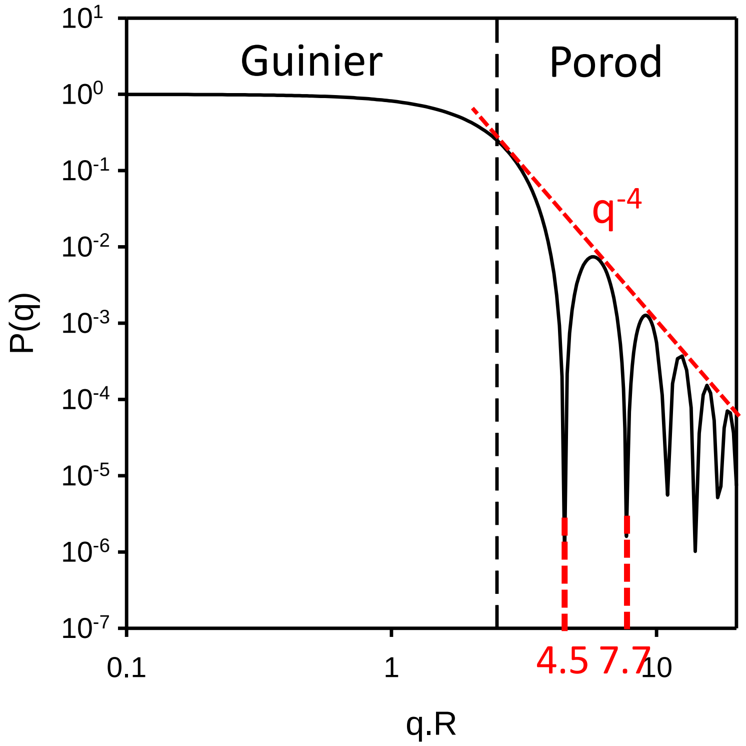
$$I(q) \cong P(q)S(q)$$

… non-interacting in dilute solution

$$S(q) = 1 \Rightarrow I(q) \cong P(q)$$

Analytical solution for a solid sphere

$$P(q) = 9\left(\frac{\sin(qR) - qR\cos(qR)}{(qR)^3}\right)^2$$

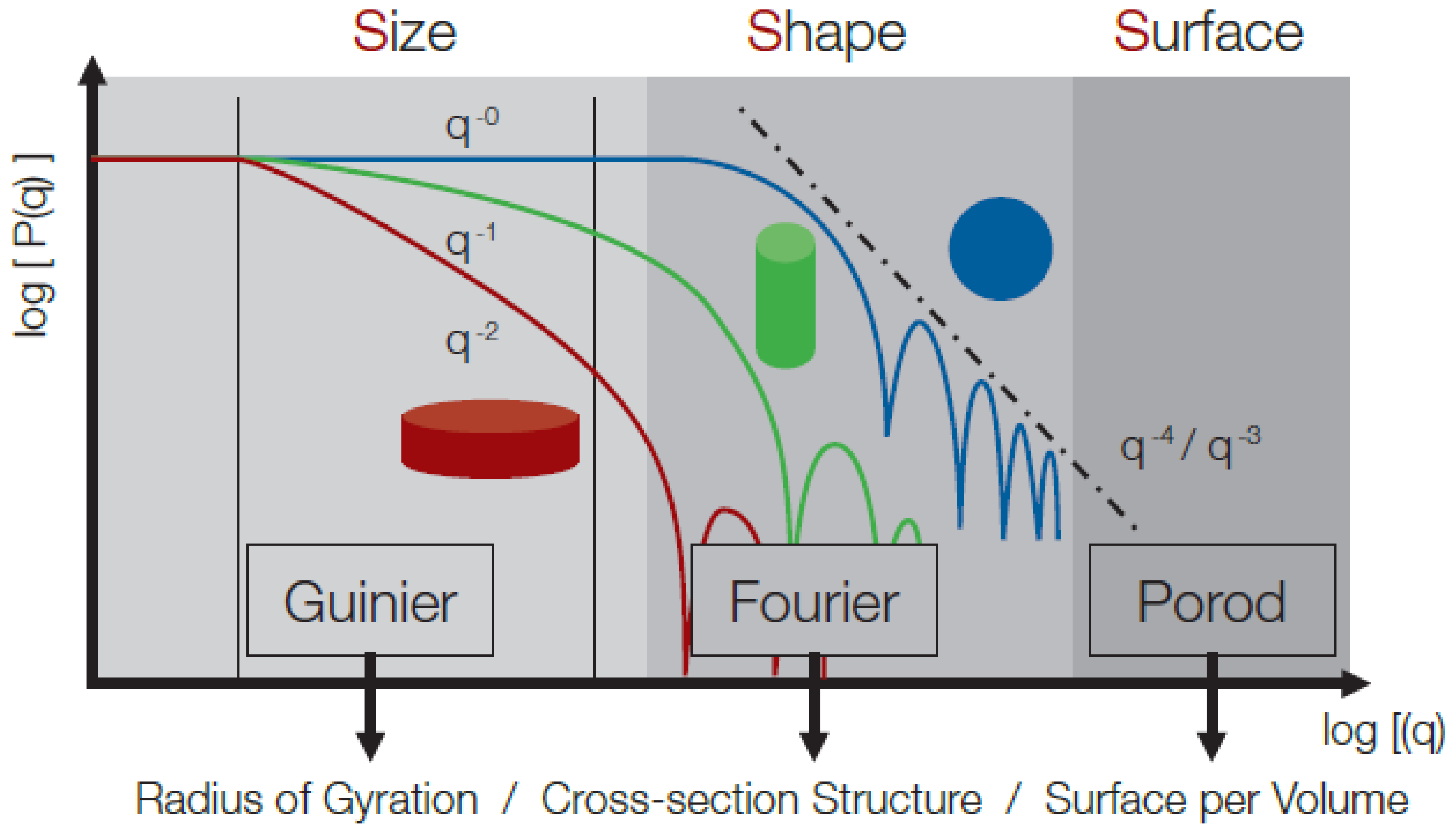


Guinier regime : $\ln(P(q)) = 1 - q^2 Rg^2/3$

Rg = Radius of gyration

TU/e

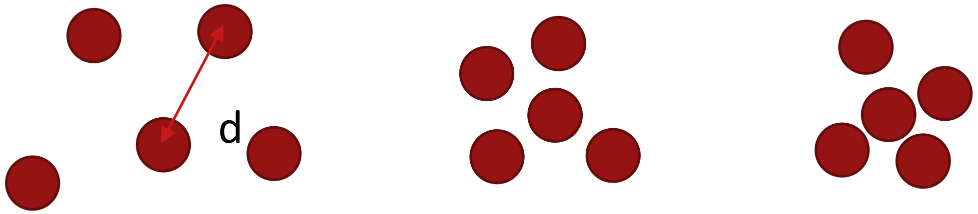
Different Shapes – Different P(q)

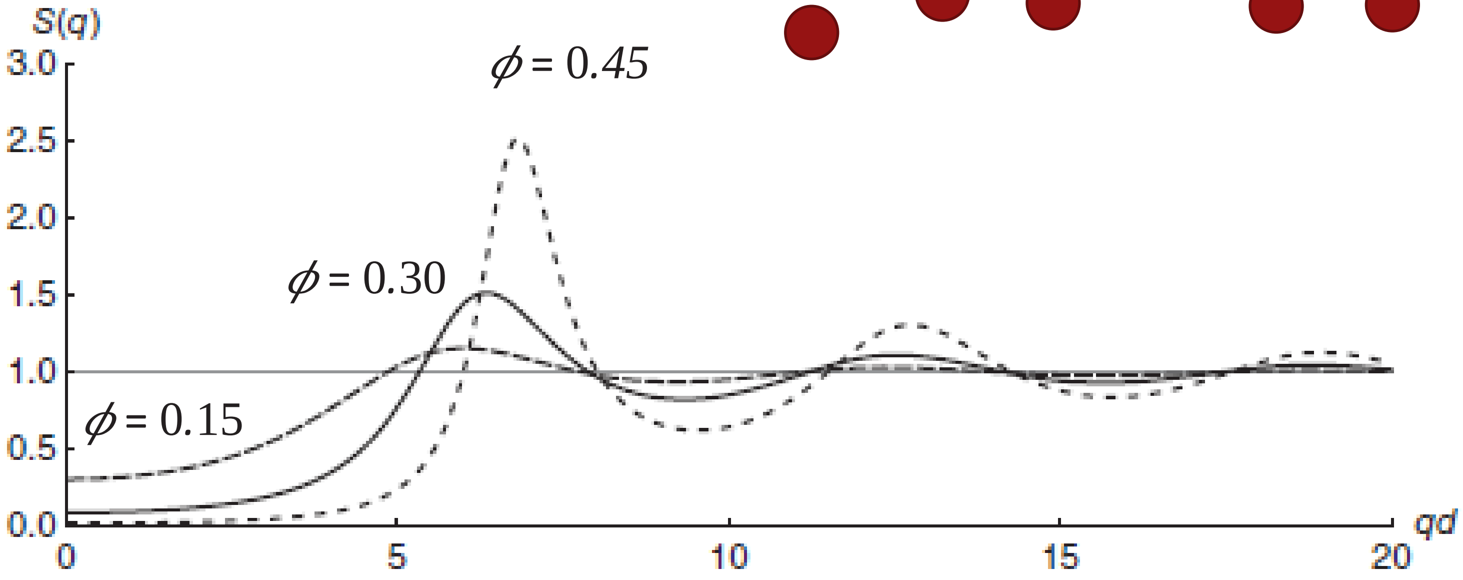


TU/e

Static Structure Factor - Fluid

In a fluid the relative positions between particles are correlated leading to typical spacing *d* between particles leads to peak

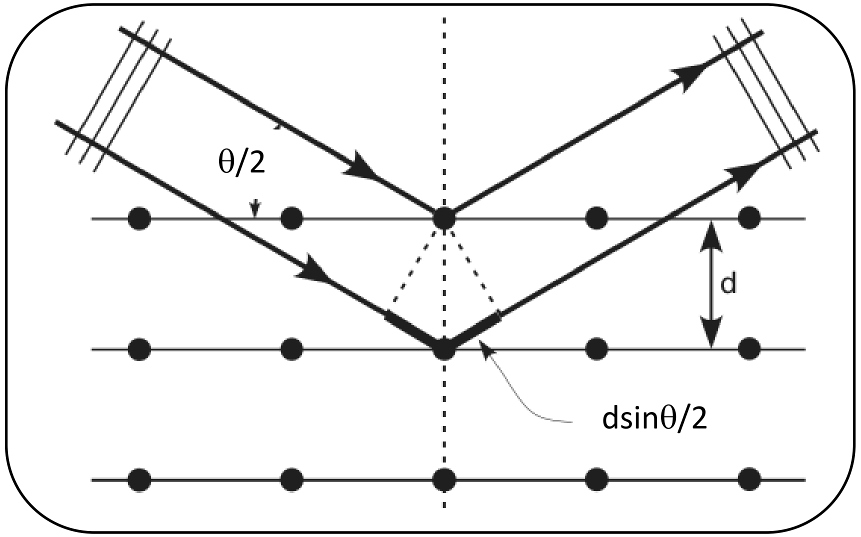


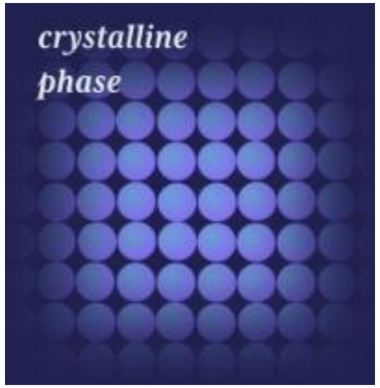


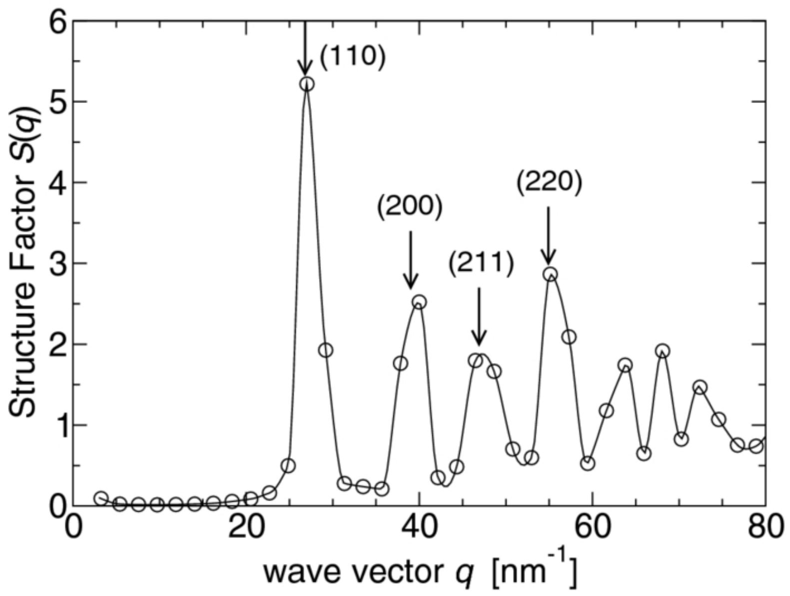
Statuuc Stucture Factor – Crystals

Bragg's law:
constructive interference when path length difference equals Nλ,

$$N\lambda = 2d\sin(\theta/2)$$







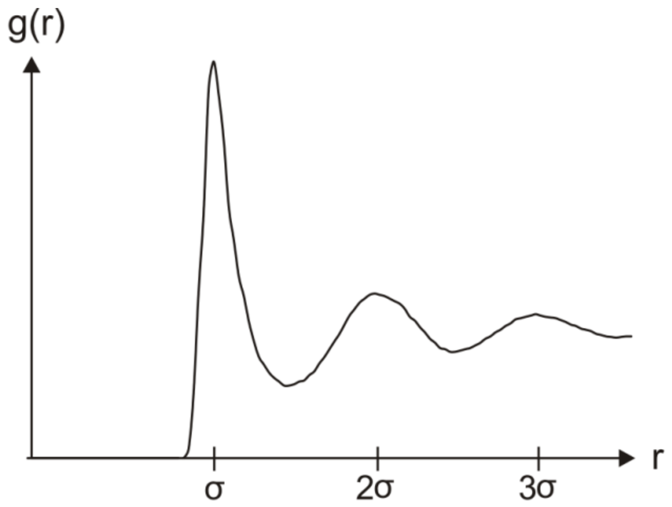
Example:
Diffraction by a grid
Is dependent on wavelength

https://www.instagram.com/p/B9CViAHBjPN/?utm_source=ig_web_copy_link

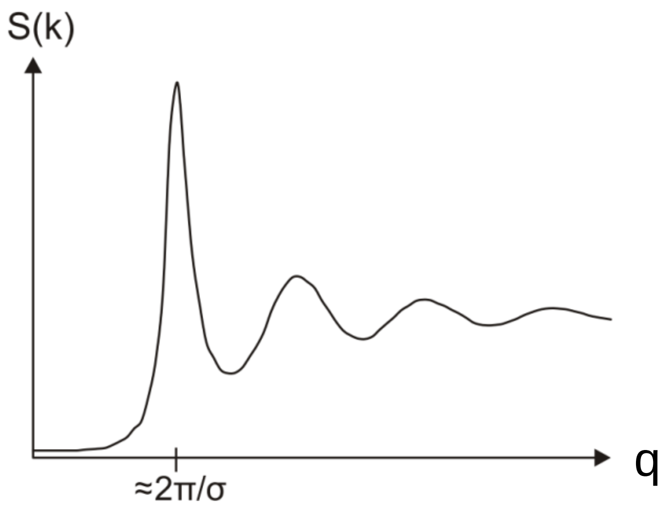
The static structure factor

- The static structure factor $S(q)$ contains a lot of information but is not necessarily easy to interpret.

- S(q) is Fourier transform of g(r) $S(q) = 1 + \rho \int d\mathbf{r} e^{-i\mathbf{q}\mathbf{r}} g(r)$



radial distribution function g(r)



static structure factor S(q)

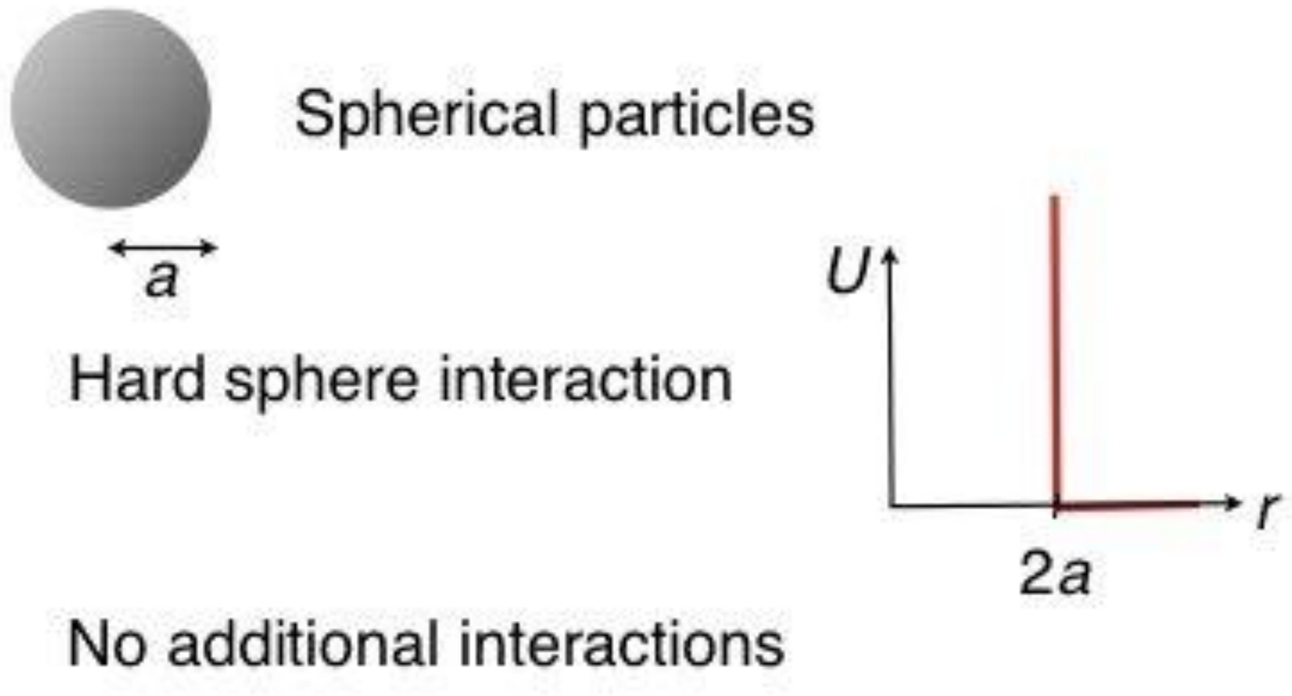
Liquid state theories AND simulations are based on interaction potentials
→ can be tested with g(r) and S(q)

TU/e

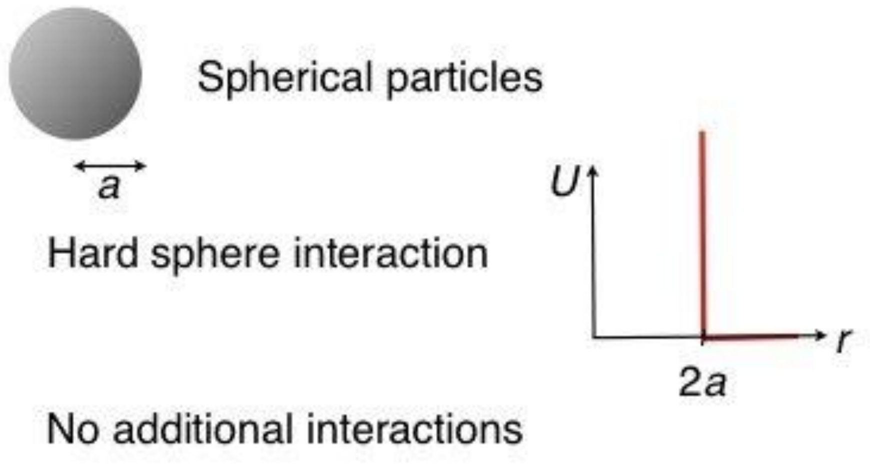
Outline

- Colloids basics + historical notes
  - Size, mechanics, systems
- Interactions between colloids
- Characterization of colloid phases
- Phase behaviour of hard spheres

Hard sphere colloids – the simples system



Hard sphere colloids



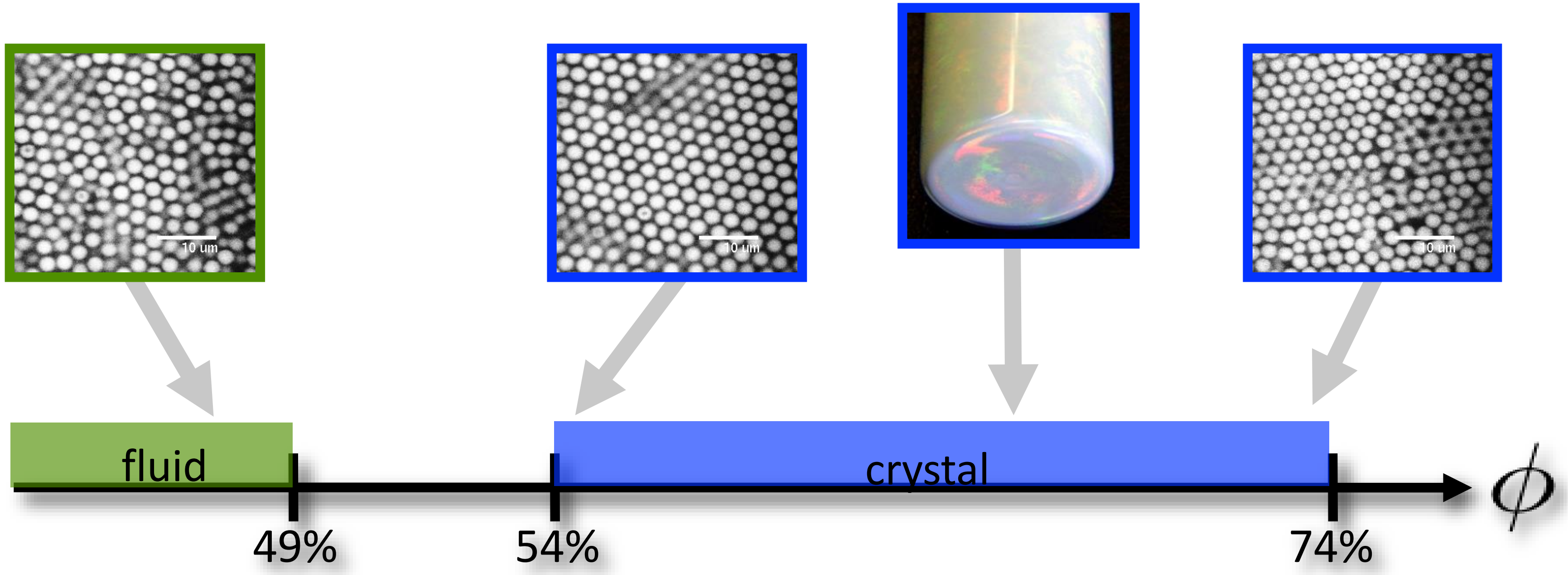
How should the phase diagram of these look?

Interaction is either zero or infinite.
=> No characteristic energy scale
=> Temperature change does not affect the phase behavior!

Hard Spheres

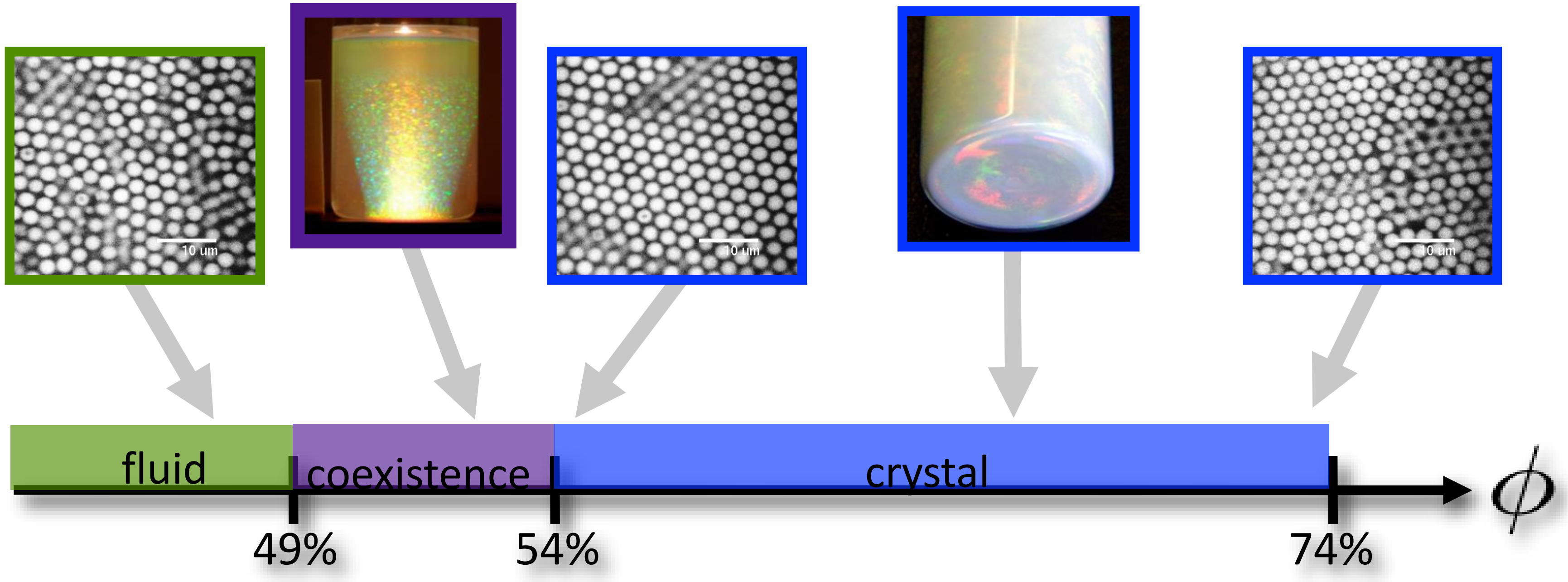
(Confocal images: E. Weeks)

Hard Spheres



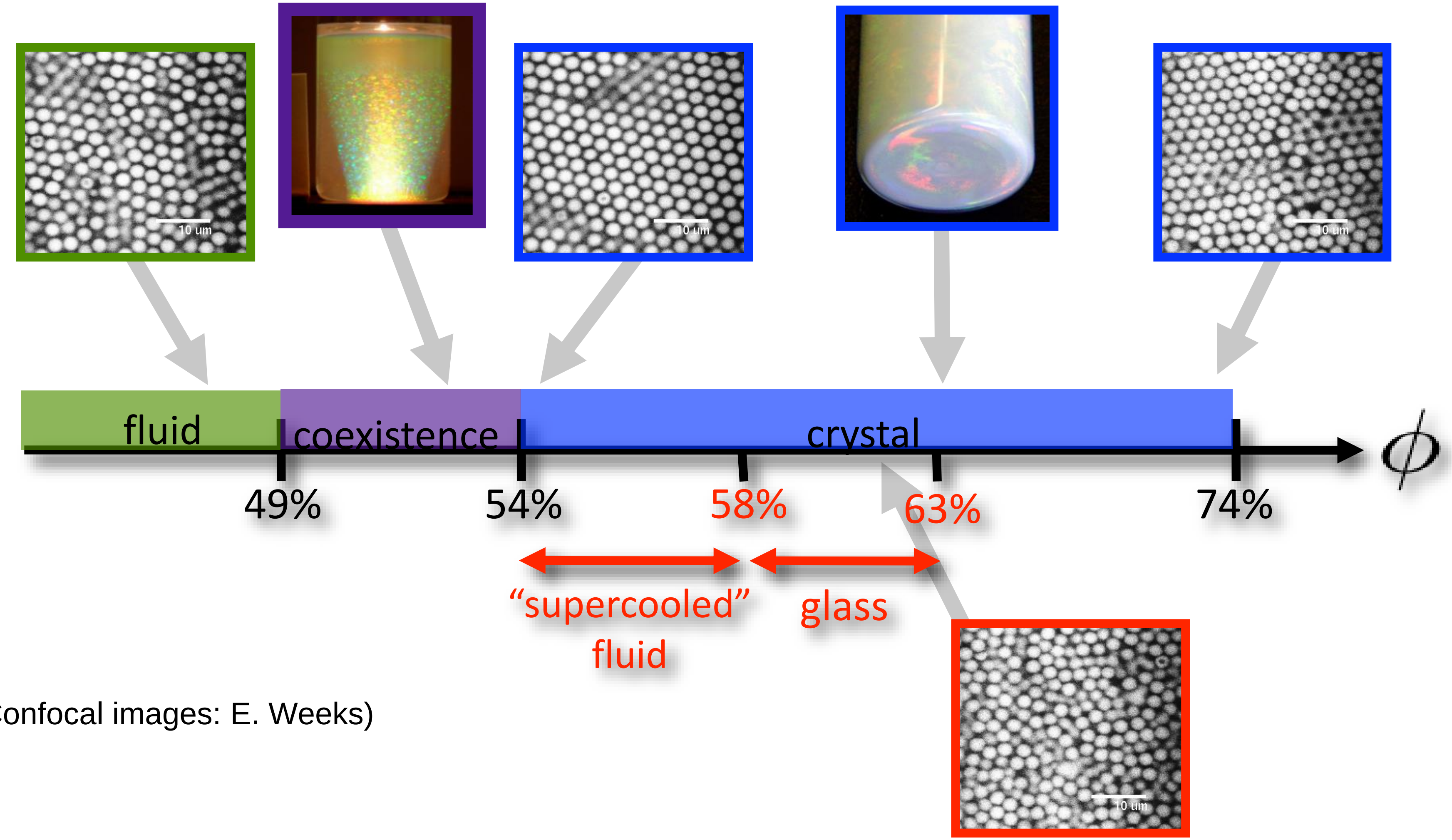
(Confocal images: E. Weeks)

Hard Spheres



(Confocal images: E. Weeks)

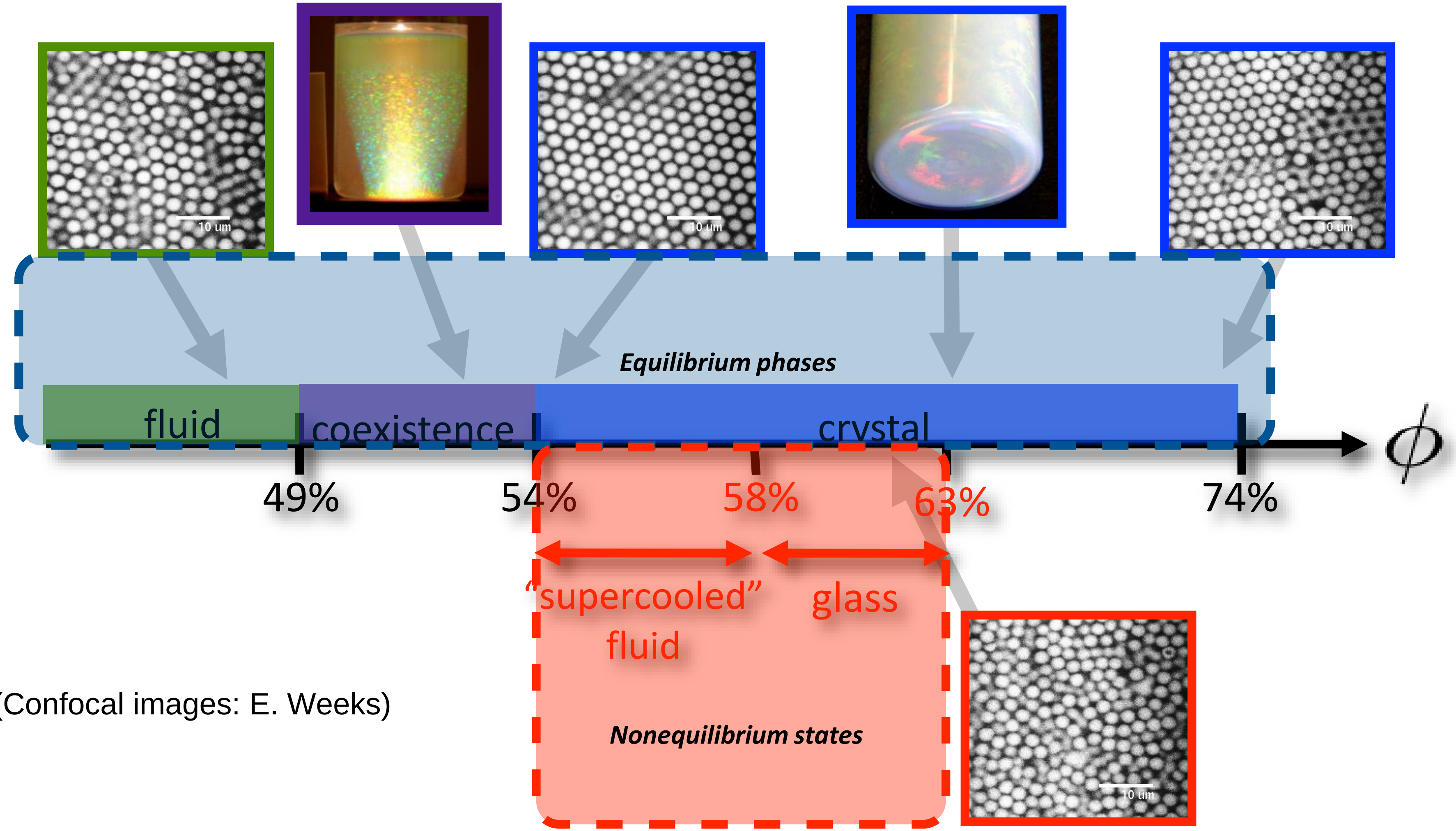
Hard Spheres



(Confocal images: E. Weeks)

TU/e

Hard Spheres



(Confocal images: E. Weeks)

=> Rich phase behavior even for this simplest system

Colloidal hard spheres

325 *nm* PMMA/decalin/CS2

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

Intermezzo: Why do hard spheres crystallize?

Computer simulations

- Alder & Wainwright (1957)
- Wood & Jacobson (1957)
- Hoover & Ree (1968)

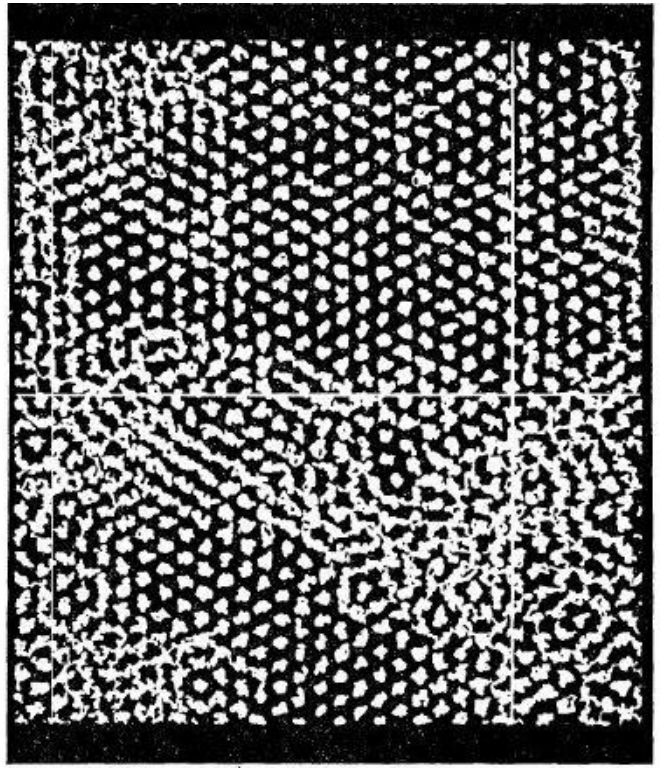
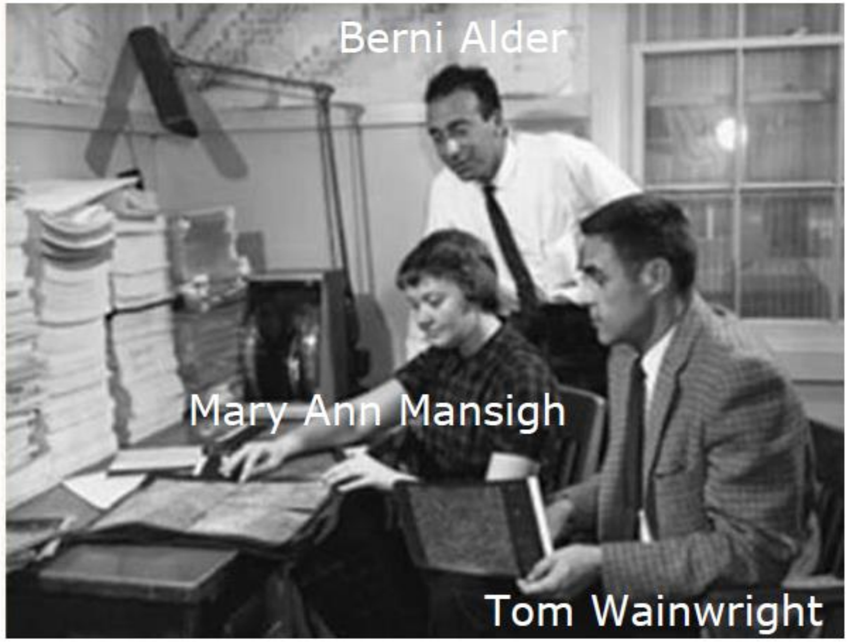
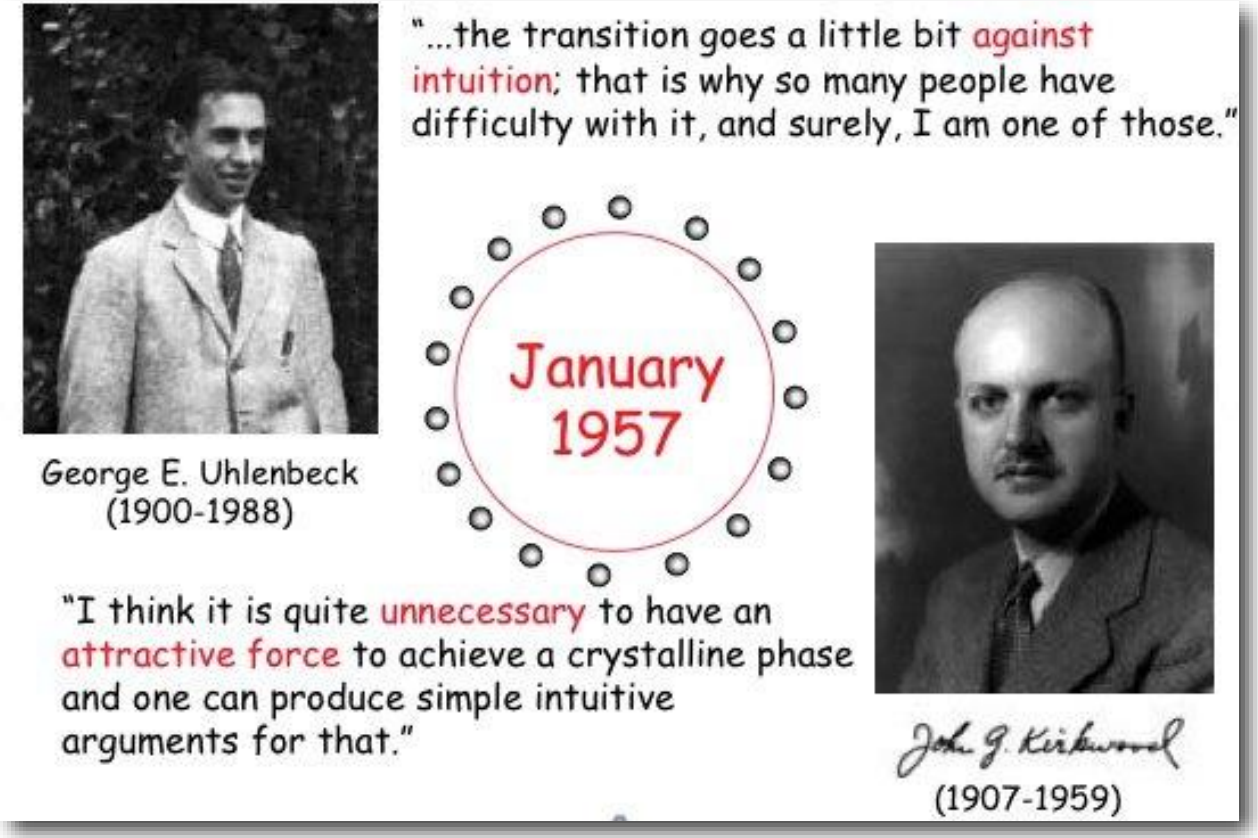


FIG. 2. The traces of the centers of particles in the phase-transition region showing fluid and crystalline regions. The horizontal and vertical lines represent an arbitrary grid.



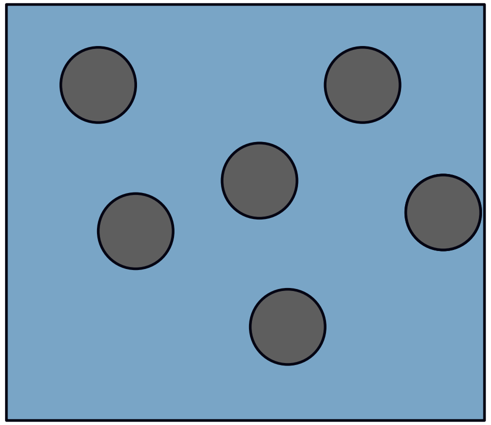
Intermezzo: Why do hard spheres crystallize?

No attractive interactions .. !



TU/e

Why do hard spheres crystallize?



Strange, because:

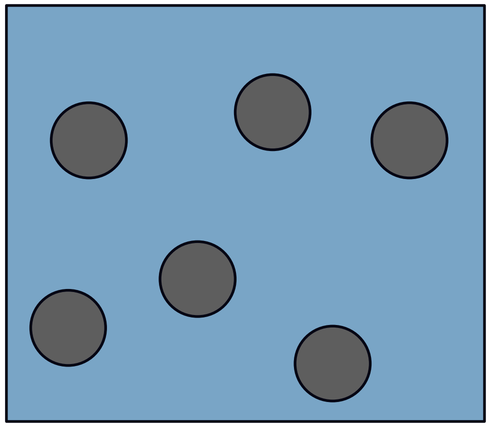
System wants to minimize free energy

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

... so why should the location of the spheres matter at all?

Ordering the spheres should <u>decrease</u> free energy, not increase it ..

Why do hard spheres crystallize



Strange, because:

System wants to minimize free energy

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

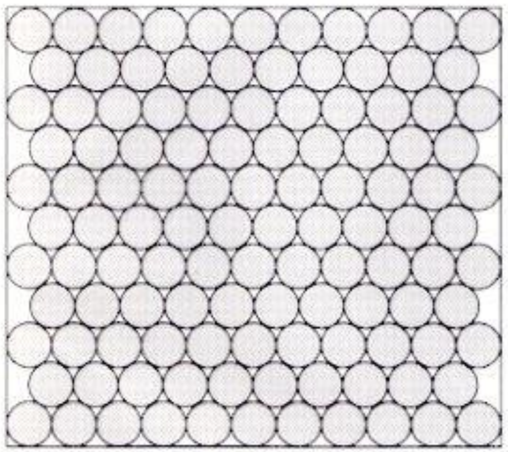
... so why should the location of the spheres matter at all?

Moving the spheres to a different place does not change the energy..

entropy of the solvent also does not depend on the position of the particles...

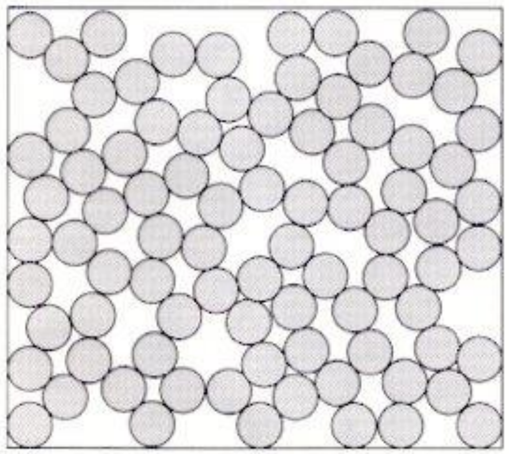
Why do hard spheres crystallize?

Maximum packing for ordered spheres



$\phi \approx 0.7404$

Maximum packing for randomly oriented spheres (random close packing)



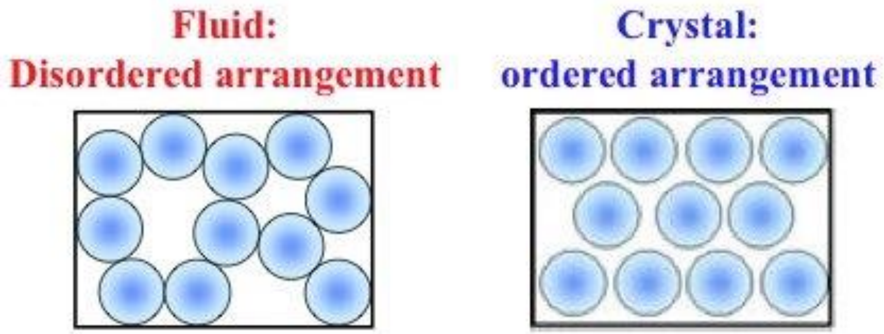
$\phi \approx 0.636$

At high volume fractions spheres would lose all degrees of freedom (zero free volume) if they do not order ...

.. So gain entropy by ordering!

TU/e

Why do hard spheres crystalliza?



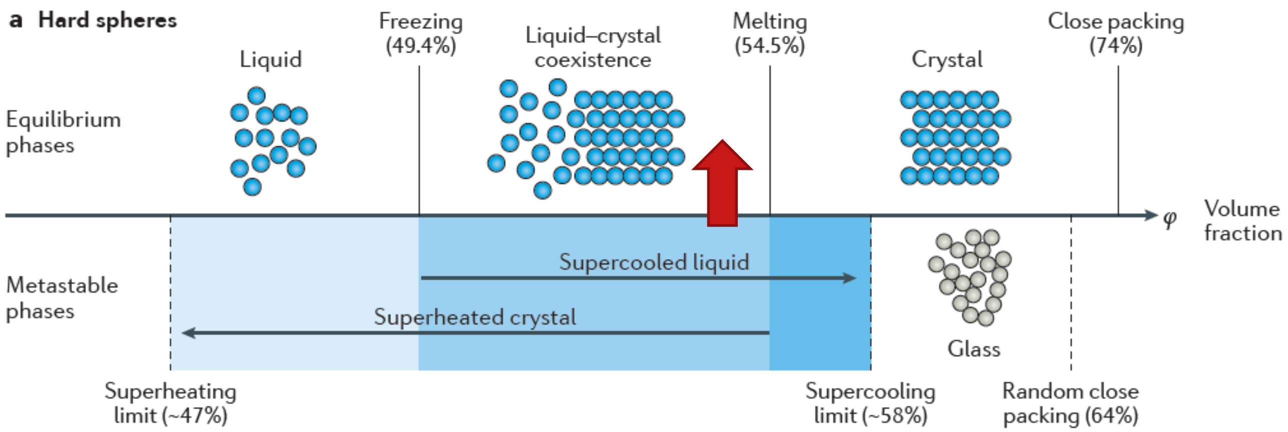
	Fluid	Crystal
$S_{packing}$	high	low
$S_{free\ volume}$	low	high

Disordered => jamming, restricted free volume => fewer degrees of freedom

Ordered => gain free volume

Please note: Equilibrium takes time!

Pusey et al. *Phil Trans R Soc A*, 2009



Li *et al*. Nature Reviews, 2016

Colloids & Soft Matter

Real systems:

Many more control parameters

- Interactions (van-der-Waals, electrostatic, depletion, ...)
- Nonspherical shapes
- Anisotropic interactions
- External fields

=> Variety of options to control system behavior