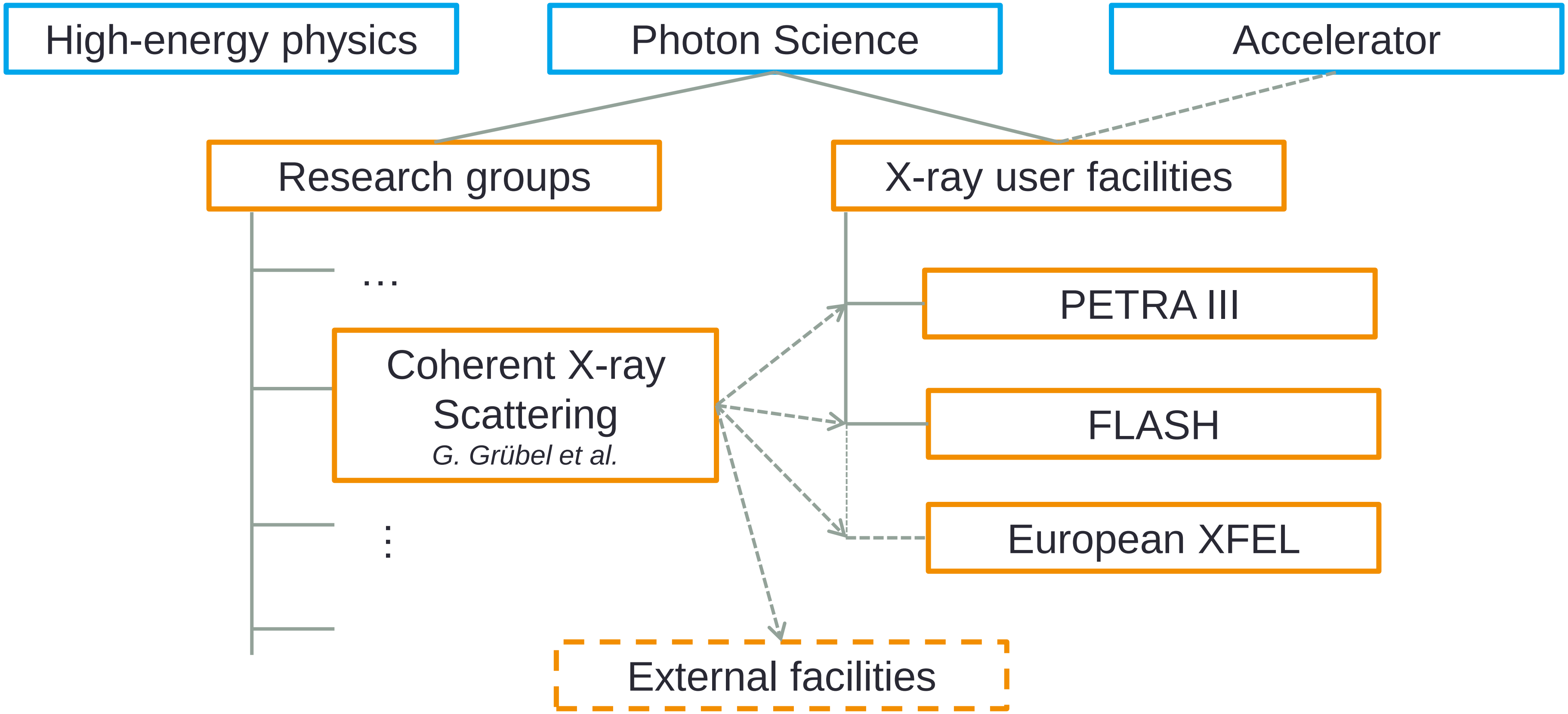
Methoden moderner Röntgenphysik: Streuung und Abbildung

Lecture 11	Vorlesung zum Haupt- oder Masterstudiengang Physik, SoSe 2019 G. Grübel, F. Lehmkühler, L. Müller, O. Seeck, L. Frenzel, M. Martins, W. Wurth		
Location	Lecture hall AP, Physics, Jungiusstraße		
Date	Tuesday	12:30 - 14:00	(starting 2.4.)
	Thursday	8:30 - 10:00	(until 11.7.)

Who & Where?



High-energy physics

Photon Science

Accelerator

Research groups

X-ray user facilities

…

Coherent X-ray Scattering
G. Grübel et al.

⋮

PETRA III

FLASH

European XFEL

External facilities

CXS Research topics

- Complex liquids (soft matter, water, …)
- Ultrafast dynamics (magnetism, FEL applications, …)
- Experiments at PETRA III, LCLS, SACLA, ESRF, APS, …

Soft Matter – Timeline

Di	07.05.2019	Soft Matter studies I: Methods & experiments *Definitions, complex liquids, colloids, storage ring and FEL experiments, setups, liquid jets,* **…**
Do	09.05.2019	Soft Matter studies II: Structure *SAXS & WAXS applications, X-ray cross correlations*, **…**
Di	14.05.2019	Soft Matter studies III: Dynamics *XPCS applications, diffusion, dynamical heterogeneities, ...*
Do	16.05.2019	XPCS and XCCA simulation and modelling
Di	21.05.2019	Case study I: Glass transition *Supercooled liquids, glasses vs. crystals, glass transition concepts, structure-dynamics relations, ...*
Do	23.05.2019	Case study II: Water *Phase diagram, anomalies, crystalline and glassy forms, FEL studies, ...*

What is Soft Matter?

"Soft matter or soft condensed matter is a subfield of condensed matter comprising a variety of physical systems that are deformed or structurally altered by thermal or mechanical stress of the magnitude of thermal fluctuations.

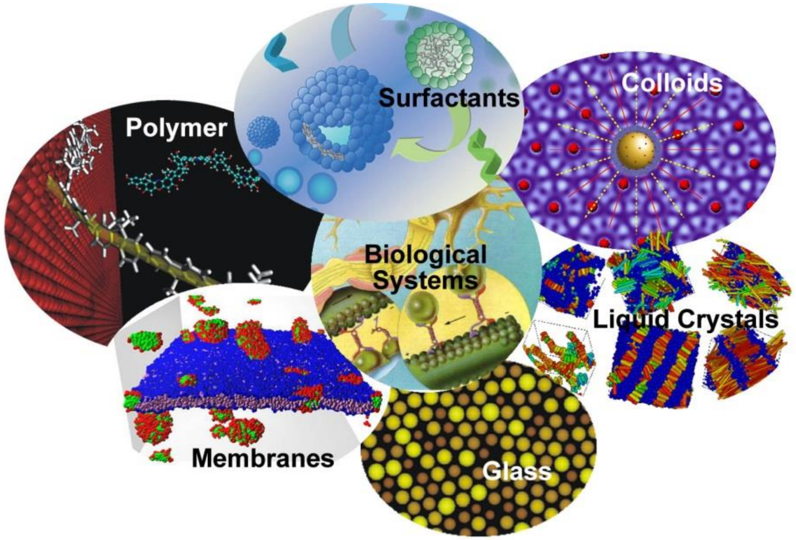
They include

- **Liquids**
- **Colloids**
- **Polymers**
- **Foams**
- **Gels**
- **Granular materials**
- **Liquid crystals**
- **Biological materials**

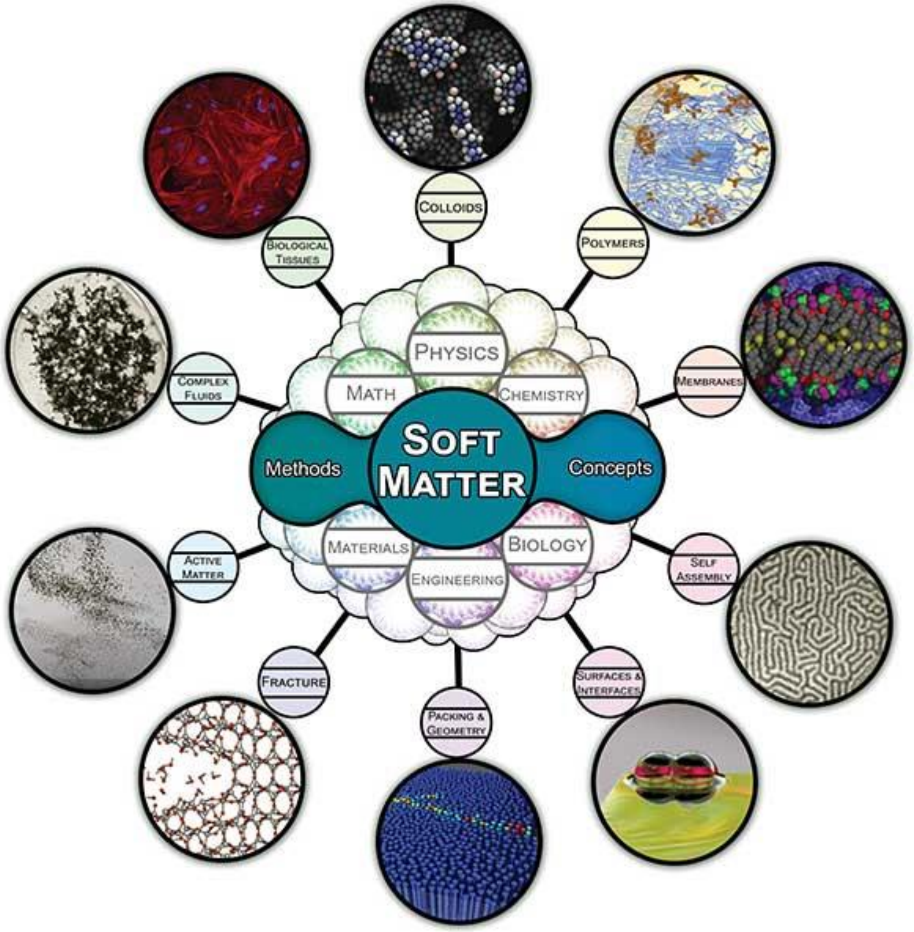
These materials share an important common feature in that predominant physical behaviors occur at an energy scale comparable with room temperature thermal energy. At these temperatures, quantum aspects are generally unimportant."
https://en.wikipedia.org/wiki/Soft_matter

What is Soft Matter?

Mesoscopic length scales
Bridging physics, chemistry and biology



https://indico.nbi.ku.dk/event/1091/overview



American chemical society

What is Soft Matter?

Why soft? → matter can be deformed easily

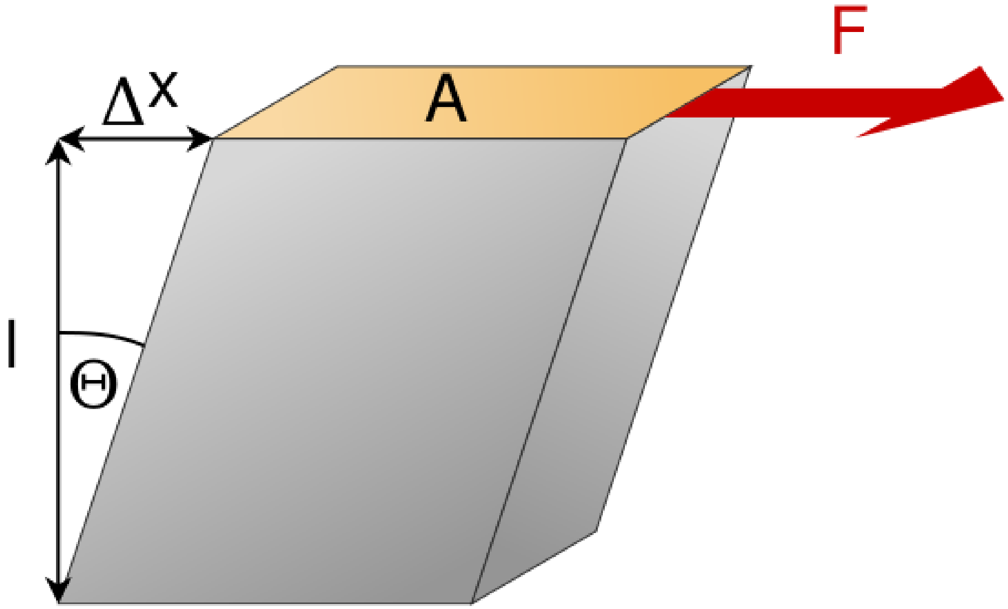
Shear modulus $G = \frac{\tau}{\gamma} = \frac{F/A}{\Delta x/l} = \frac{Fl}{A\Delta x}$,

Shear stress $\tau = \frac{F}{A}$, *shear strain* $\gamma = \frac{\Delta x}{l}$

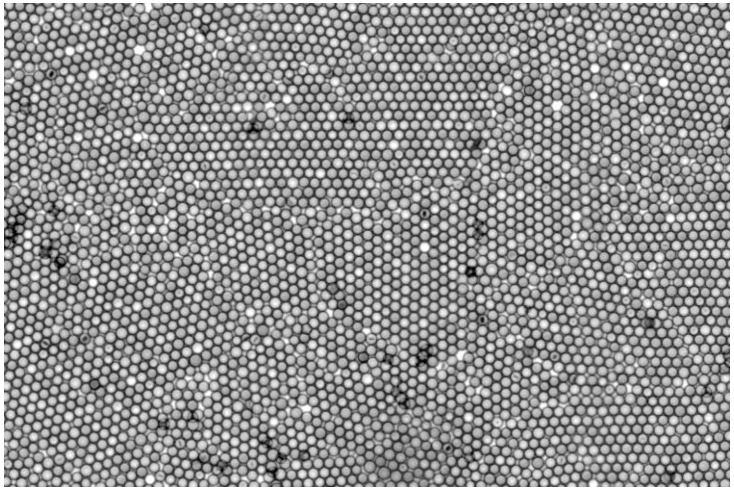
Metals: $G \sim$ some 10 GPa

Soft Matter: $G \leq$ 0.1 GPa typically

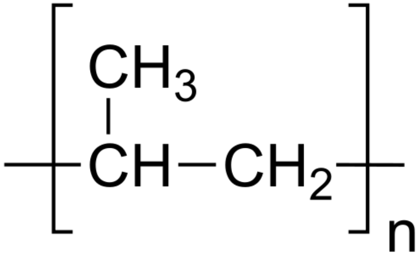
Liquid: $G \sim$ 0



What is Soft Matter – examples



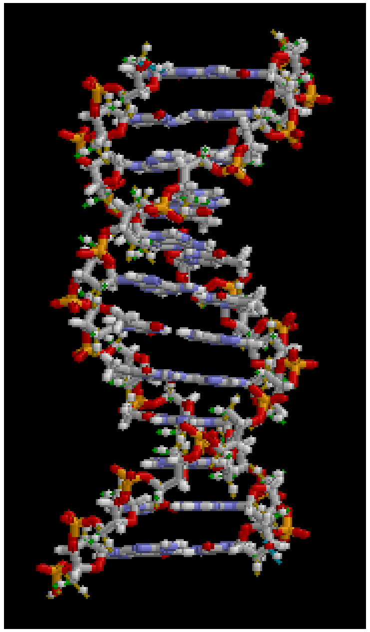
Colloids

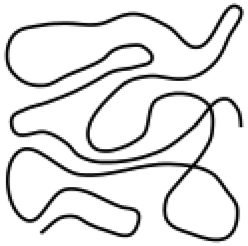
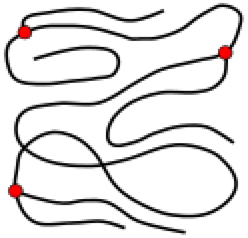
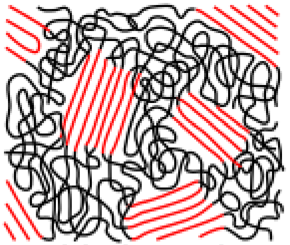
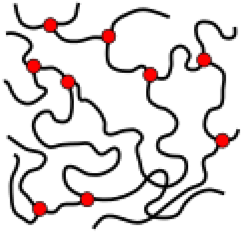
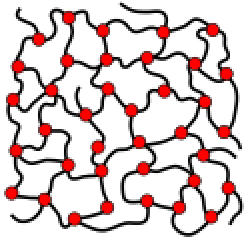


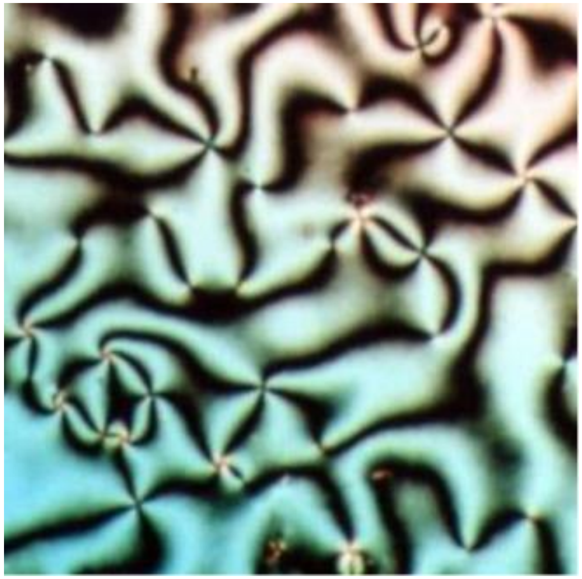
$$\left[-\underset{}{\overset{CH_3}{\overset{|}{CH}}}-CH_2- \right]_n$$

polypropylene

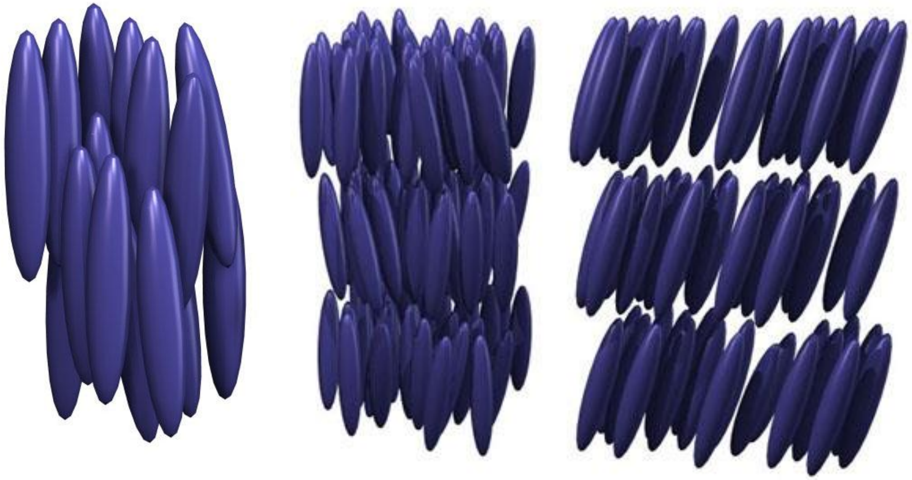
Polymers



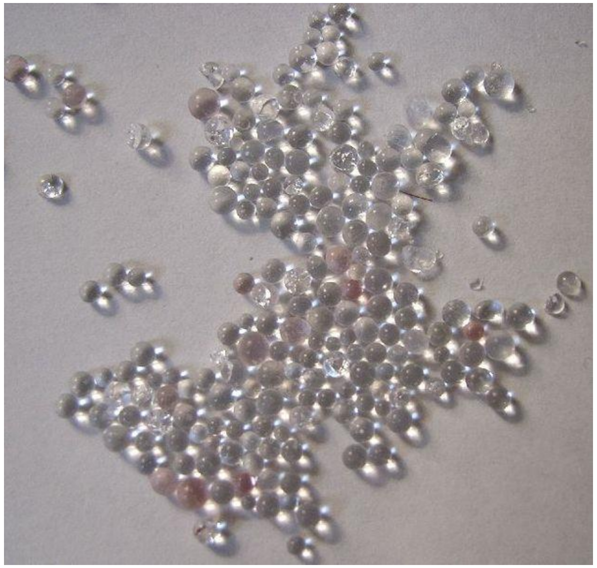
 lineares Makromolekül	 verzweigtes Makromolekül	 teilkristalline Struktur linearer Polymere	 weitmaschig vernetztes Polymer	 engmaschig vernetztes Polymer

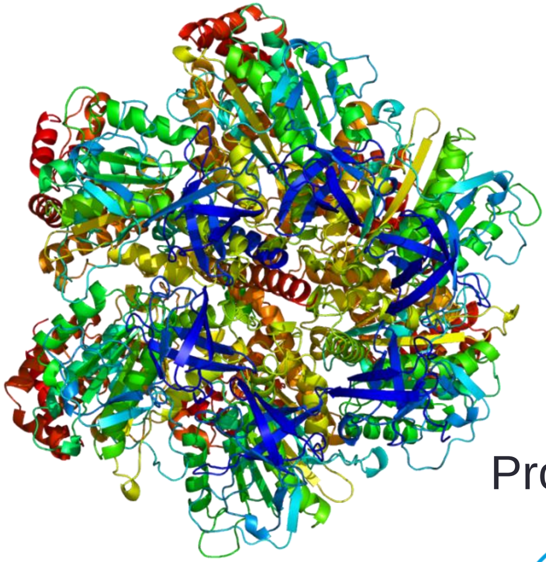


Liquid
Crystals



Gels





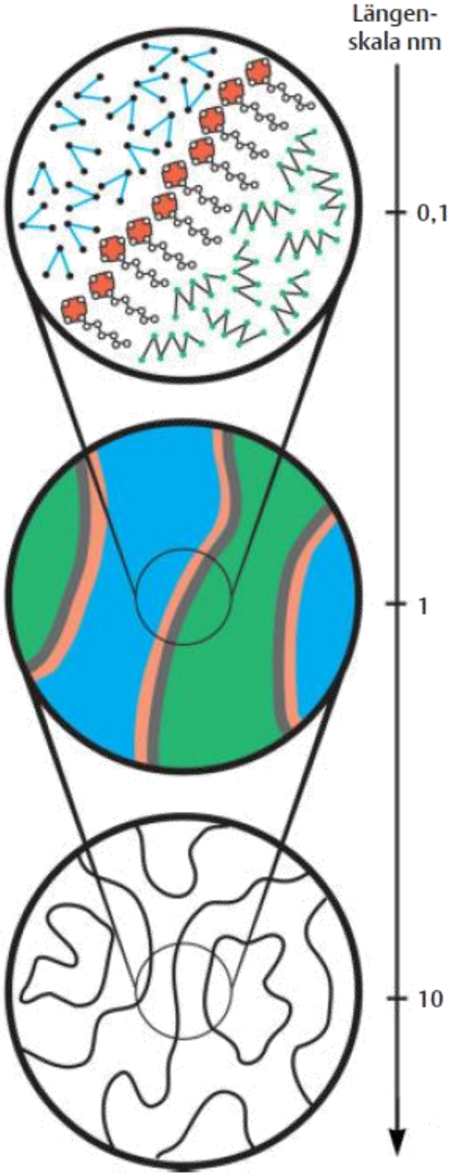
Proteins

What is Soft Matter?

Bridging physics, chemistry and biology

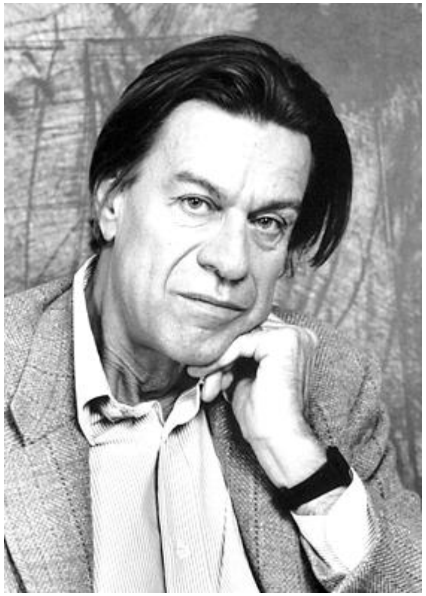
- Mesoscopic length scales
- Self-organization
- Bond energy in soft matter ~ thermal energies

Every day life & technology:
Milk, blood
Yoghurt
Cosmetics
LCD displays
Paints
Rubber
Plastica
….



Phys. Unserer Zeit 2003

"Father of soft matter": Pierre-Gilles de Gennes (1932-2007)



https://www.nobelprize.org/

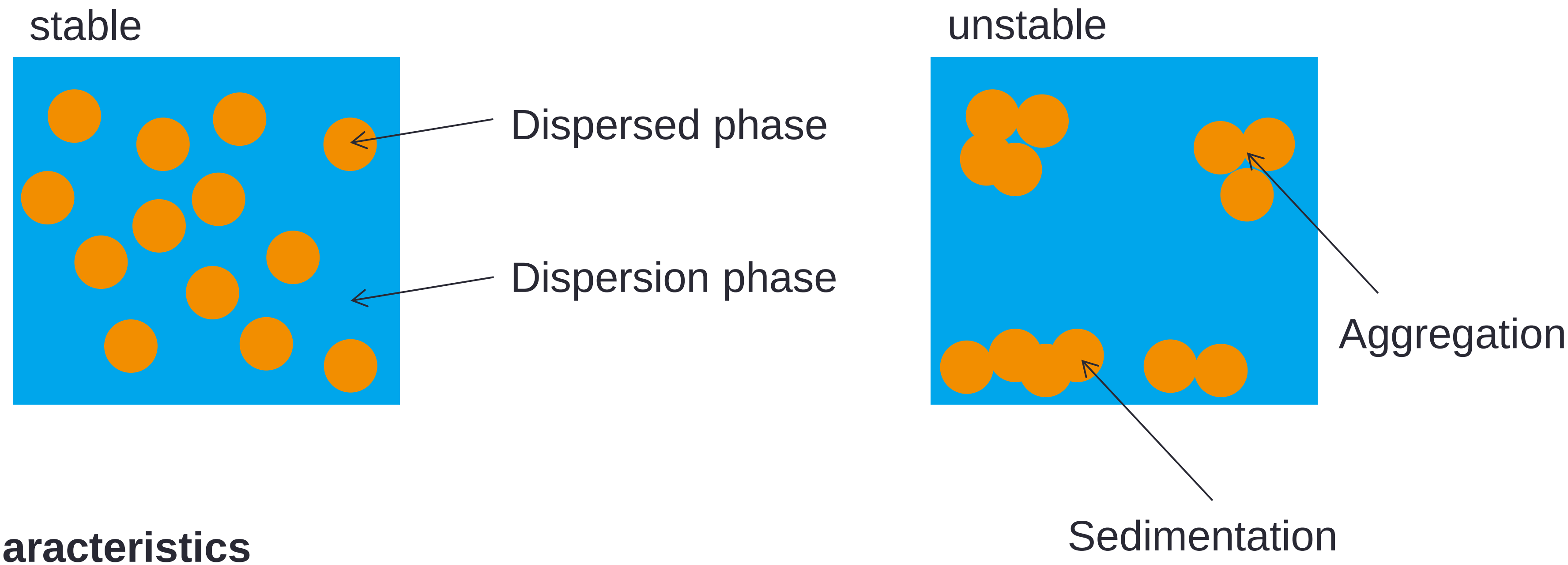
Nobel Prize in physics 1991 "*for discovering that methods developed for studying order phenomena in simple systems can be generalized to more complex forms of matter, in particular to liquid crystals and polymers*".

→ Soft Matter as model systems!

E.g. for study of
- Phase transitions
- Glass transition
- Liquid phases

Colloids

Homogeneous mixtures of two different substances where one is dispersed in the other

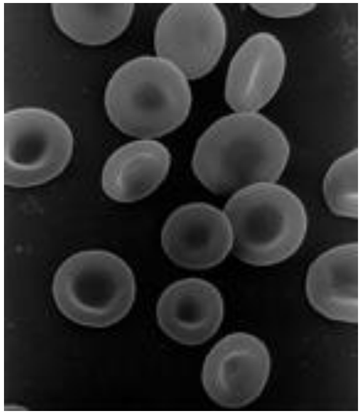


Characteristics

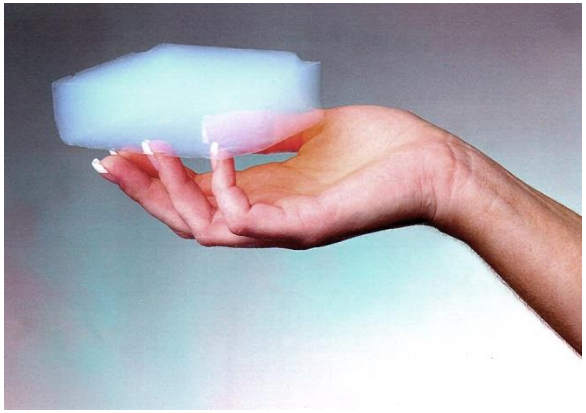
- Not a dissolved phase! (e.g. salt in water)
- Dispersed phase: sizes ~ 1 nm to 1000 nm → between atomic/molecular and macroscopic length scales
- Interactions: entropic, van-der-Waals, electrostatic, repulsion, …

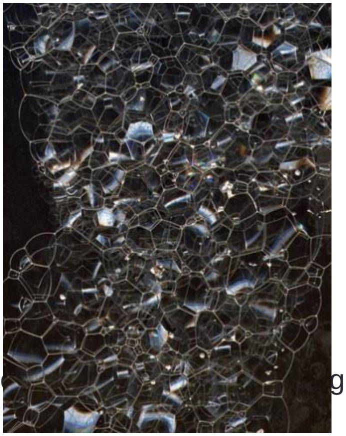
Colloids

Medium/Phase		**Dispersed phase**		
		Gas	**Liquid**	**Solid**
Dispersion medium	**Gas**	---	Aerosol *Clouds, fog, mist*	Solid aerosol *smoke*
	Liquid	Foam *Whipped cream*	Emulsion *Milk, mayonnaise*	Sol *blood*
	Solid	Solid foam *Aerogel, styrofoam*	Gel *Gelatin, jelly*	Solid sol *Cranberry glass*



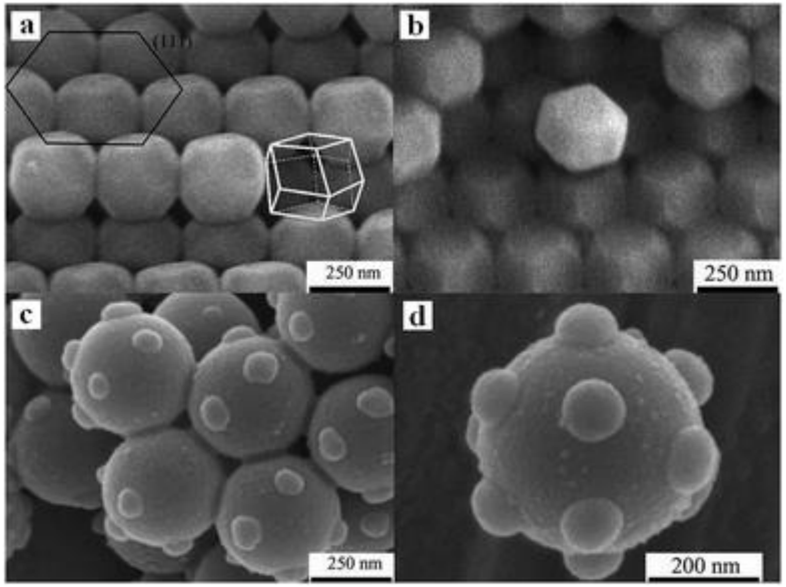

cm.
Camlin
Exam



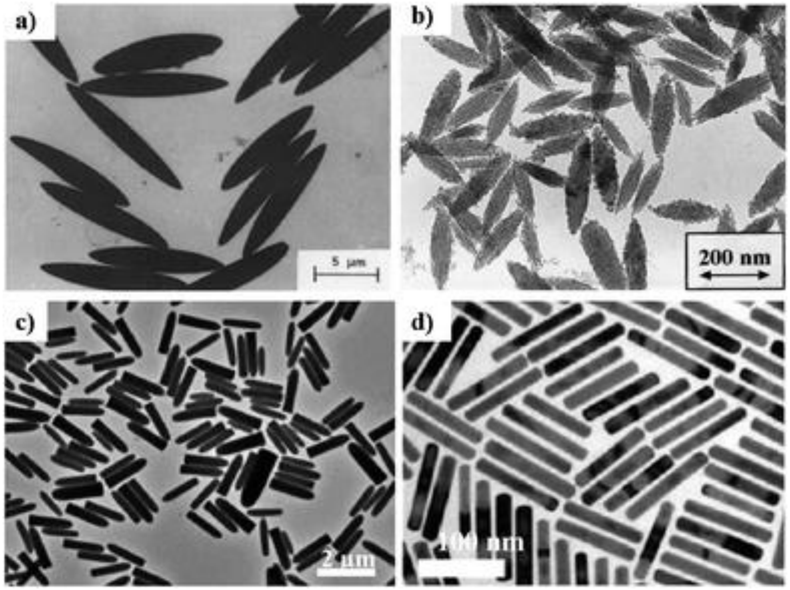


Colloids – Sol (solid particles in liquid)

Shapes
Dimensions
Materials
…



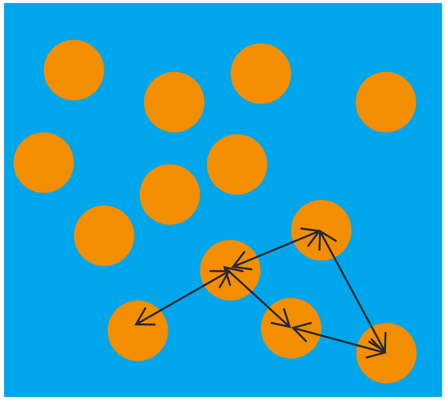
Chem. Soc. Rev. 42, 7774 (2013)



Soft Matter 9, 6711 (2013)

Colloids: interactions

Coarse-grain descripton:
- Dispersion medium considered as continuum with macroscopic properties
- Dispersed particles interact via effective pair potential
- Analogy to atomistic systems

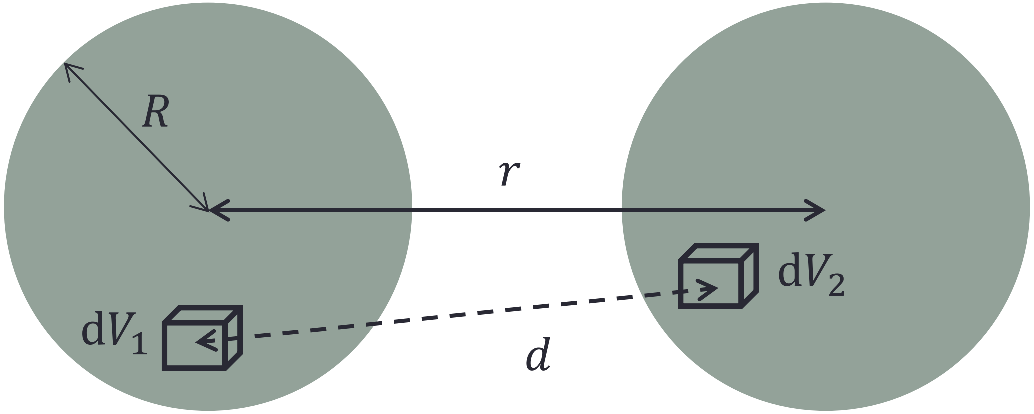


1. Van der Waals interactions

Attraction between particles due to (induced) dipoles:

$$U_{vdW}(r) = -\frac{C}{r^6}$$

Macroscopic objects: equations hold for all pairs of molecules in the two interacting objects (Hamaker theory)



$$U_{vdW}(r) = -C \iint \frac{1}{r^6}\,\mathrm{d}V_1 \mathrm{d}V_2$$

It follows for spherical particles of the same radius:

$$U_{vdW}(r) = -\frac{A_H}{6}\left(\frac{2R^2}{r^2-4R^2} + \frac{2R^2}{r^2} + \ln(1-\frac{4R^2}{r^2})\right)$$

With the Hamaker-constant $A_H \sim 10^{-20} - 10^{-19}$ J as Amplitude for the forces between the particles.

Hamaker constant: $A_H \propto \rho_1 \rho_2$, with number densities ρ_i.

For dielectric media, the Hamaker constant can be approximated to

$$A_H \approx \frac{3}{4} k_B T \, \frac{\epsilon_1 - \epsilon_s}{\epsilon_1 + \epsilon_s} \frac{\epsilon_2 - \epsilon_s}{\epsilon_2 + \epsilon_s} + \frac{3h\nu_e}{8\sqrt{2}} \frac{(n_1^2 - n_s^2)(n_2^2 - n_3^2)}{\sqrt{n_1^2 + n_s^2}\sqrt{n_2^2 + n_s^2}\left(\sqrt{n_1^2 + n_s^2} + \sqrt{n_2^2 + n_s^2}\right)}$$

With the dielectric constants ϵ_i, refractive indices n_i, and a „typical“ absorption frequency ν_e. ($\nu_e \sim 3 \cdot 10^{15}$ Hz)

For two identical phases in a solvent one obtains:

$$A_H \approx \underbrace{\frac{3}{4} k_B T \left(\frac{\epsilon_1 - \epsilon_s}{\epsilon_1 + \epsilon_s}\right)^2}_{\leq 3 \cdot 10^{-21}\ \text{J}} + \underbrace{\frac{3h\nu_e}{16\sqrt{2}} \frac{(n_1^2 - n_s^2)^2}{(n_1^2 + n_s^2)^{3/2}}}_{\leq 2.6 \cdot 10^{-19}\ \text{J, for } T = 300\ \text{K.}}$$

Note: index s marks the solvent → $n_1 = n_2 \Rightarrow A_H \approx 0$ → index matching

Int. J. Mol. Sci. 13, 12773 (2012)

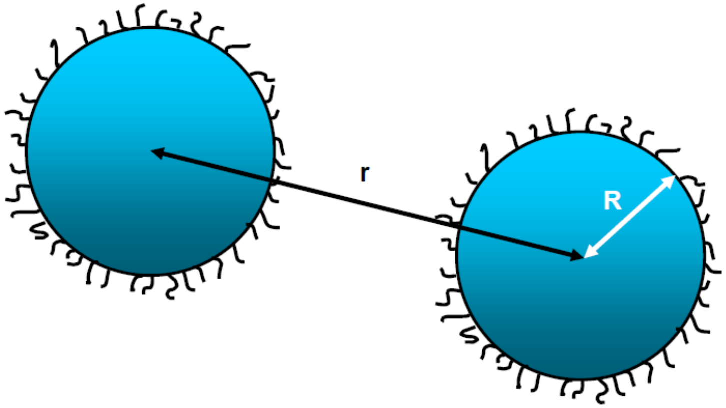
Colloids: stabilization

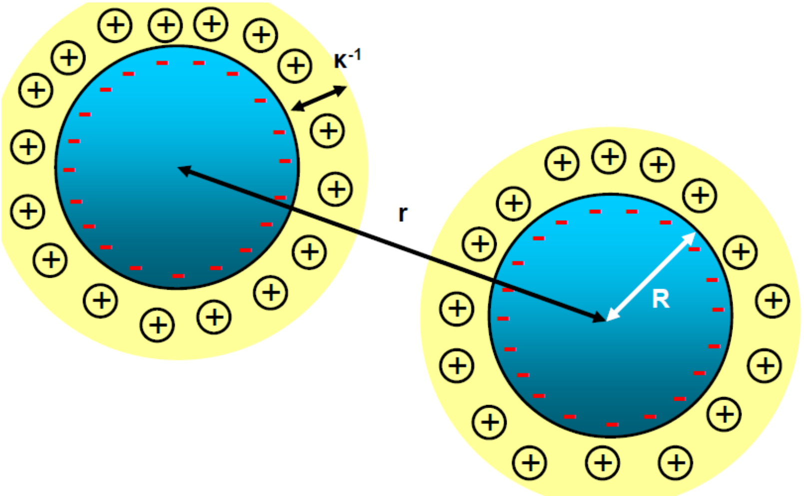
2. Steric stabilization

- Surface covered with polymer chains (or similar)
- Chemically bonded or physically adsorbed
- At small distances: compression of polymers →repulsion

3. Electro-static stabilization

- Ionisable groups on surface
- Dissociation of counter-ions in polar solvent
  - charged particles
  - Ionic cloud → electric double layer
  - Overlap → repulsion





2. Steric stabilization: hard spheres

- Thin polymer layer: particles only "feel" each other at very short distances
- Idealized: non-interpenetrating hard spheres

$$U_{HS}(r) = \begin{cases} \infty, & r \leq 2R \\ 0, & r > 2R \end{cases}$$

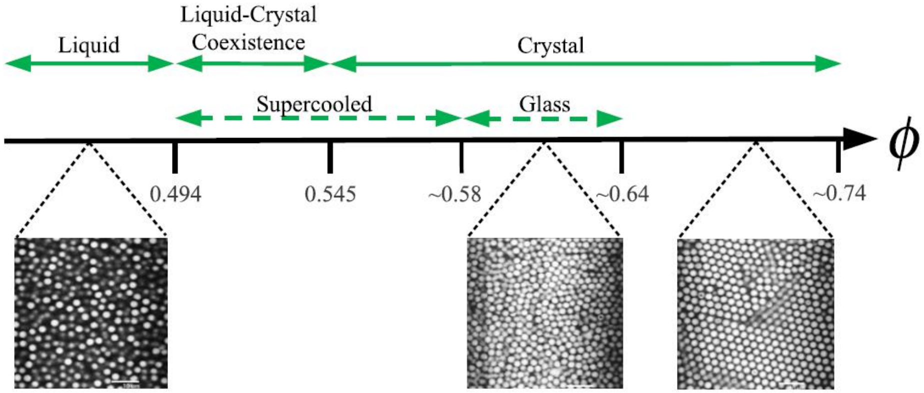
W. Oxtoby *Nature* 413, 694(2001)

Poly(methyl methacrylate) (PMMA) particles in decalin
With steric layer (~10 nm)

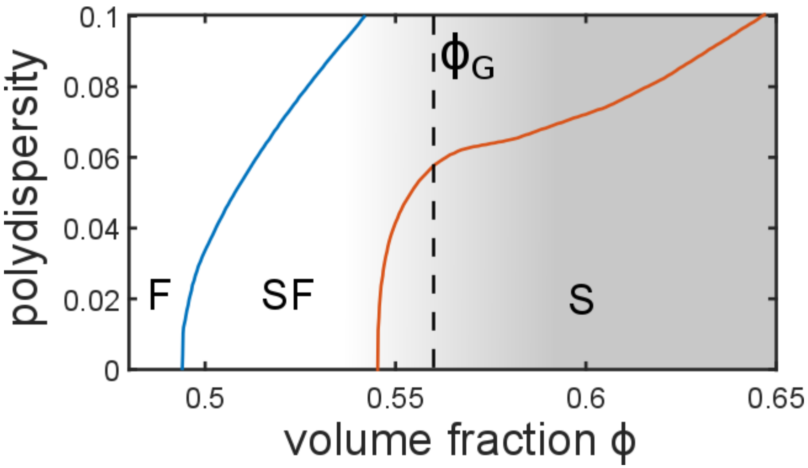
→ Increasing volume fraction

Hard spheres

- Volume fraction $\phi = V_p/(V_s + V_p)$
- Phase diagram:
  - Liquid state for $\phi < 0.494$
  - Liquid-crystal coexistence for $0.494 < \phi < 0.545$
  - Crystal for $\phi > 0.545$
  - Metastable states: supercooled liquid and glasses
  - Particle size polydispersity shifts phase borders
- Model for crystallisation and glass transition (→ lecture 15)



Rep. Prog. Phys. 75, 066501 (2012)

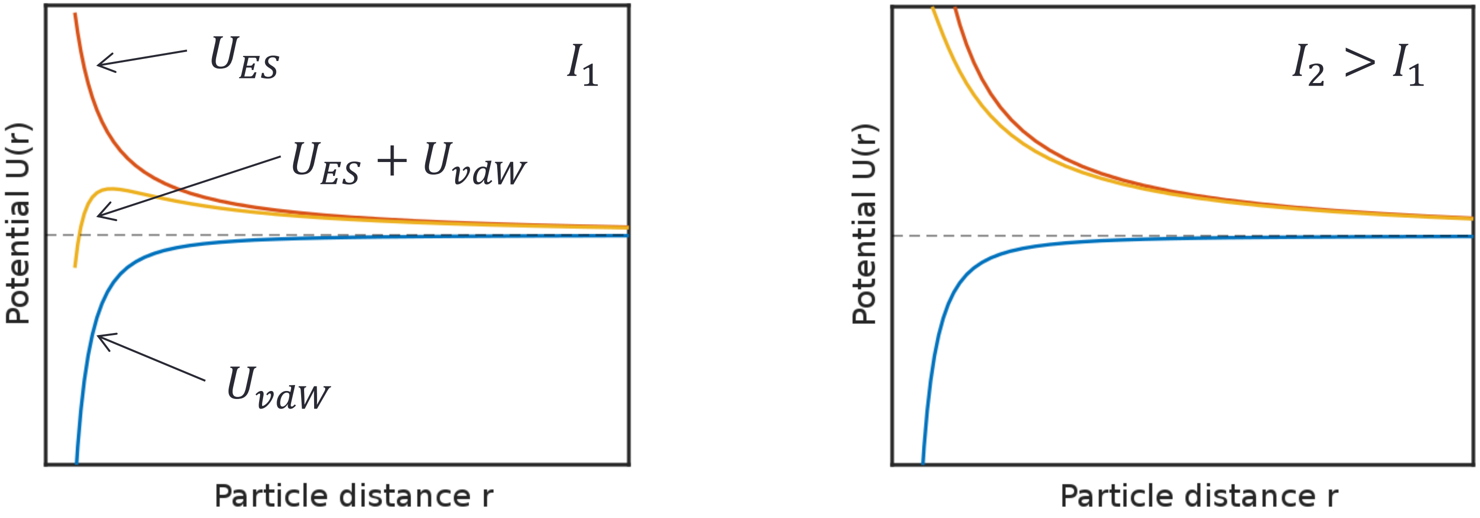


3. Electro-static stabilization

- Derjaguin-Landau-Verwey-Overbeek (DLVO) theory
- Screened Coulomb (Yukawa) potential: degree of "softness"

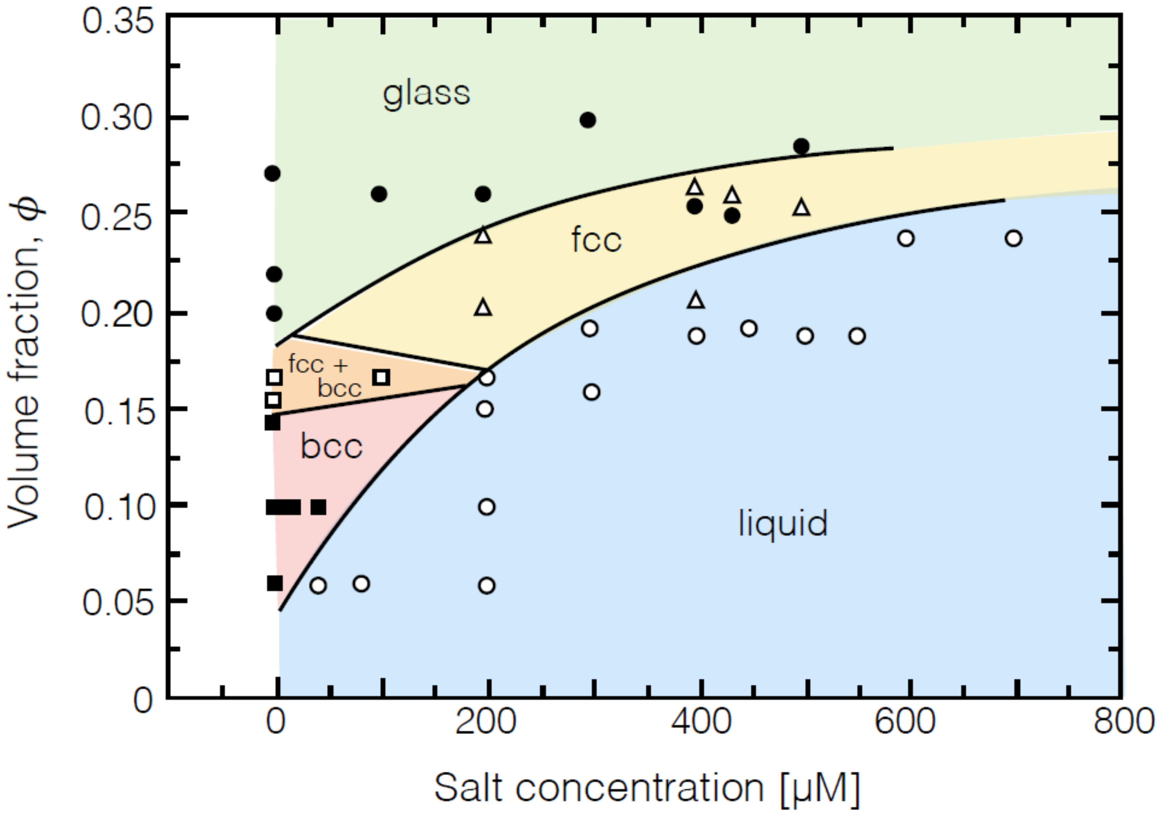
$$U_{ES}(r) = \begin{cases} \infty, & r \leq 2R \\ \dfrac{Z_{\text{eff}}^2 e_0^2}{4\pi\epsilon_0\epsilon_r}\left(\dfrac{\exp(\kappa R)}{1+\kappa R}\right)^2 \dfrac{\exp(-\kappa r)}{r}, & r > 2R \end{cases}$$

- Debye-Hückel screening length $\kappa^{-1} = \sqrt{\frac{\epsilon_0\epsilon_r k_B T}{2e_0^2 N_A I}}$, ionic strength $I = \frac{1}{2}\sum_j c_j q_j^2$



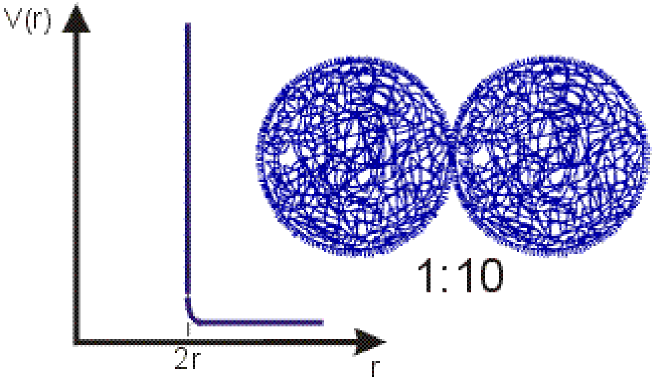
Electro-static stabilization

- Screening tunable by e.g. electrolytes (salt)
- Rich phase behavior
- E.g. silica spheres in water

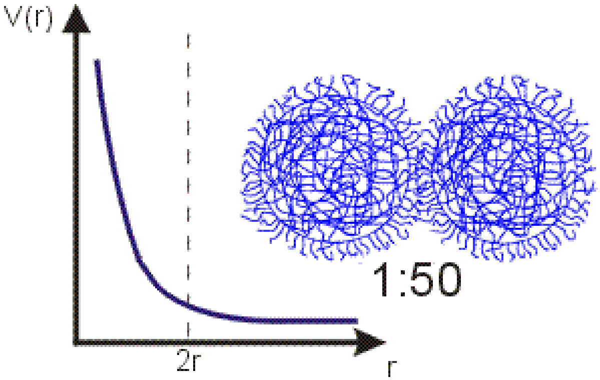


D. Sheyfer. Dissertation, Universität Hamburg (2018)
Sirota et al. Phys. Rev. Lett. 62, 1524 (1989).

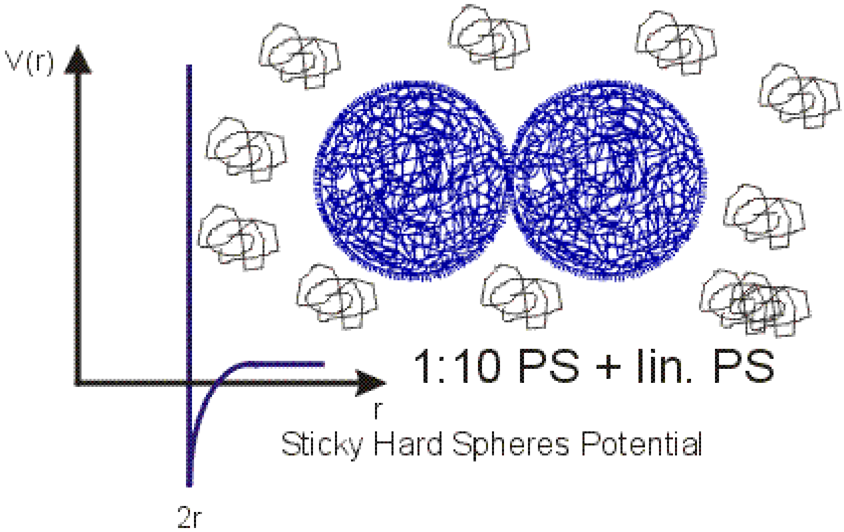
From hard to soft spheres



Hard Spheres Potential



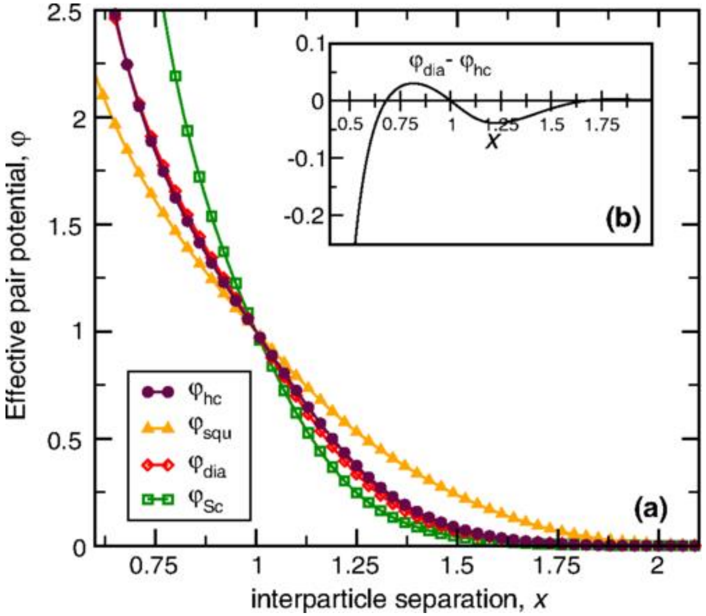
Soft Spheres Potential



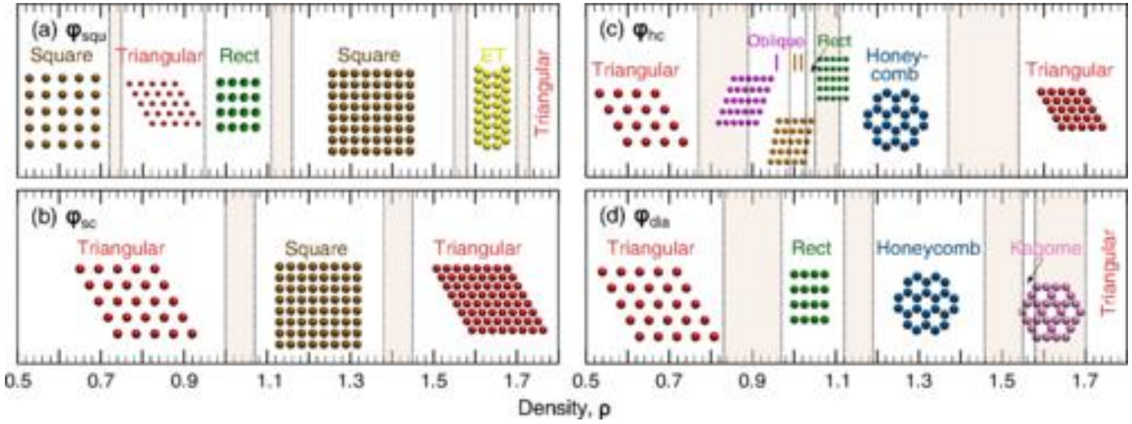
Sticky Hard Spheres Potential

https://www.colloids.uni-freiburg.de/Methoden/polymer.html

Example for phase behaviour



Small modfications of the potential may dramatically change the phase behaviour



A. Jain et al. Phys. Rev. X 4, 031049 (2014).

Soft matter – X-ray studies

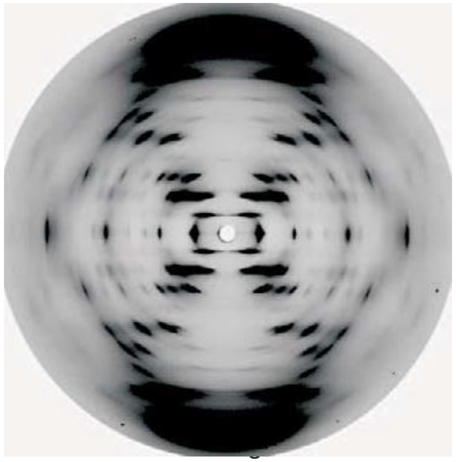
- Colloidal systems as model systems for phase transitions
    - Change of structure and dynamics while crossing phase borders
- Structure of soft matter: in-situ
    - Polymers: from macromolecules to networks
    - Colloids: form factors, function and synthesis
    - Order-disorder transition in liquid crystals
    - …
- Biomolecules: understand function
- Liquid surfaces – water & membranes → lectures by O. Seeck

Soft matter – X-ray methods

- Length scales of ~nm to µm: **Small-angle X-ray scattering**
- Surfaces & interfaces: **X-ray reflectivity & GISAXS**
- Sample dynamics: **XPCS**
- **Crystallography**, e.g. Proteins
- …

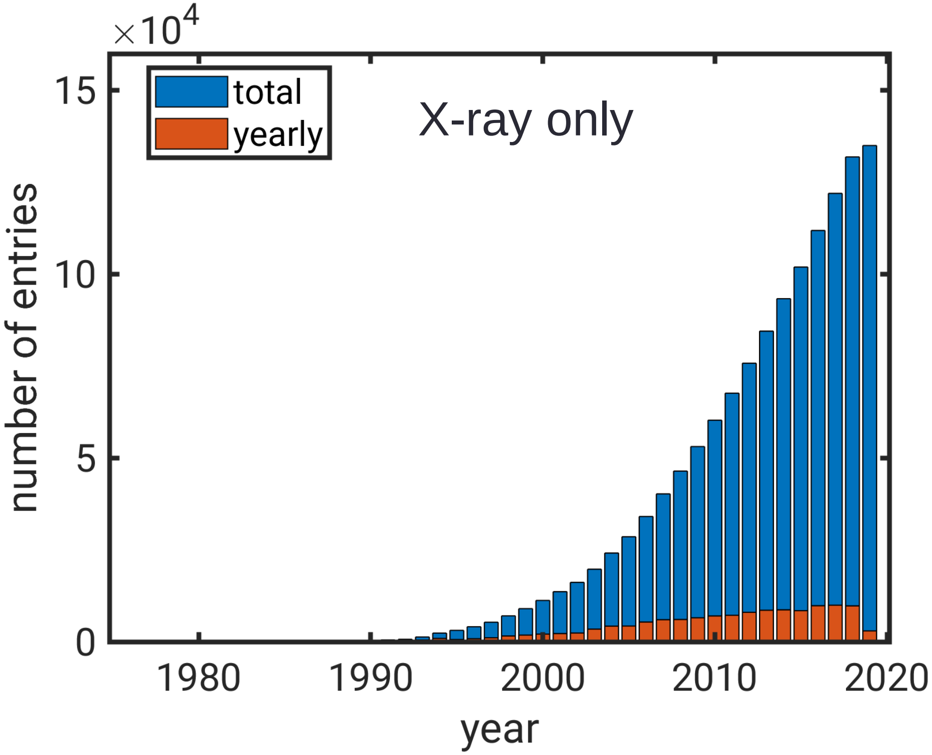
Sample environments

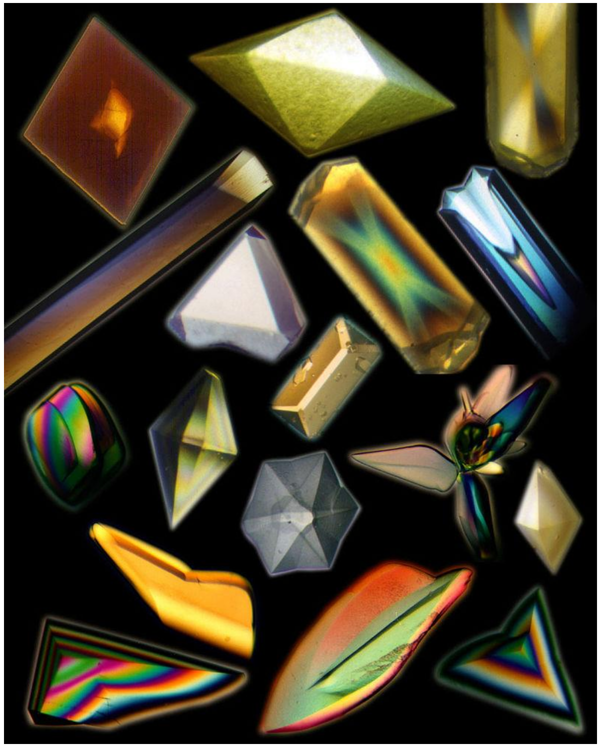
- Structure under flow and shear
- Rheology & SAXS
- Liquid Jets
- …



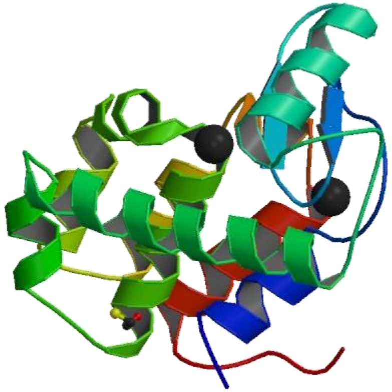
Protein Crystallography

- Access protein structures by X-ray scattering
- Scattering from single particles too weak → use of crystals instead
- Macromolecular crystallography at beamlines all around the world (e.g. P13 & P14 at PETRA III)





Protein databank
https://www.rcsb.org/



SAXS in a nutshell

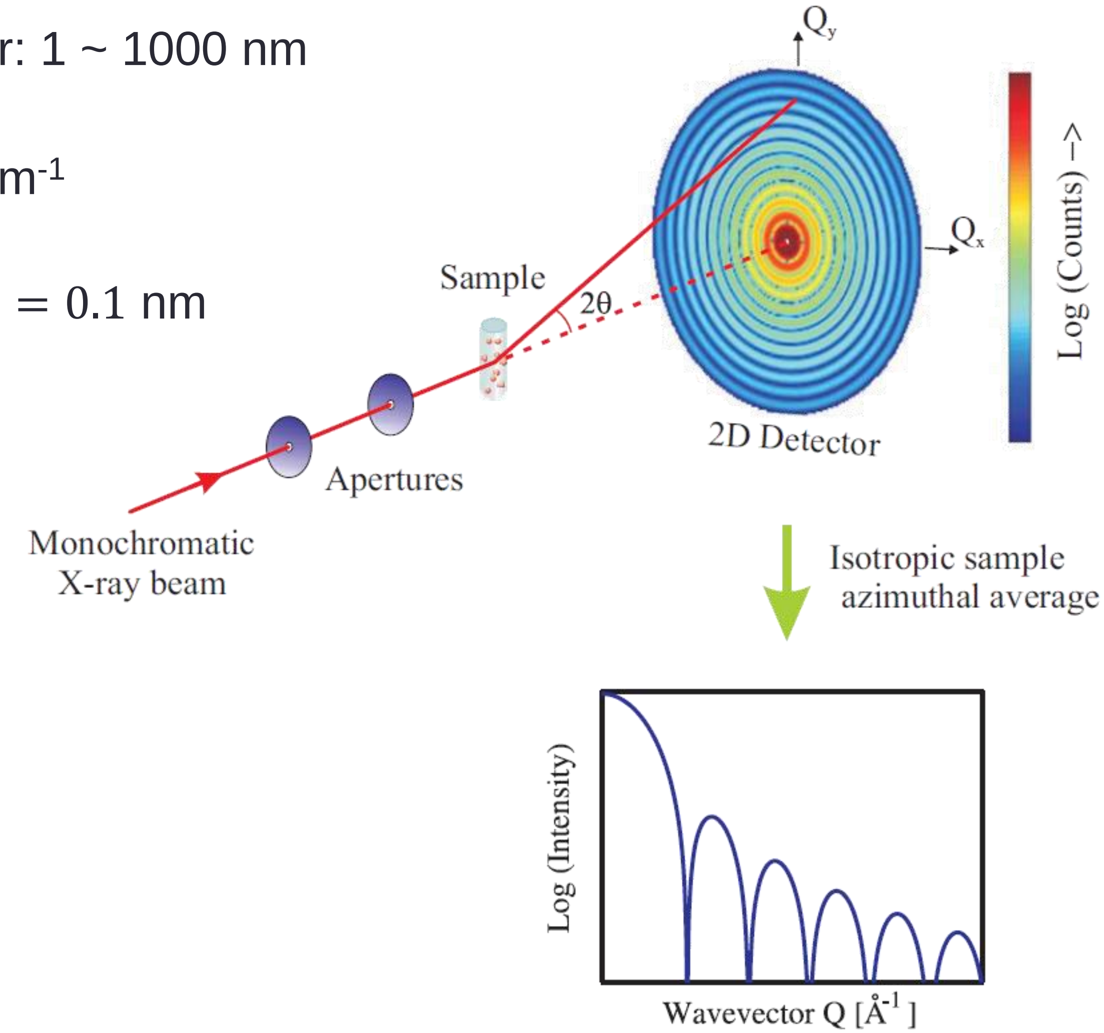
Typical dimensions of soft matter: 1 ~ 1000 nm

$$q = \frac{4\pi}{\lambda}\sin\left(\frac{\theta}{2}\right) = \frac{2\pi}{100\ nm} = 0.063\ \text{nm}^{-1}$$

$$\Rightarrow \theta = \arcsin\left(\frac{q\lambda}{2\pi}\right) = 0.057° \ \text{ for } \lambda = 0.1\ \text{nm}$$

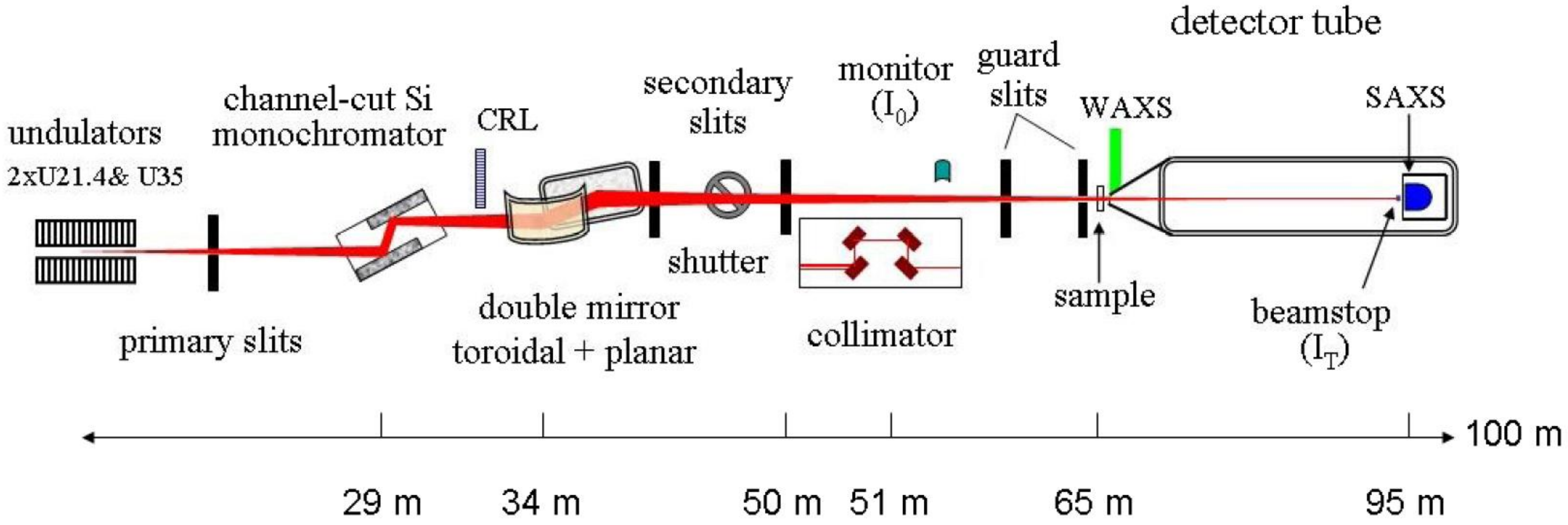
→ Need small angles for soft matter studies!

See Lecture 7 (& 12) for more details



SAXS – beamlines

ID02 @ ESRF



P10 @ PETRA III

P12 @ PETRA III

P10 @ PETRA III

- Sample-detector distance ~ 5m
- Lab visit!

SAXS

Accessible q-range in SAXS experiments

- Sample-detector distance ~m, e.g. $D = 5$ m

- State-of-the-art detectors: 2D
  - Assume Eiger 4M → size 155.2 x 162.5 mm
  - Read-out 750 Hz, 75 µm pixels
  - Larger detectors available, in particular at dedicated beamlines

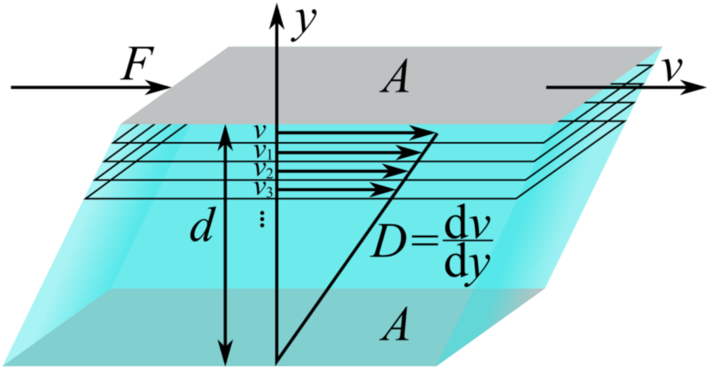
- Assume beam impinging to the center of the detector ($2p$ diagonal of detector)
  - $q_{max} = \frac{4\pi}{\lambda} \cdot \sin(\arctan(\frac{p}{D})/2) \; = 12.57 \cdot \sin(\arctan(\frac{112.4\text{ mm}}{5\text{ m}})/2) \approx 1.4$ nm^{-1}

  - Minimum q defined by beamstop (~ 3 mm size): $q_{min} \approx 0.018$ nm^{-1}

  - Length scales ~ 5-350 nm in this setting

  - Typically: tuning of λ, D, …

Rheology & SAXS



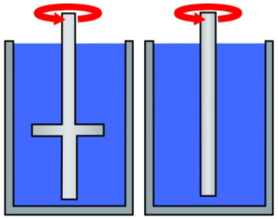
Rheology = study of flow of matter

- Applications range from liquids, soft matter to geophysics

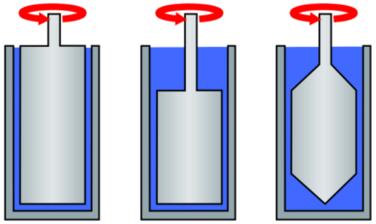
- (Dynamic) Viscosity η: resistance to shear stress $\tau = F/A$
  - $F = \eta A \frac{\mathrm{d}v}{\mathrm{d}y} = \eta A \dot{\gamma}$
  - Shear rate $\dot{\gamma} = \frac{\mathrm{d}v}{\mathrm{d}y}$
  - Newtonian liquids: $\tau = \eta\dot{\gamma}$ with $\eta = const.$

- Rheometers for measuring rheological properties ($\dot{\gamma} \leq 1000$ s^{-1})

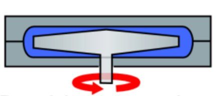
- Péclet-number: Pe =advective/diffusive= $\dot{\gamma}R^2/D$



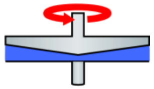
Spindle type



Concentric cylinder



Double cone-plate



Cone-plate

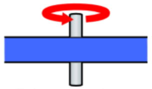


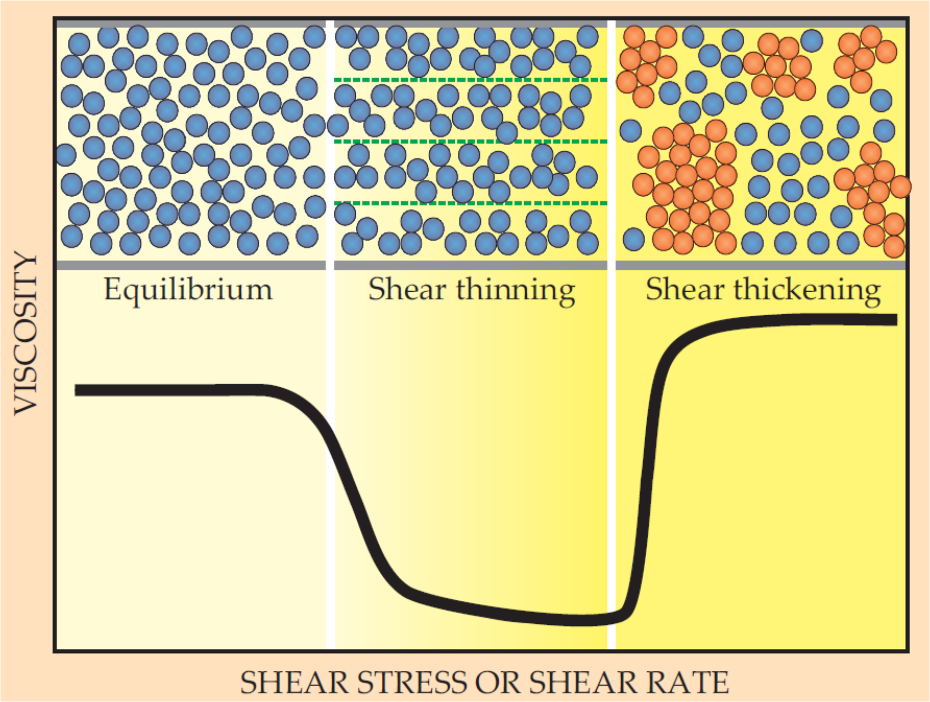
Plate-plate

Cone-cone

Rheology & SAXS

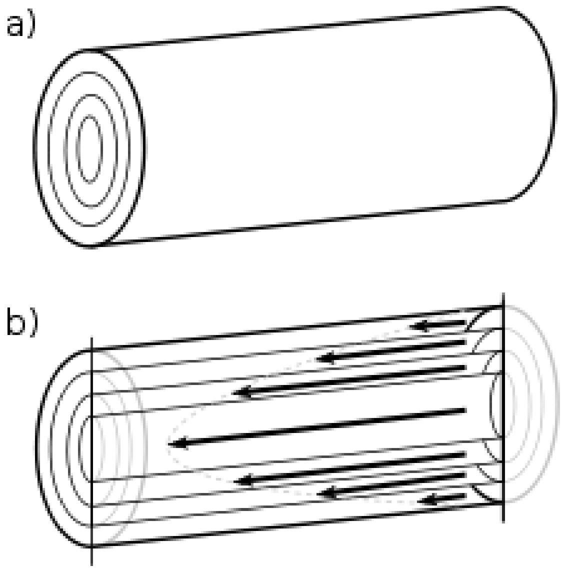
Goals:

- Structural origin of non-Newtonian behavior
- Phase transitions and gelation



P10 @ PETRA III

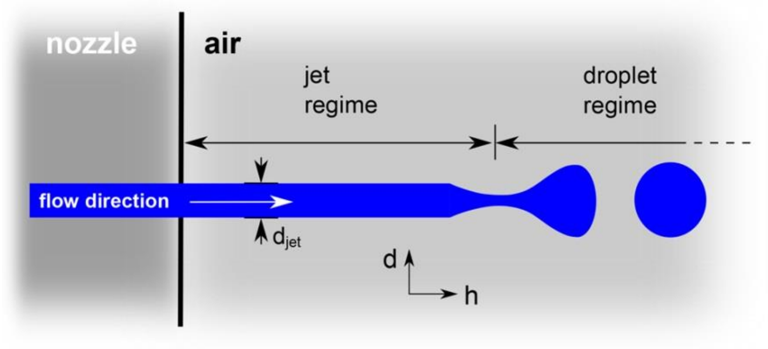
Microfluidics & SAXS



- Higher shear rates can be achieved in microfluidic flows (cf. blood transport)
- Motion of fluids: Navier-Stokes-equations → partial differential equations
- Hagen–Poiseuille flow (laminar flow through a pipe): $\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial u_z}{\partial r}\right) = \frac{1}{\eta}\frac{\partial p}{\partial z}$, with u_z velocity in pipe direction z.
- This can be solved exactly yielding $u_z = -\frac{1}{4\eta}\frac{\partial p}{\partial z}\,(R^2 - r^2)$, with pipe radius r → parabolic flow profile!
- Shear rate $\dot{\boldsymbol{\gamma}} = \frac{8u}{2R}$
- $u = 1$ m/s, $R = 50$ µm → $\dot{\boldsymbol{\gamma}} = 8 \cdot 10^4$ s^{-1}
- SAXS: µm X-ray beam

Liquid Jets

In recent years well-established sample injection method for soft matter experiments



Typical: $d_{jet} \approx 1 - 100\ \mu m$


Fig. 3.


Fig. 4.

Lord Rayleigh. Some applications of photography. Nature 44 (1133), 249-254 (1891).

Liquid Jets in X-ray scattering experiments

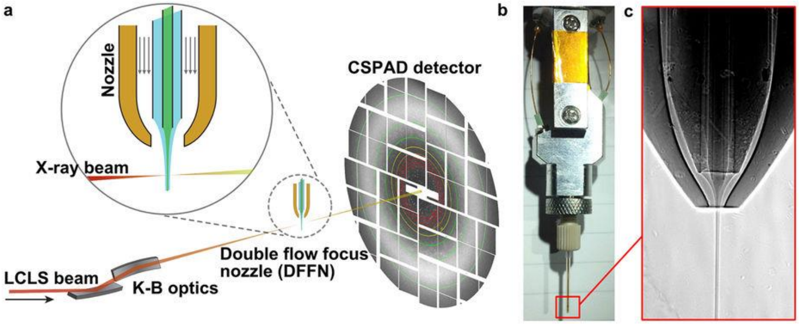
Advantages

- Free-standing sample, no sample chamber/container
- Refreshing sample (avoid influence from radiation damage)
- In-situ reactions possible by mixing jets
- Flow experiments at high shear rates
- Study of deeply supercooled liquids possible (see lecture 16)

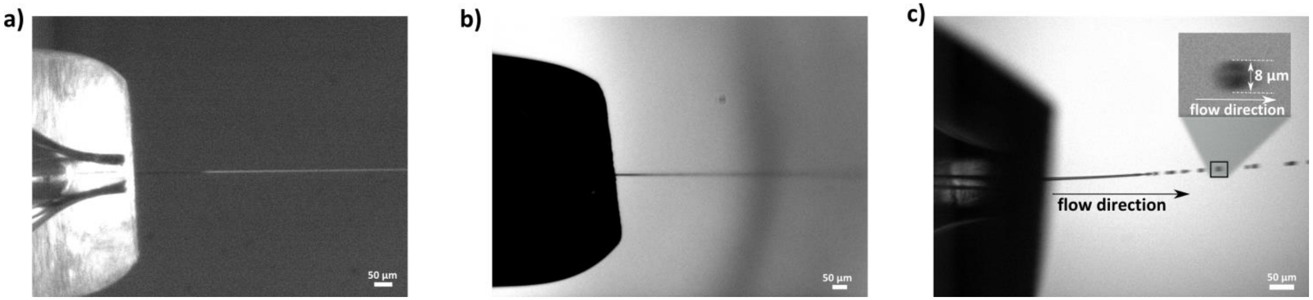
…

Nozzles

- Rayleigh nozzles (pipe)
- Gas-dynamic virtual nozzle
  → flow-focussing

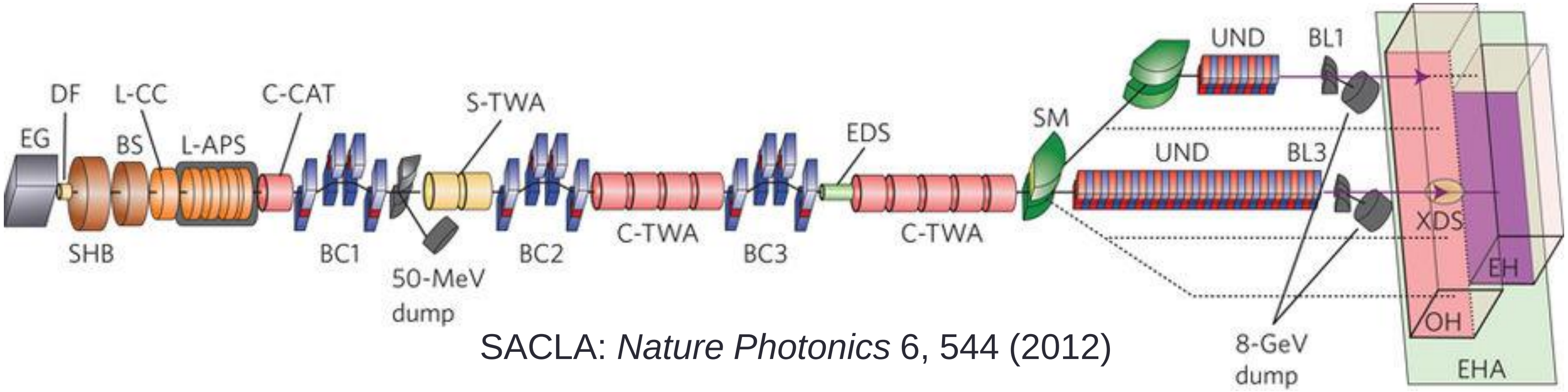


Sci. Rep. 7, 44628 (2017)



Rev. Sci. Instrum. 87, 063905 (2016)

Free-electron lasers



SACLA: *Nature Photonics* 6, 544 (2012)

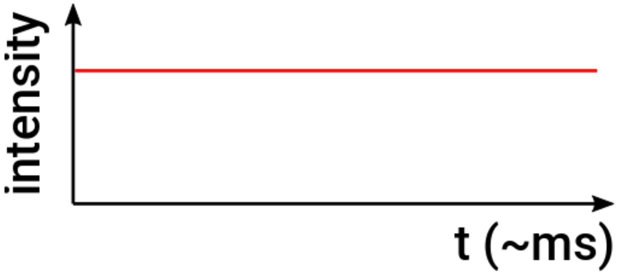
Characteristics

- Ultrashort pulses: $\sim 5 - 100$ fs
- Typically 10^{12} X-ray photons per pulse (i.e. similar to storage rings per s)
- (Transversely) fully coherent
- Repetition rates
  - LCLS (California): 120 Hz
  - SACLA (Japan), PAL-FEL (Korea): 60 Hz
  - European XFEL: 4.5 MHz (in pulse trains)

Free-electron lasers vs. Storage rings

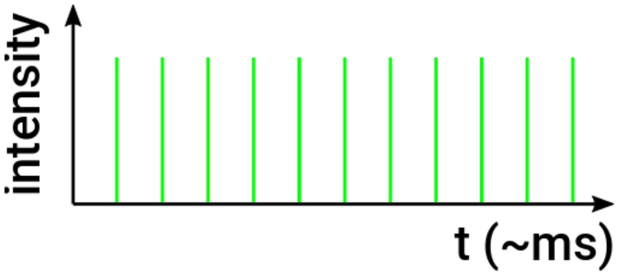
Storage ring

- Quasi-continuous light source
- $\sim 10^{12}$ photons per second



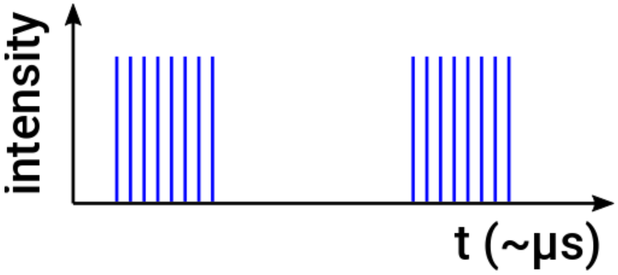
LCLS / SACLA / PAL-FEL

- 60 – 120 Hz repetition rate
- ~10 – 100 fs long pulses
- $\sim 10^{12}$ photons per pulse



European XFEL

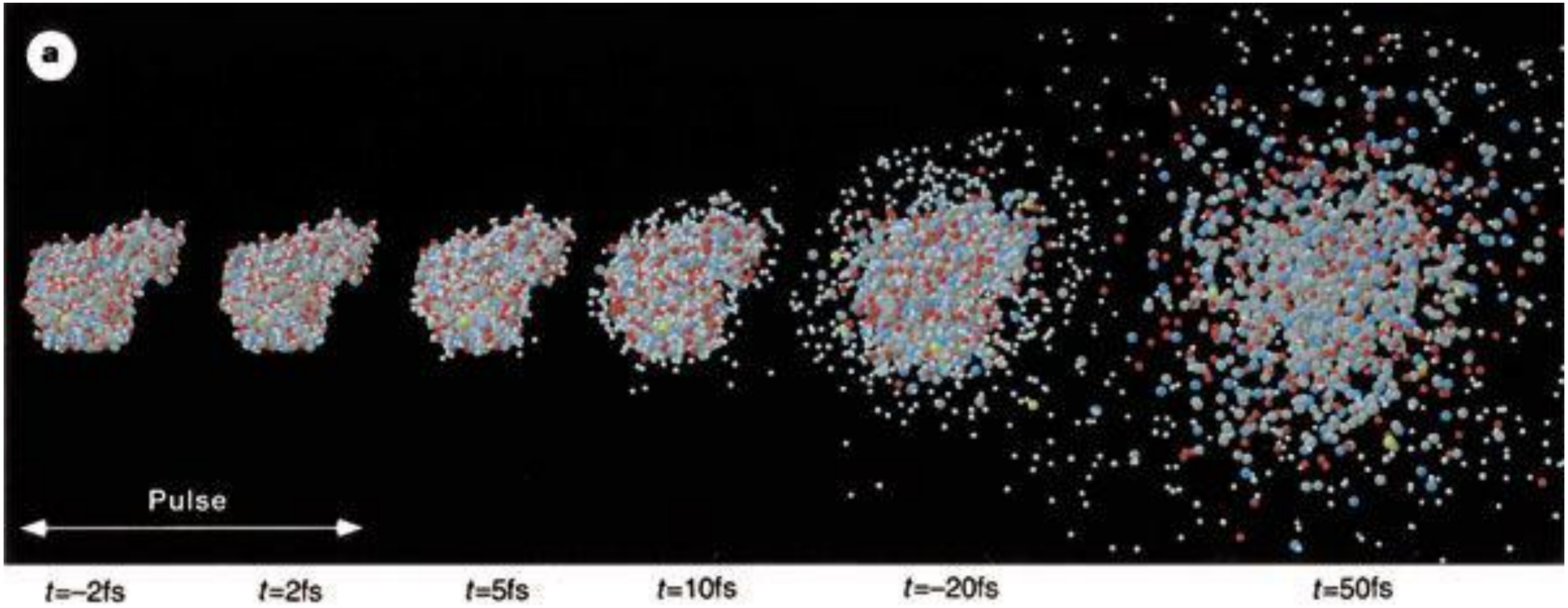
- Pulse trains of 2700 pulses
- Train repetition rate: 10 Hz
- Pulse repetition rate: 4.5 MHz#
- ~10 – 100 fs long pulses
- $\sim 10^{12}$ photons per pulse



Free-electron lasers

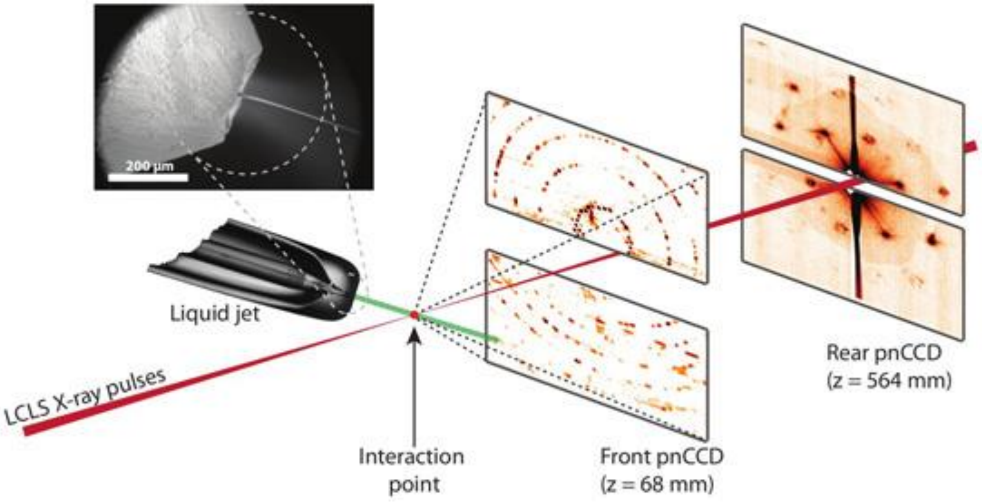
Diffract before destroy

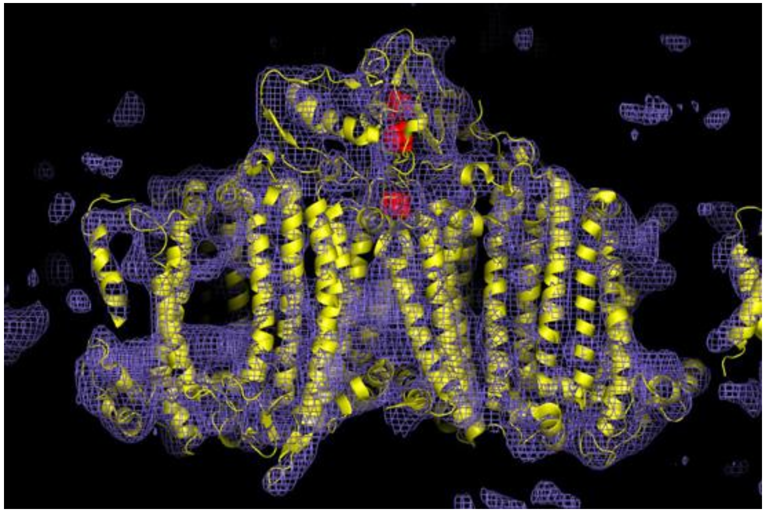
→ Radiation-sensitive samples can be studied at FEL sources



R. Neutze et al. Nature 406, 752 (2000)

Structure of bio-molecules at FEL: Serial-femtosecond crystallography

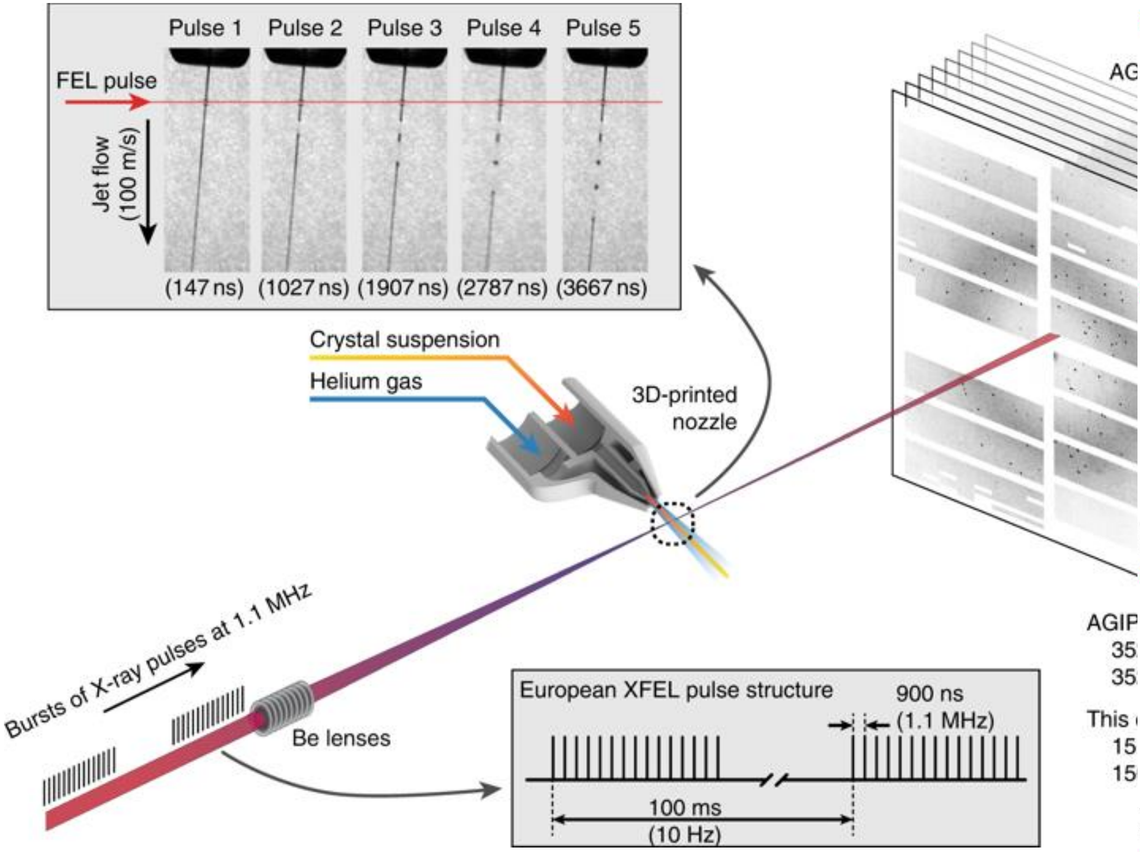


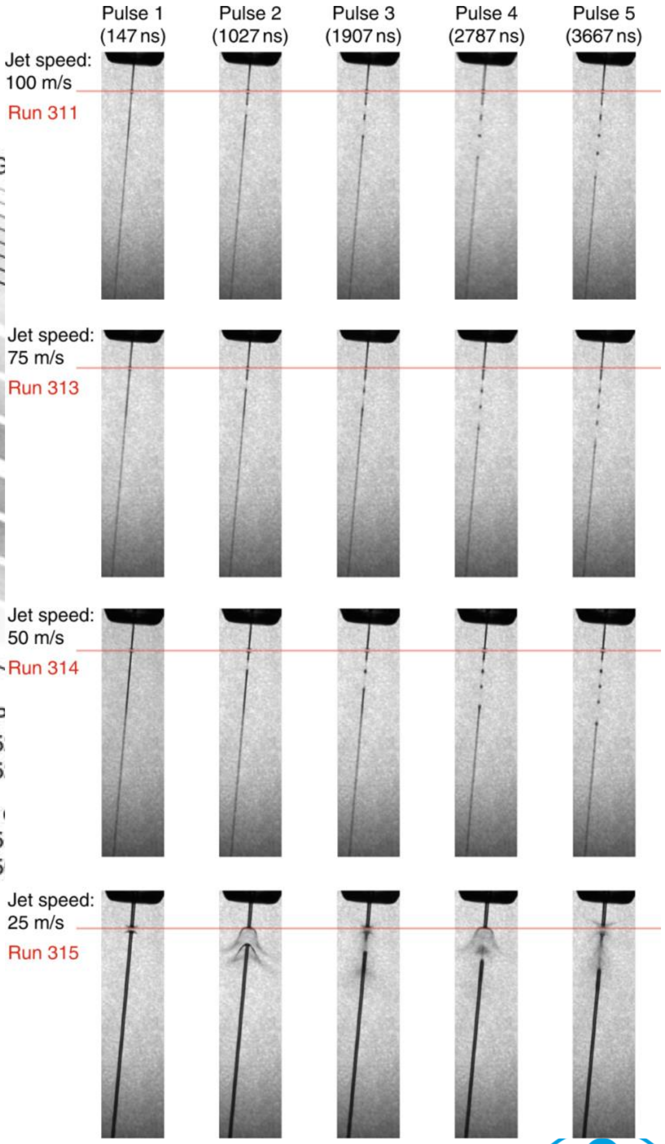


Nature 470, 73-78 (2011)

- Protein crystals not always available
- Liquid jet sample injection
- Run experiment on 120 Hz → 4.5 MHz pulse trains at European XFEL
- >10^5 diffraction patterns to obtain sample structure

Free-electron lasers





First European XFEL studies – experiments at MHZ repetition rate

Wiedorn et al. Nat. Commun. 9, 4025 (2019).