

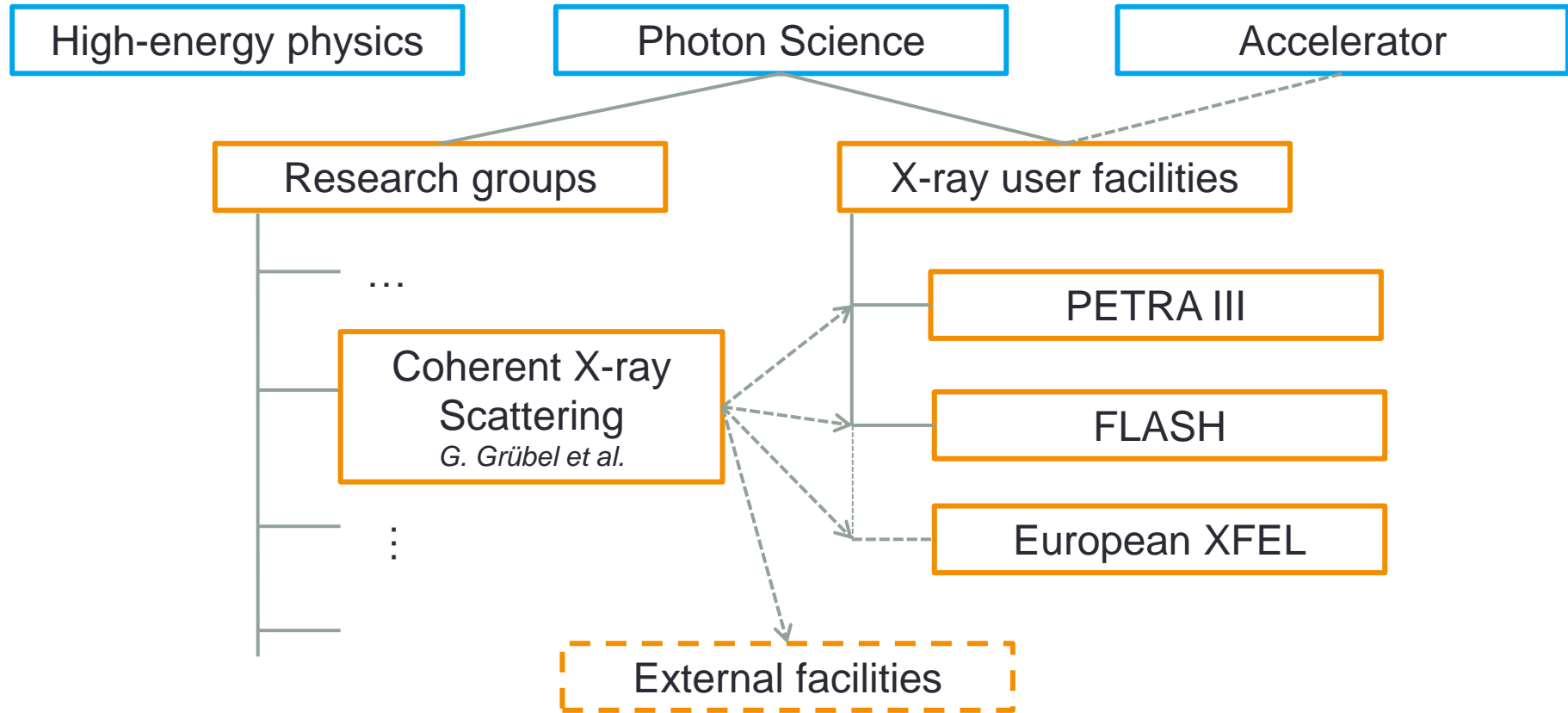
Methoden moderner Röntgenphysik: Streuung und Abbildung

Lecture 13	Vorlesung zum Haupt- oder Masterstudiengang Physik, SoSe 2018 G. Grübel, A. Philippi-Kobs, <u>F. Lehmkuhler</u> , O. Seeck, L. Frenzel, M. Martins, W. Wurth		
Location	Lecture hall AP, Physics, Jungiusstraße		
Date	Tuesday	13:00 - 14:30	(starting 3.4.)
	Thursday	8:30 - 10:00	(until 12.7.)





Who & Where?



- 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 29.05.2018** **Soft Matter studies I: Methods & experiments**
Definitions, complex liquids, colloids, storage ring and FEL experiments, setups, liquid jets, ...
- **Do 30.05.2018** **Soft Matter studies II: Structure**
SAXS & WAXS applications, X-ray cross correlations, ...
- **Di 05.06.2018** **Soft Matter studies III: Dynamics**
XPCS applications, diffusion, dynamical heterogeneities, ...
- **Do 07.06.2018** **Excursion to DESY (L. Frenzel)**
- **Di 12.06.2018** **Case study I: Glass transition**
Supercooled liquids, glasses vs. crystals, glass transition concepts, structure-dynamics relations, ...
- **Do 14.06.2018** **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

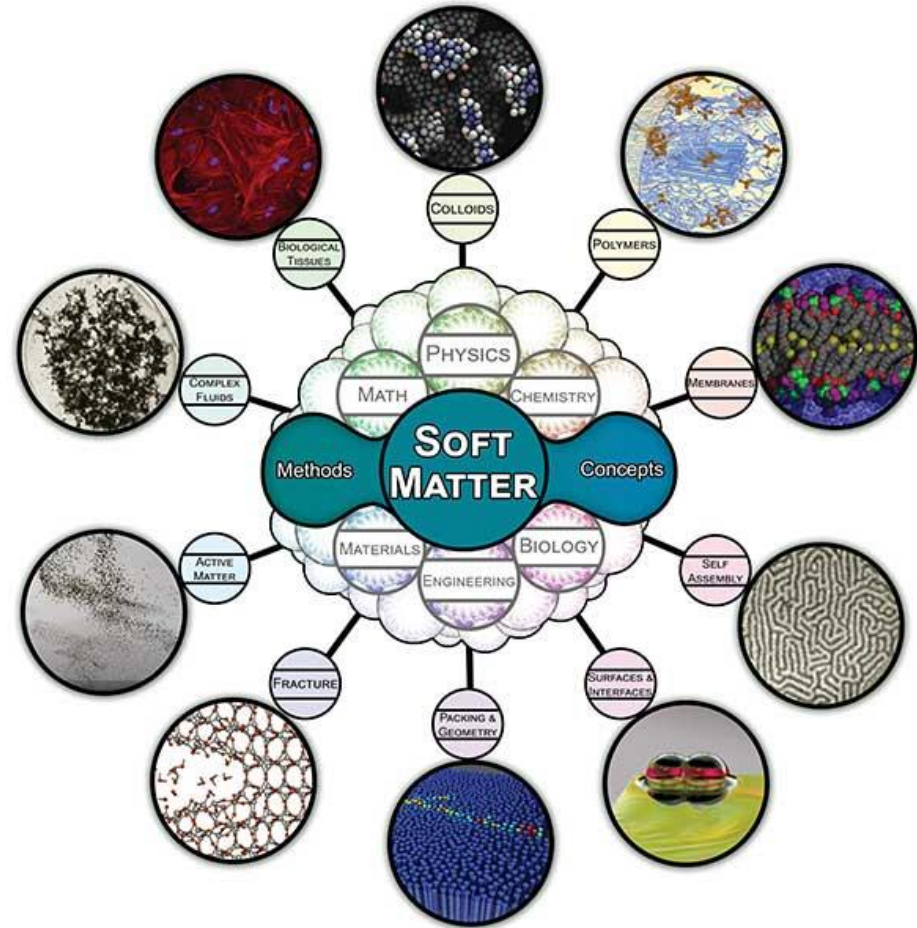
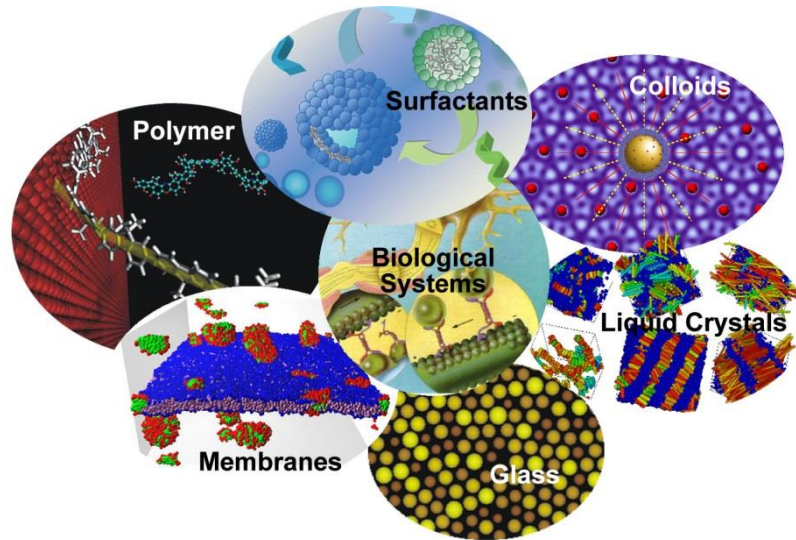
- **Liquids**
- **Colloids**
- **Polymers**
- **Foams**
- **Gels**
- **Granular materials**
- **Liquid crystals**
- **Biological materials**

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



American chemical society

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

What is Soft Matter?

Why soft? → matter can be deformed easily

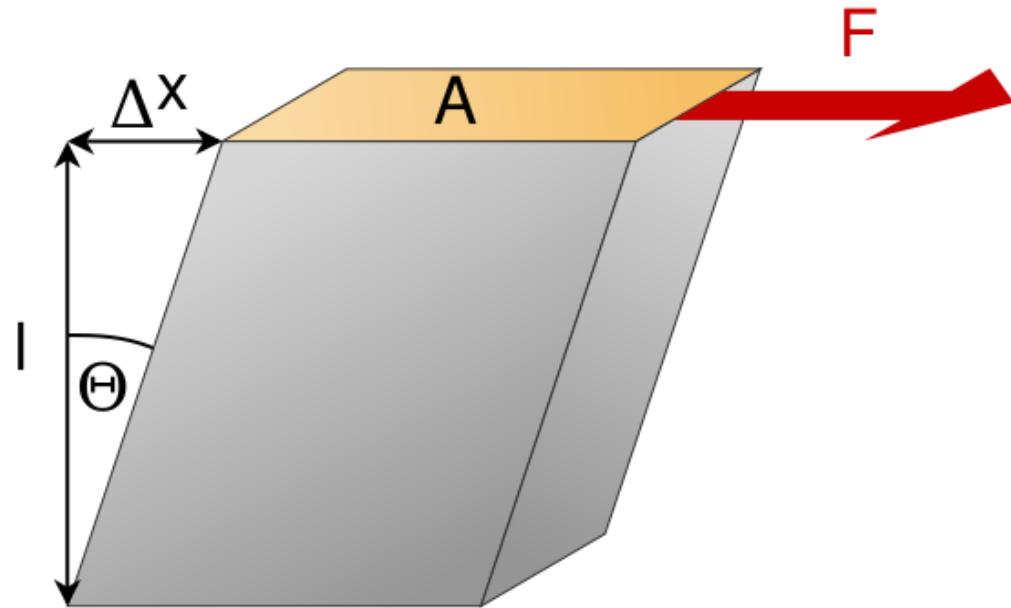
$$\text{Shear modulus } G = \frac{\tau}{\gamma} = \frac{F/A}{\Delta x/l} = \frac{Fl}{A\Delta x},$$

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

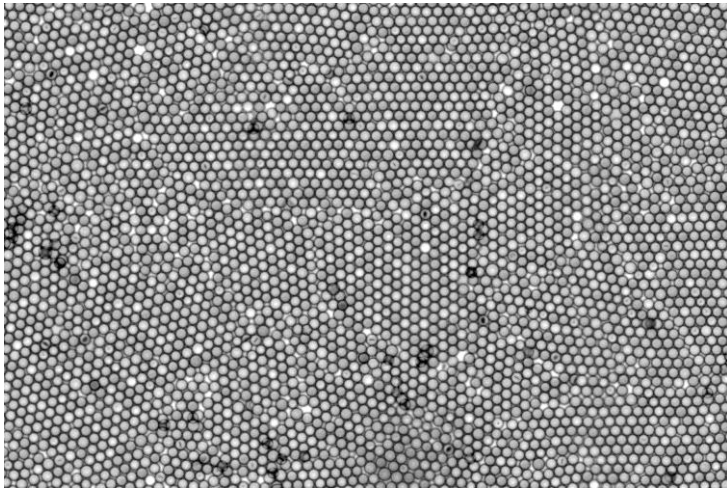
Metals: $G \sim$ some 10 GPa

Soft Matter: $G \leq 0.1$ GPa typically

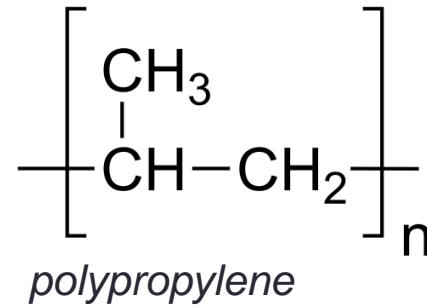
Liquid: $G \sim 0$



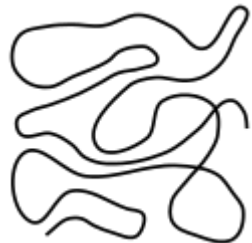
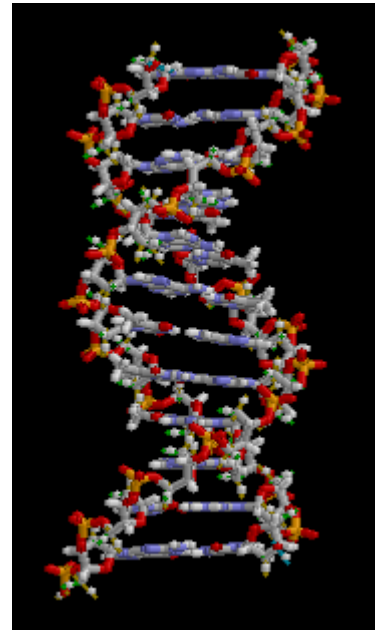
What is Soft Matter – examples



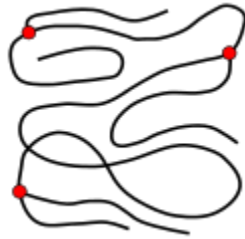
Colloids



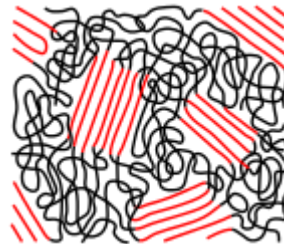
Polymers



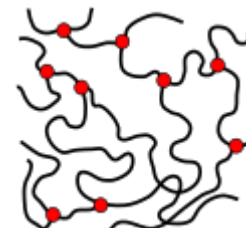
lineares
Makromolekül



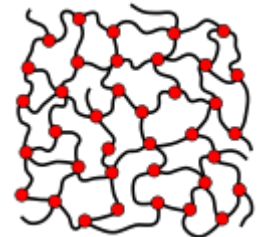
verzweigtes
Makromolekül



teilkristalline
Struktur linearer
Polymere

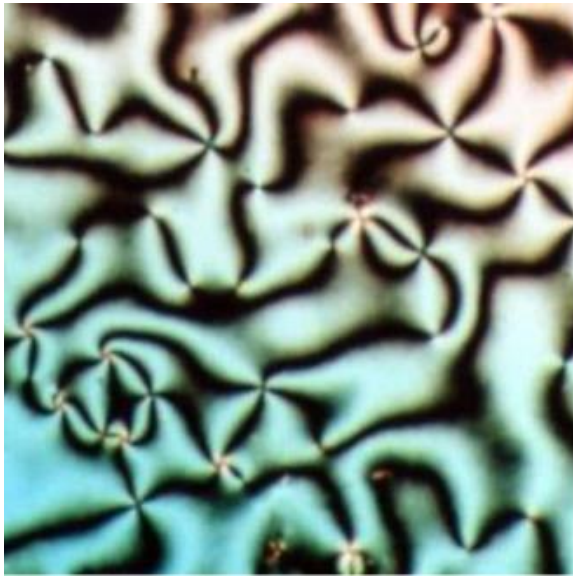


weitmaschig
vernetztes
Polymer

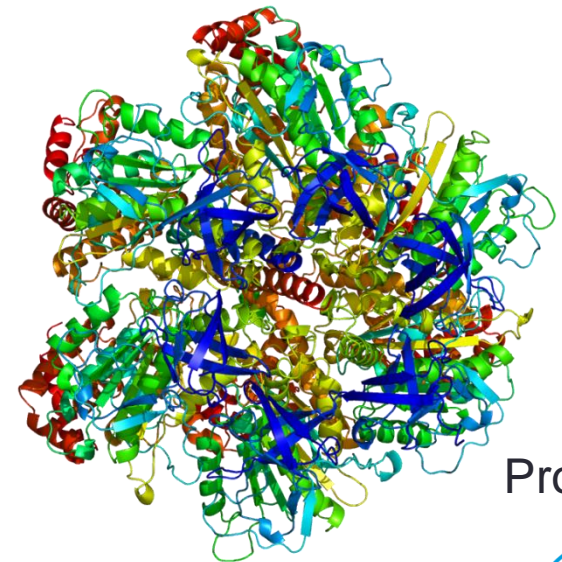
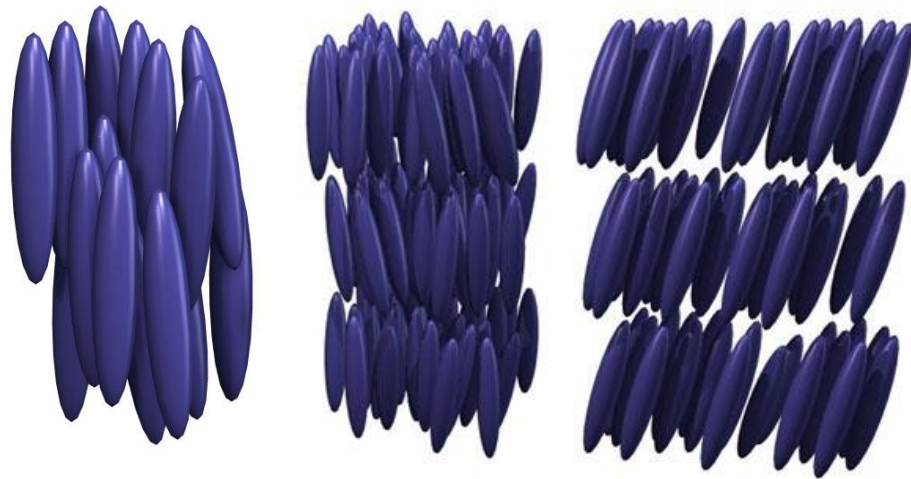


engmaschig
vernetztes
Polymer

Liquid
Crystals



Gels



Proteins

What is Soft Matter?

Bridging physics, chemistry and biology

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

Every day life & technology:

Milk, blood

Yoghurt

Cosmetics

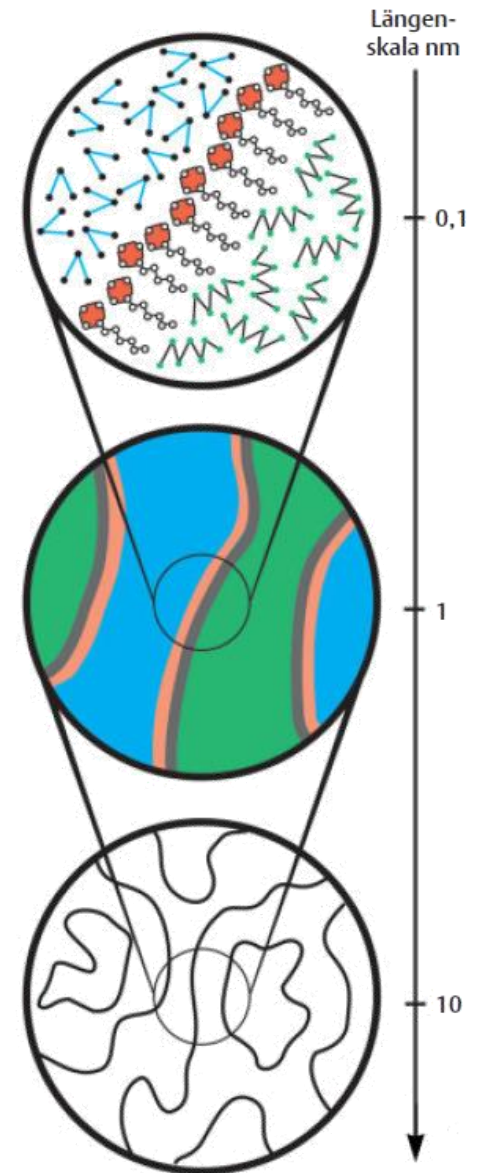
LCD displays

Paints

Rubber

Plastica

.....



Phys. Unserer Zeit 2003



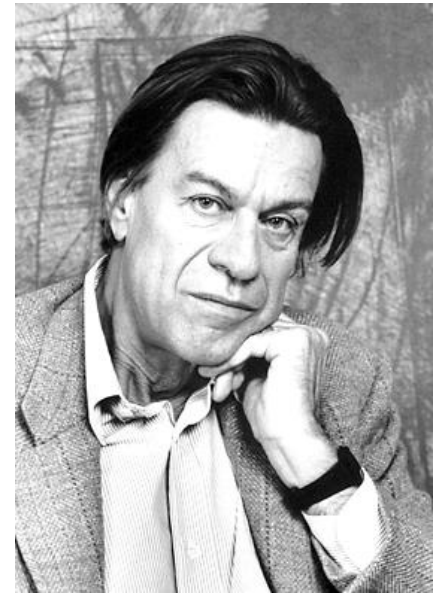
"Father of soft matter": Pierre-Gilles de Gennes (1932-2007)

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

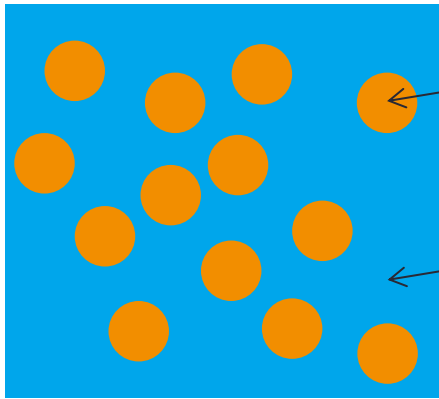


<https://www.nobelprize.org/>

Colloids

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

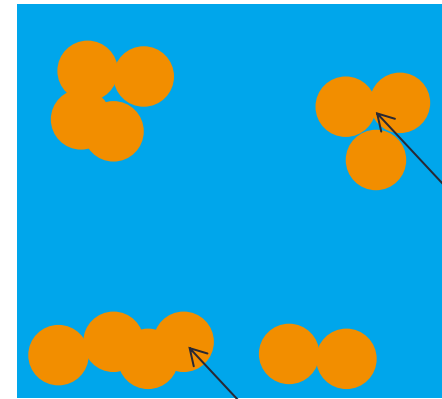
stable



Dispersed phase

Dispersion phase

unstable



Aggregation

Sedimentation

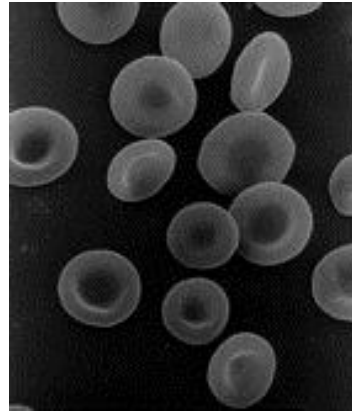
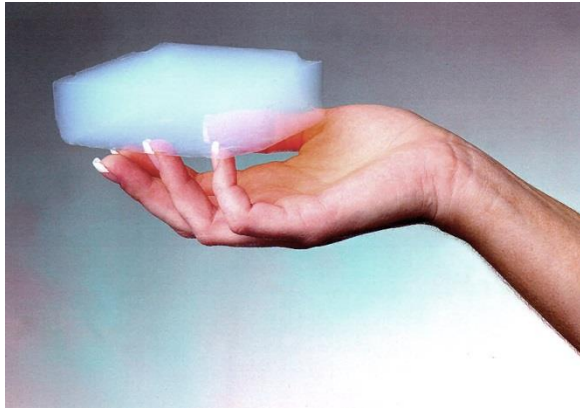
Characteristics

- No dissolved phase! (e.g. salts)
- Dispersed phase: sizes ~ 1 nm to 1000 nm \rightarrow 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 <i>Clouds, fog, mist</i>	Solid aerosol <i>smoke</i>
	Liquid	Foam <i>Whipped cream</i>	Emulsion <i>Milk, mayonnaise</i>	Sol <i>blood</i>
	Solid	Solid foam <i>Aerogel, styrofoam</i>	Gel <i>Gelatin, jelly</i>	Solid sol <i>Cranberry glass</i>

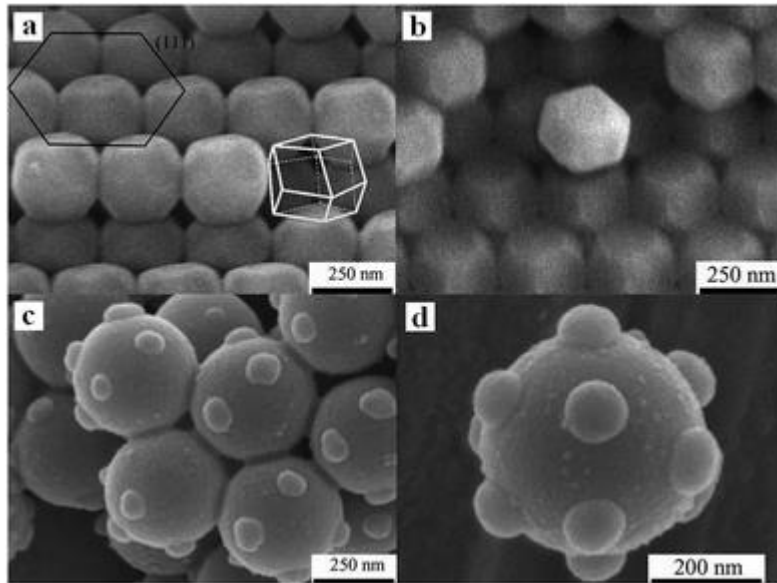




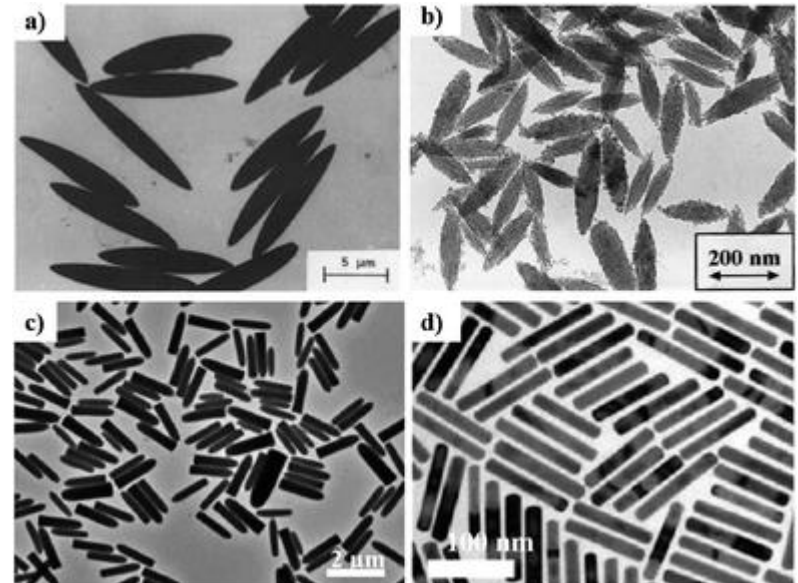
Colloids – Sol (solid particles in liquid)

Shapes
Dimensions
Materials

...



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

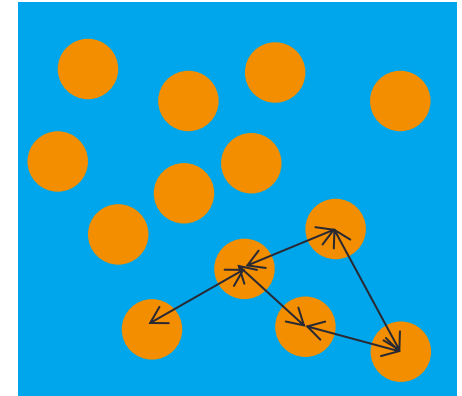


Soft Matter 9, 6711 (2013)

Colloids: interactions

Coarse-grain descripton:

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

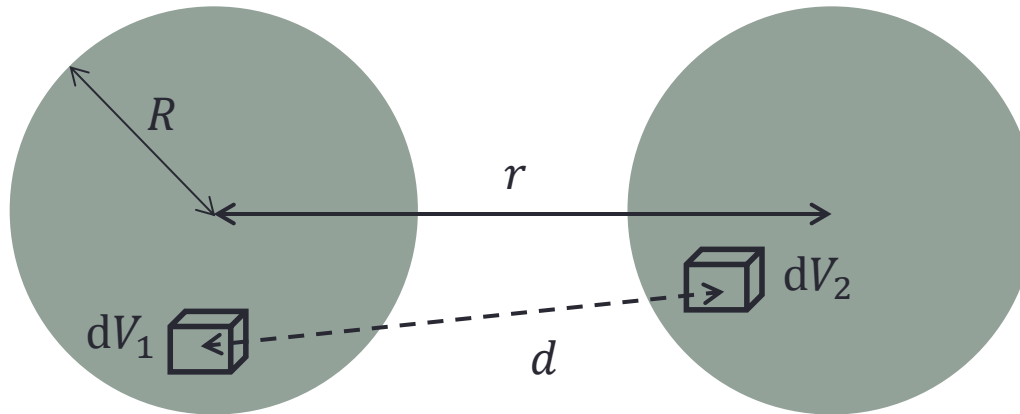


1. Van der Waals interactions

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)



$$U_{vdW}(r) = -C \iint \frac{1}{r^6} dV_1 dV_2$$

It follows for spherical particles of the same radius:

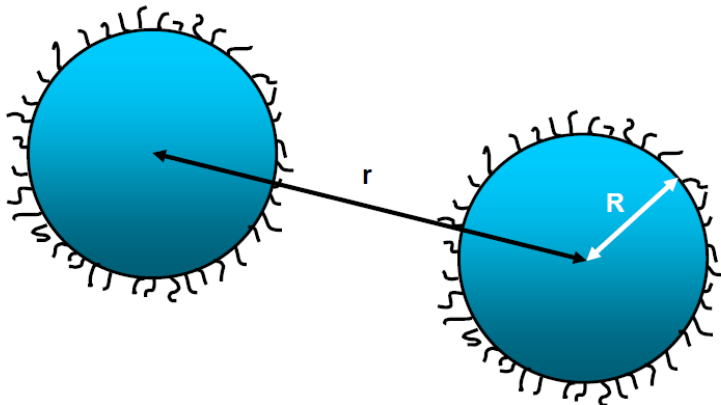
$$U_{vdW}(r) = -\frac{A_H}{6} \left(\frac{2R^2}{r^2 - 4R^2} + \frac{2R^2}{r^2} + \ln\left(1 - \frac{4R^2}{r^2}\right) \right)$$

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

Colloids: stabilization

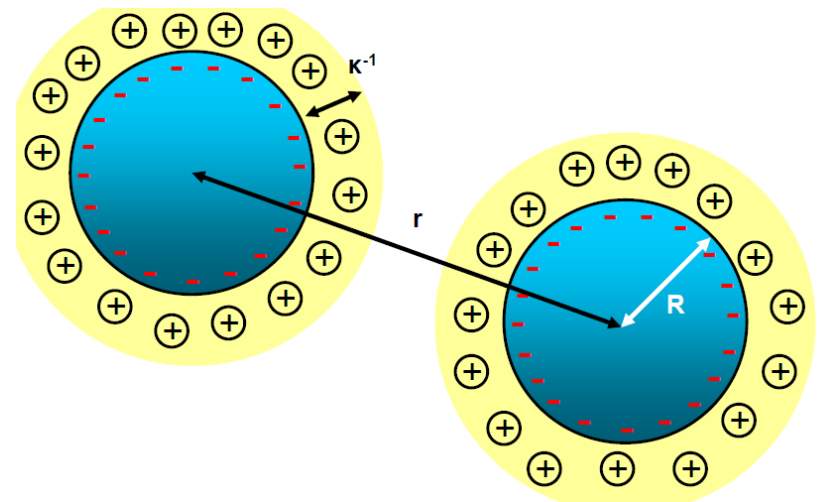
2. Steric stabilization

- 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



Steric stabilization: hard spheres

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

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



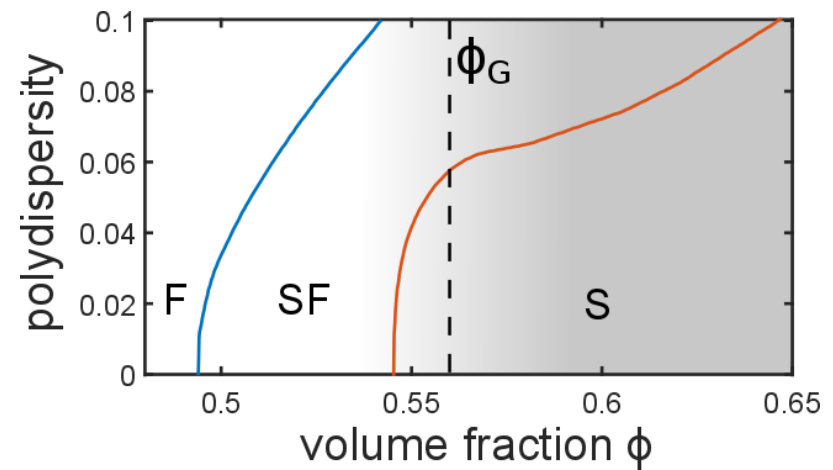
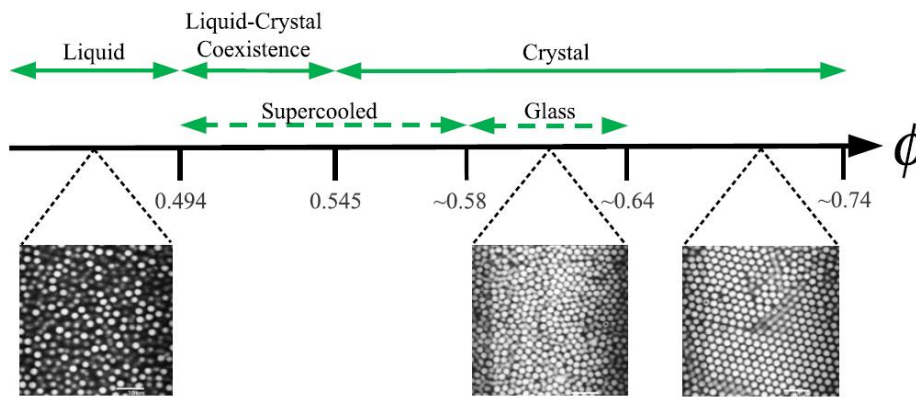
Poly(methyl methacrylate)
 (PMMA) particles in
 decalin
 With steric layer (~10 nm)



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 (\rightarrow lecture 16)



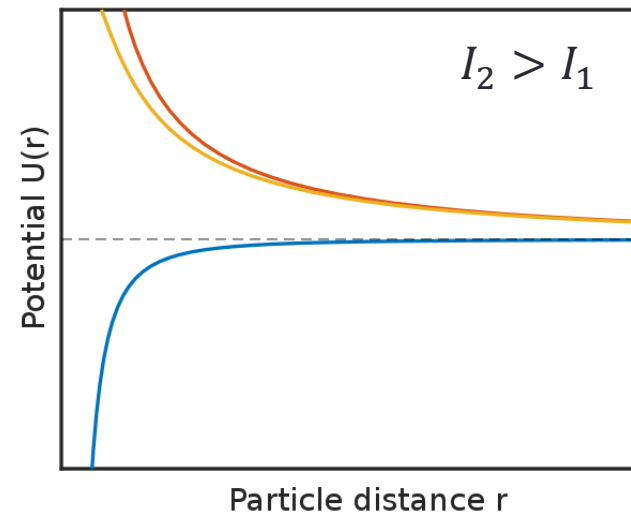
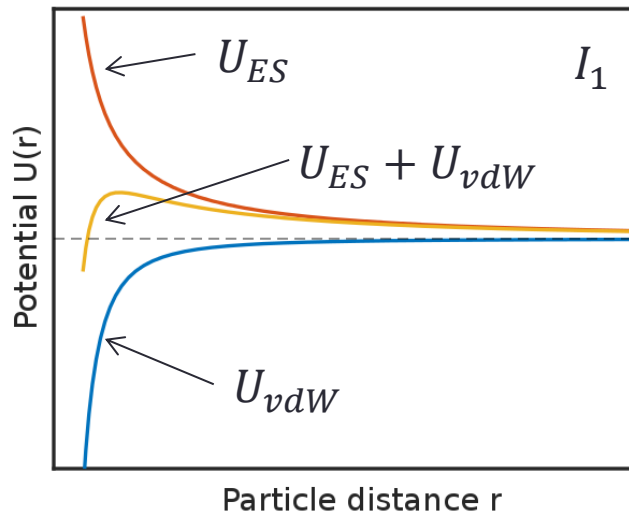
Rep. Prog. Phys. 75, 066501 (2012)

Electro-static stabilization

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

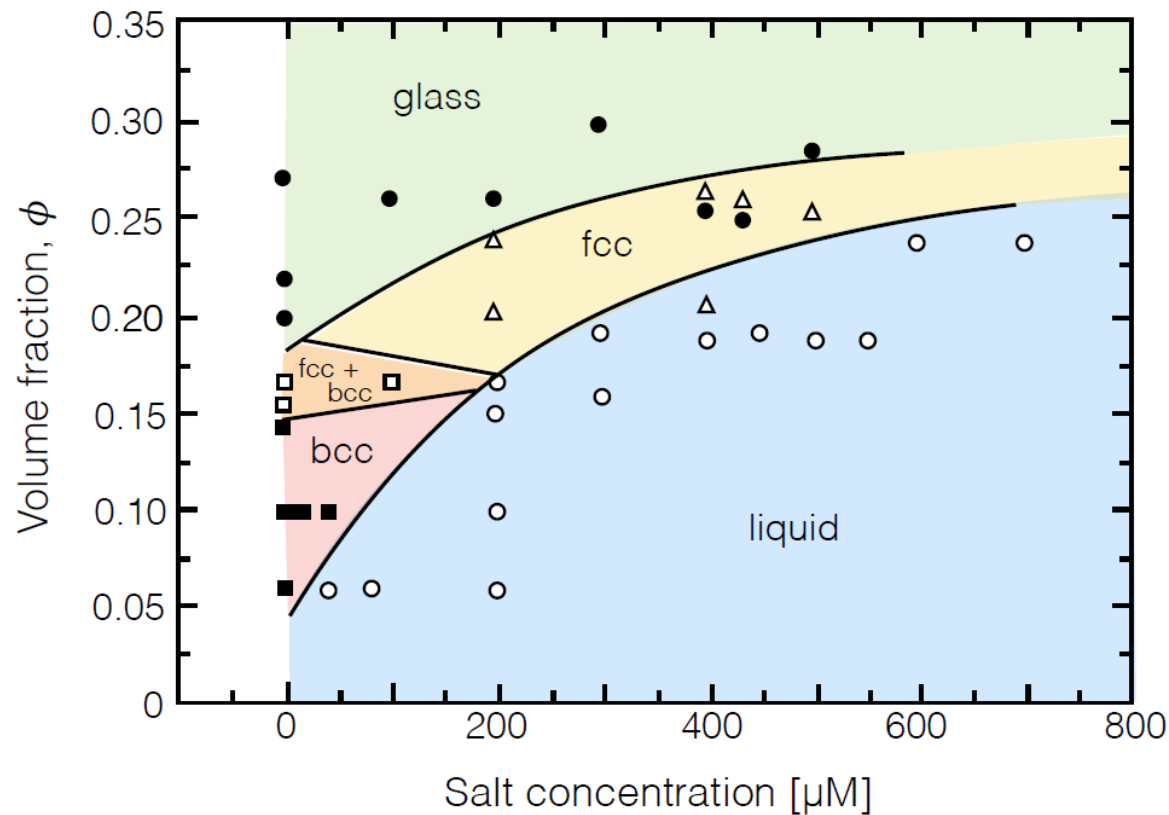
$$U_{ES}(r) = \begin{cases} \infty, & r \leq 2R \\ \frac{Z_{eff}^2 e_0^2}{4\pi\epsilon_0\epsilon_r} \left(\frac{\exp(\kappa R)}{1 + \kappa R} \right)^2 \frac{\exp(-\kappa r)}{r}, & r > 2R \end{cases}$$

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



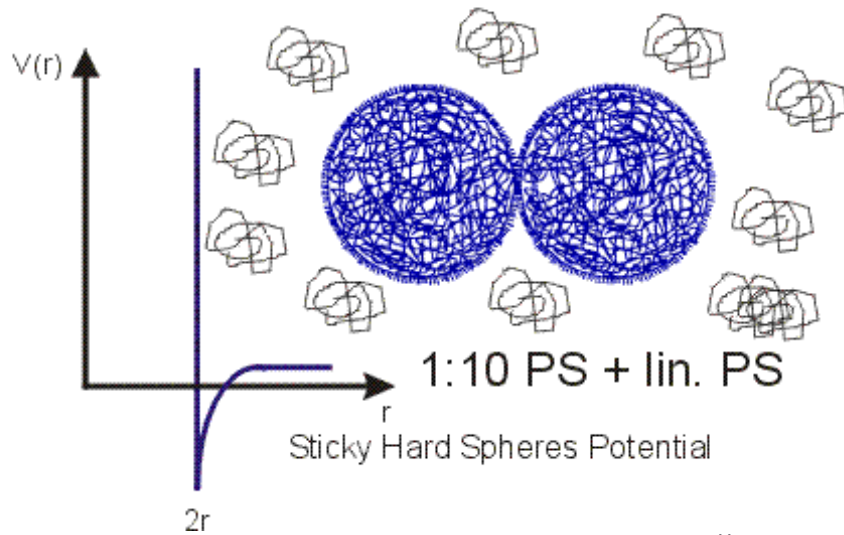
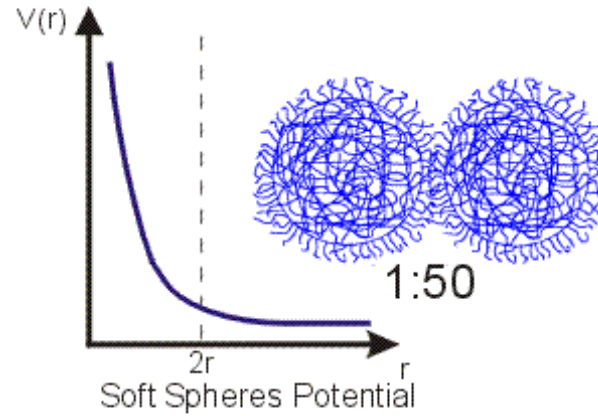
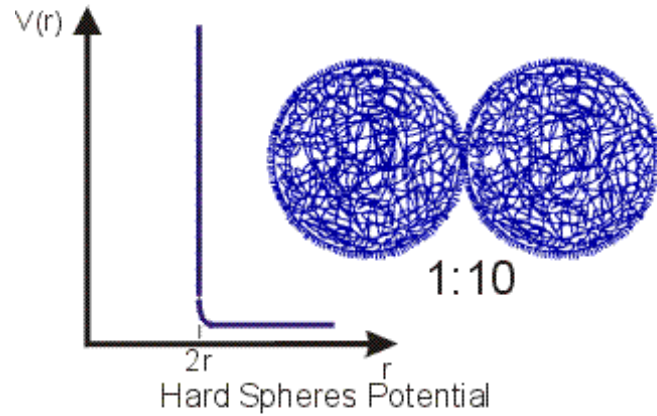
Electro-static stabilization

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



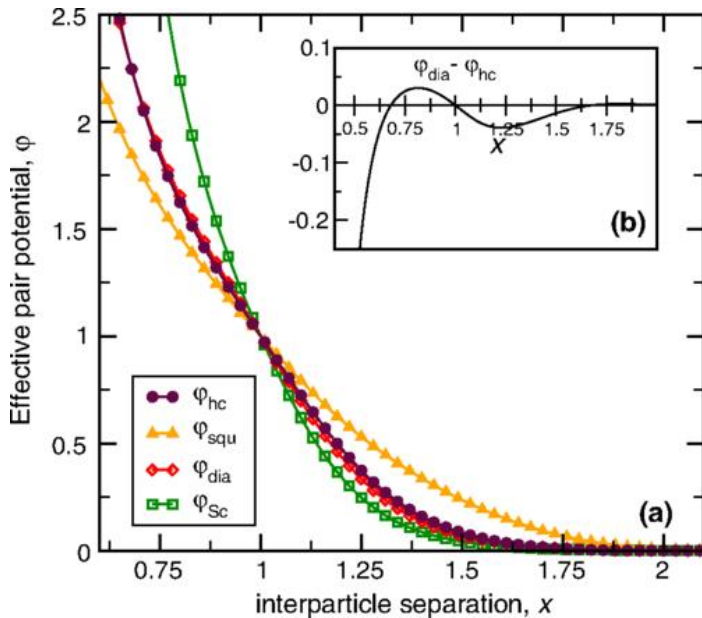
D. Sheyfer. Dissertation, Universität Hamburg (2018)
 Sirota et al. Phys. Rev. Lett. 62, 1524 (1989).

From hard to soft spheres

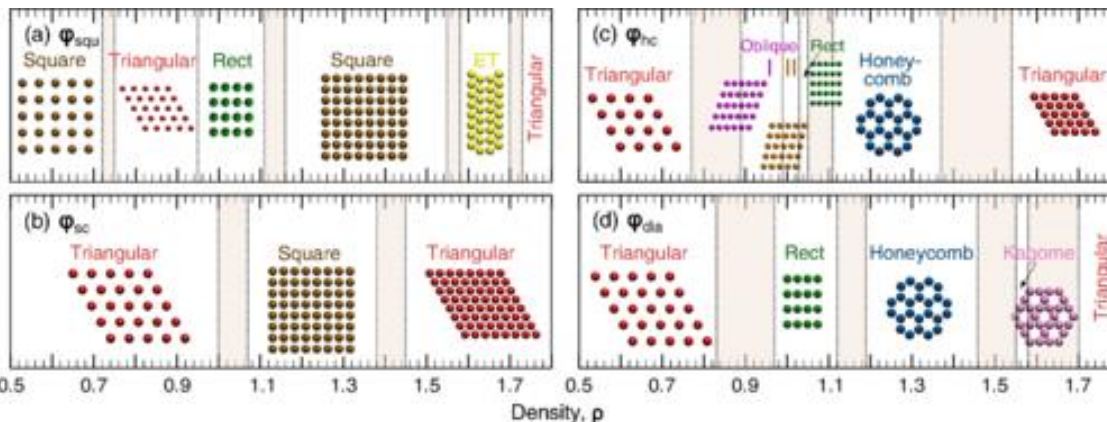


<https://www.colloids.uni-freiburg.de/Methoden/polymer.html>

Example for phase behaviour



Small modifications of the potential may dramatically change the phase behaviour



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

Soft matter – X-ray studies

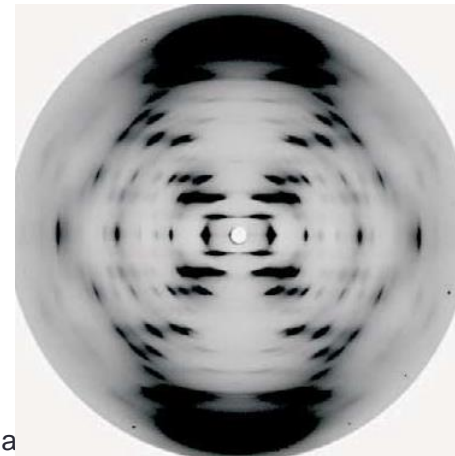
- Colloidal systems as model systems for phase transitions
 - Change of structure and dynamics while crossing phase borders
- Structure of soft matter: in-situ
 - Polymers: from macromolecules to networks
 - Colloids: form factors, function and synthesis
 - Order-disorder transition in liquid crystals
 - ...
- 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
- ...

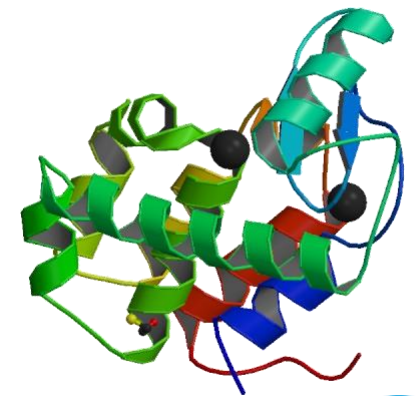
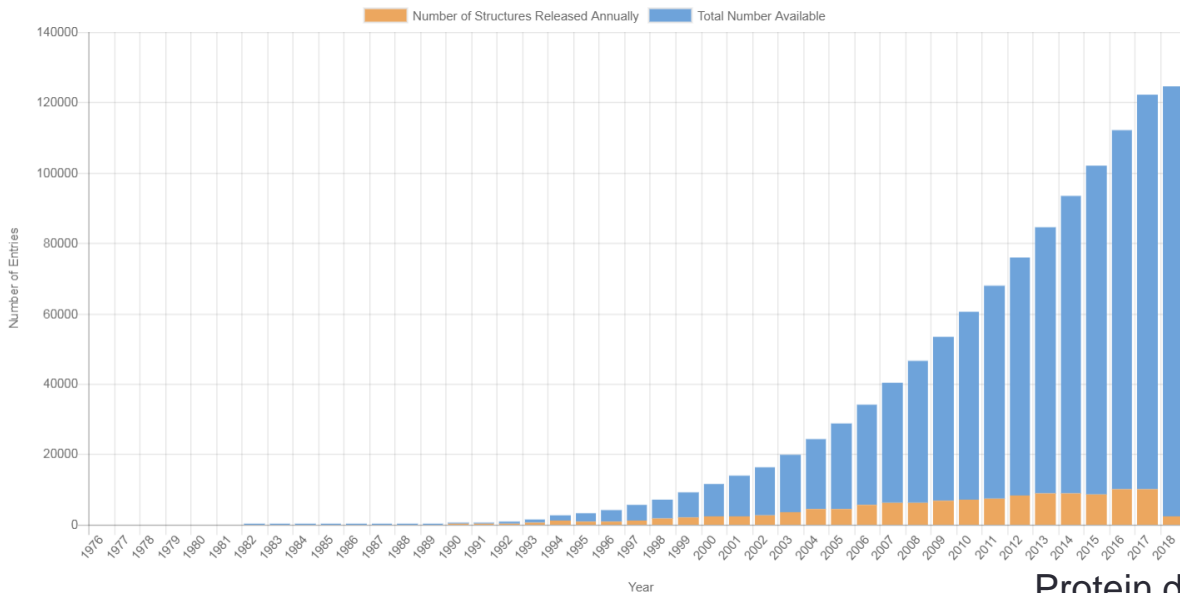
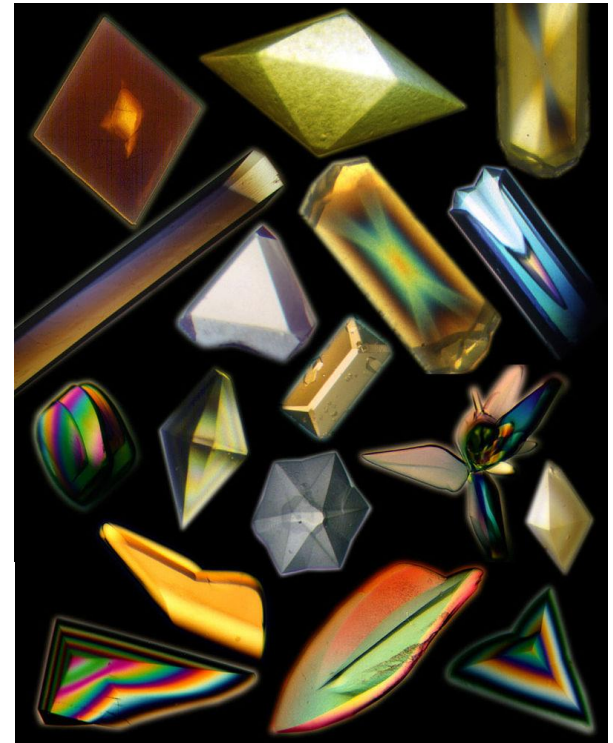
Sample environments

- 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

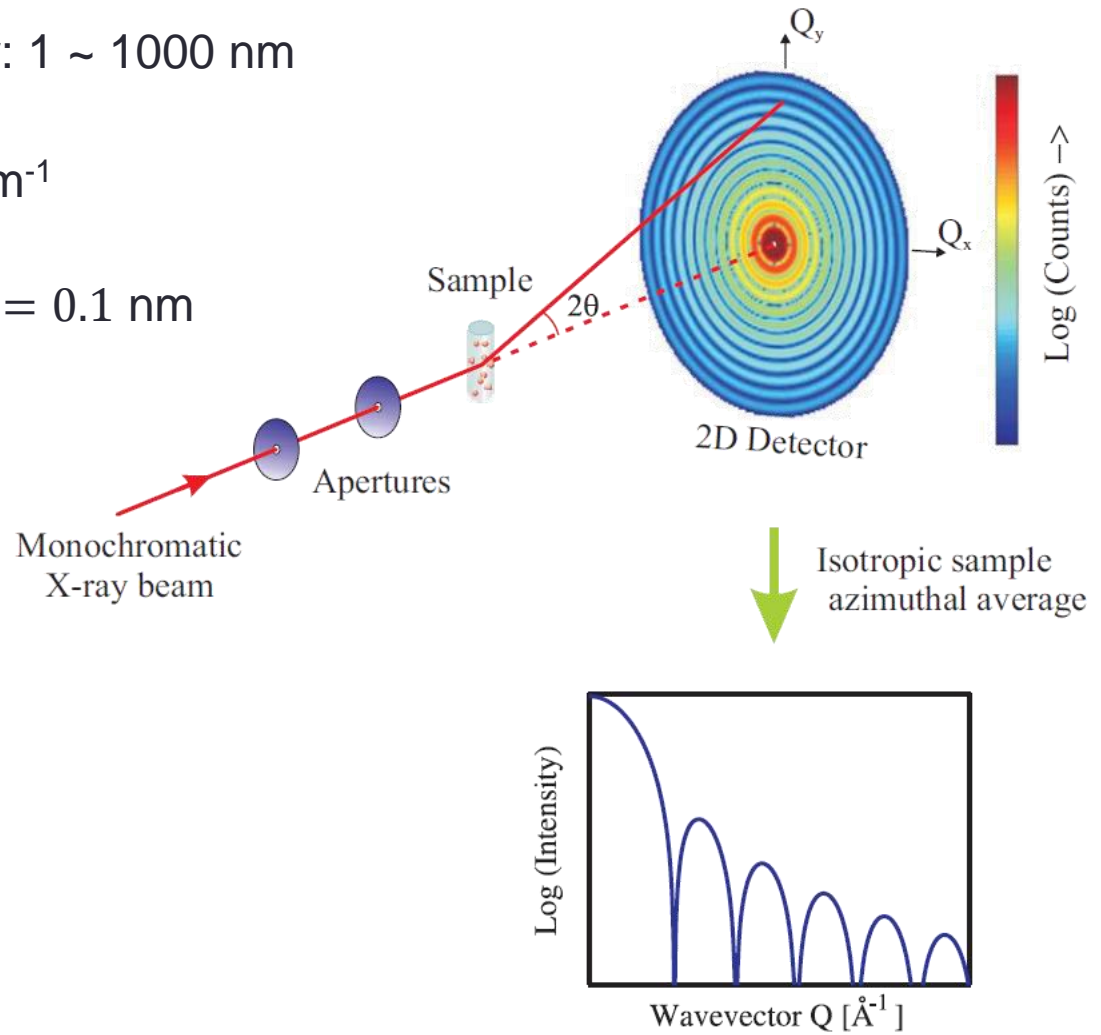
Typical dimensions of soft matter: 1 ~ 1000 nm

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

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

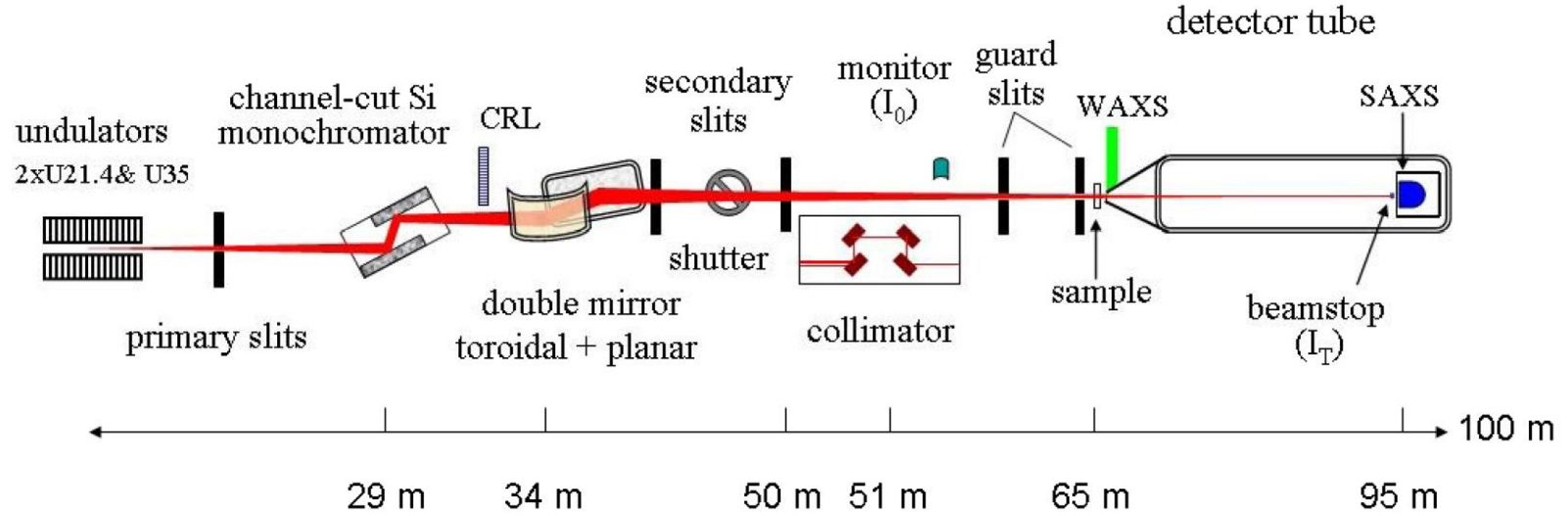
→ Need small angles for soft matter studies!

See Lecture 7 (& 14) for more details



SAXS – beamlines

ID02 @ ESRF



P10 @ PETRA III



P12 @ PETRA III

P10 @ PETRA III



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

SAXS

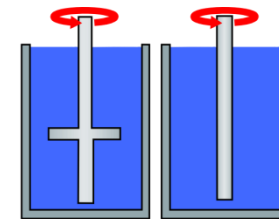
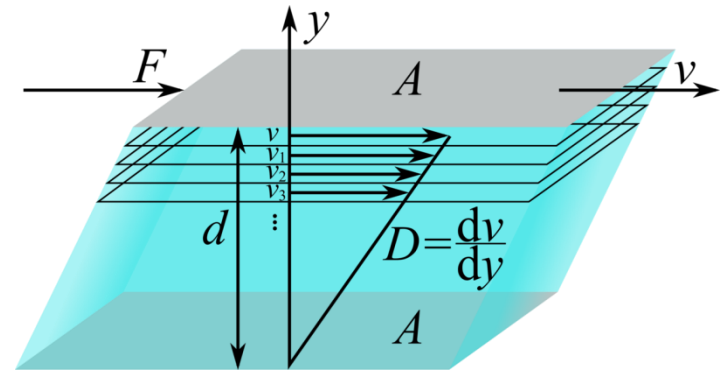
Accessible q-range in SAXS experiments

- Sample-detector distance \sim m, e.g. $D = 5$ m
- State-of-the-art detectors: Assume Eiger 4M \rightarrow size 155.2 x 162.5 mm
 - Read-out 750 Hz, 75 μ m pixels
 - Larger detectors available, in particular at dedicated beamlines
- Assume beam impinging to the center of the detector ($2p$ diagonal of detector)
 - $q_{max} = \frac{4\pi}{\lambda} \cdot \sin(\arctan(\frac{p}{D})/2) = 12.57 \cdot \sin(\arctan(\frac{112.4 \text{ mm}}{5 \text{ m}})/2) \approx 1.4 \text{ nm}^{-1}$
 - Minimum q defined by beamstop (~ 3 mm size): $q_{min} \approx 0.018 \text{ nm}^{-1}$
 - Length scales ~ 5 -350 nm in this setting
 - Typically: tuning of λ , D , ...

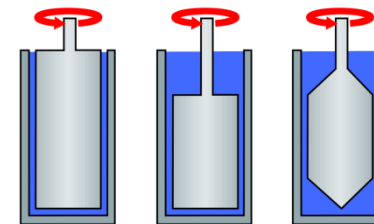
Rheology & SAXS

Rheology = study of flow of matter

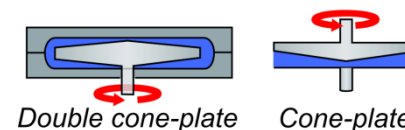
- Applications range from liquids, soft matter to geophysics
- (Dynamic) Viscosity η : resistance to shear stress $\tau = F/A$
 - $F = \eta A \frac{dv}{dy} = \eta A \dot{\gamma}$
 - Shear rate $\dot{\gamma} = \frac{dv}{dy}$
 - Newtonian liquids: $\tau = \eta \dot{\gamma}$ with $\eta = \text{const.}$
- Rheometers for measuring rheological properties ($\dot{\gamma} \leq 1000 \text{ s}^{-1}$)
- Péclet-number: $Pe = \text{advective/diffusive} = \dot{\gamma} R^2 / D$



Spindle type



Concentric cylinder



Double cone-plate



Cone-plate

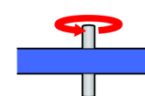


Plate-plate



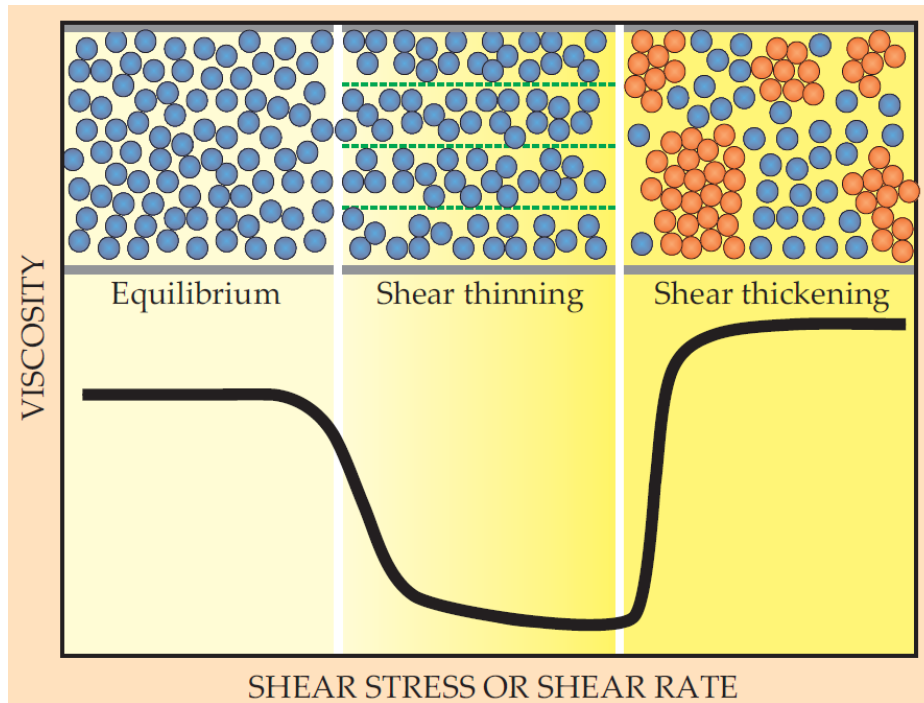
Cone-cone



Rheology & SAXS

Goals:

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

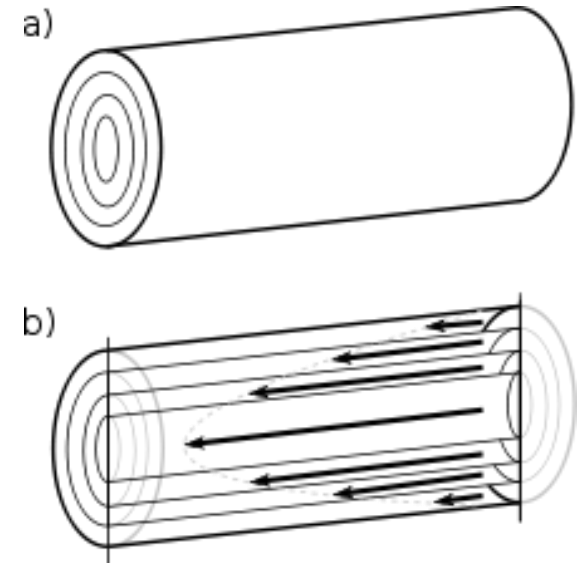


P10 @ PETRA III

Microfluidics & SAXS

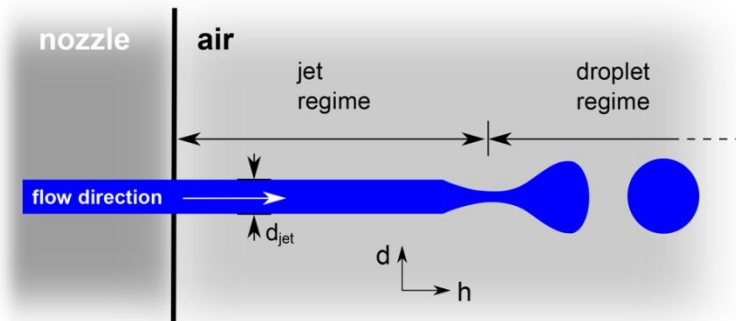
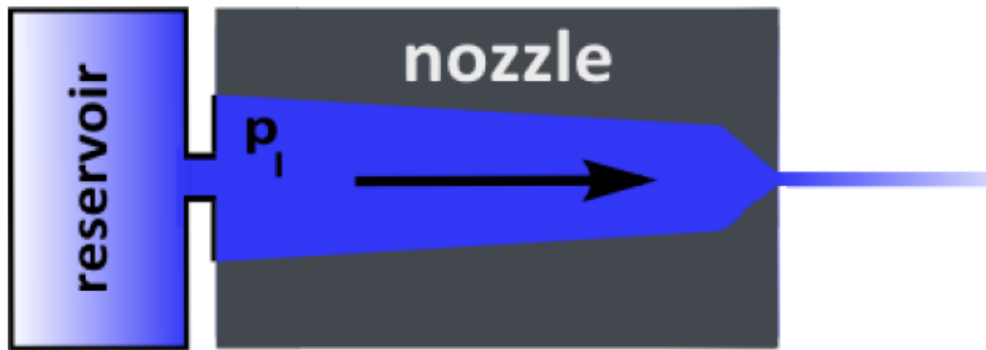
- Higher shear rates can be achieved in microfluidic flows (cf. blood transport)
- Motion of fluids: Navier-Stokes-equations \rightarrow partial differential equations
- Hagen–Poiseuille flow (laminar flow through a pipe):

$$\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial u_z}{\partial r} \right) = \frac{1}{\eta} \frac{\partial p}{\partial z},$$
 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 $r \rightarrow$ parabolic flow profile!
- Shear rate $\dot{\gamma} = \frac{8u}{2R}$
- $u = 1 \text{ m/s}, R = 50 \text{ }\mu\text{m} \rightarrow \dot{\gamma} = 8 \cdot 10^4 \text{ s}^{-1}$
- SAXS: μm X-ray beam



Liquid Jets

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



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



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

Liquid Jets in X-ray scattering experiments

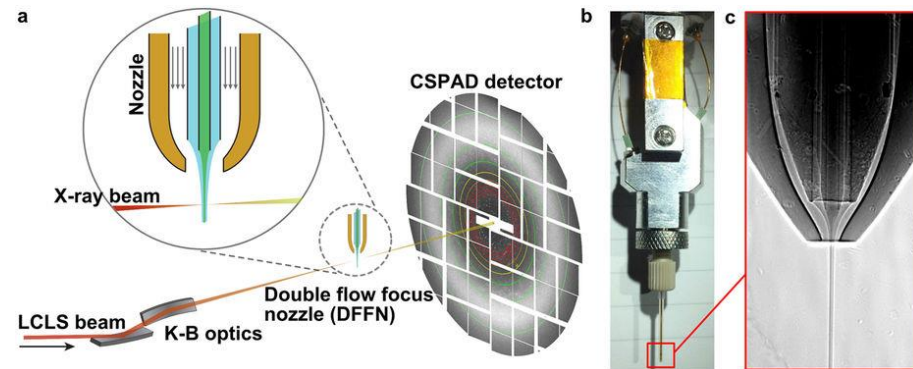
Advantages

- 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

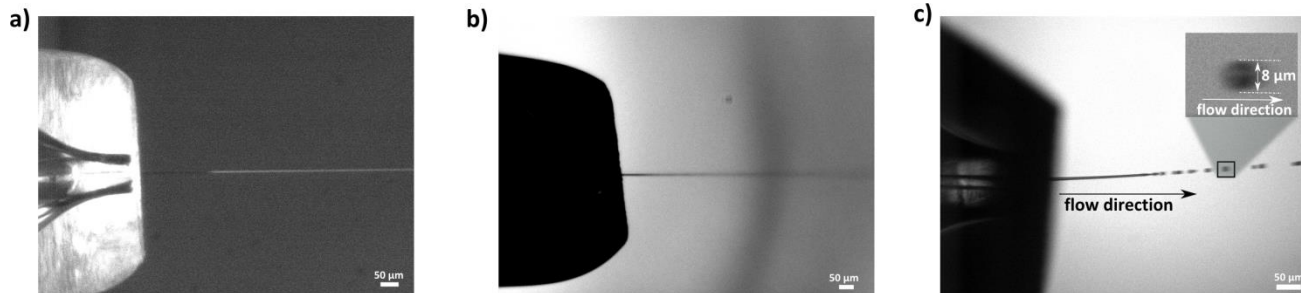
...

Nozzles

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



Sci. Rep. 7, 44628 (2017)

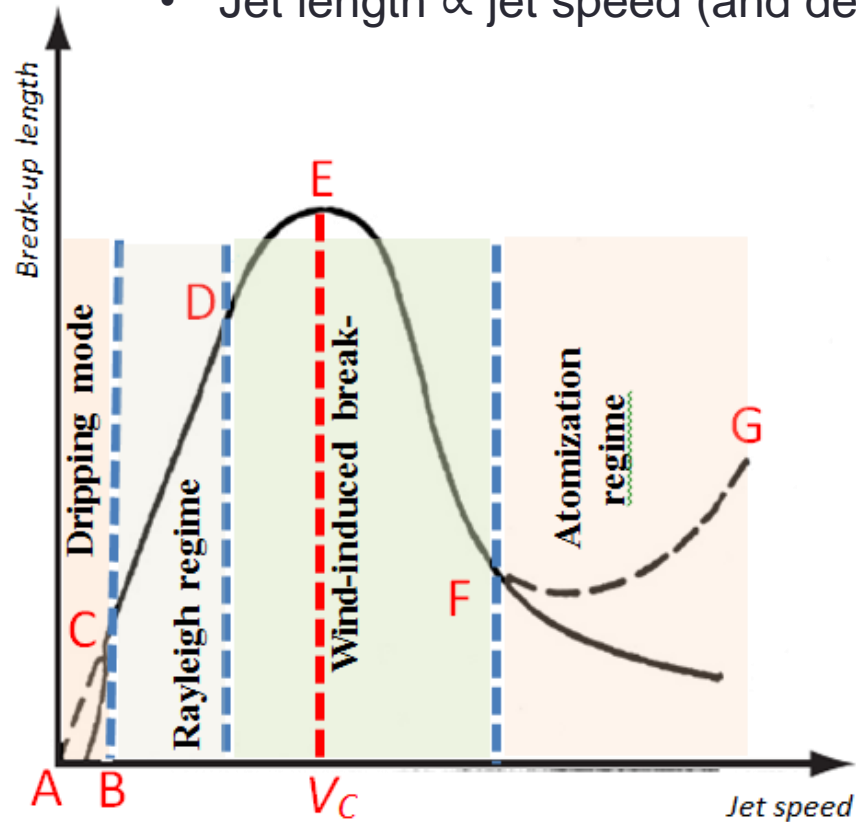


Rev. Sci. Instrum. 87, 063905 (2016)



Liquid Jets – stability and droplets

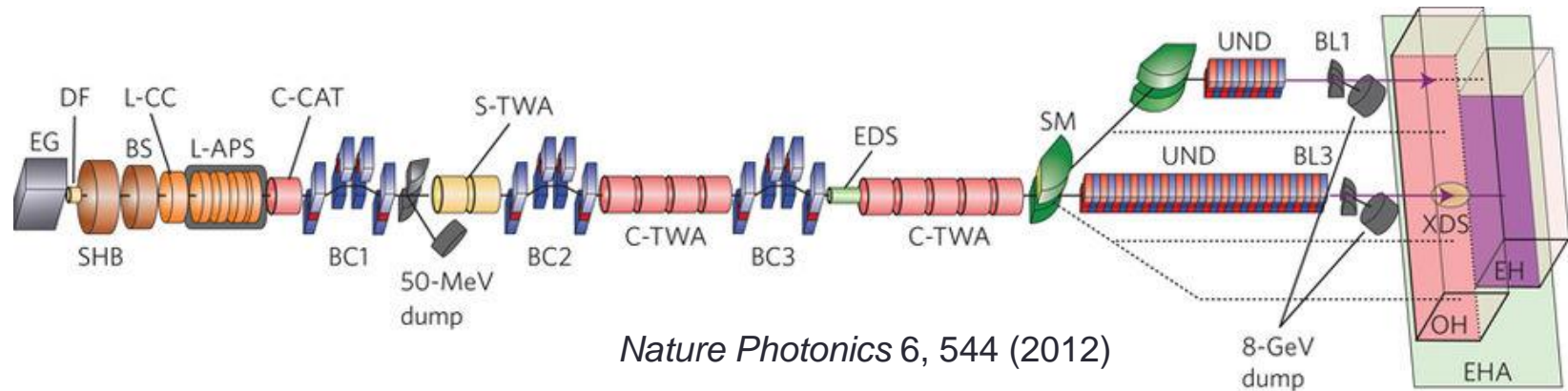
- After a certain distance liquid jets break-up into train of droplets
- Linear regime (Rayleigh) → capillary waves on jet surface trigger jet break-up.
 - Characteristic droplet size $r_{droplet} \approx 1.89r_{jet}$
 - Jet length \propto jet speed (and density, viscosity, surface tensions, ...)



Droplets in vacuum

- Evaporation of liquid
- Fast cooling rate
- Study of deeply supercooled liquids possible (see lecture 17)

Free-electron lasers



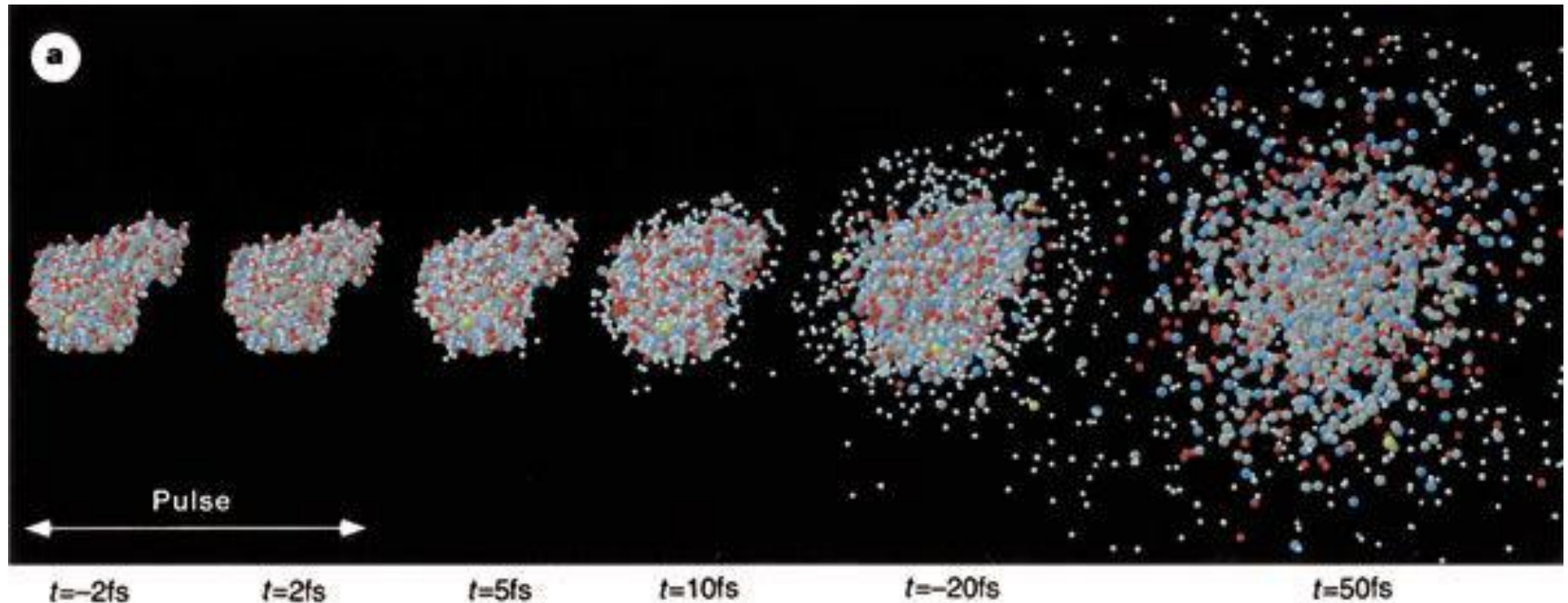
Characteristics

- 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

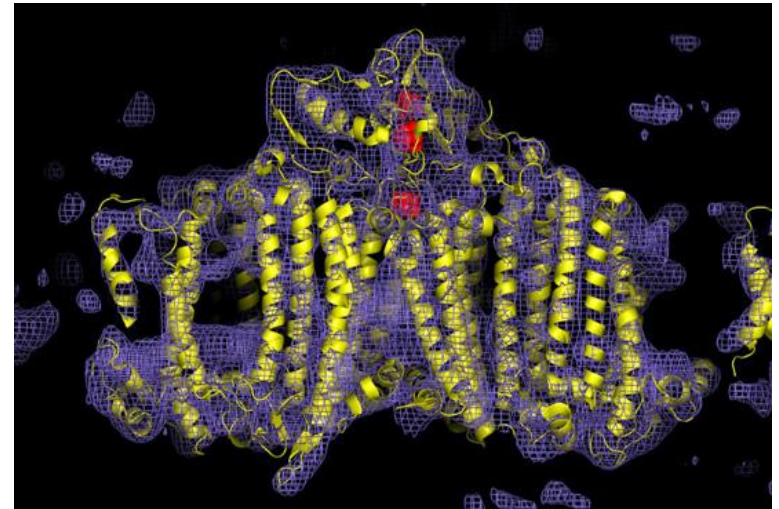
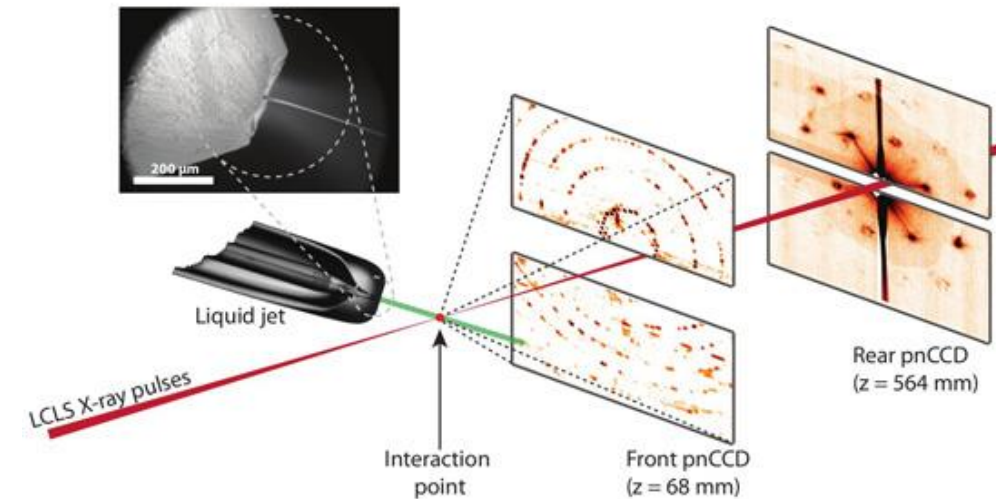
Diffract before destroy

→ 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