Introduction to Soft Matter Physics

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提纲

- 软物质物理的定位
- 胶体间的基本相互作用
- 主要实验方法简介

Lecture 1

- 胶体在平衡态研究中的应用

布朗运动
微流变学
胶体自组装
胶体晶体的固液相变

Lecture 2

- 胶体玻璃与非平衡态

Lecture 3

Useful books

1. Richard Jones, “**Soft Condensed Matter**”

A small book with much information

2. R. Pathria, “**Statistical Mechanics**”

Probably the best Stat Mech book for non-theorists

3. Jeffrey Olafsen edt., “**Experimental and computational techniques in Soft condensed matter physics**”

A handbook written by active researchers in the field, very informative

4. Wilson Poon and David Andelman, “**Soft Condensed Matter Physics in Molecular and Cell Biology**”

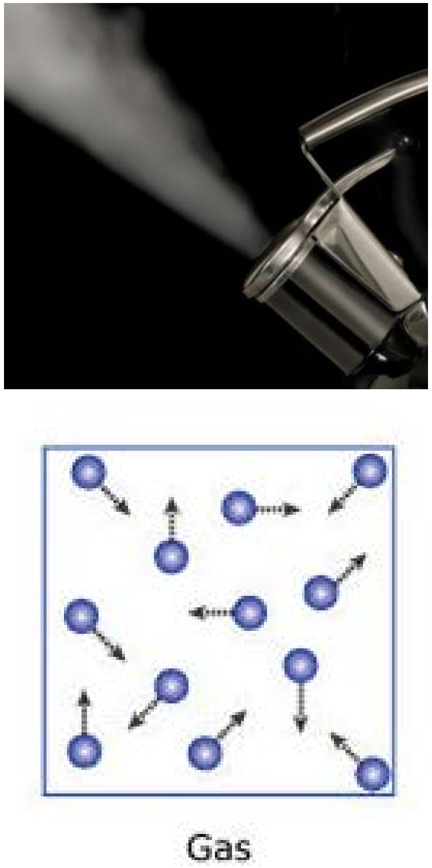
Bio-related handbook with detailed information in both theory and experiment.

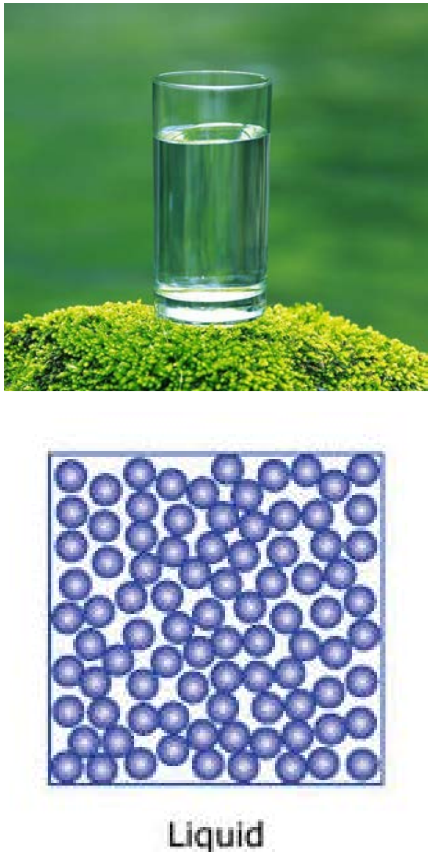
5. Shinya Inoué, “**Video microscopy**”

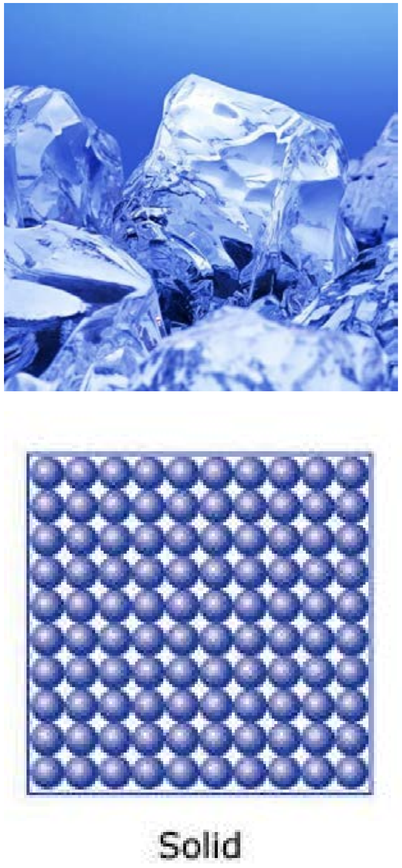
Everything you need to know about video microscopy

Lecture 1

States of matter





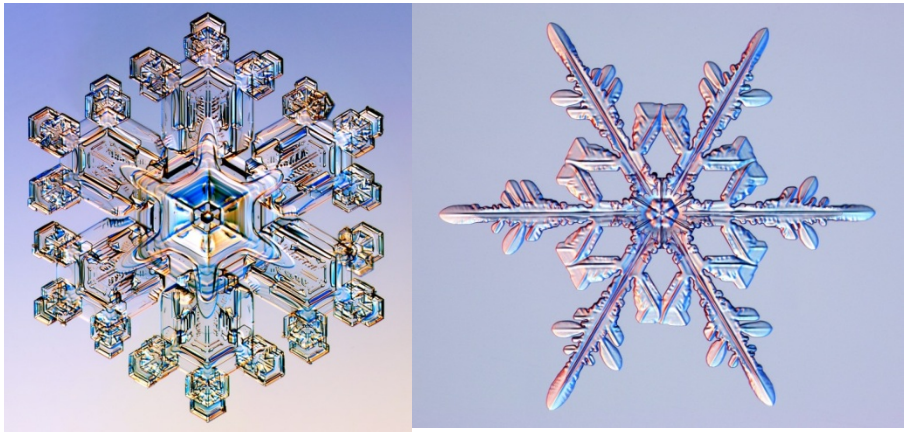


Structure:	**Disordered**	**Disordered**	**Ordered**
Interaction:	**Weak**	**Strong**	**Strong**

Condensed Matter

Liquid and solid are in condensed states, where interaction between individual elements are important.

water vapor condenses into liquid droplets



Snow flakes are frozen water

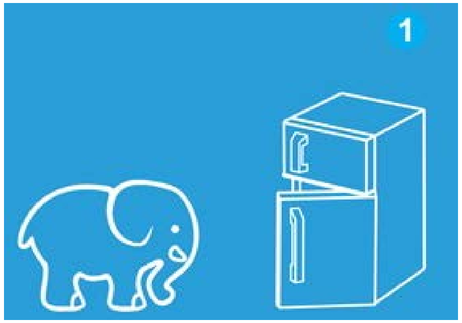
Statistical mechanics with interactions
Complex phase behaviors

Statistical Mechanics is easy

Statistical mechanics connects microscopic motions to macroscopic properties.

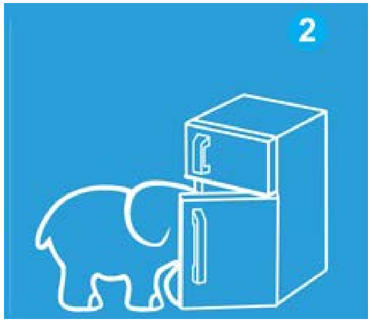
1. **Write down the Hamiltonian,**

$$H = \sum_{\alpha} \left(\text{kinetic energy and ALL possible interactions}\right)$$



2. **Write down the partition function,**

$$Q = \sum_{r} e^{-\beta H_r} \left(\text{summed over ALL possible states}\right)$$



3. **Do your physics….**

$$\bar{f} = \int f\left(\mathbf{x},\mathbf{p}\right)\rho\left(\mathbf{x},\mathbf{p}\right) d\mathbf{x}\, d\mathbf{p}$$

Ideal Stat Mech

For ideal gases, there is only kinetic energy, the Hamiltonian is

$$H = \sum_{\alpha} \frac{p_{\alpha}^{2}}{2m}$$

And the partition function is

$$Z_N(T,V) = \frac{1}{N!h^{dN}} \int d\mathbf{R} e^{-\beta H} = \frac{V^N}{N!}\left(\int \frac{dp}{h} e^{-\beta p^2/2m}\right)^{3N} = \frac{1}{N!}\frac{V^N}{\lambda^{3N}}, \qquad \lambda = \frac{h}{(2\pi m T)^{1/2}}$$

The free energy is

$$F(T,N,V) = -T\ln\left(\frac{1}{N!}\frac{V^N}{\lambda^{3N}}\right) = TN\ln\left(\frac{\lambda^3}{V}\right) - T\ln(N!), \quad \ln(N!) \approx N\ln(N) - N$$

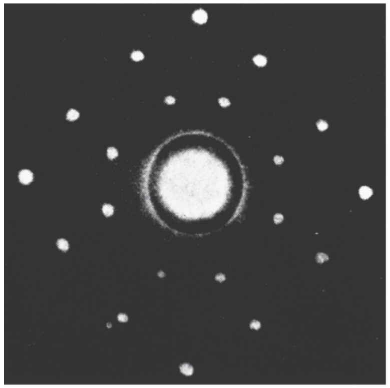
$$= TN\ln\left(\frac{\lambda^3}{V}\right) - TN\ln(N) = TN\left[\ln\left(\frac{N\lambda^3}{V}\right) - 1\right]$$

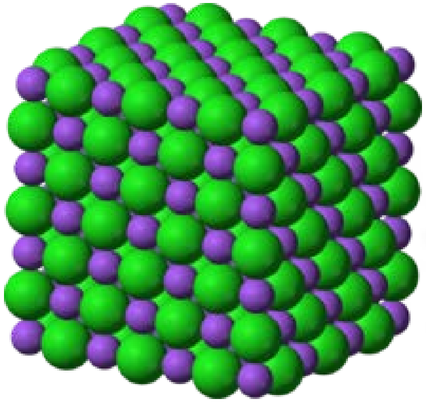
From the free energy we can obtain

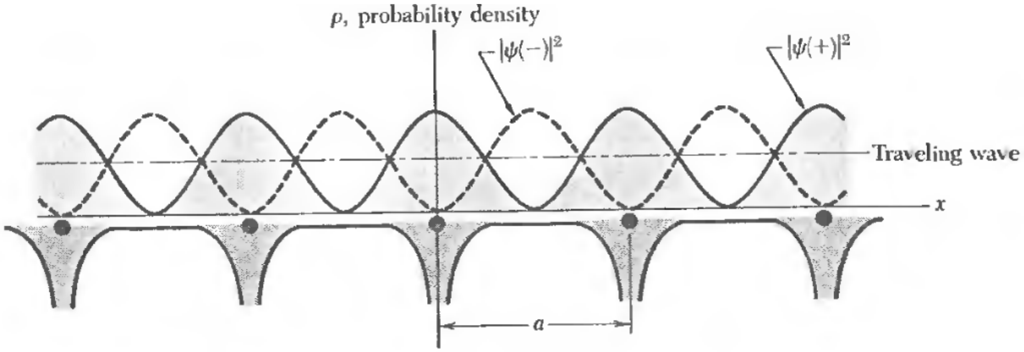
$$E = \frac{3}{2}NT, \quad \mu = T\ln\left(\frac{N\lambda^3}{V}\right), \quad p = T\frac{N}{V}, S = N\left[\frac{5}{2} - \ln\left(\frac{N\lambda^3}{V}\right)\right]$$

Hard condensed matter

For crystalline solids, the periodicity in atom positions greatly reduces the complexity of the problem, although it is still hard.





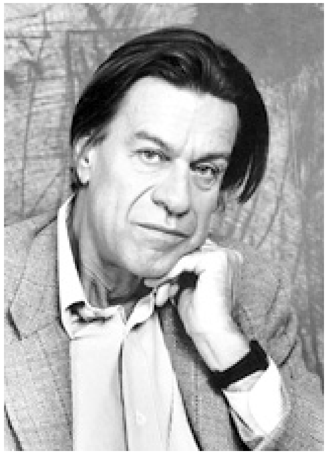


Periodicity requires physical quantities to obey the symmetry of the lattice.

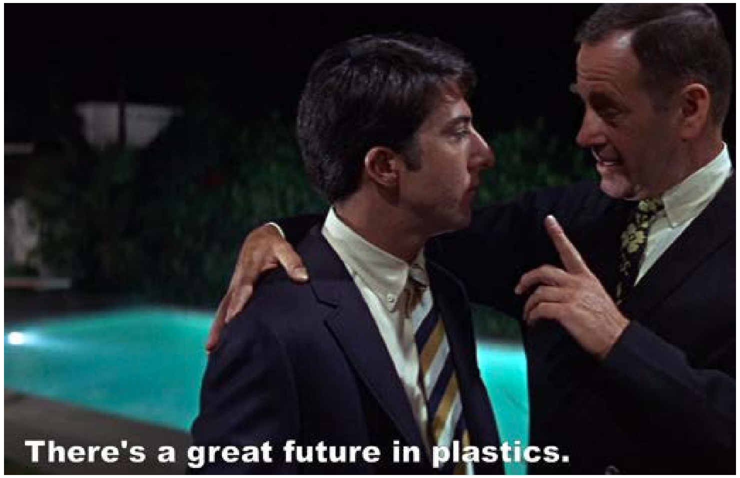
Quite often, one needs to consider only the property of a unit cell

Soft Condensed Matter Physics

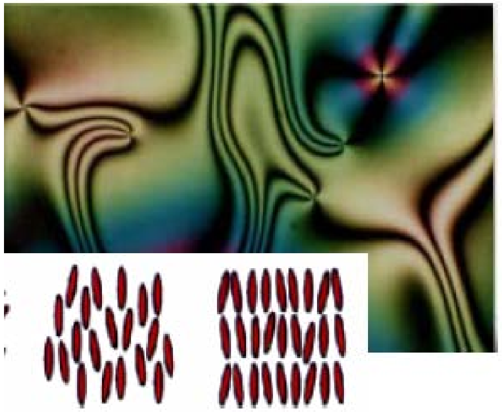
Soft matter physics study systems with strong interactions but with weak or no structural order (sort of the worst deal).



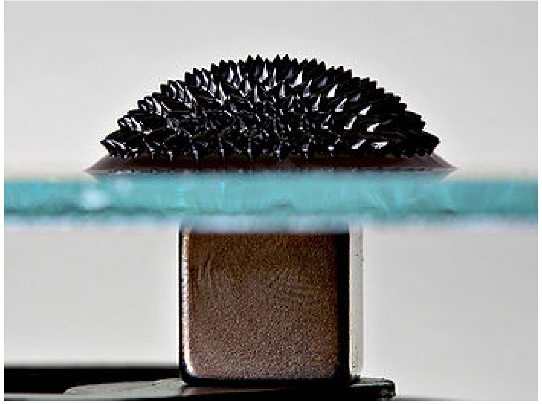
Pierre-Gilles de Gennes
1991 Nobel Prize in Physics



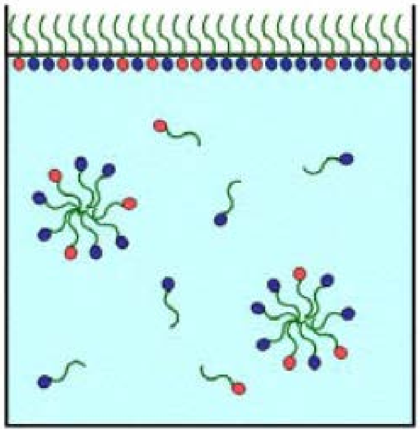
Polymer



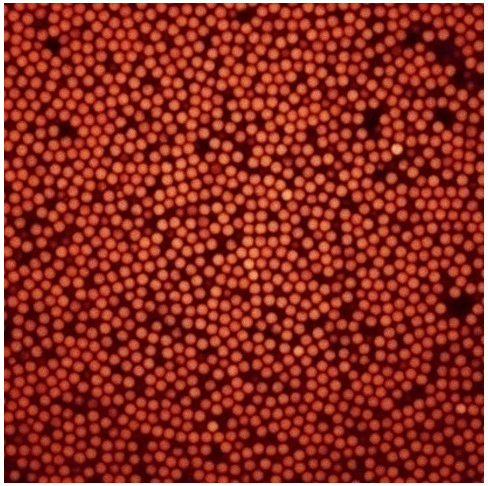
Liquid Crystal



Complex Fluids



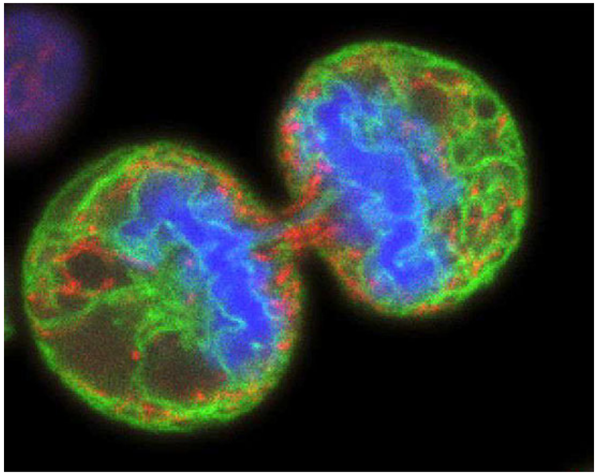
Surfactant

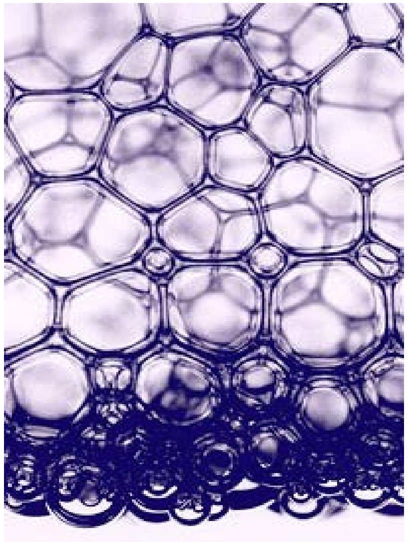


Colloids

Soft Condensed Matter Physics


Granular materials


Biological systems


Foams

Common features of soft matters:

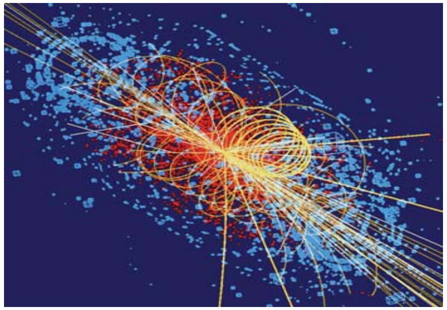
1. Length scale between atomic and macroscopic

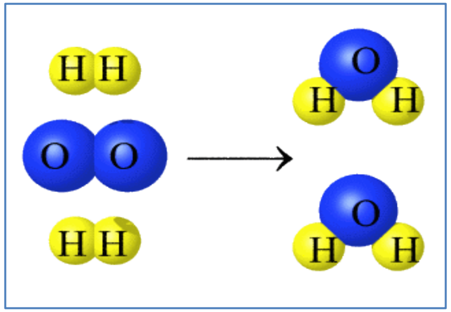
2. Thermal fluctuations significant, easy to flow

3. Entropy plays an important role, rich phase behaviors

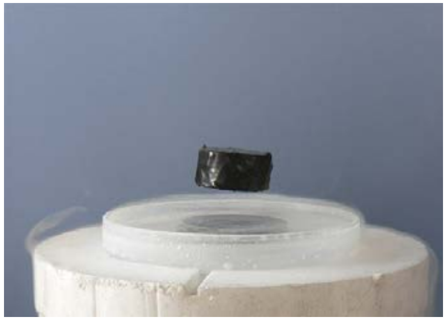
Where is the science?

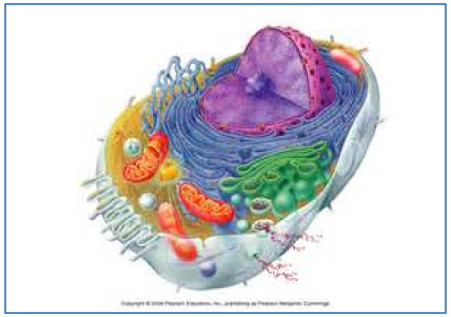
“Fundamental”

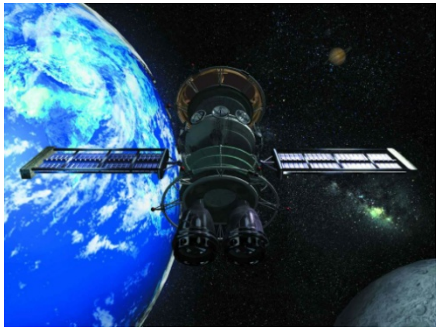




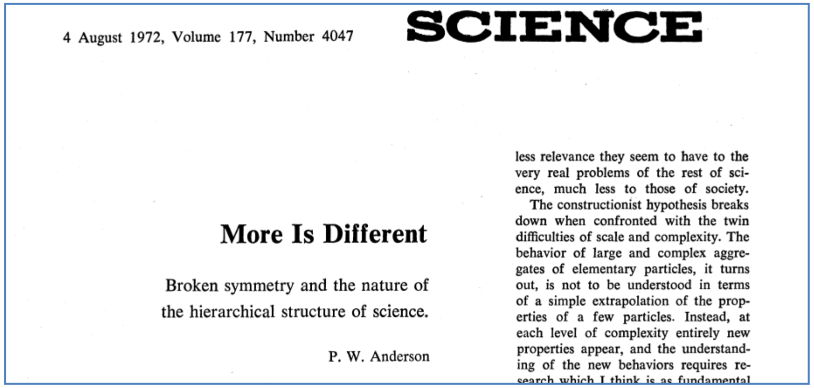
“Applications”







People used to believe that as long as we can understand the “fundamental” laws in physics, the real world can be constructed by “applying” these fundamental laws.



4 August 1972, Volume 177, Number 4047

SCIENCE

More Is Different

Broken symmetry and the nature of the hierarchical structure of science.

P. W. Anderson

less relevance they seem to have to the very real problems of the rest of science, much less to those of society.

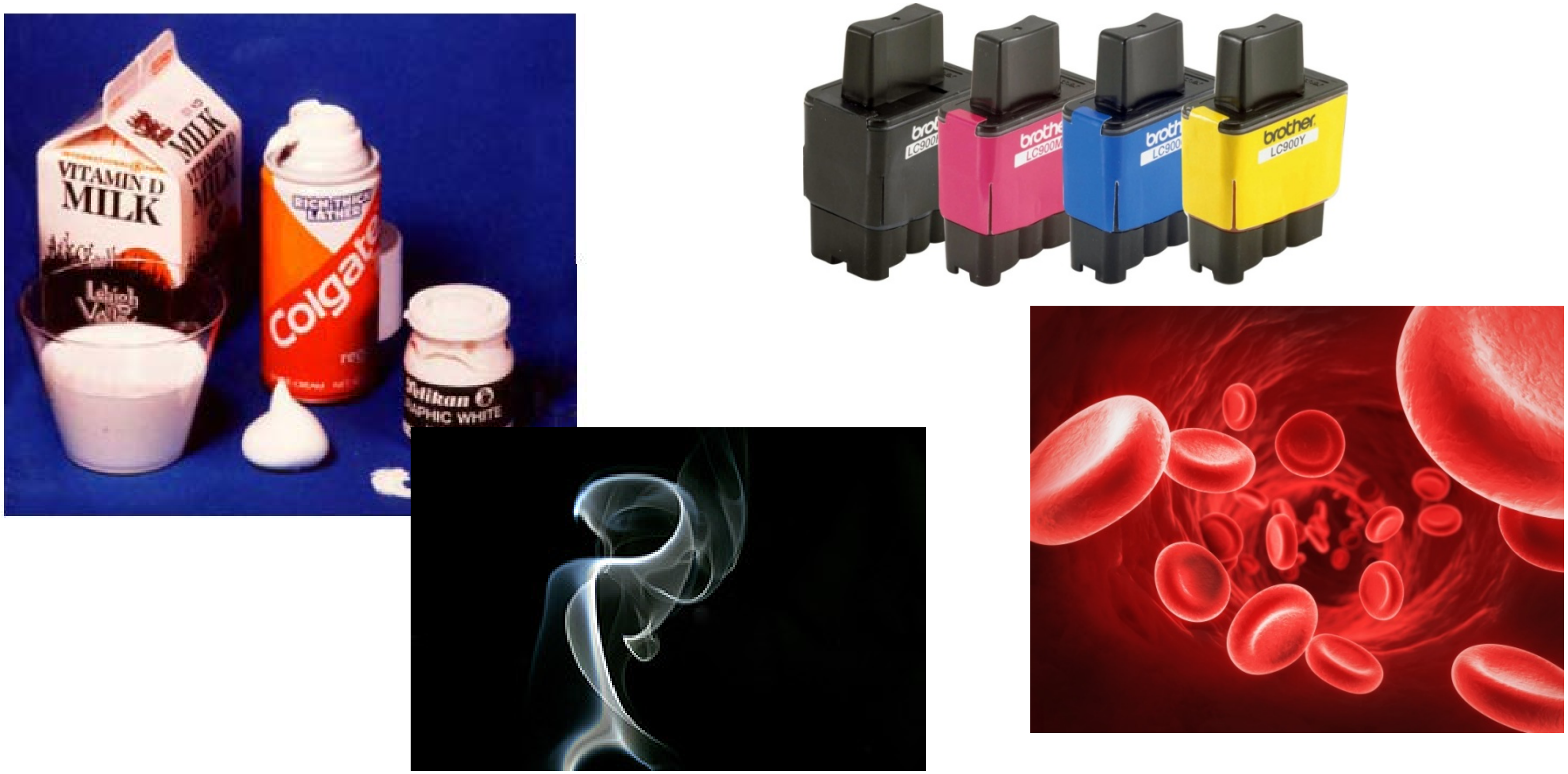
The constructionist hypothesis breaks down when confronted with the twin difficulties of scale and complexity. The behavior of large and complex aggregates of elementary particles, it turns out, is not to be understood in terms of a simple extrapolation of the properties of a few particles. Instead, at each level of complexity entirely new properties appear, and the understanding of the new behaviors requires research which I think is as fundamental

“The ability to reduce everything to simple fundamental laws does not imply the ability to start from those laws and reconstruct the university ”

- P. W. Anderson

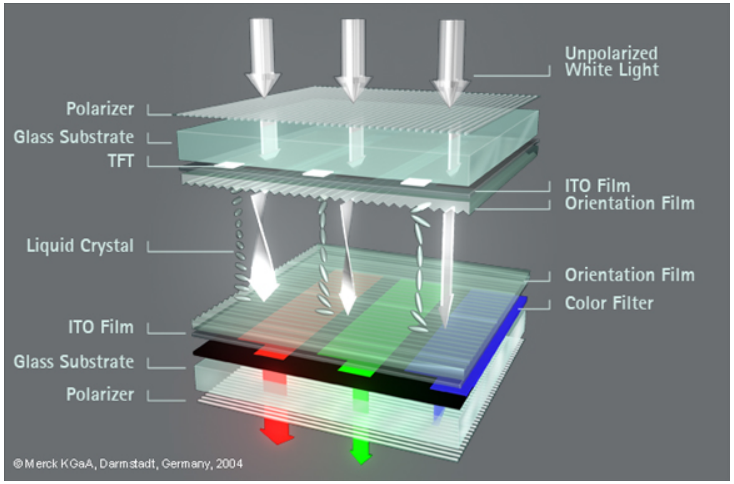
Colloids

Colloids are small particles (nanometer to micron sized) dispersed in a continuous medium



ExxonMobil P&G BASF Johnson&Johnson

Colloidal displays



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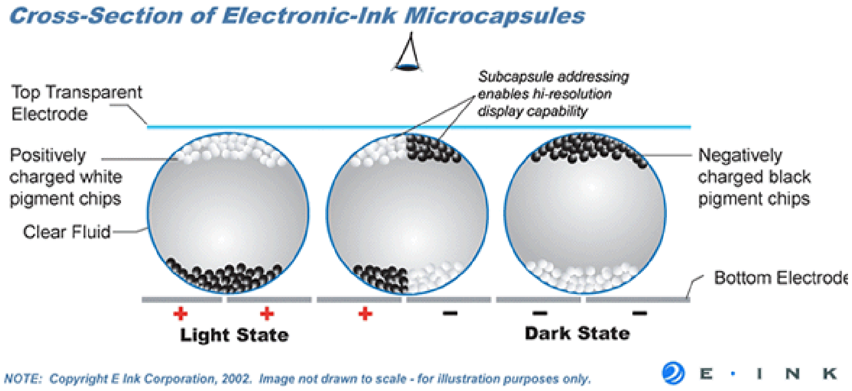
Conventional LCD

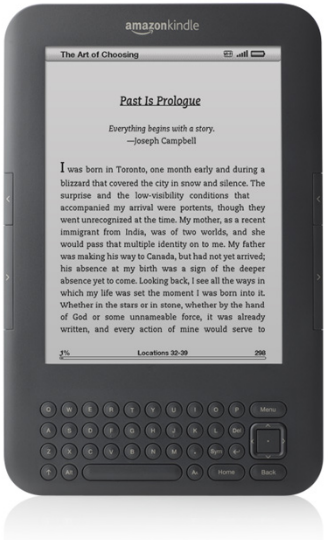
Energy consuming, generate heat



Cross-Section of Electronic-Ink Microcapsules

NOTE: Copyright E Ink Corporation, 2002. Image not drawn to scale - for illustration purposes only.

Reflective colloidal display（E-ink）



The Art of Choosing

Past Is Prologue

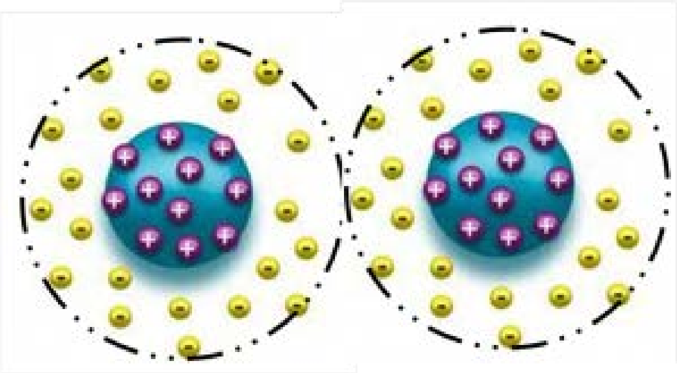
Everything begins with a story.
—Joseph Campbell

I was born in Toronto, one month early and during a blizzard that covered the city in snow and silence. The surprise and the low-visibility conditions that accompanied my arrival were portents, though they went unrecognized at the time. My mother, as a recent immigrant from India, was of two worlds, and she would pass that multiple identity on to me. My father was making his way to Canada, but had not yet arrived; his absence at my birth was a sign of the deeper absence yet to come. Looking back, I see all the ways in which my life was set the moment I was born into it. Whether in the stars or in stone, whether by the hand of God or some unnameable force, it was already written, and every action of mine would serve to

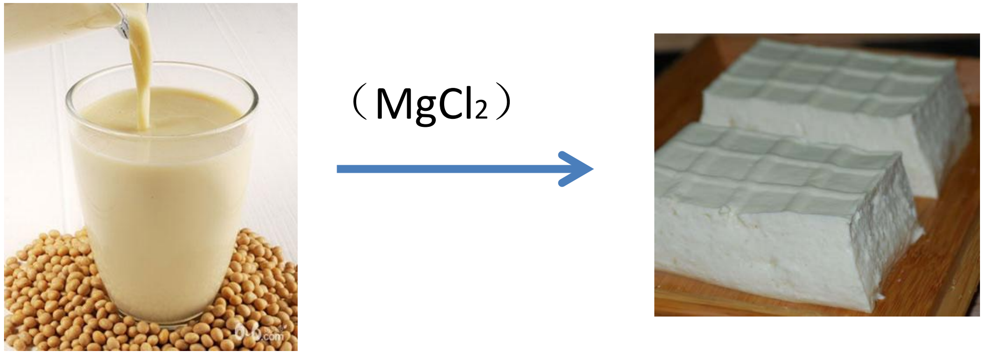
1% Locations 32-39 298

Energy efficient

Colloidal Stabilization

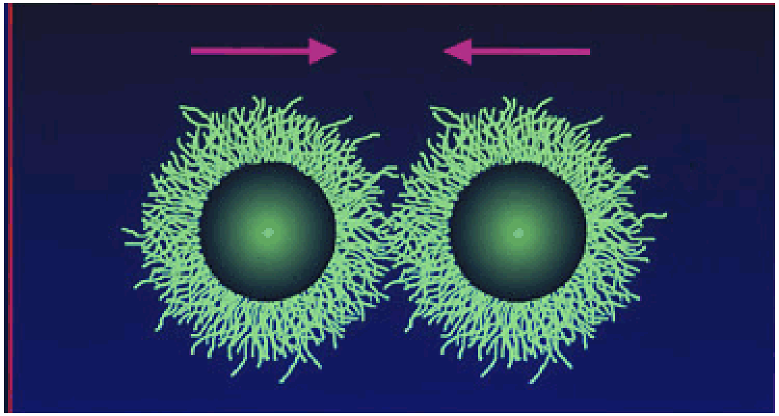


(charge stabilization)

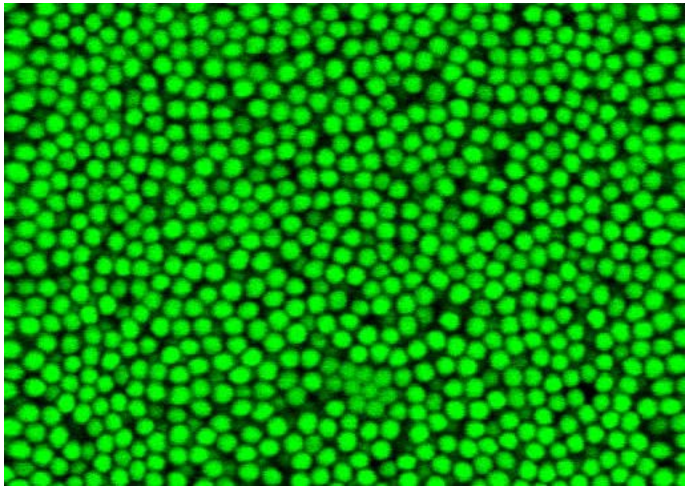


（$MgCl_2$）

Colloidal particles coalesce when charges are screened



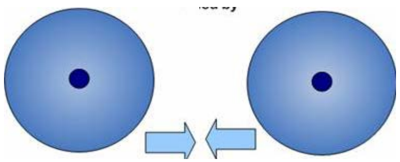
(steric stabilization)



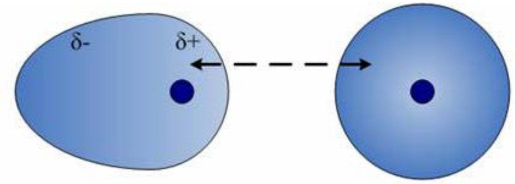
PMMA particles in organic solvent

Van der Waals Interactions

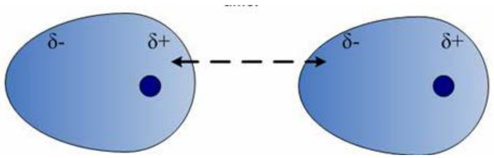
Van der Waals forces arise from fluctuating dipole interactions between atoms or molecules



Two approaching atoms

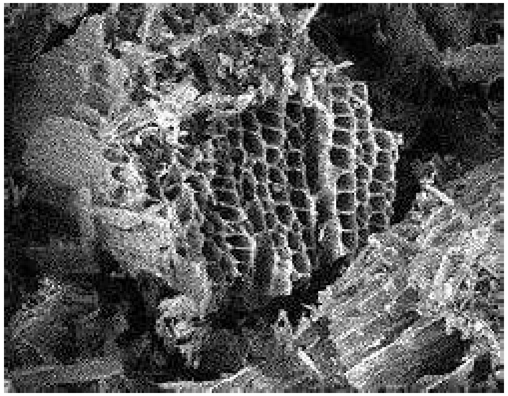


An instantaneous dipole is induced in one atom



Another dipole is induced from interacting with the first one, causing attraction

A gecko foot



Activated carbon

For Van der Waals forces to be significant, the separation between atoms must be small to effectively induce dipoles

Van der Waals interactions are always attractive.

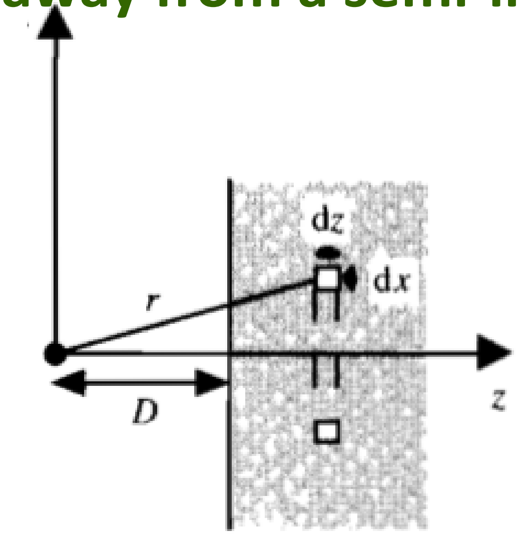
Van der Waals Interactions

The force between two neutral atoms can be evaluated from quantum mechanical perturbation theory.

$$\begin{aligned} V(r) &= -\frac{3}{4}\left(\frac{1}{4\pi\epsilon_0}\right)^2 \frac{\alpha^2}{r^6}\hbar\omega, \\ &= -C/r^6 \end{aligned}$$

where, α is the polarisability and the ionisation energy is $h\omega$.

First consider the interaction between a single atom at a distance D away from a semi-infinite wall of density ρ, by integral, we obtain:



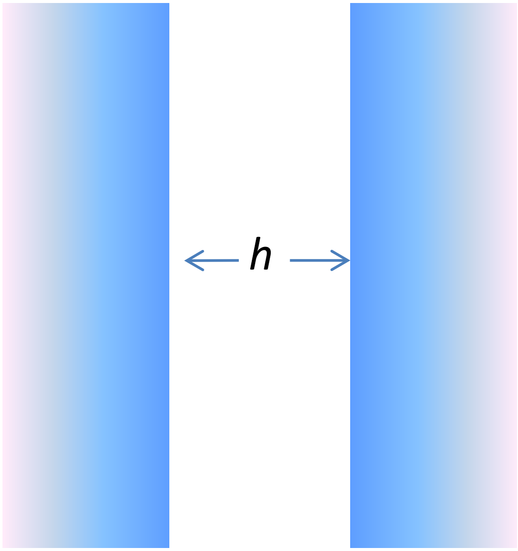
$$\begin{aligned} w(D) &= -2\pi\rho C \int_D^\infty \mathrm{d}z \int_0^\infty \frac{x\,\mathrm{d}x}{(z^2+x^2)^3} \\ &= -\frac{2\pi\rho C}{12D^3}. \end{aligned}$$

Van der Waals Interactions

We now replace the single atom with a sheet of atoms of unit area and thickness *dz*, at a distance *z* from the semi-infinite wall, the interaction potential becomes:

$$-2\pi\rho^2 C/12z^3$$

Finally, by integrating over z to infinity, the interaction potential between two semi-infinite walls separated by h becomes



$$U(h) = -\frac{2\pi\rho^2 C}{12}\int_h^\infty \frac{dz}{z^3} = -\frac{A}{12\pi h^2},$$

$$A = \pi\rho^2 C$$

Hamaker constant ~10^{-19} J

At atomic scales (e. g. 0.2 nm), the attractive force between two plates can reach 10^9 Pa or 10000 atm. Even at 10 nm separation, the pressure is still greater than 1 atm.

Van der Waals Interactions

Another reason that Van der Waals interactions require close distances between surfaces is the Retardation Effects. At room temperature, the typical vibration period of an electron is

$$T = 10^{-16} s$$

The electromagnetic field of the dipole needs to reach the other surface before the current dipole de-correlates. With the speed of light at

$$c = 3 \times 10^{8} m / s$$

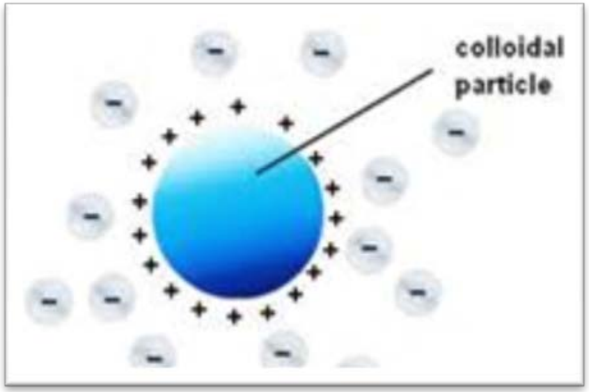
the characteristic length at which "retardation" becomes significant is

$$r_r \cong cT \approx 30 \, \mathrm{nm}$$

In real systems, this distance is even shorter, since the propagation of electromagnetic wave is slower in a medium (e. g. water)

Interactions between charged colloids

Colloids have large specific surface areas, uncharged colloidal suspensions are unstable due to strong attractions induced by Van der Waals interactions. In order to counter this attraction, colloidal particles are usually charged.



The colloids obtain charges by ionizing in a solution, creating a charged surface and equal amount of counter-ions in the solutions. Other ions may still be present.

Electrostatic interaction will attract counter-ions to the surface, and repel co-ions away from the surface of the colloidal particle, creating an uneven distribution of ions in its surroundings or *double layer*. Determination of this distribution is crucial to understanding interactions between charged colloids.

Interactions between charged colloids

The distribution of ions near a charged surface is described by Poisson-Boltzmann equation.

Things need to be considered include, ion charges (+/-)ion type (i), ion valency (z), and ion concentration (n). At any point M in the solution we have the total charge density to be

$$\rho(\mathrm{M}) = e \sum_{i,j} (z_i^+ n_i^+ + z_j^- n_j^-),$$

To maintain overall neutrality of the solution, the total charge should be zero

$$\int_V \rho(\mathrm{M})\, dV + \int_\Sigma \sigma\, d\Sigma = 0,$$

Where σ is the concentration of surface ions per unit area

At any point in the solution, the local electric field obeys the Poisson equation.

$$-\mathrm{div}\, \mathbf{E} \equiv \nabla^2 \varphi = \frac{-1}{\varepsilon \varepsilon_0} \rho(\mathrm{M}),$$

Interactions between charged colloids

On the other hand, the distribution of each specie of charges are statistically determined by the Boltzmann equation:

$$n_i = n_{i,0} \exp - \frac{e z_i \varphi}{k_B T},$$

Note that the Boltzmann equation must be satisfied for individual ion type.

The Poisson-Boltzmann equation is obtained by combining the two equations above

$$\nabla^2 \varphi = - \frac{e}{\varepsilon \varepsilon_0} \sum_i z_i n_{i,0} \exp - \frac{e z_i \varphi}{k_B T}.$$

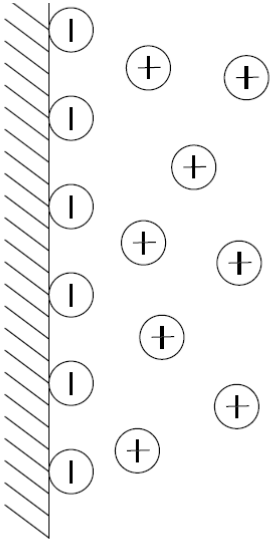
The PB equations require solution for both charge distribution and electric potential, and are generally difficult to solve, particularly when there are several types of ions with different valencies.

When the valencies of the charged particles are all equal, and the charged boundaries have a simple geometry, simple solutions are possible.

Interactions between charged colloids

Weak Electrolyte:

Consider a planar infinite, charged surface, in contact with a solvent with no electrolyte added, so that the only species of ions are the counterions from the ionization of the surface. The PB equation can be written as



$$\frac{d^2\varphi}{dx^2} = -\frac{en_0}{\varepsilon\varepsilon_0} \exp -\frac{e\varphi}{k_B T},$$

The solution is this equation is analytically available by integration

$$\varphi(x) = \frac{2k_B T}{e} \ln\left(\frac{x+b}{\xi}\right).$$ and $$n(x) = \frac{1}{2\pi\ell(x+b)^2}$$

With $$b = -\frac{2\varepsilon\varepsilon_0}{\sigma}\frac{k_B T}{e}, \qquad \ell = \frac{e^2}{4\pi\varepsilon_0\varepsilon k_B T}$$

Here, ***b*** is called **Gouy-Chapman** length. It is the thickness of a solvent layer that contains half of the total counterions.

l is called **Bjerrum** length, counterions within ***l*** are considered immobile, while counterions outside of ***l*** have significant thermal motions.

Interactions between charged colloids

Strong Electrolyte:

The opposite situation is when the boundary is in the presence of a strong electrolyte. For simplicity, let’s consider a single valance salt such as NaCl in water. The PB equation is summed over two ion types of equal charges.

$$\nabla^2\varphi = \frac{2en_0}{\varepsilon_0\varepsilon}\sinh\frac{e\varphi(\mathbf{r})}{k_BT},$$

Where n_0 is the electrolyte concentration in the reservoir at infinity.

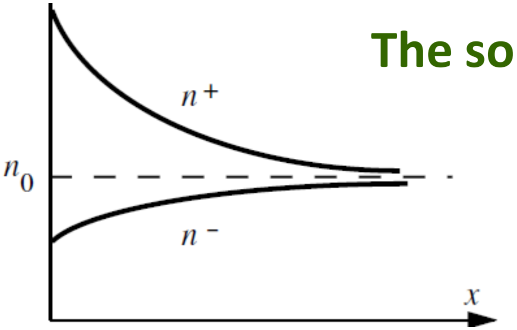
when $\varphi < k_BT/e$, the PB equation can be linearized

$$\nabla^2\varphi = \frac{2e^2n_0}{\varepsilon\varepsilon_0k_BT}\varphi(\mathbf{r}) = k_D^2\varphi(\mathbf{r}) \quad \text{with} \quad k_D = \lambda_D^{-1} = \left(\frac{2e^2n_0}{\varepsilon\varepsilon_0k_BT}\right)^{1/2}$$

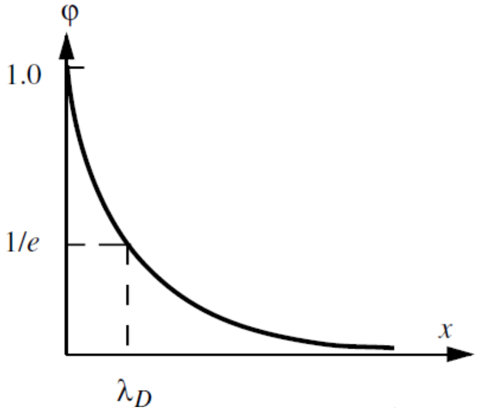
The solution to the linearized PB equation is

$$\varphi(x) = \varphi_s\exp(-x/\lambda_D)$$

Where λ_D is known as Debye length or screening length



Ion concentration

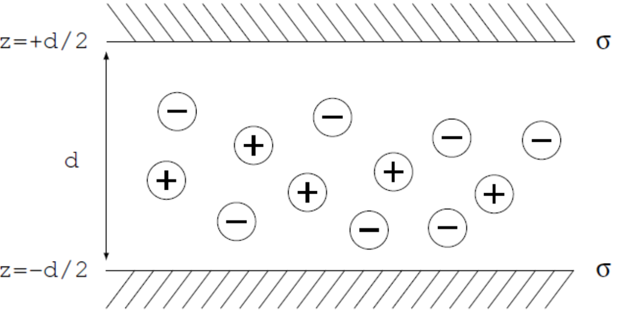


Electric potential

Interactions between charged colloids

Two planar surfaces:

Finally, let’s consider the interaction between two equally charged plates in a solution



The free energy of the system can be written in two parts

First, the potential energy stored the field

$$F_{\text{bulk}} = \frac{1}{2}\varepsilon\varepsilon_0 \int E^2\, dV = \frac{1}{2}\varepsilon\varepsilon_0 \int (\nabla\varphi)^2\, dV\,,$$

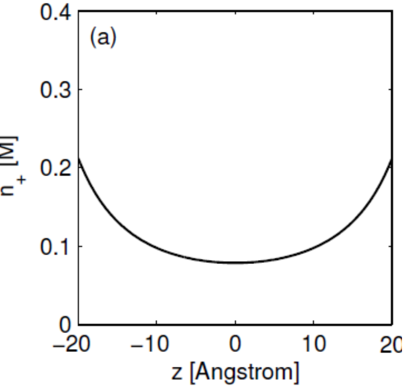
And secondly, the entropy from mixing different ions

The total free energy is thus

$$F_{\text{entropy}} = k_B T \int \left[\sum_{i=\pm} n_i \ln \frac{n_i}{n_0} - \sum_{i=\pm} n_i + 2n_0 \right] dV$$

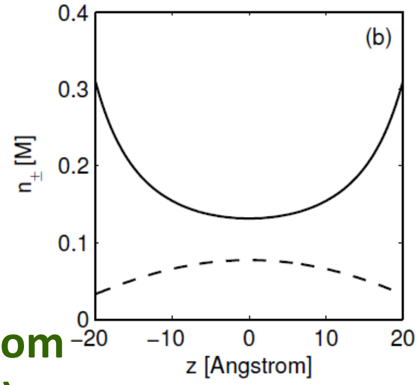
$$F_{\text{el}} \equiv F_{\text{bulk}} + F_{\text{entropy}}$$

Considering that one plate is kept fixed, the force exterted on the other is



$$p_d = -\frac{\partial F_{\text{el}}}{\partial d}\Big|_{T,n_i}$$

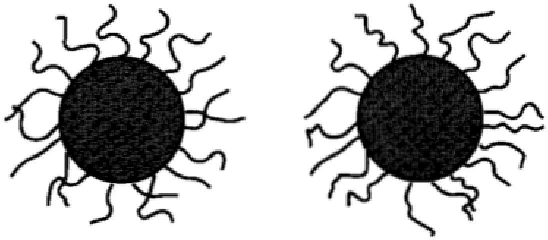
$$p_d = k_B T\left(n_{mid} - \sum_i n_{i,0} \right)$$



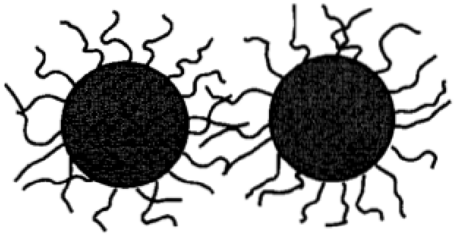
The repulsion between charged plates originated from the osmotic pressure (entropy instead of electric)

Steric interactions

When ions are not present (e. g. in an organic solvent), steric stablization has been developed to prevent colloidal particles from aggregation.



Freely extending polymer chains



Overlapping polymer chains

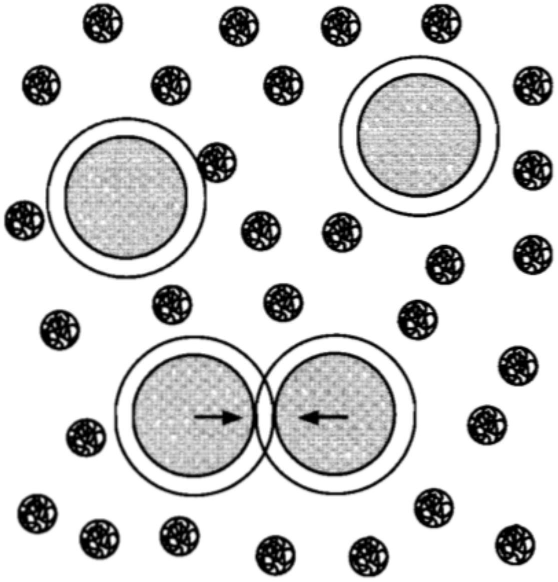
Polymer chains are attached to colloidal spheres. When dispersed in a good solvent for the attached polymer, these chains will extend. When two colloidal particles come close to each other, the polymer concentration between the spheres is higher than in the solution, creating repulsive osmotic pressure.

The range of interaction is governed by the distance from the surface to the extended polymer chain.

Sterically interacting colloids can be well modeled as hard spheres

Depletion forces

When polymer chains are not attached to the colloidal sphere, instead dispersed in the solvent, depletion interactions may arise.



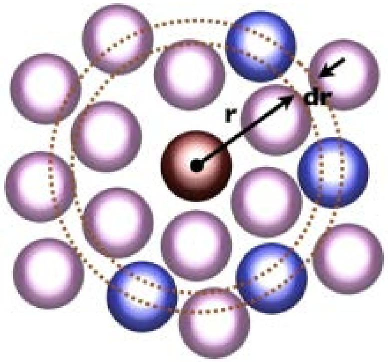
Polymer coils are excluded from the space between two colloidal spheres, when the separation between the spheres becomes smaller than the coil size, creating a depletion zone. Unbalanced osmotic pressure induces a net attractive force between the particles.

Measuring colloidal interactions

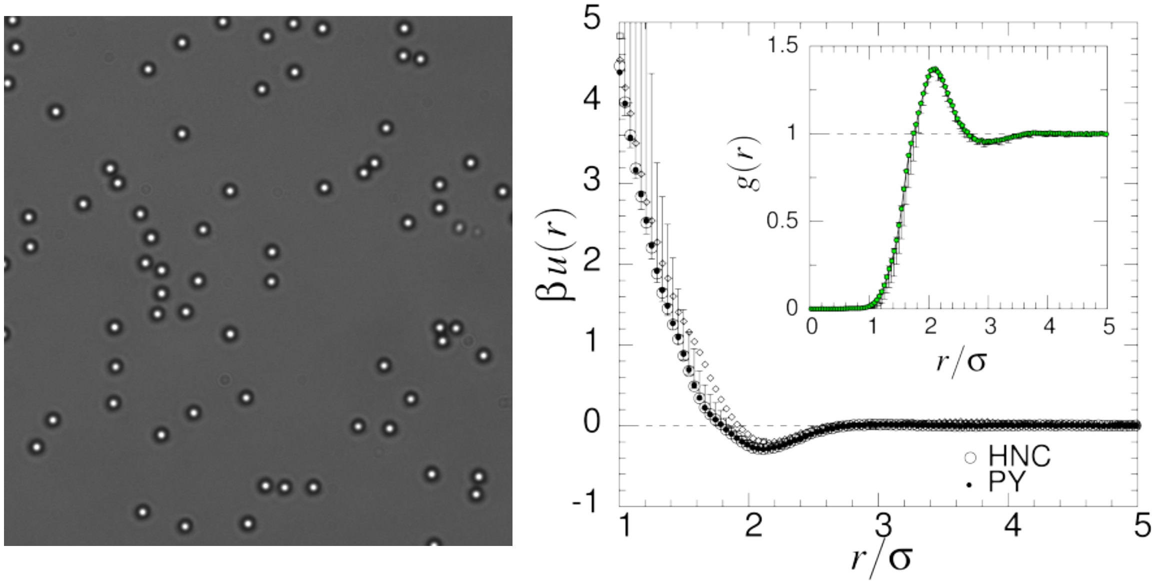
At equilibrium, the probability of finding a particle at a distance r from another particle is determined by the Boltzmann relation:

$$g(r) = e^{\frac{-U(r)}{kT}}$$

$$U(r) = -kT\ln(g(r))$$



Pair correlation function g(r)



Interaction between colloidal particles

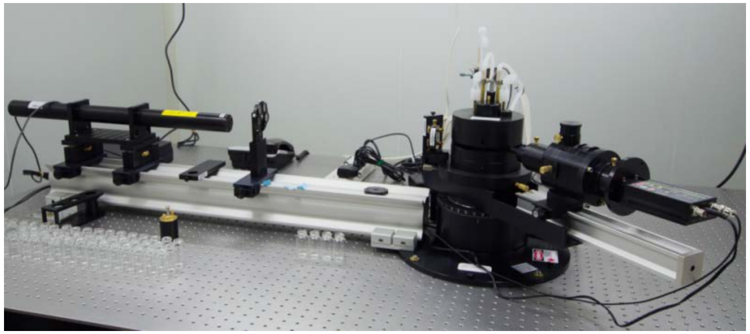
Han and Grier, **PRL** (2003)

Experiment tools

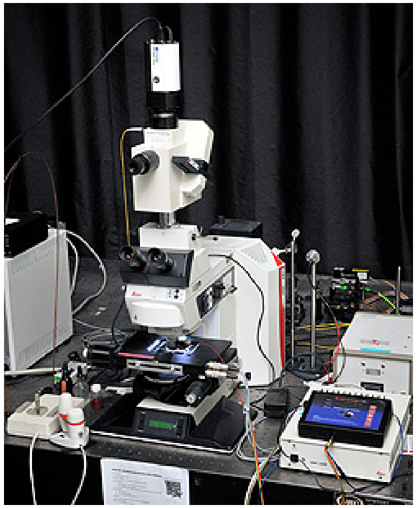
For soft material, we are interested in the bulk mechanical property, the underlying structure and dynamics. Different tools are available to probe and observe.

Rheology:
Bulk measurement

Light scattering:
Microscopic, averaged

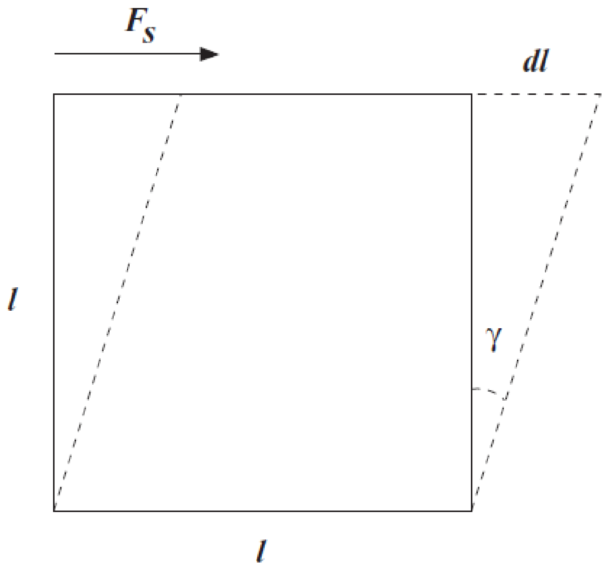


Microscopy:
Local, mesoscopic



Materials under shear

Materials response to shear stress differently.



Shear stress: $\sigma = F_s/A.$

Shear strain: $\gamma = d\ell/\ell.$

An ideal elastic solid (Hookean solid) deforms proportionally to applied shear stress

$$\sigma = G'\gamma$$

An ideal viscous liquid (Newtonian liquid) flows at a rate proportional to applied shear stress

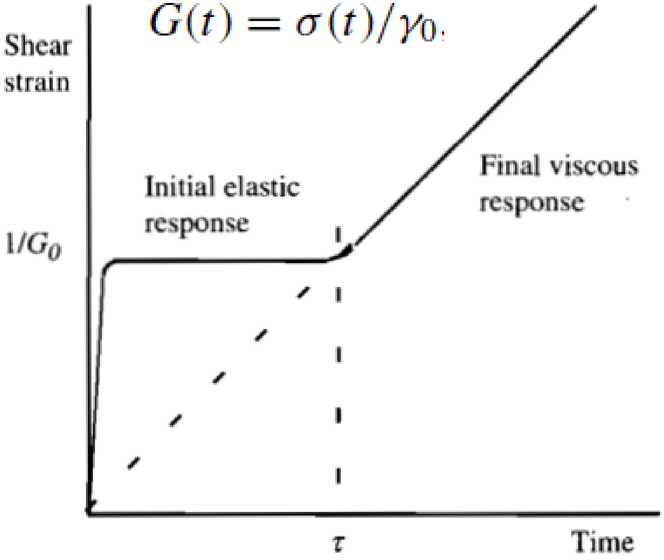
$$\sigma = \eta\dot{\gamma},$$

Real materials, particularly soft materials, often behave in a way between these two ideal limits, a behavior known as viscoelasticity (both viscous and elastic)

Viscoelasticity and Non-Newtonian fluids

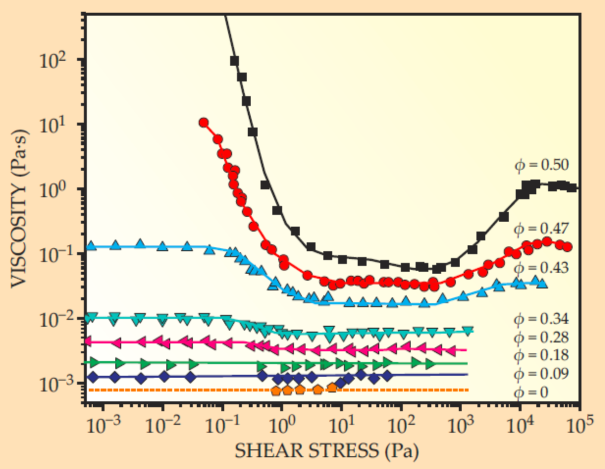
How a material responses to shear stress depends on the relaxation time.
If the stress is applied on a time scale shorter than relaxation time, the material behave like a solid. If the stress is applied on a longer time scale, the material flows.

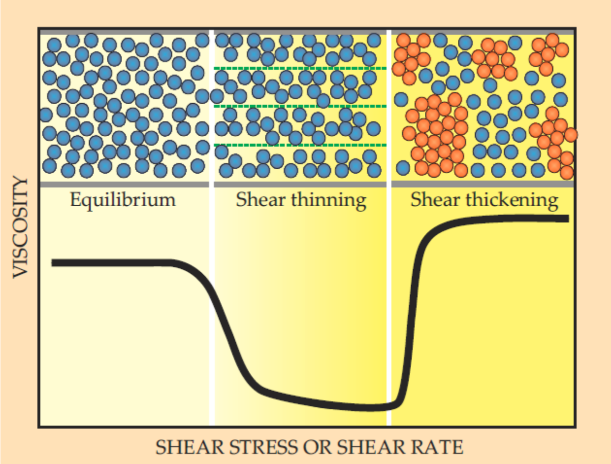
$$G(t) = \sigma(t)/\gamma_0.$$



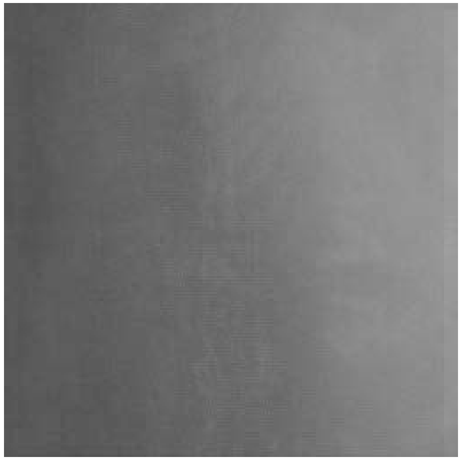
$$d\sigma = G(t)d\gamma.$$

Eventually, everything flows!





Shear thinning

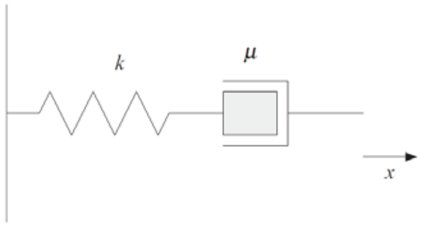


Shear thickening

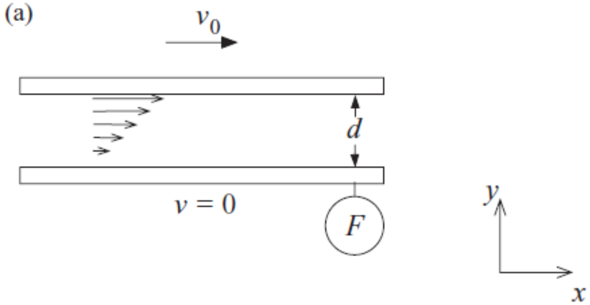
Rheology

Rheology measures both the viscous and elastic responses of soft materials under shear.
A simple spring-dashpot model can be used to understand the viscoelasticity materials:
When deformed, a stress will develop, but the stress will gradually decay to zero if the strain is maintained.

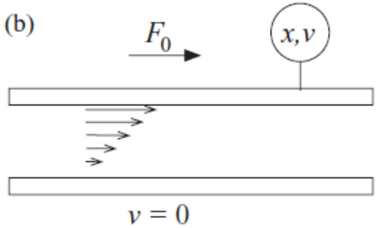
In rheology measurements, a controlled deformation or stress is applied to the material, and stress or deformation is measured.



Spring-dashpot model

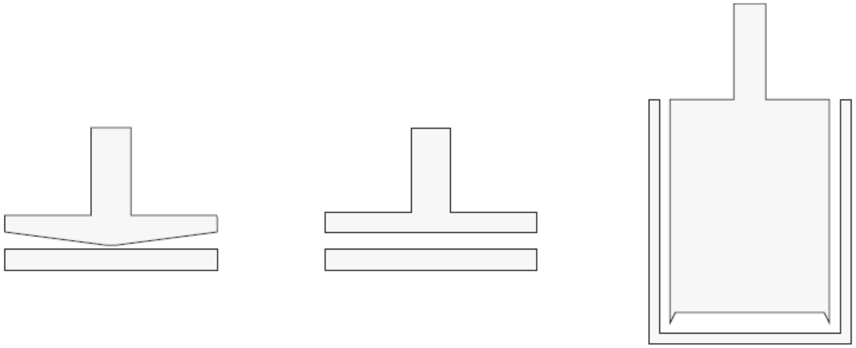


Strain controlled deformation



Stress controlled deformation

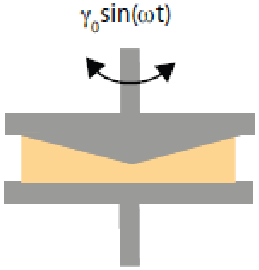
In practice, a rheometer rotates to shear the sample, and measure the torque (stress) or angular displacements (strain)



Commonly used rheometer geometry

Rheology

For viscoelastic materials, the most commonly used measurement is small-amplitude oscillatory measurements. In which a small sinusoidal strain is applied to at a frequency ω.



$$\gamma = \gamma_0 \sin \omega t,$$

The resulting stress is

$$\sigma = \sigma_0 \sin(\omega t + \phi).$$

Note the phase difference between the stress and strain, due to the viscosity of the material.

The stress can be decomposed into two parts

$$\sigma = \sigma' + \sigma'' = \sigma_0' \sin \omega t + \sigma_0'' \cos \omega t.$$

We define elastic modulus as $G' = \dfrac{\sigma_0'}{\gamma_0}$, and the viscous modulus as $G'' = \dfrac{\sigma_0''}{\gamma_0}$.

A complex modulus can thus be defined as

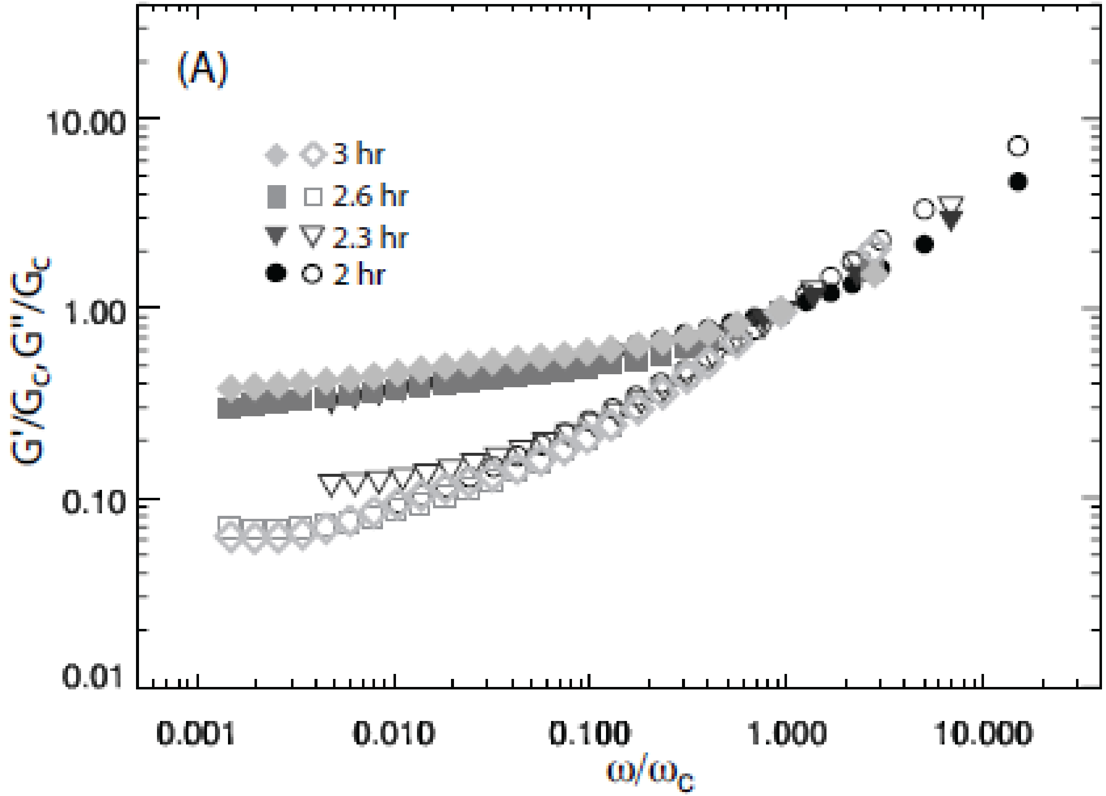
$$G^* = G' + iG''$$

Where G’ is a measure of the elastic energy stored per unit volume per cycle (storage)

Where G” is a measure of the energy dissipated per unit volume per cycle (loss)

Rheology

Both G’ and G” depend on the frequency (or time scale). For a certain frequency, when G’ dominates, the material behave like a solid, when G” dominates, the material behave more like a fluid.



Cross-over from fluid-like behavior to solid like behavior at high frequencies

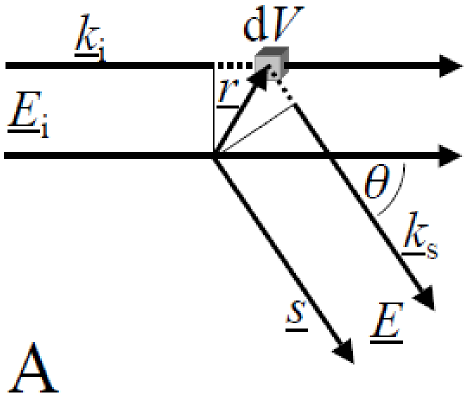
Light scattering

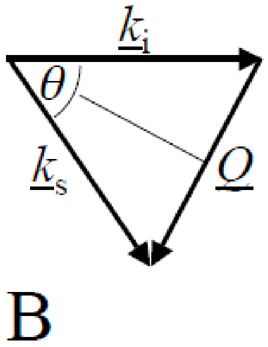
Light is scattered when refractive index fluctuates in a solution.

By measuring the spatial or temporal distributions of the scattered light, one can learn a lot about the microscopic details of the subject.

Scattering - basics

We start by considering quasi-elastic scattering of a small volume element *dV* at location *r*, the local scattering ability is characterized by *ρ*.





$$\underline{Q} = \underline{k}_s - \underline{k}_i$$

$$Q = |\underline{Q}| = 2k\sin\frac{\theta}{2} = \frac{4\pi}{\lambda}\sin\frac{\theta}{2}.$$

The scattered field by *dV* is $\mathrm{d}\underline{E}(\underline{r},t) = \underline{E}_0\,\rho(\underline{r})\,\frac{1}{s}e^{i(k_s s-\omega t)}\,e^{i\delta\phi(t)}\,\mathrm{d}V.$

The phase difference is caused by the extra distance *dL(t*) travelled (dashed lines)

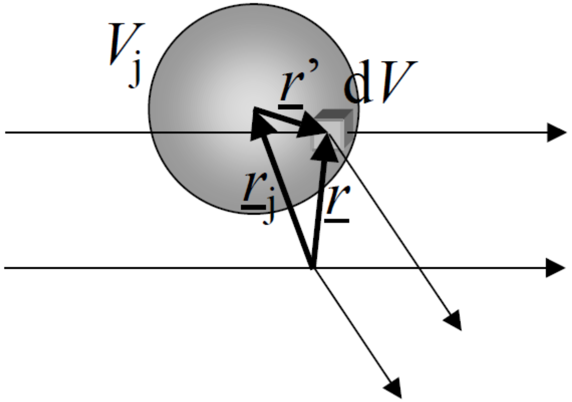
$$\delta\phi(t) = \frac{2\pi}{\lambda}\delta L(t) = \underline{k}_i\cdot\underline{r}(t) - \underline{k}_s\cdot\underline{r}(t) = -\underline{Q}\cdot\underline{r}(t),$$

If we only keep the terms relevant to the local scattering volume, we have the most basic relation for scattering.

$$\mathrm{d}\underline{E}(\underline{Q},t) \sim \rho(\underline{r})e^{-i\underline{Q}\cdot\underline{r}(t)}\,\mathrm{d}V.$$

Scattering by a particle

To calculate the scattered field of an extended particle, we integrate the elementary signals from each volume elements over the volume of the particle V_j.



$$\underline{r}(t) = \underline{r}_j(t) + \underline{r}'.$$

$$\begin{aligned}\underline{E}_j(\underline{Q},t) &= \int_{V_j} \mathrm{d}\underline{E}(\underline{Q},t) \sim \int_{V_j} \rho(\underline{r}) e^{-i\underline{Q}\cdot\underline{r}(t)}\,\mathrm{d}V \\ &= \int_{V_j} \rho(\underline{r}') e^{-i\underline{Q}\cdot\underline{r}'}\,\mathrm{d}V\ e^{-i\underline{Q}\cdot\underline{r}_j(t)} = b_j(\underline{Q})\ e^{-i\underline{Q}\cdot\underline{r}_j(t)}.\end{aligned}$$

Where $b_j(\underline{Q}) = \int_{V_j} \rho(\underline{r}') e^{-i\underline{Q}\cdot\underline{r}'}\,\mathrm{d}V$ **, which is the Fourier transformation of ρ *(r')***

Scattering by an ensemble of particles

It is straight forward to write down the total field scattered by N particles

$$\underline{E}(\underline{Q},t) = \sum_{j=1}^{N} \underline{E}_j(\underline{Q},t) \sim \sum_{j=1}^{N} b_j(\underline{Q})\, e^{-i\underline{Q}\cdot\underline{r}_j(t)}$$

In experiments, it is the time averaged intensity of the scattered light that is measured.

$$\begin{aligned}\langle I(\underline{Q})\rangle &= \sqrt{\frac{\epsilon}{\mu}}\ \langle \underline{E}(\underline{Q})\cdot\underline{E}^*(\underline{Q})\rangle \\ &\sim \left\langle \sum_{j=1}^{N}\sum_{k=1}^{N} b_j(\underline{Q})\, b_k(\underline{Q})\, e^{-i\underline{Q}\cdot[\underline{r}_j(t)-\underline{r}_k(t)]} \right\rangle\end{aligned}$$

It is reasonable to assume b_j(Q) is independent of position, we obtain,

$$\begin{aligned}\langle I(\underline{Q})\rangle &\sim \sum_{j=1}^{N}\sum_{k=1}^{N} \langle b_j(\underline{Q})\, b_k(\underline{Q})\rangle \left\langle e^{-i\underline{Q}\cdot[\underline{r}_j(t)-\underline{r}_k(t)]}\right\rangle \\ &= \langle b^2(\underline{Q})\rangle \sum_{j=1}^{N}\sum_{k=1}^{N} \left\langle e^{-i\underline{Q}\cdot[\underline{r}_j(t)-\underline{r}_k(t)]}\right\rangle \\ &= N\langle b^2(0)\rangle \frac{\langle b^2(\underline{Q})\rangle}{\langle b^2(0)\rangle}\frac{1}{N}\sum_{j=1}^{N}\sum_{k=1}^{N} \left\langle e^{-i\underline{Q}\cdot[\underline{r}_j(t)-\underline{r}_k(t)]}\right\rangle \\ &= N\langle b^2(0)\rangle\ P(\underline{Q})S(\underline{Q}),\end{aligned}$$

$$P(\underline{Q}) = \frac{\langle b^2(\underline{Q})\rangle}{\langle b^2(0)\rangle}$$

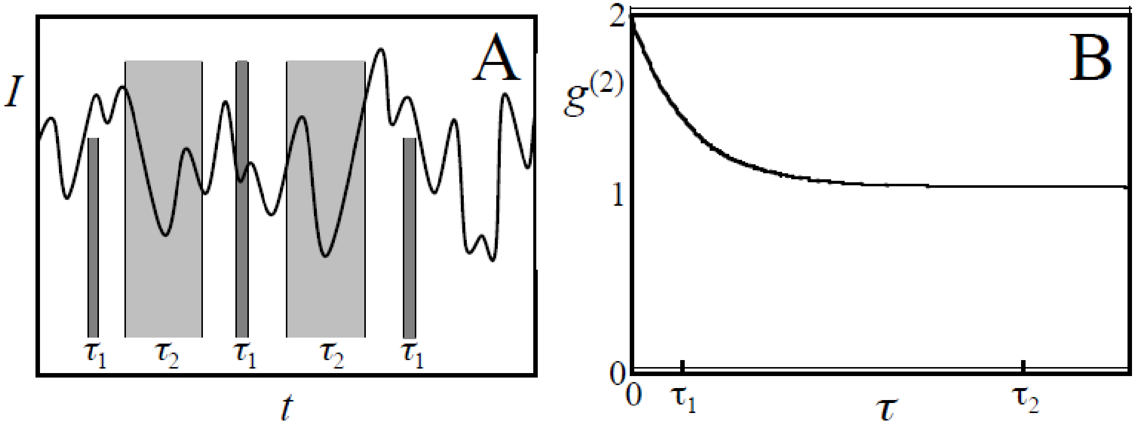
Form factor

$$S(\underline{Q}) = \frac{1}{N}\sum_{j=1}^{N}\sum_{k=1}^{N} \left\langle e^{-i\underline{Q}\cdot[\underline{r}_j(t)-\underline{r}_k(t)]}\right\rangle$$

Structure factor

Dynamic light scattering

When the scattering centers move, the intensity of scattered light also varies with time



Define time correlation function of the intensity

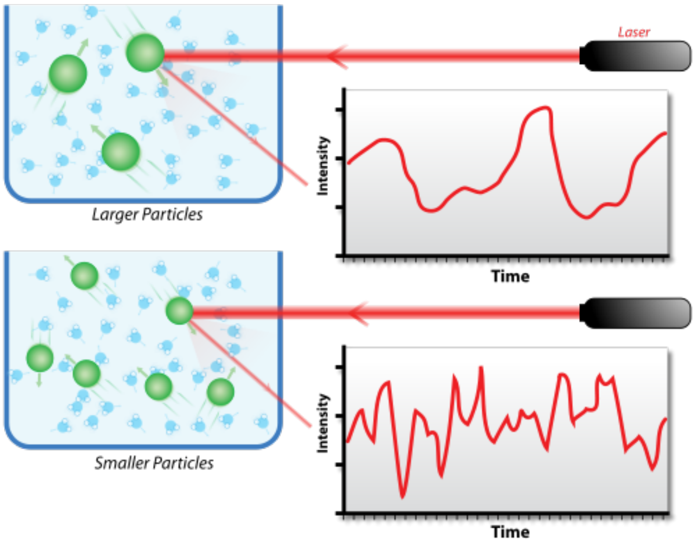
$$g^{(2)}(\underline{Q},\tau) = \frac{\langle I(\underline{Q},0)I(\underline{Q},\tau)\rangle}{\langle I(\underline{Q})\rangle^2}$$

For Brownian particles, the correlation function is

$$g^{(2)}(\underline{Q},\tau) = 1 + f^2(\underline{Q},\tau) = 1 + \left(e^{-DQ^2\tau}\right)^2$$

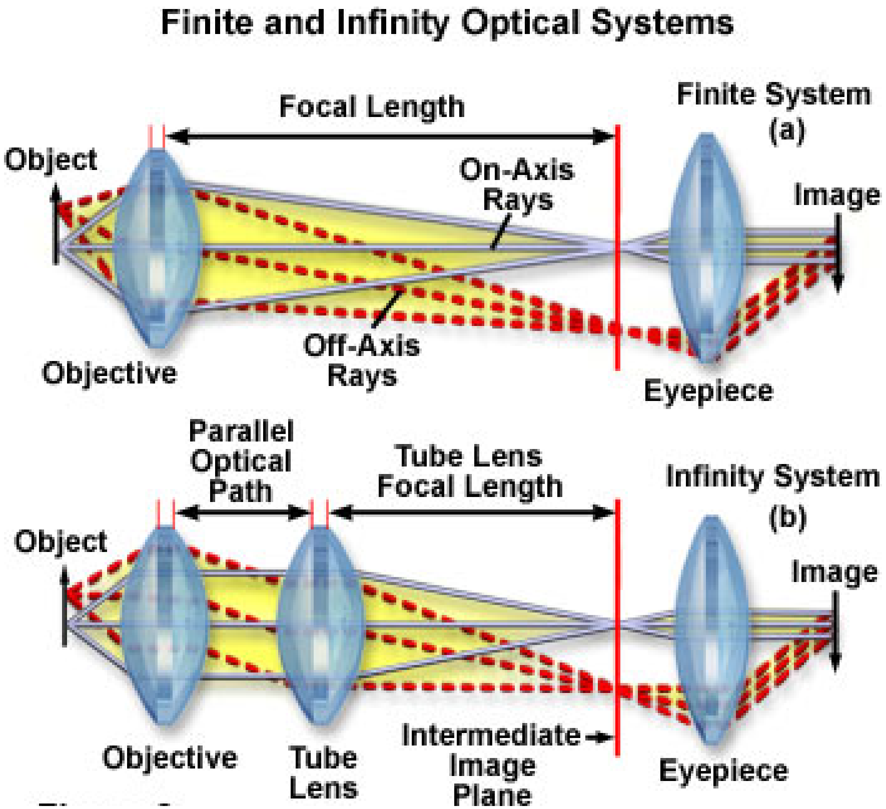
Where D is the diffusion constant of the Brownian particle

$$D = \frac{k_\mathrm{B}T}{6\pi\eta R_h}$$



Optical microscopy

Optical microscopy enables direct observations of soft matter samples



Principles of optical (brightfield)microscopy

No Pictures,
No Truth!

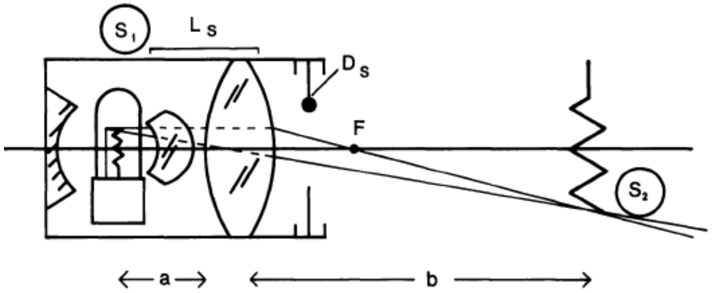
Inverted microscope

upright microscope

A microscope uses a series of lenses to magnify the images of small objects. Modern microscopes employ infinite focus design with a tube length of 200 mm

Koehler illumination

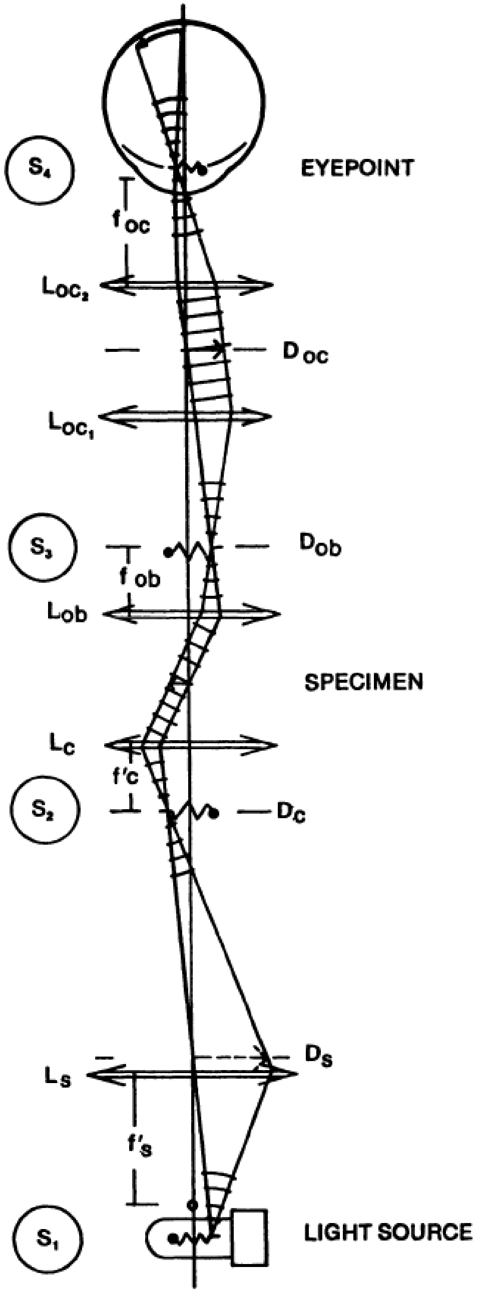
Optical microscopy enables direct observations of soft matter samples



Light source for a microscope

To achieve optimal image quality, the illumination on the specimen need to be homogeneous and intense.

For a properly aligned Koehler illumination, the image of the light source is placed on the back focal plane of the condenser, and the sample is illuminated by a converging set of plane-wave fronts.



Principles for Koehler illumination

Condenser

Condenser is used to collect light to illuminate the samples, and it critical to proper imaging

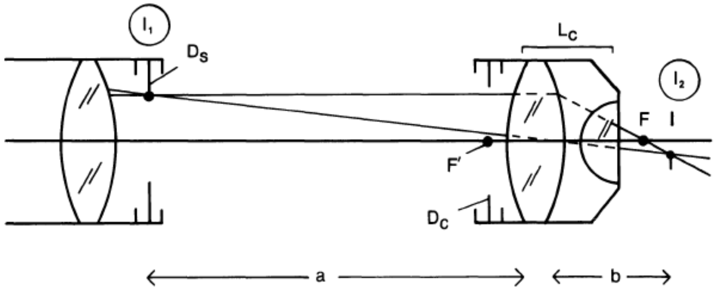
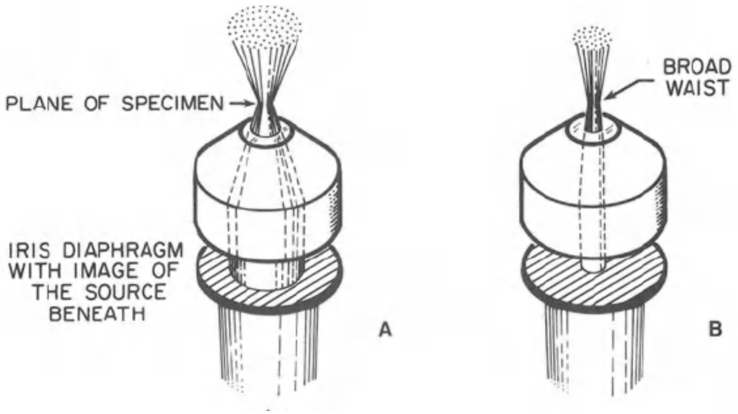
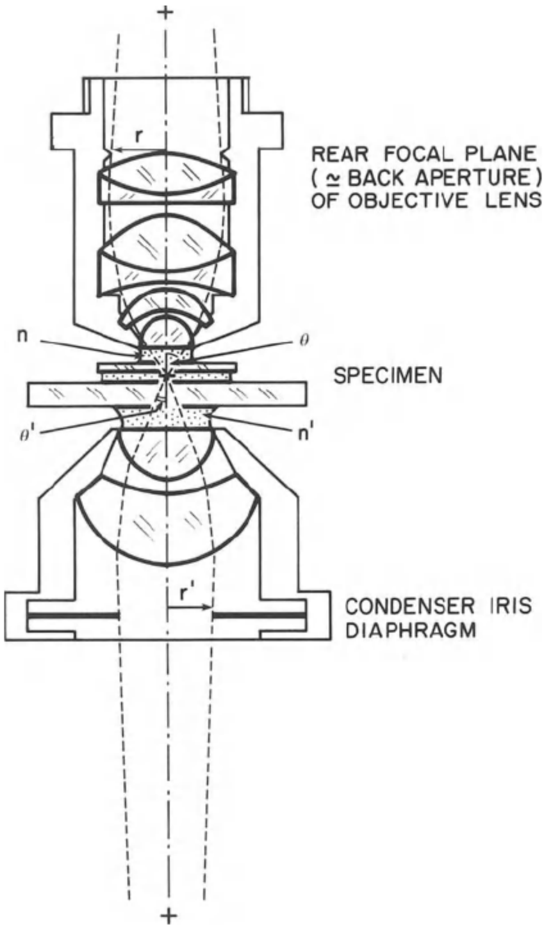


Image planes of a condenser
Dc is the iris diaphragm



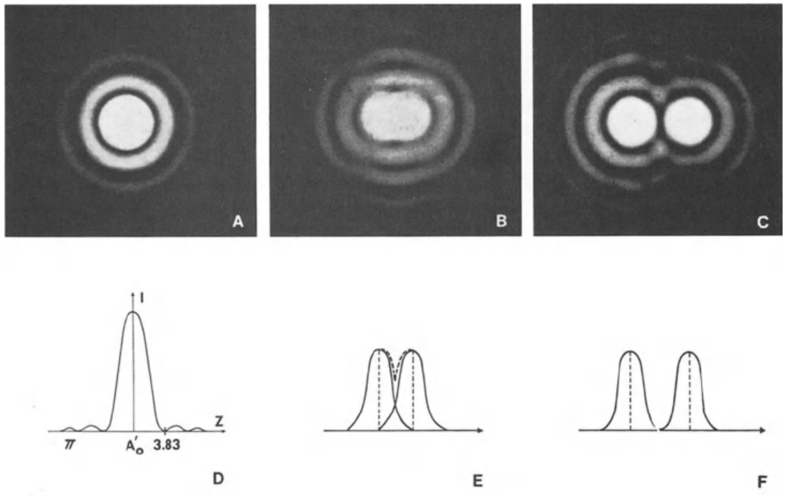
The illuminating cone can be adjusted by iris diaphragm



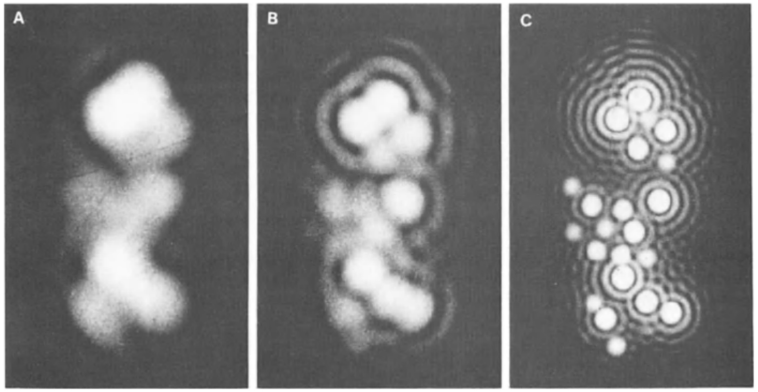
Ideally, the illuminating light cone should be adjusted to match the light collecting angle of the objective to achieve the best resolution

Resolution and depth of field

The resolution of optical microscope is limited by the diffraction of light



Two approaching Airy disk



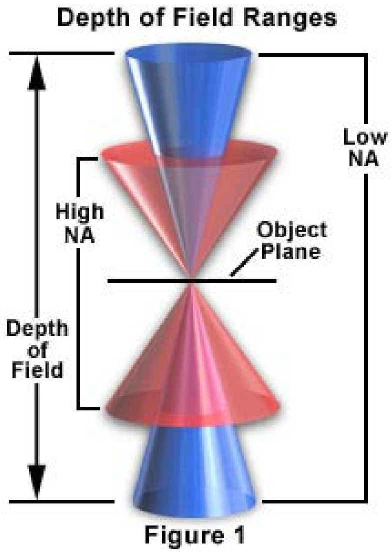
Improved resolution with NA.

For a self-luminous body the lateral resolution is

$$r = 1.22\,\lambda_0/(2\mathrm{NA}_{obj}) \qquad \mathrm{NA}_{obj} = n\sin\theta$$

When a condenser if used

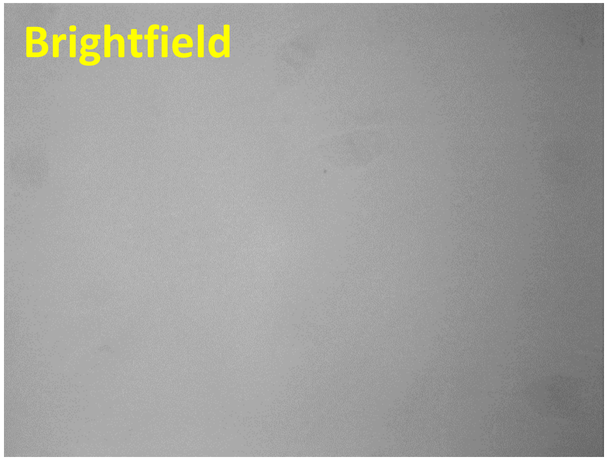
$$d = 1.22\,\lambda_0/(\mathrm{NA}_{obj} + \mathrm{NA}_{cond})$$

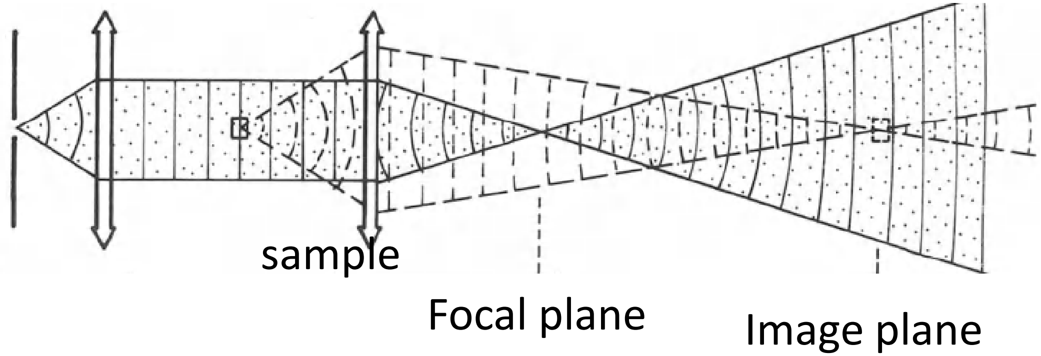


The depth of field suffers from large NA

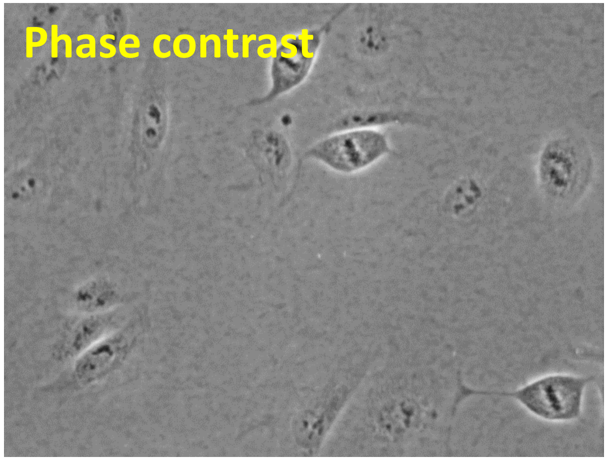
Phase contrast

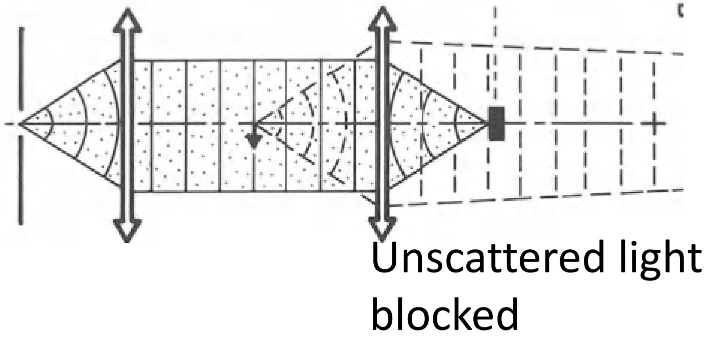
Many biological samples contains large amount of water and have refractive indices very close to water, resulting in very low contrast under brightfield microscopy. The intensity at the image plane comes largely from the unscattered illumination





Light train of brightfield microscopy for low contrast sample



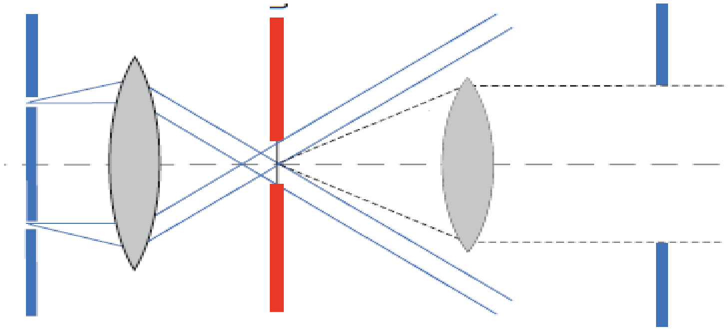


Light train of phase constrast microscopy

By blocking unscattered illumination in the objective lens, Zernike developed phase contrast microscopy.

Phase contrast

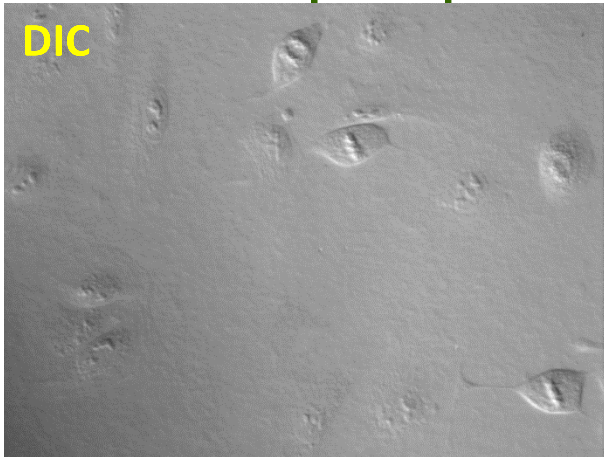
Other techniques are also developed to generate contrast in weakly-scattering samples, including darkfield and differential interference contrast (DIC)

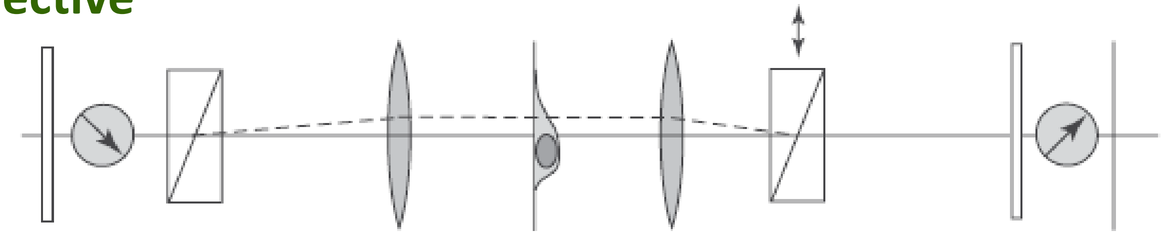


Principles of darkfield microscopy

the illumination light completely avoids the objective, leaving only scattered light to form images;

Does not require special objective





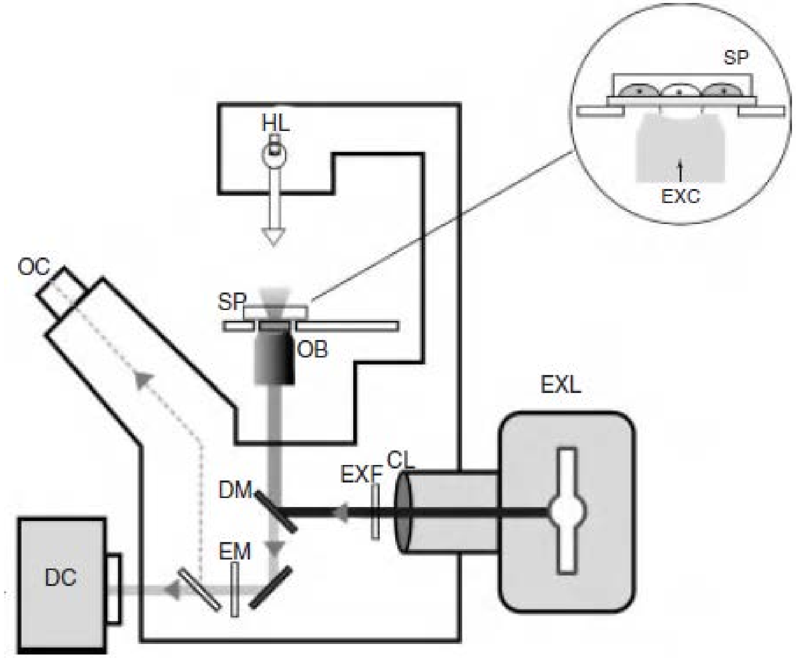
Principles of DIC

The illumination is spit into two perpendicularly polarized beam that recombine at the image plane. An analyzer can pick up the phase differences from different passages.

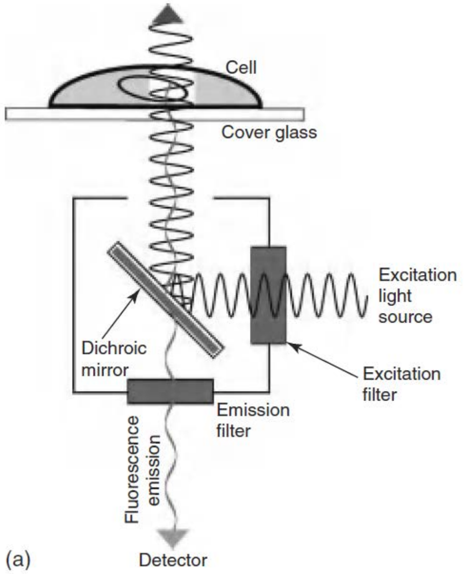
Fluorescence microscopy

The story of fluorescence microscopy

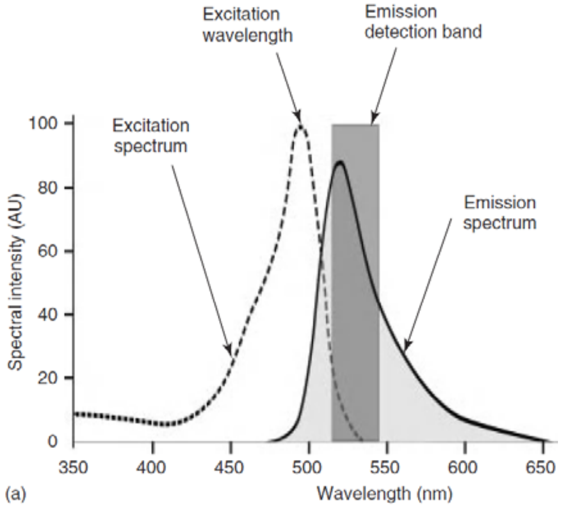
Fluorescence microscopy



Typical fluorescence microscopy setup



A fluorescence filter block



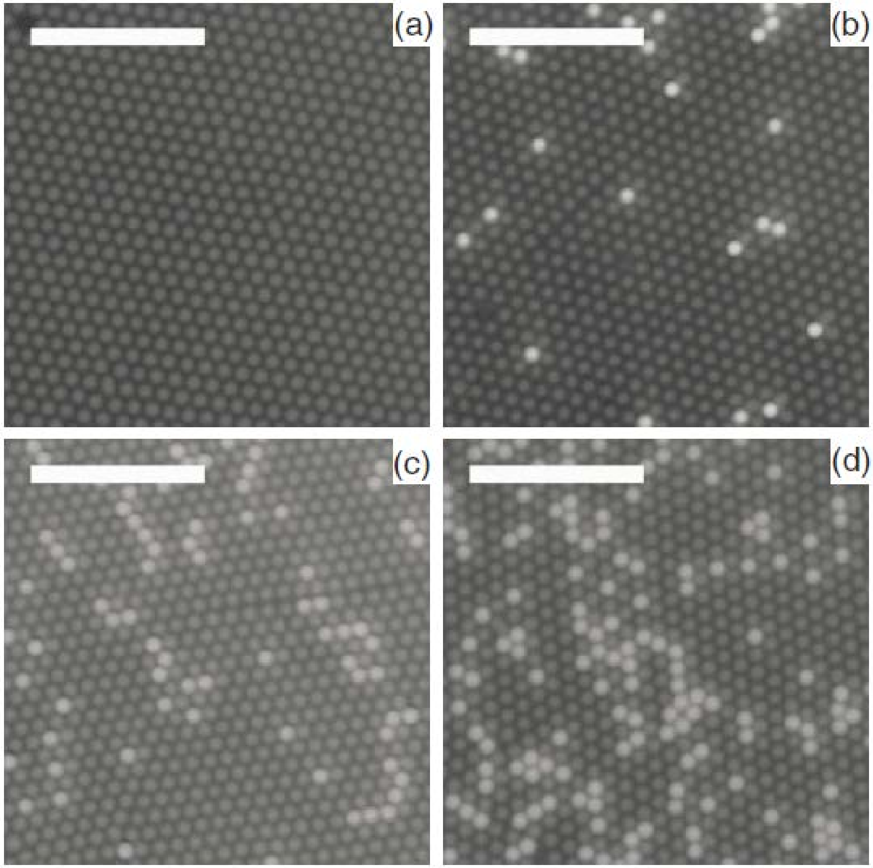
Excitation and emission

Many molecules can be excited by a photon of high frequency and emission a photon of lower frequency.

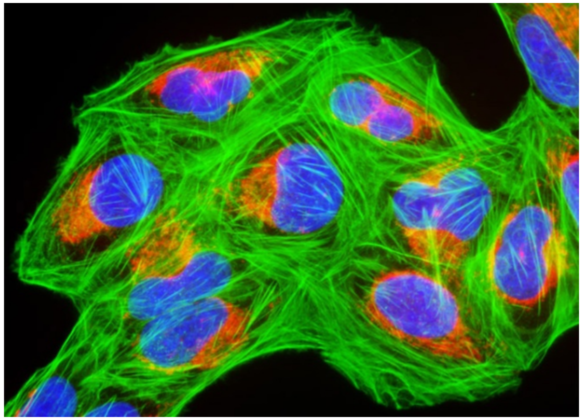
When the difference between the excitation and emission bands are large enough, a dichroic filter can be use to separate exiction signal from emission signals.

Only regions labeled by exited dye molecules will be visible under fluorescence microscopy.

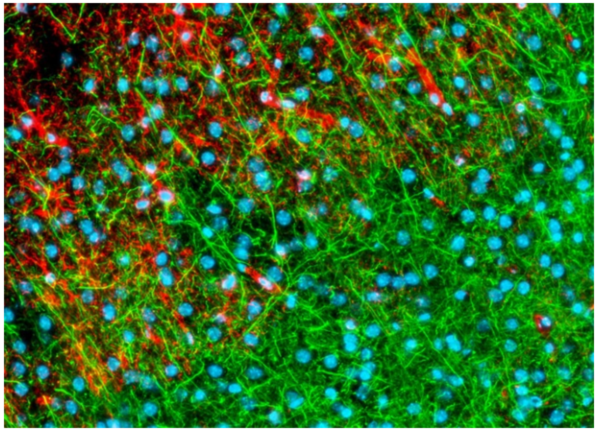
Fluorescence microscopy



Doped colloidal crystals



Human bone cells



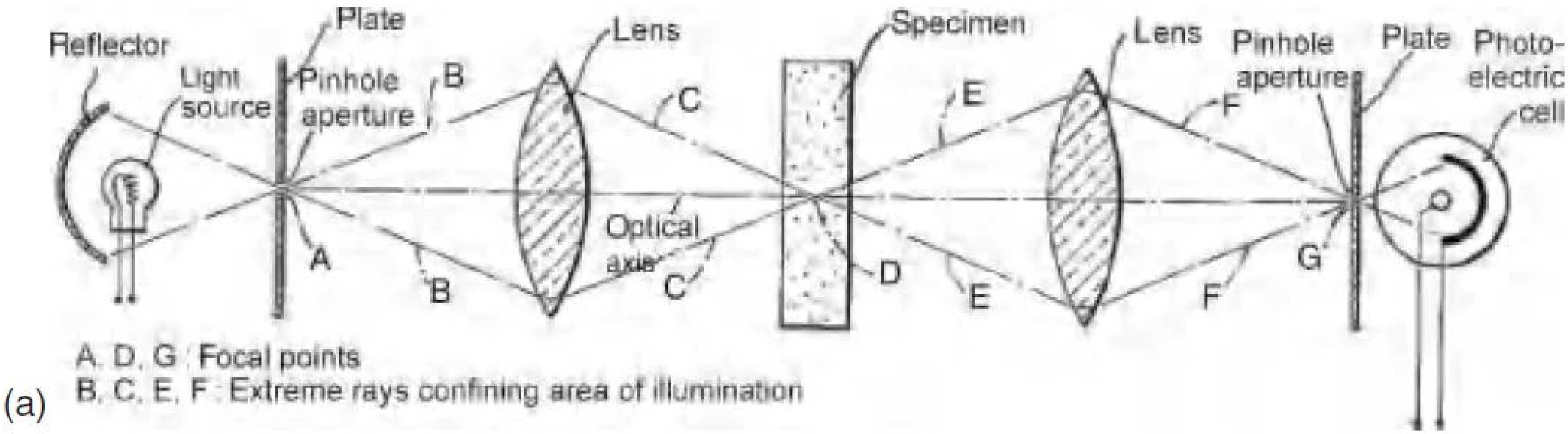
Mouse brain tissues

Multiple dyes can be used in fluorescence microscopy, revealing details that would otherwise be buried in other methods.

When pseudo-colors are applied, creates beautiful cover images

Confocal microscopy

Confocal microscopy is derived from fluorescence microscopy



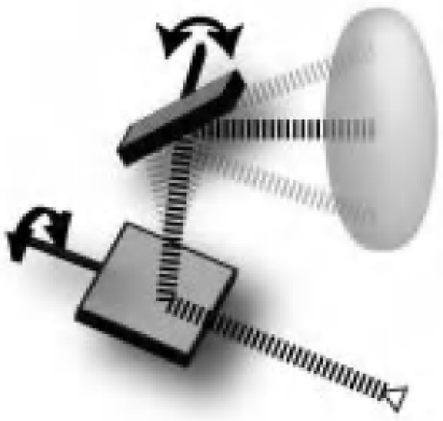
M. Minsky filed patent application for confocal microscopy in 1957

A confocal microscope employs a pair of conjugate pinholes to selectively block out-of-focus signals, to achieve very high signal-noise ratio in images.

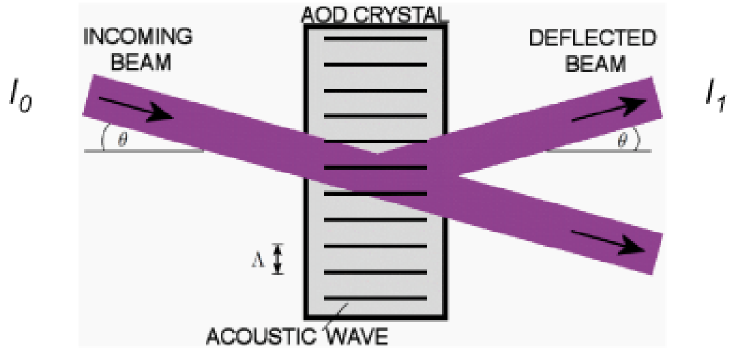
This idea was way ahead of its time, many of the needed technologies have not been invented (laser, CCD, faster scanners etc.), thus had been dormant for quite some time.

Confocal microscopy

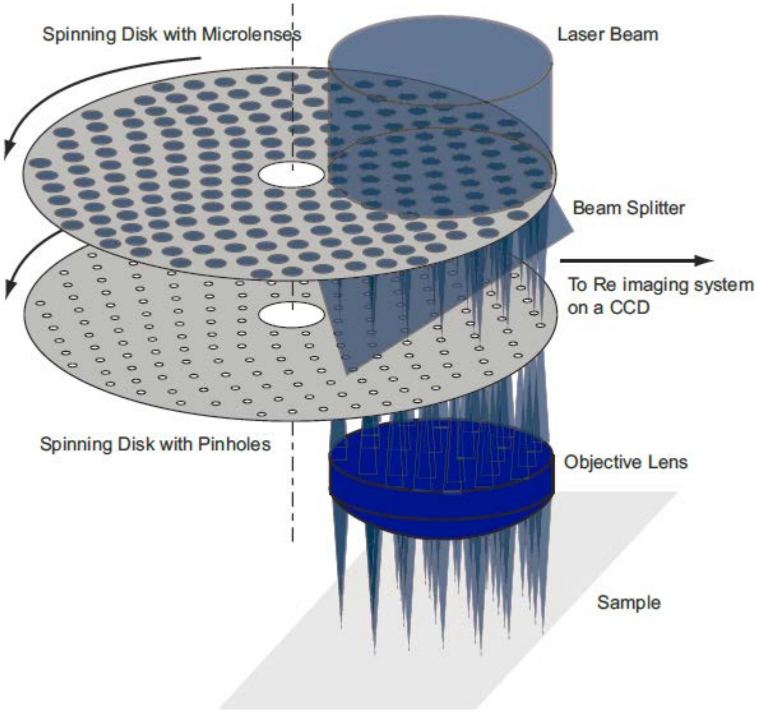
With the invention of laser, confocal microscopy became a real possibility. The main challenge has been how to improve the scanning rate. Many ways have been devised to achieve that .



Point-scanning galvo-mirros



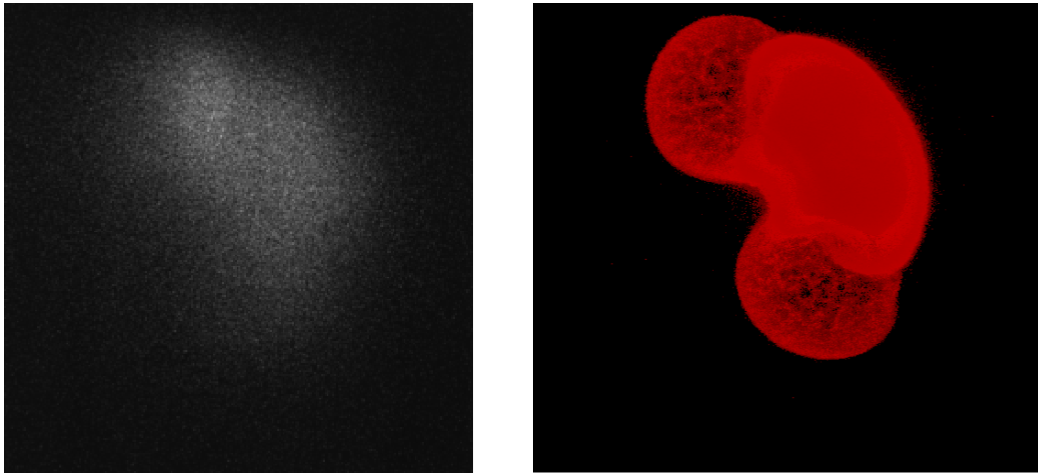
Acoustic-Optical Deflector (AOD



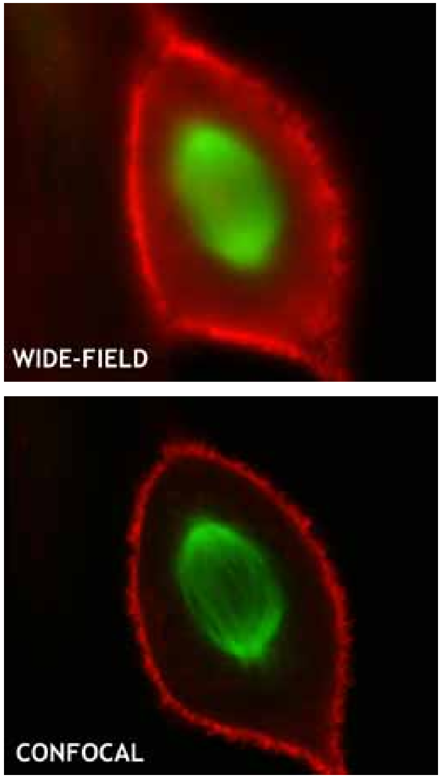
Spinning disk configuration
High speed scanning, lower light, cross-talk between pixels

Confocal microscopy

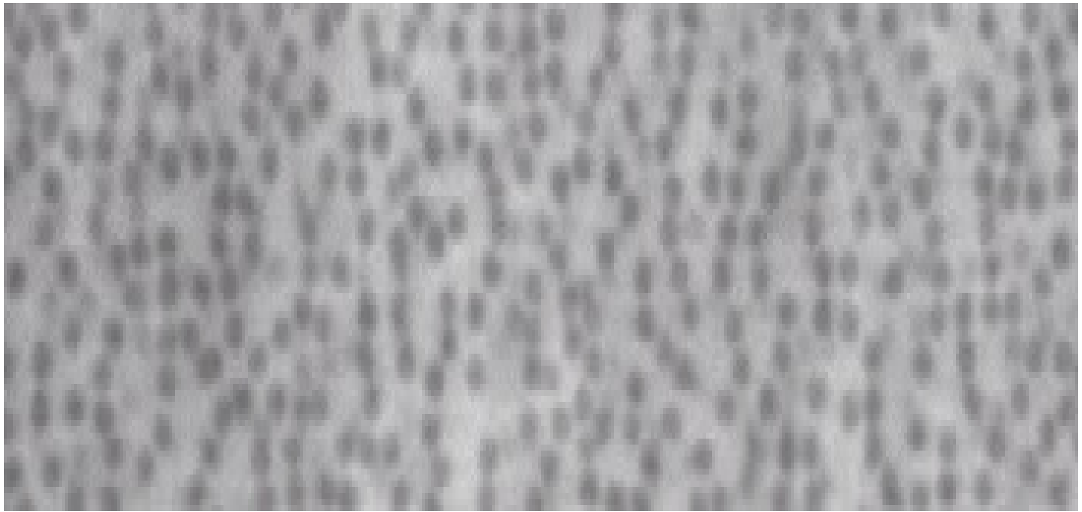
Confocal microscopy provides clearer images, enables depth scanning and 3D reconstruction. Modern fast scanning confocal microsope can follow fast flows of colloidal particles



3D scanning and reconstruction



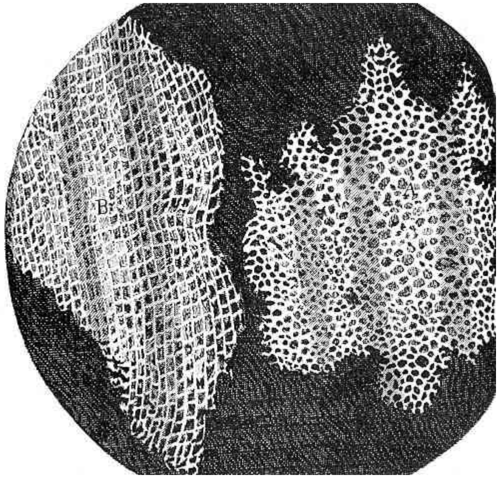
Comparison between wide-field fluorescence and confocal images



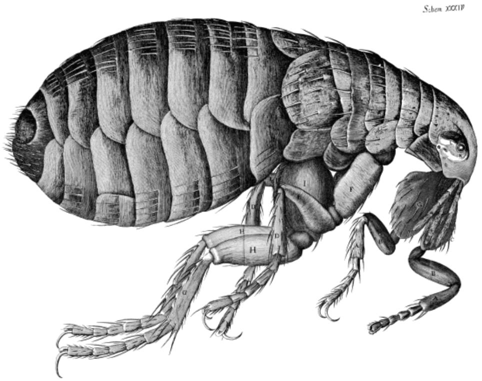
Colloidal flows under shear

Digital image analysis

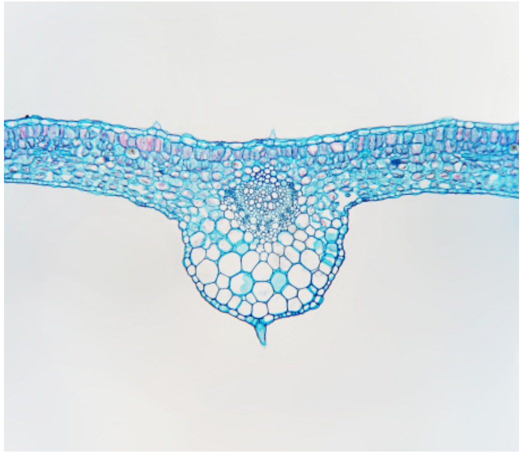
Before the age of photograph, all microscope observations were recorded by hand. With the invention of CCD cameras, it is now possible to generate and analyze images digitally.



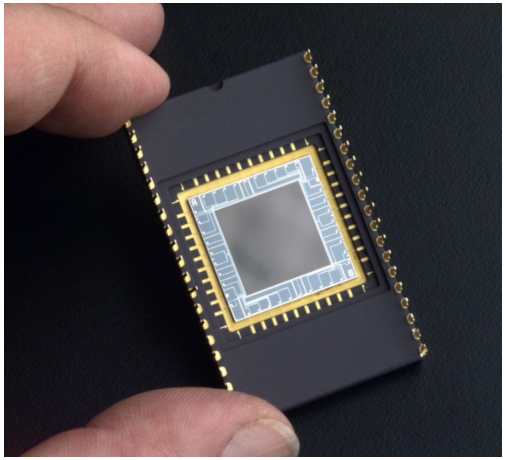
Hooke’s Cells

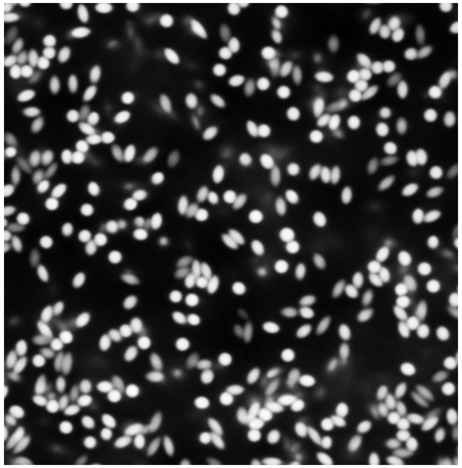


A flea under microscope



Cell images

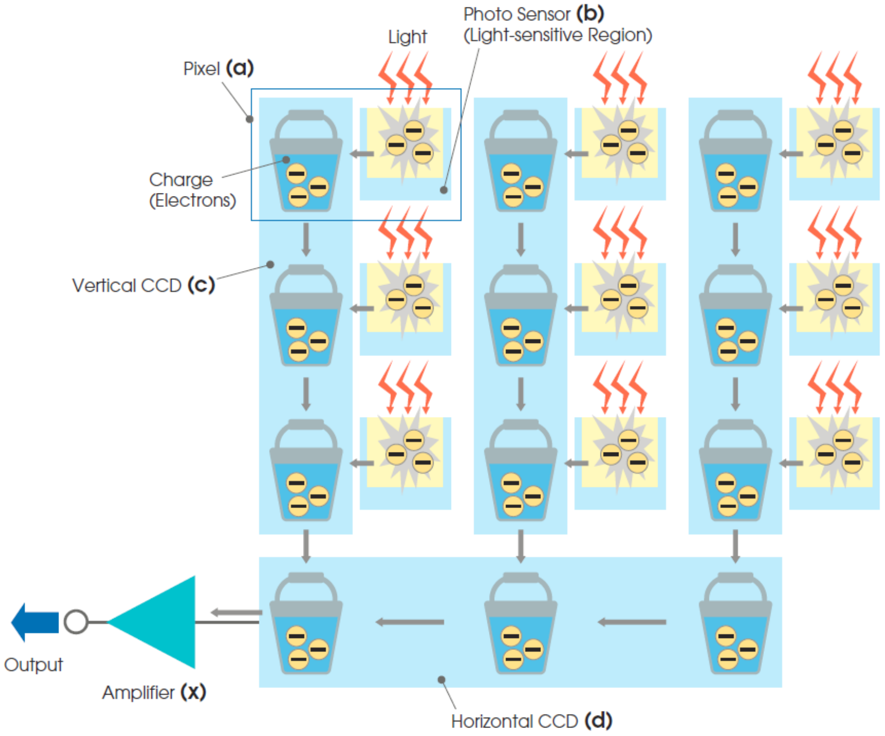


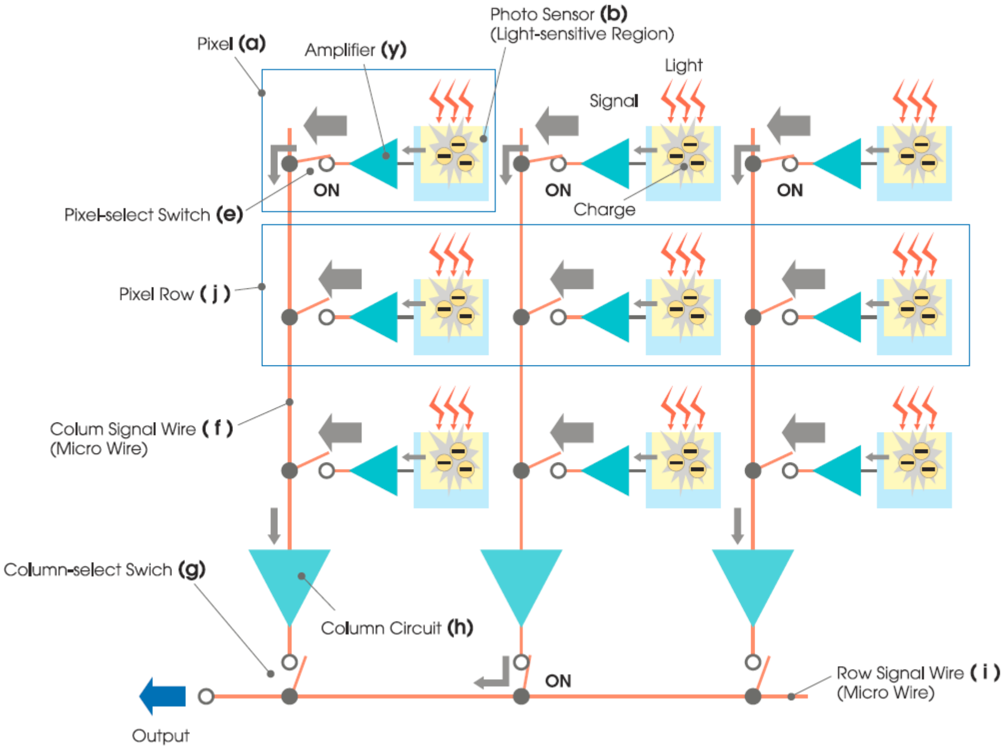


Moving colloids

CCD and CMOS

Charge coupled devices (CCD) and Complementary metal oxide semiconductor (CMOS) are the two most commonly used devices to obtain digital images. Both devices convert light into charges.





In a CCD, the charges are converted to voltage one by one, through the same amplifier

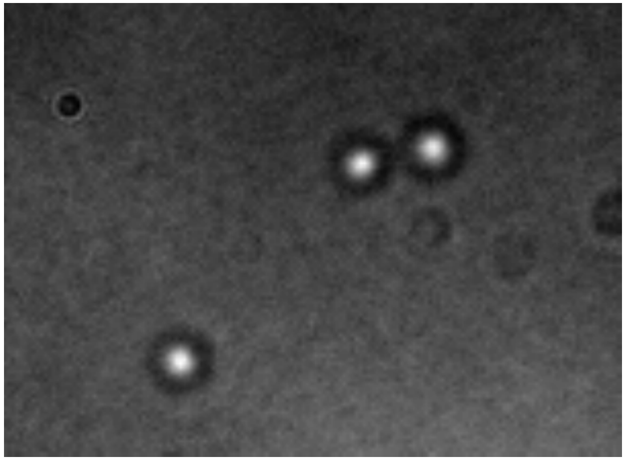
Good linearity, slow speed

In a CMOS, the charges are converted to voltage locally, each pixel has its own amplifier.

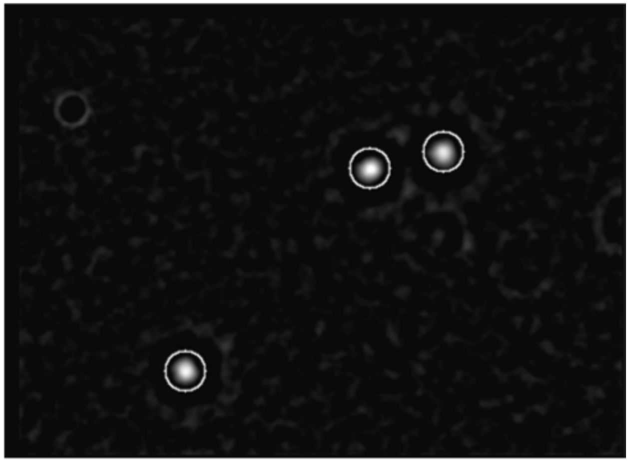
Lower image quality, fast speed

Particle tracking

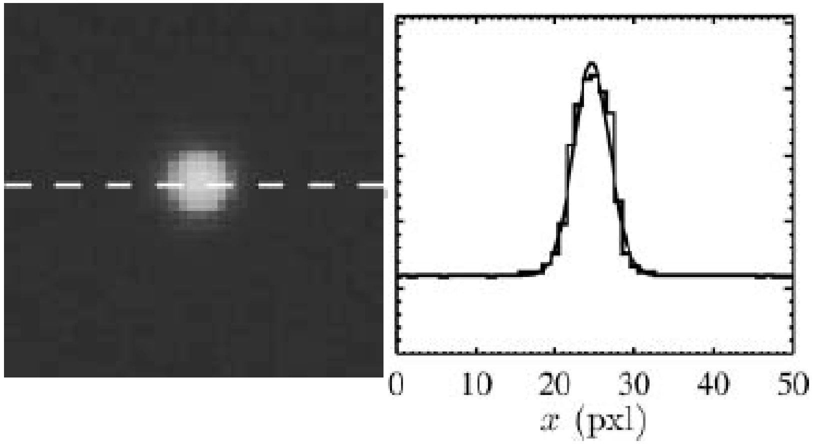
From the digitized microscopy images, the locations of particles can be accurately identified, down to 1/20 of a pixel, or 10 nm under ideal situations.



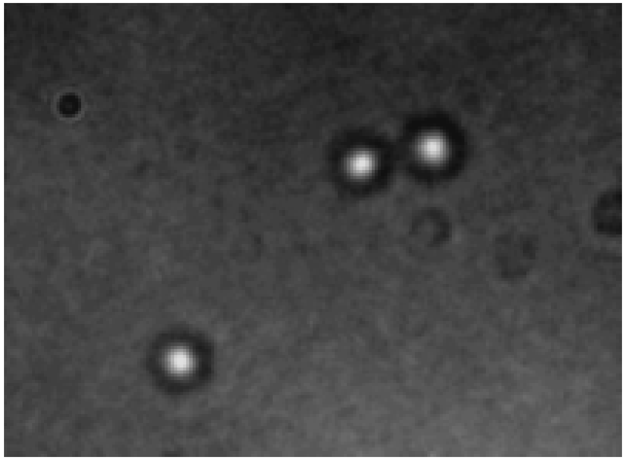
Raw image



Particle centers estimated from local maxima



Particle centers are refined by fitting to a Gaussian



Particle trajectories

Summary

1. 软物质物理的定位

Systems with strong interactions but with weak structural order

2. 胶体间的基本相互作用

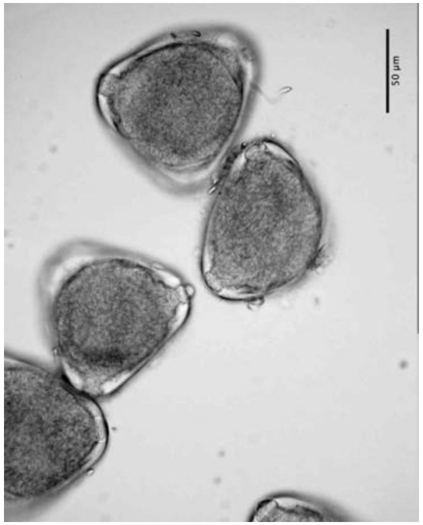
Van Der Waals interactions
Double layer charge interactions
Steric interactions
Depletion interactions

3. 主要实验方法简介

Rheology
Light scattering
Microscopy

Lecture 2

Brownian motion



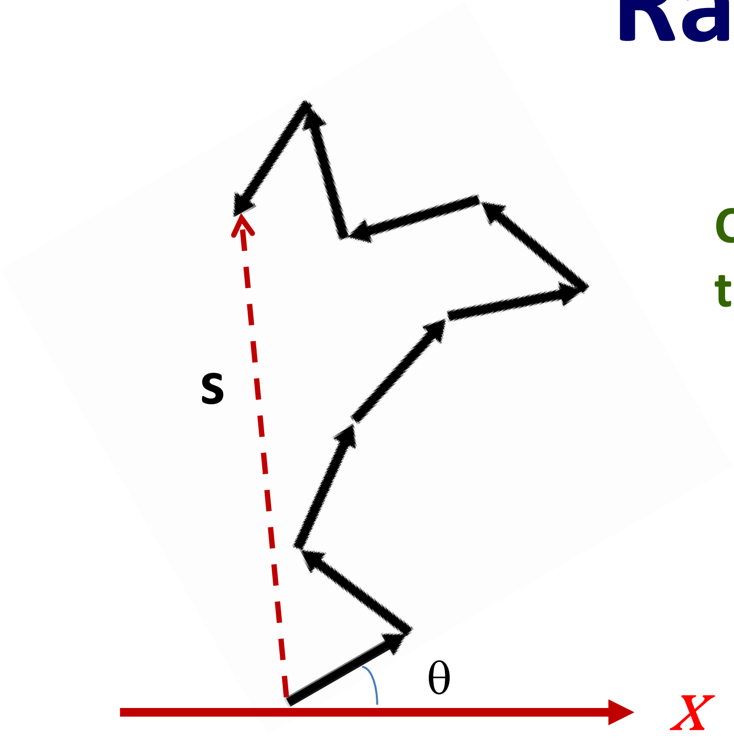
In 1827 Robert Brown (a botanist) discovered the random motion of small particles using a microscope

$$kT \geq mgd$$

$$d \leq 5\mu m$$

Particles less than 5 microns experience significant thermal motion

Random Walk



Consider 2D random walk with fixed step size of 1, the direction of each step is determined randomly

$$x_N = \sum_{i=0}^{N} \cos\theta_i \qquad y_N = \sum_{i=0}^{N} \sin\theta_i$$

After *N* steps, the distance to the origin is

$$s^2 = x_N^2 + y_N^2 = \left(\sum_{i=0}^{N} \cos\theta_i\right)^2 + \left(\sum_{i=0}^{N} \sin\theta_i\right)^2$$

$$= \left(\sum_{i=0}^{N} \cos^2\theta_i\right) + \left(\sum_{i=0}^{N} \sin^2\theta_i\right)$$

$$= N$$

$$\left\langle s^2 \right\rangle \propto t$$

The mean square displacement increases linearly with time.

No Physics Needed!

Stokes-Einstein relation

A more physical treatment of Brownian motion was proposed by Einstein in 1905, resulting in the Stokes-Einstein relation.

Diffusional flux is proportional to concentration gradient ,

$$j(x,t) = -D\frac{\partial c}{\partial x},$$

Now consider an external field *U* that will exert a force *F* on diffusing particles, resulting in additional velocity

$$F = -\frac{\partial U}{\partial x} \qquad\qquad v = M \cdot F = -M \cdot \frac{\partial U}{\partial x},$$

Where *M* is the mobility of a particle

The flux under external potential then becomes

$$j(x,t) = -D\frac{\partial c}{\partial x} - c(M \cdot \frac{\partial U}{\partial x})$$

Stokes-Einstein relation

Eventually, an equilibrium distribution of concentration will be established under the external field, determined by Boltzmann relation.

$$c_{eq}(x) \propto \exp(-U(x)/k_B T)$$

At equilibrium, the net flux at any point is zero

$$j(x,t) = -D\frac{\partial}{\partial x}c_{eq} - M c_{eq}\frac{\partial U}{\partial x} = 0$$

Plug in $c_{eq}(x)$, we obtain the Einstein relation

$$D = k_B T M.$$

(Notice the potential is no longer relevant)

The mobility of a sphere of radius a is determined by Stokes relation,

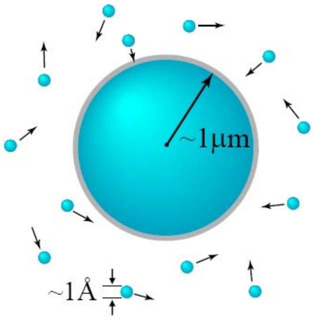
$$\vec{F} = 6\pi\eta a\vec{v} \qquad M = (6\pi\eta a)^{-1}.$$

Finally, we arrive at the Stokes-Einstein relation

$$\boxed{D = \frac{k_B T}{6\pi\eta a}}$$

Measuring Avogardro Number

From the definition of Boltzmann constant $k_B = \frac{R}{N_A}$ the diffusion constant of a small particle becomes

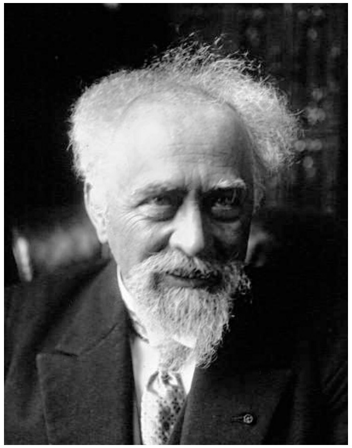


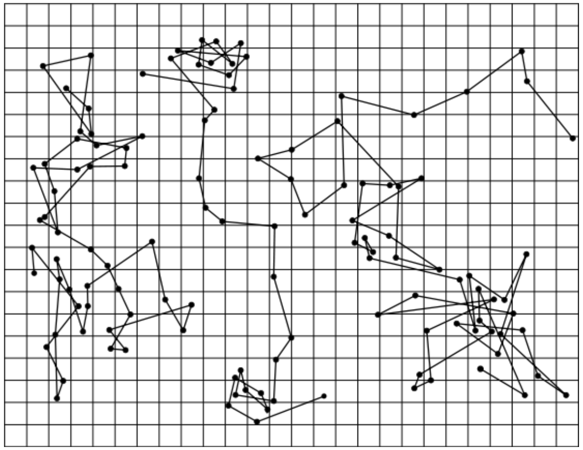
$$D = \frac{RT}{6\pi\eta a N_A}$$

D is related to the mean square displacement by

$$\langle \Delta x^2(\tau) \rangle = 2D\tau$$

Thus by measuring the MSD of a small particle, the Avogardro number can be determined.





Jean Perrin measured the Avogardro number to be 6.5-6.9x10^{23} in 1909, and received the Nobel prize in 1925.

Microrheology

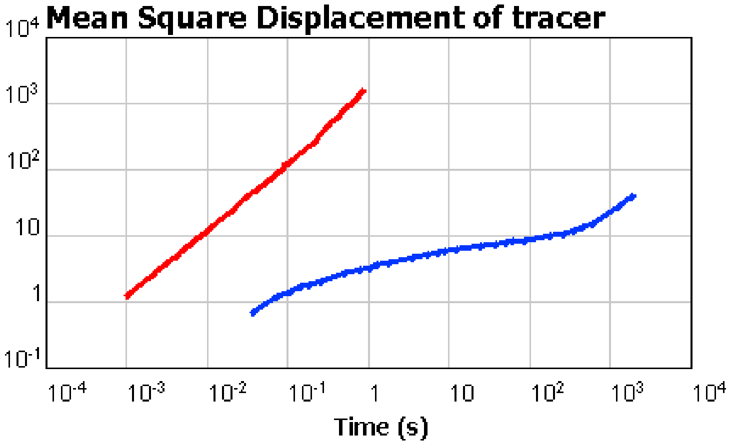
Directly from the Stokes-Einstein relation, one can measure the viscosity of a simple fluid where the MSD increases linearly with time.

A more general form of MSD can be written as

$$\langle r^2(\tau)\rangle \propto \tau^{\alpha} \quad \text{with} \quad 0 \le \alpha \le 1$$

At the limit where $\alpha = 1$, we recover the pure viscous fluid, and the the limit of $\alpha = 0$, the particle is trapped in a purely elastic medium.

For viscoelastic materials whose rheological responses depend on the relaxation time, the MSD curve will have different α at different time scales



MSD of a tracer particle in viscous fluid (red) and viscoelastic material (blue)

Microrheology

Starting with a generalized Langevin equation

$$m\dot{v}(t) = f_R(t) - \int_0^t \zeta(t-\tau)v(\tau)\,d\tau$$

Mason and Weitz show that the shear modulus can be related to the MSD of a particle by

$$\tilde{G}(s) = s\,\tilde{\eta}(s) = \frac{s}{6\pi a}\left[\frac{6k_BT}{s^2\langle\Delta\tilde{r}^2(s)\rangle} - ms\right]$$

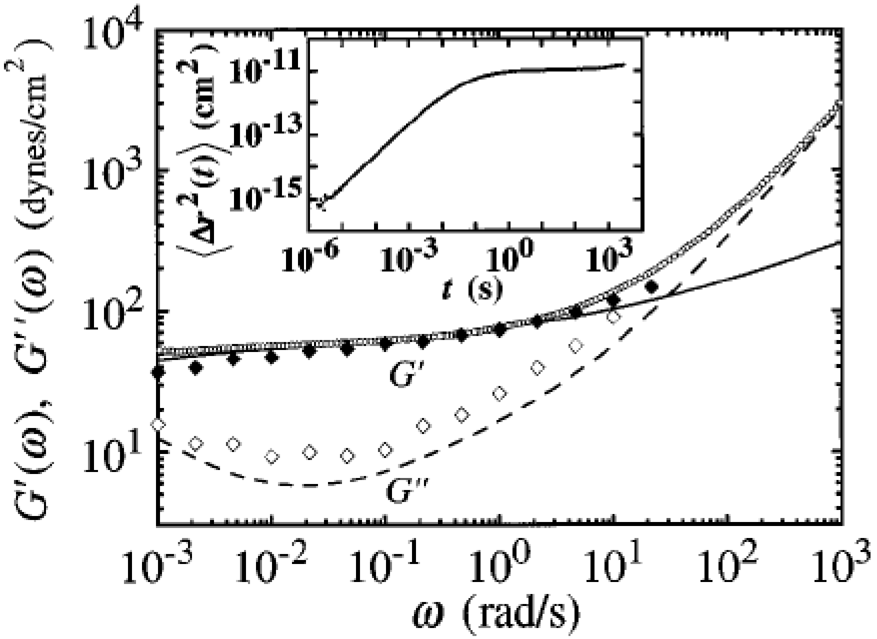
Where the ~ indicate a Laplace transformation, by replacing *s* with *iω*, one can obtain the complex shear modulus *G*(ω)*.

In practice, instead of doing numerical Laplace transformation, the local slope *α(ω)* is used to calculate *G*(ω)*.

$$|G^*(\omega)| = \frac{k_BT}{\pi a\langle r^2(1/\omega)\rangle\Gamma\,(1+\alpha(\omega))}$$

$$G'(\omega) = |G^*|\cos(\pi\alpha(\omega)/2) \qquad G''(\omega) = |G^*|\sin(\pi\alpha(\omega)/2)$$

Microrheology



Comparison between bulk (symbols) and micro-rheology (lines)

Advantages of microrheology:

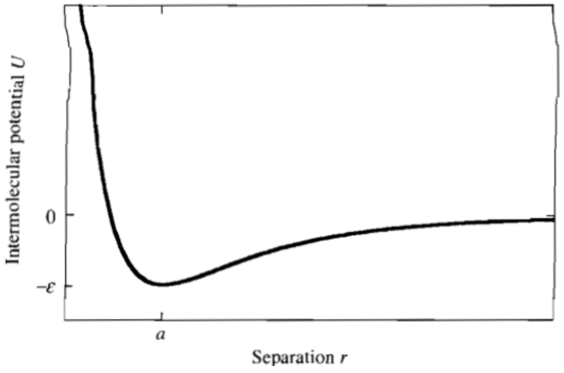
1. **Small sample volume ~μl**
2. **Probe a wide frequency range in one measurement**
3. **Able to probe local heteorgeneities**

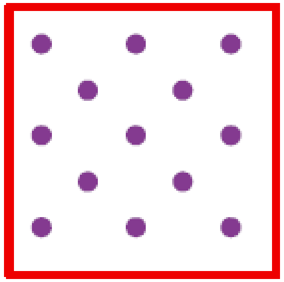
Phase Transitions

Matters can change from one thermodynamically stable state to another, this is known as phase transitions.

The driving force behind the phase transitions is the free energy

$$F = E - TS$$

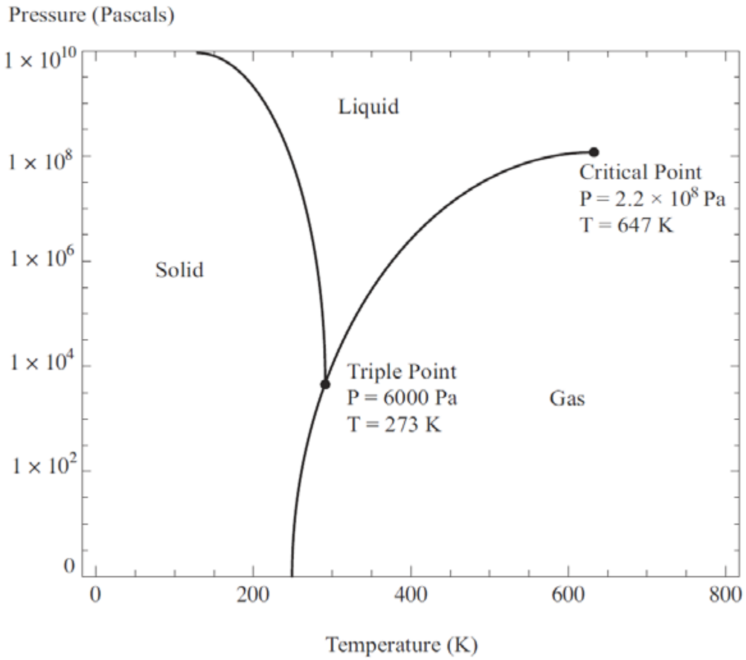


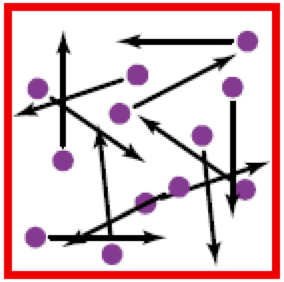


solid

Low T

E dominated





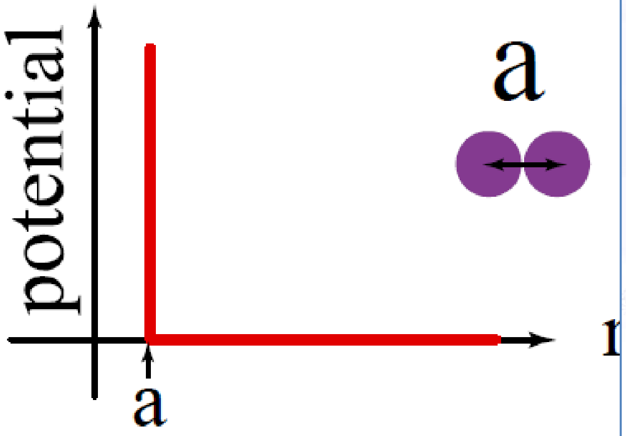
liquid, gas

High T

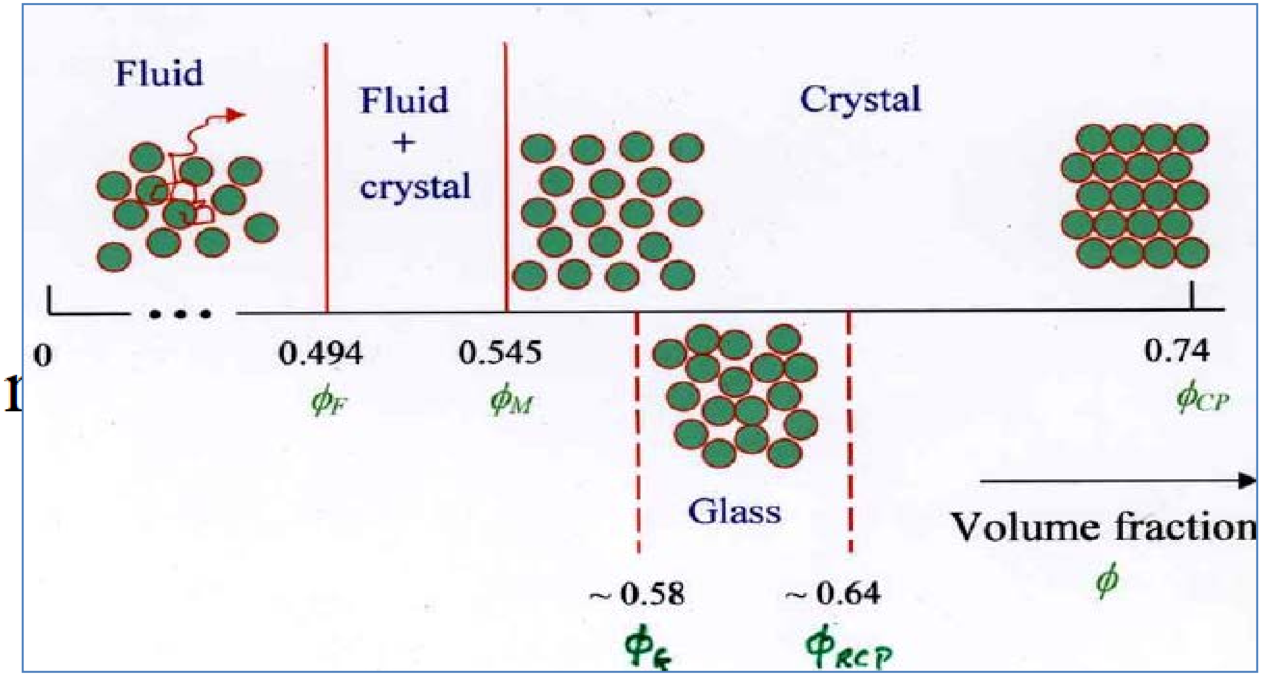
S dominated

Hard sphere interactions

Many colloidal system can be well described by hard sphere interactions, with which two particle repel each other upon contact and have no interactions once separated.



$$F = -TS$$



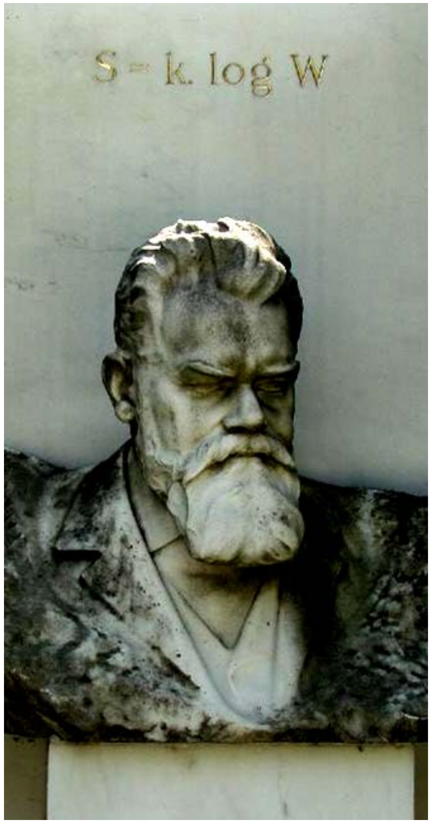
In a hard sphere system, phase behaviors are driven only by entropy

Entropy

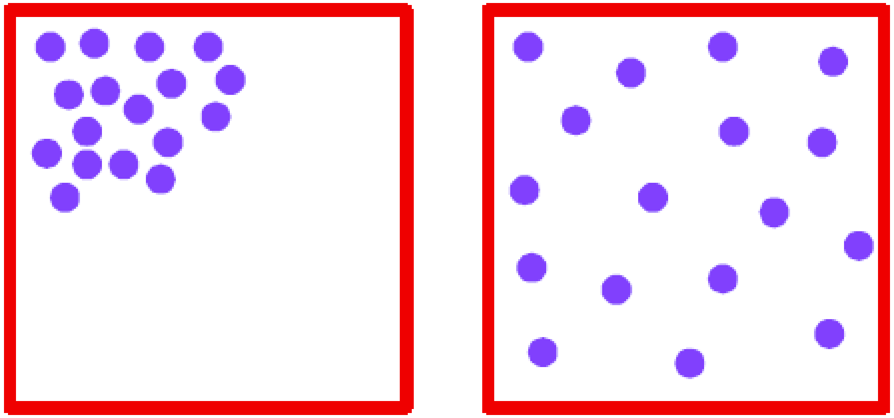
Entropy describes the number of states accessible to a system

The second law of thermodynamics states:

In an equilibrium system, entropy never decreases



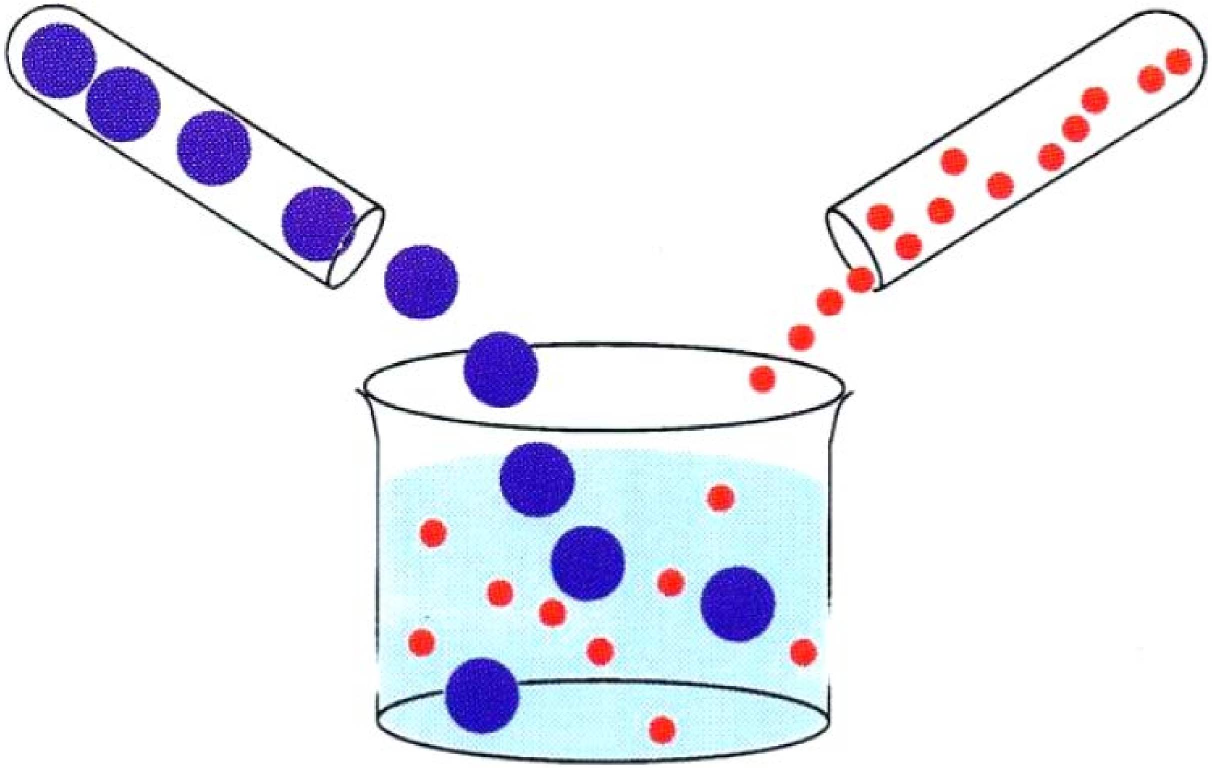
Boltzmann



Entropy increase through expansion

$\Delta S = nR\ln(V_2/V_1)$

Question

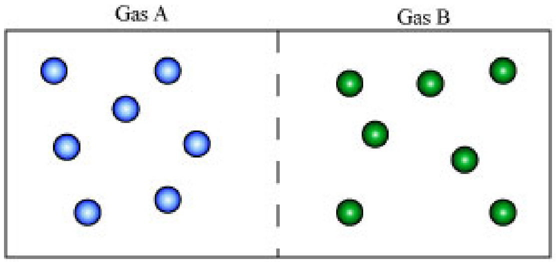


When mixing two kinds of hard spheres, when will the entropy be at the maximum?

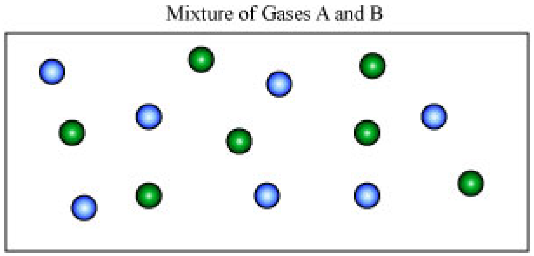
Mixing entropy

In the dilute limit $\frac{N\lambda^3}{V} << 1,$ $S \approx N \ln\left(\frac{V}{N\lambda^3}\right)$

Consider mixing of two kinds of gases



$$\Delta S_A \approx N_A \left[\ln\left(\frac{V_A + V_B}{N_A\lambda^3}\right) - \ln\left(\frac{V_A}{N_A\lambda^3}\right) \right] > 0$$

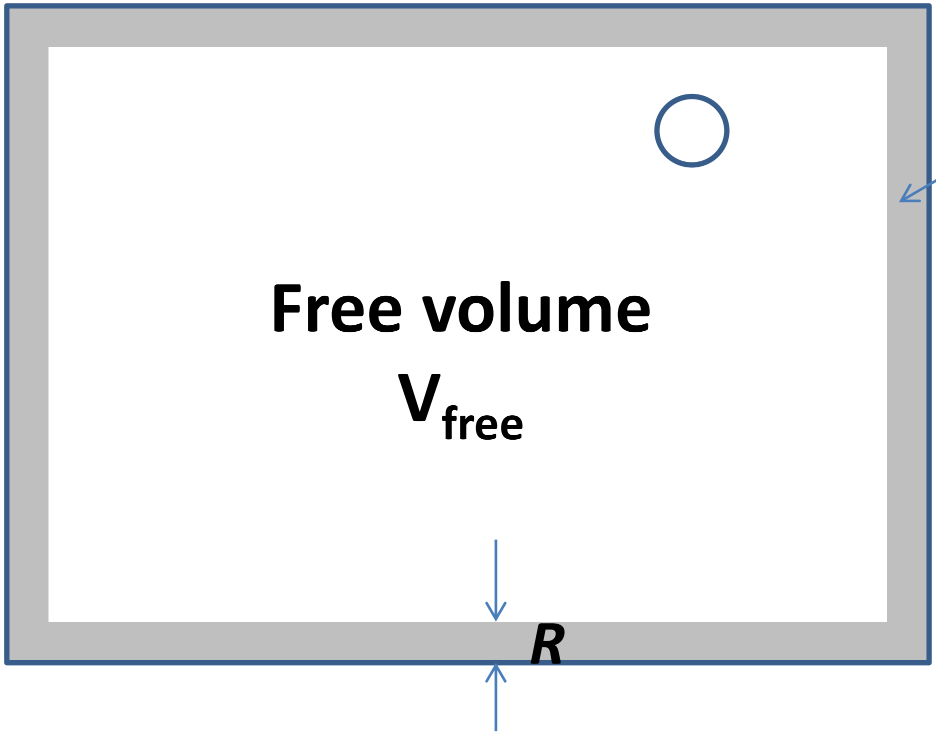


$$\Delta S_B \approx N_B \left[\ln\left(\frac{V_A + V_B}{N_B\lambda^3}\right) - \ln\left(\frac{V_B}{N_B\lambda^3}\right) \right] > 0$$

Entropy increases after mixing
Irreversible
More disorder (really?)

Getting down to the basics

Consider the entropy of just ONE single sphere of radius R in a box



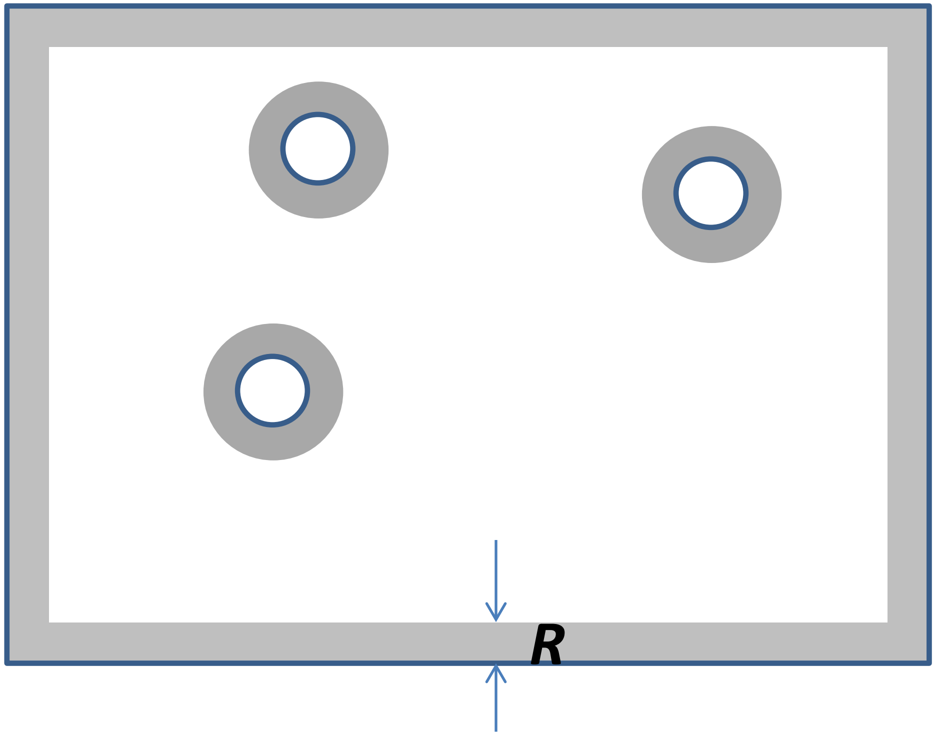
Gray areas are not accessible to the sphere

The number of states available Ω to the sphere is proportional to V_{free}/λ^3, where V_{free} is the free volume available to the particle

Entropy for hard spheres

Continue to introduce hard spheres, as long as the system is still dilute, the total entropy can be roughly written as

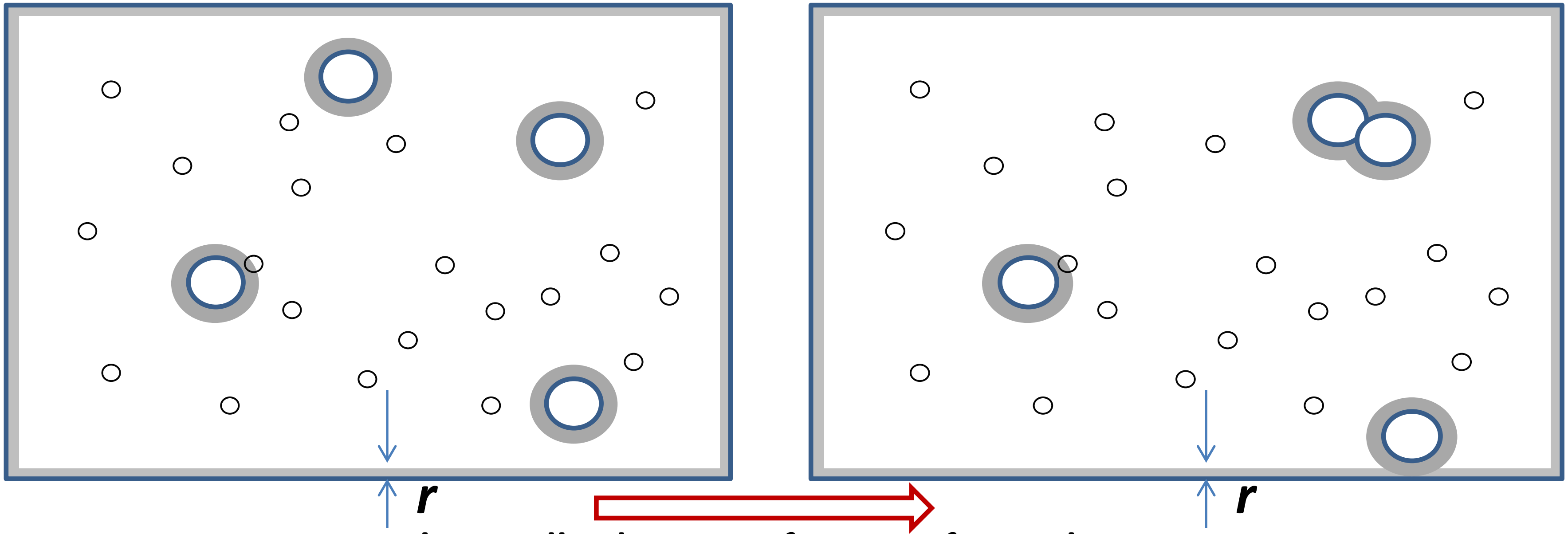
$$S = kN\ln(V_{free}/\lambda^3)$$



Each sphere will also create areas that are inaccessible to other spheres, so the overall free volume decreases with more spheres.

Entropic forces

Now let’s introduce small spheres, in large numbers, so that the entropy of the whole system is largely determined by the small spheres instead of the larges ones.

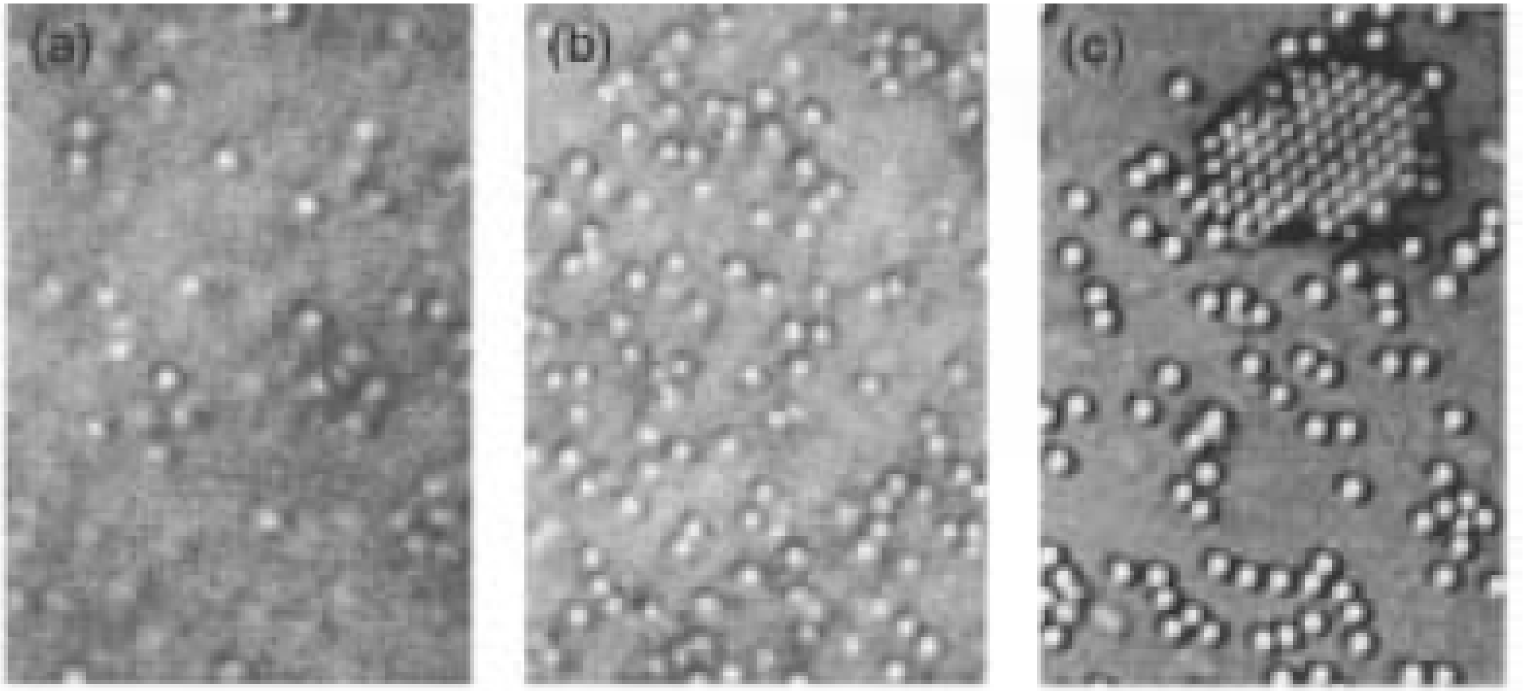


The small spheres prefer more free volumes

$$F = \frac{kT\phi_S^*}{\left(2a_S^*\right)^3}\left(2a_S^* + 2a_L - r\right)^2 \times \left(2a_S^* + 2a_L + \frac{r}{2}\right)$$

When two large particles come to contact to each other or to the wall, the free volume for small particles increases, at the cost of decrease degree of freedom for large particles

Entropy-driven crystallization

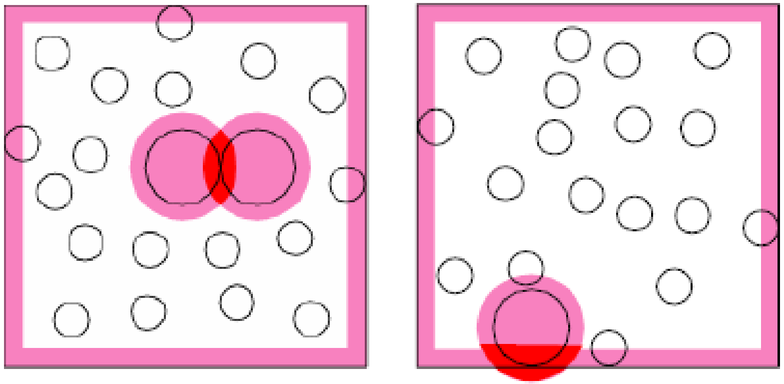


Mixture of polymers (invisible) and colloidal particles.
Colloidal particles crystallize as the concentration of polymers increases

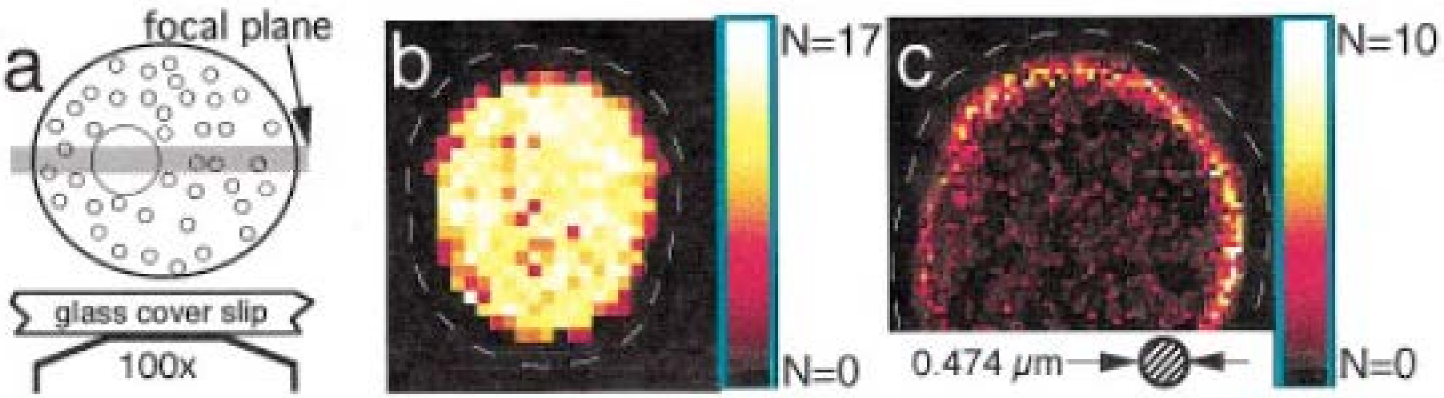
As the entropy increases, part of the system becomes more ordered!

A. Dinsmore, **EPL** (1997)

Pushed to the wall



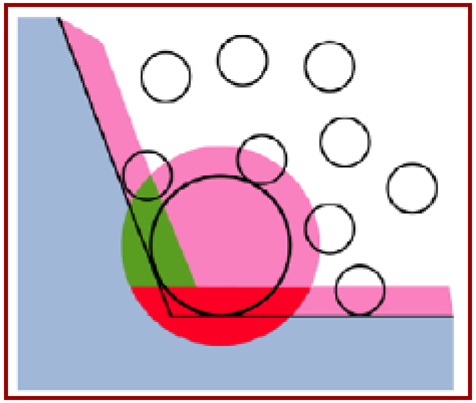
Moving a large particle to the wall increases free volumes for small particles even more than simply pushing two large particles together

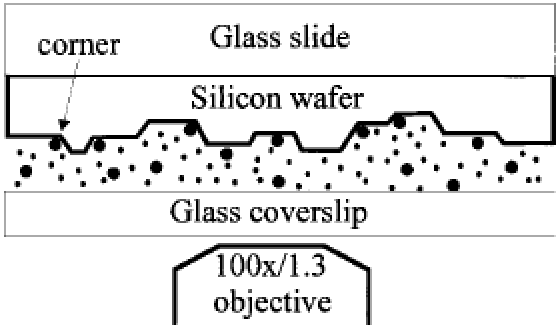


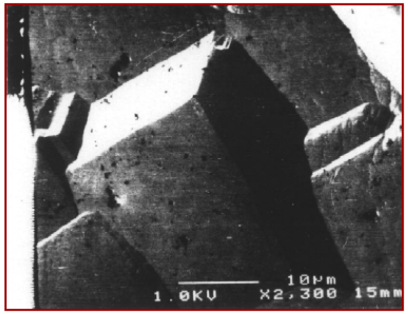
A vesicle containing colloidal particles.
Particles are uniformly distributed when only large particles are contained (b)
When small particles are also introduced, large particles are pushed to the wall of the vesicle (c).

Dinsmore **PRL** (1998)

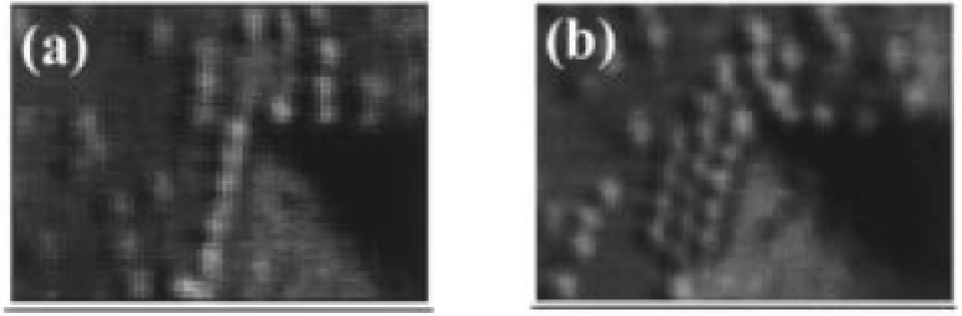
Cornered







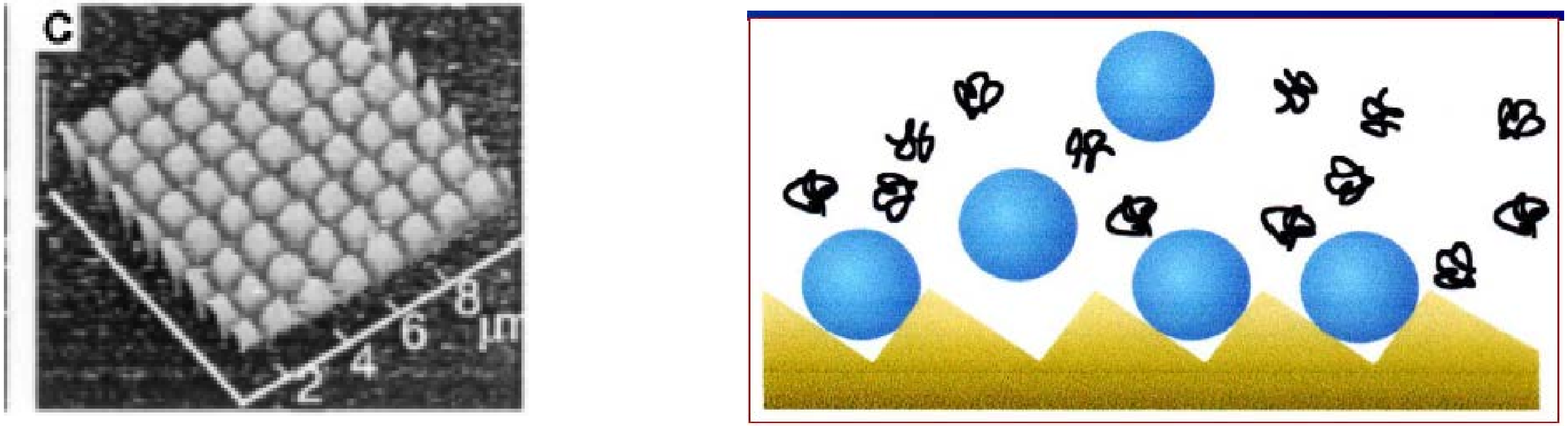
Even more free volume will be created if a particle comes to contact with two surfaces, i. e. a corner



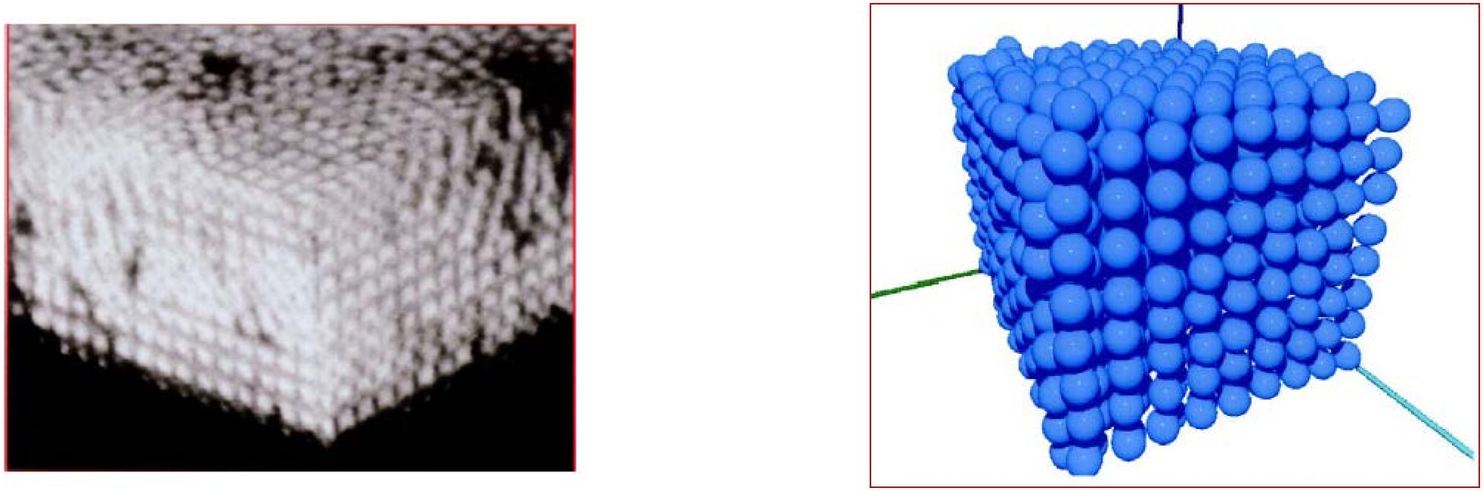
Colloidal crystal grows from a corner

Dinsmore, Langmuir (1999)

Self-assembly: going 3D



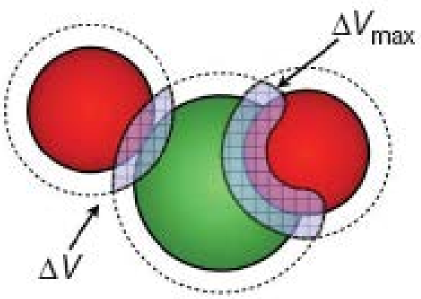
Colloidal particles will be driven to corners on a patterned surface. Or to crystalline sites at higher layers



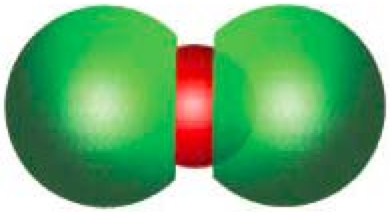
Colloidal crystal image obtained by confocal microscopy and its 3D reconstruction

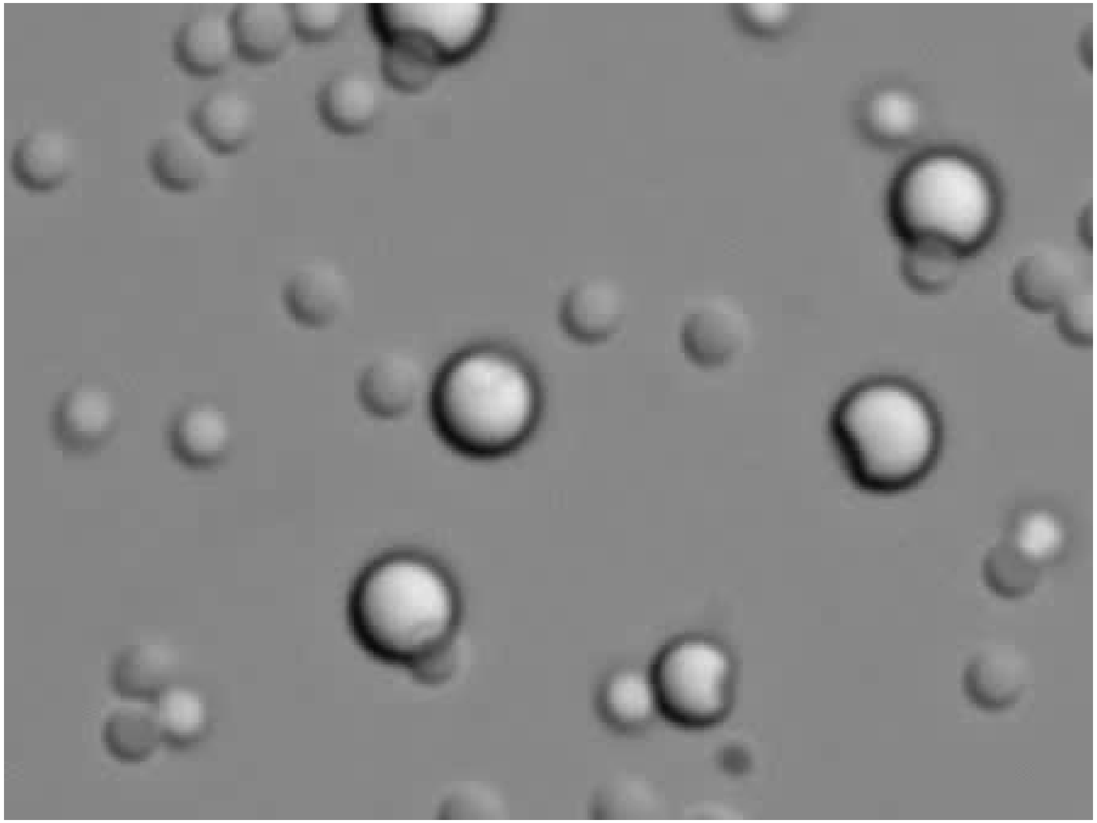
Lin PRL (2000)

Entropic forces: beyond spheres



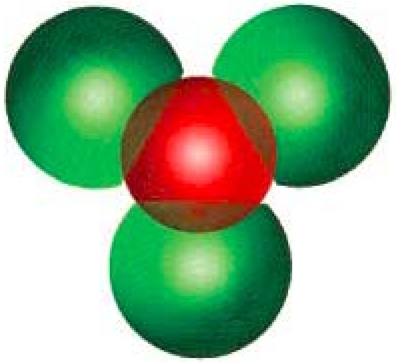
Properly matched curvatures maximize the increase of free volume



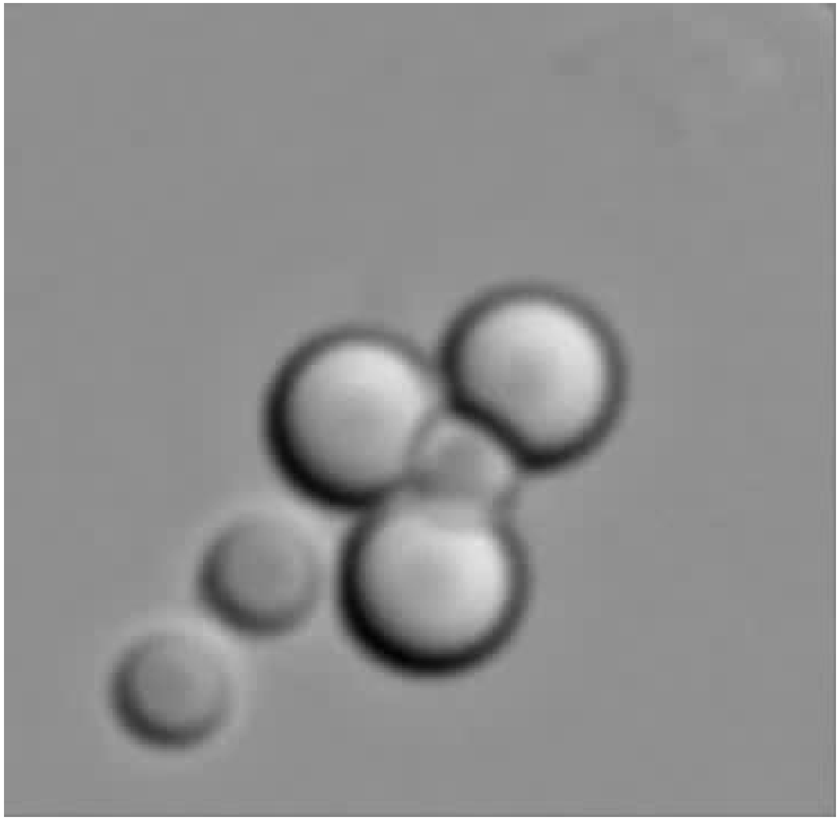


Self-assembly of lock-and-key colloidal particles
S. Sacanna, **Nature** (2010)

Lock and key experiment

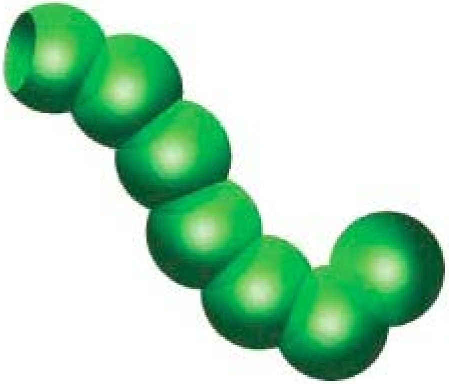


Particles choose configurations that maximize entropy gain

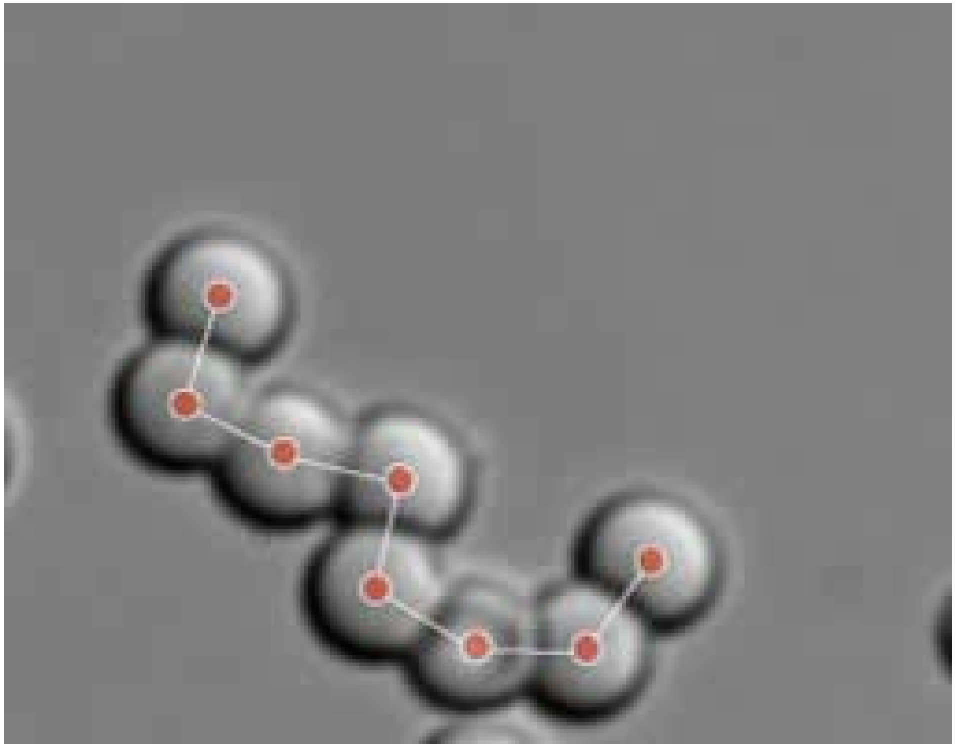


Self-assembly of lock-and-key colloidal particles
S. Sacanna, **Nature** (2010)

Lock and key experiment



Particles choose configurations that maximize entropy gain



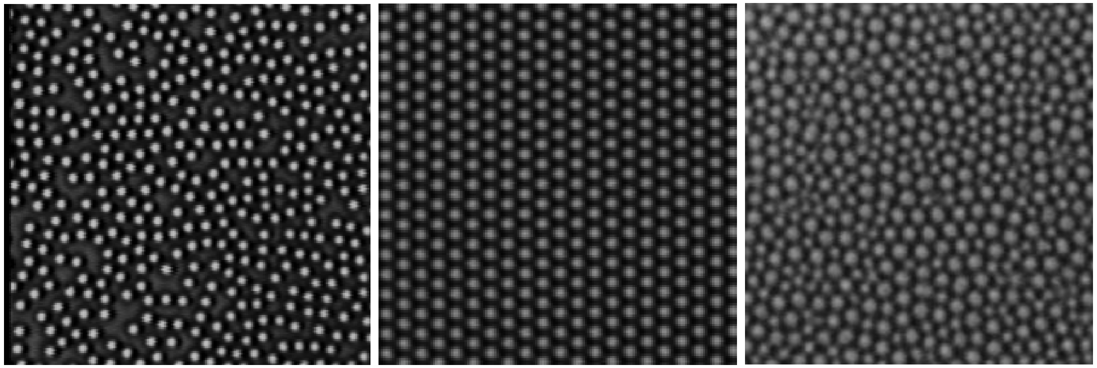
Self-assembly of lock-and-key colloidal particles
S. Sacanna, **Nature** (2010)

Colloids as a model system

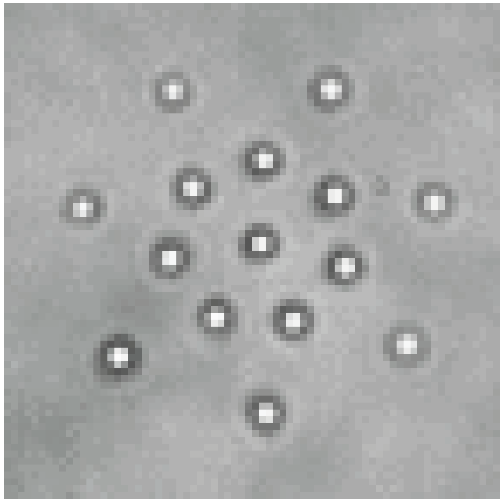
The entropy of colloidal systems is determined by the volume fraction.

Higher packing fractions correspond to lower temperatures.

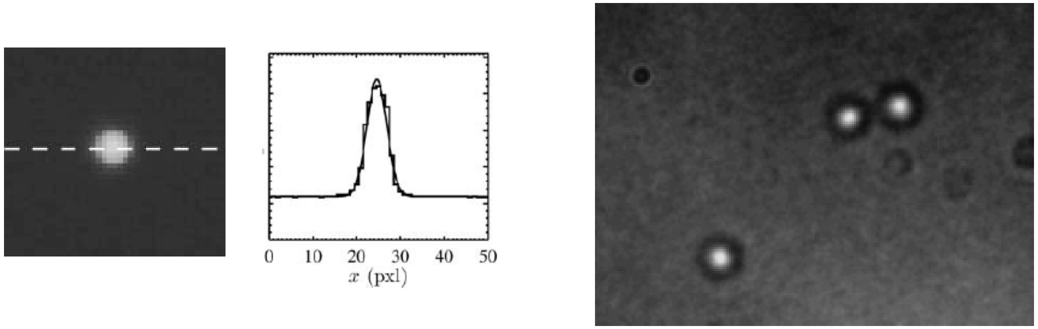
Colloidal systems can be use to study phase behaviors in condensed matter physics.



Different phases of colloids



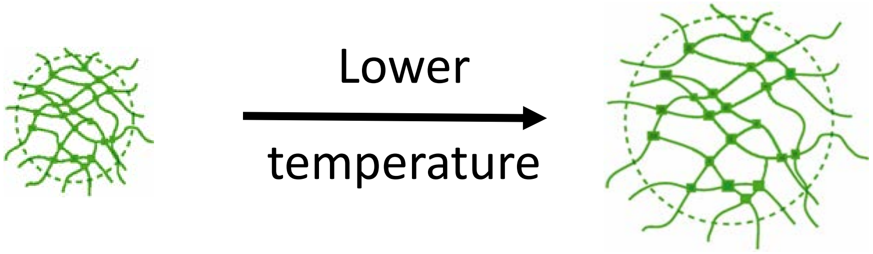
Manipulation of colloidal particles with optical tweezers



Accurate tracking of colloidal particles

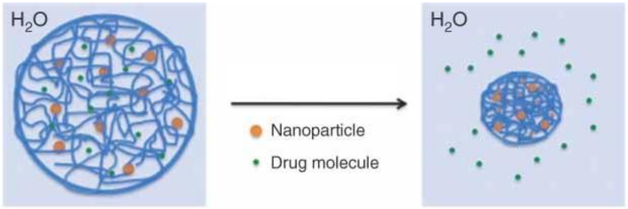
Temperature sensitive colloids（PNIPAm）

PNIPAm (Poly-N-isopropylacrylamide) particles are temperature sensitive, the diameters of PNIPAm particles increase when temperature decreases.

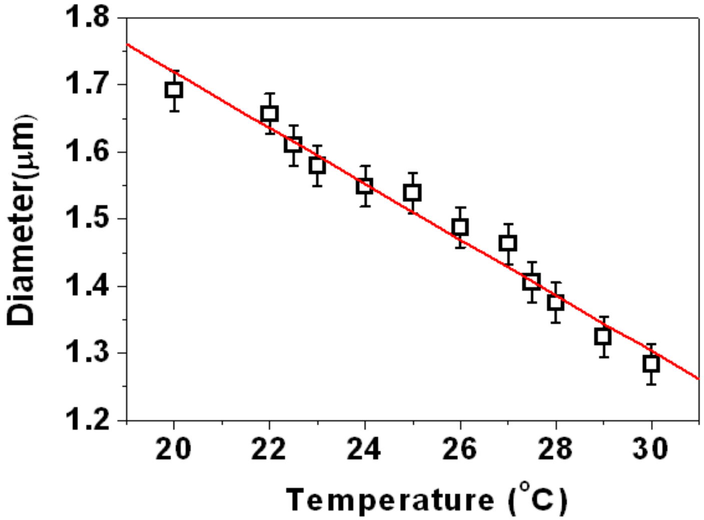


Lower

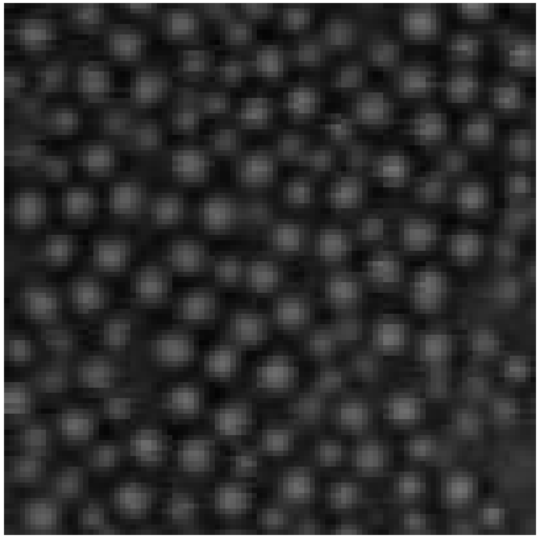
temperature



Drug delivery using PNIPAm particles

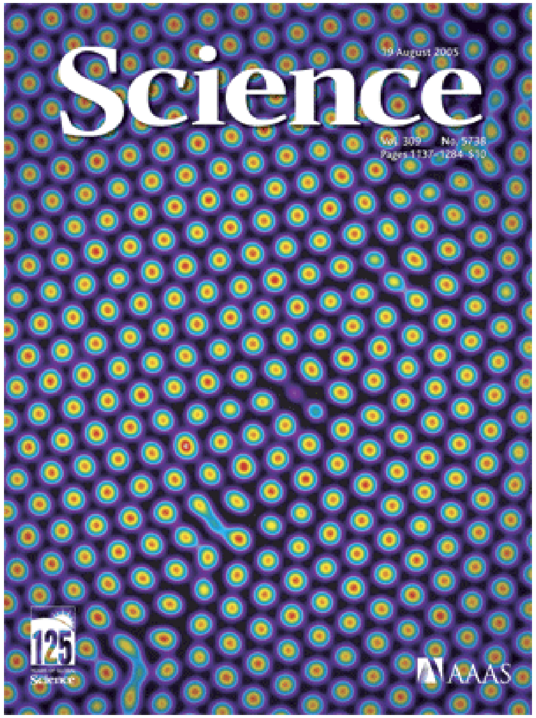


Free volume decreases
Slower Brownian motion

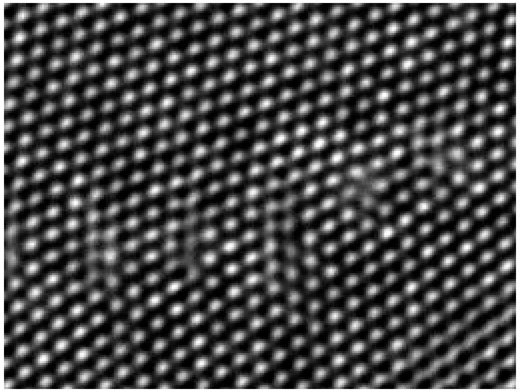


Rapid quenching of a PNIPAm fluid to a glass

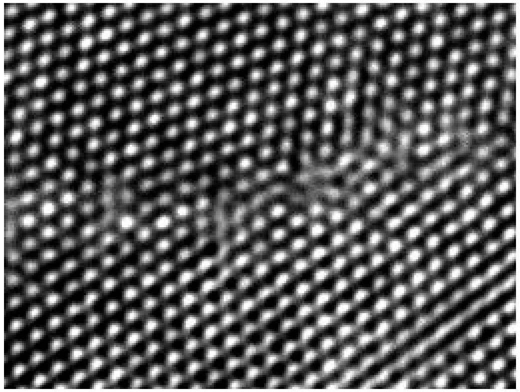
Pre-melting of colloidal crystals



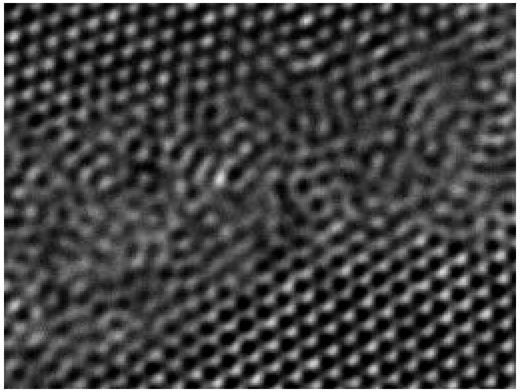
A. Alsayed et al, **Science** (2005)



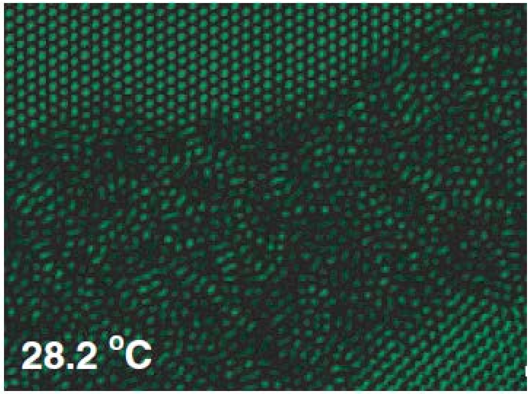
27.2



28.0



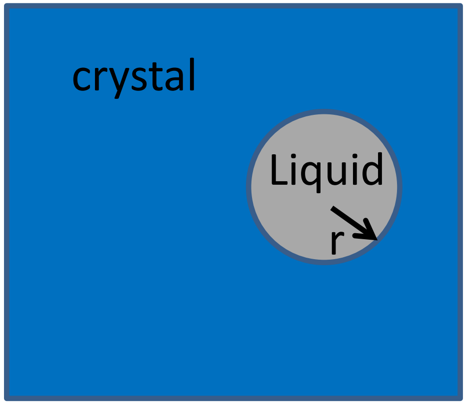
28.1



28.2

Before reaching the bulk melting temperature, pre-melting starts at grainboundares

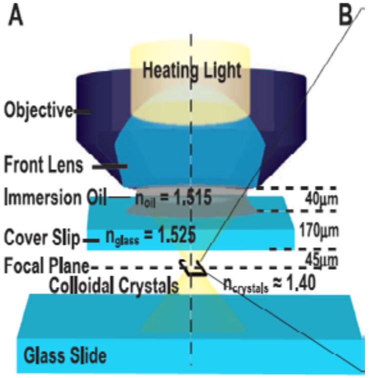
Melting of Superheated Colloidal



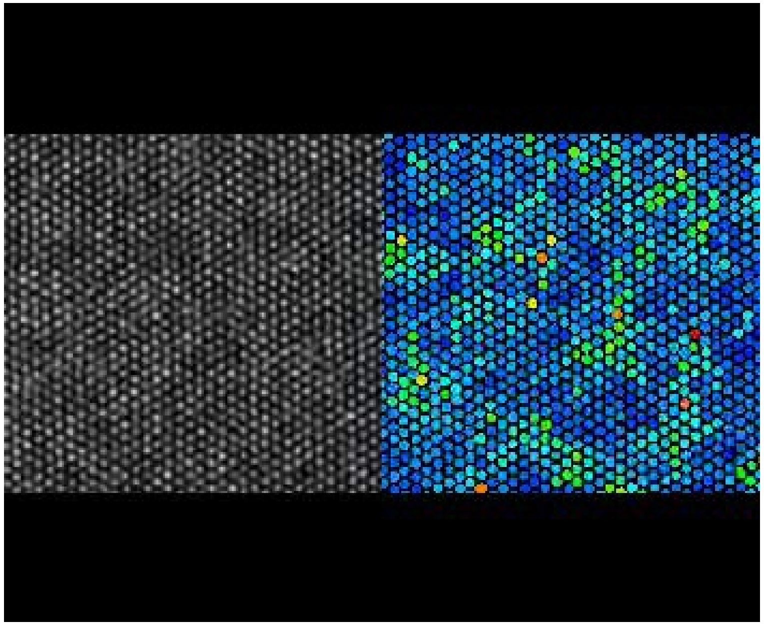
Melting starts with an nucleus created by thermal fluctuation

$$\Delta G = 4\pi r^2 \gamma - \frac{4}{3}\pi r^3 n \Delta\mu + E_{strain}$$

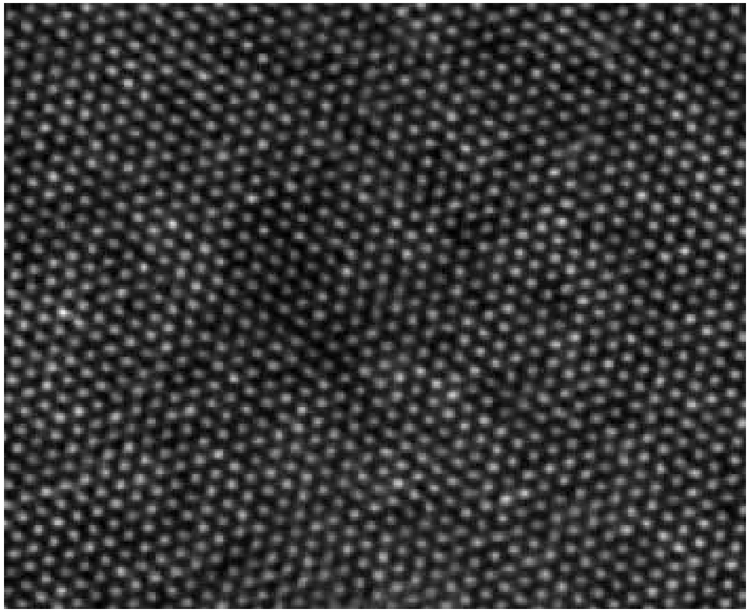
Small nuclei recrystalize, Large nuclei grow



均匀加热晶体



Nucleation process

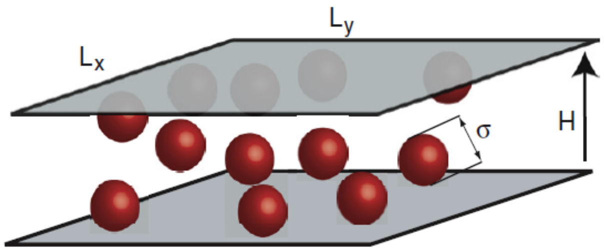


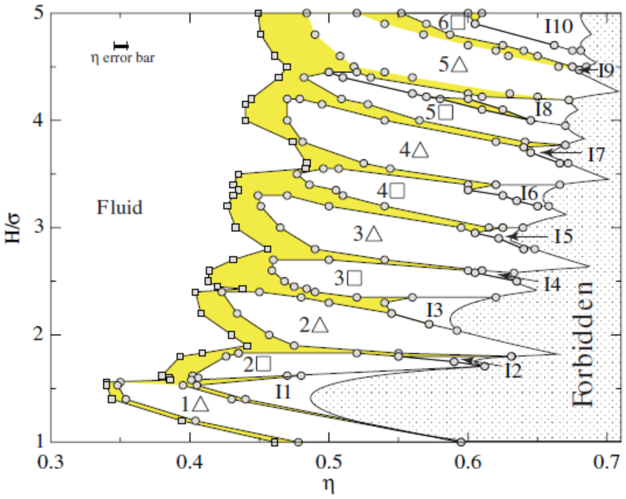
Catastrophic Melting

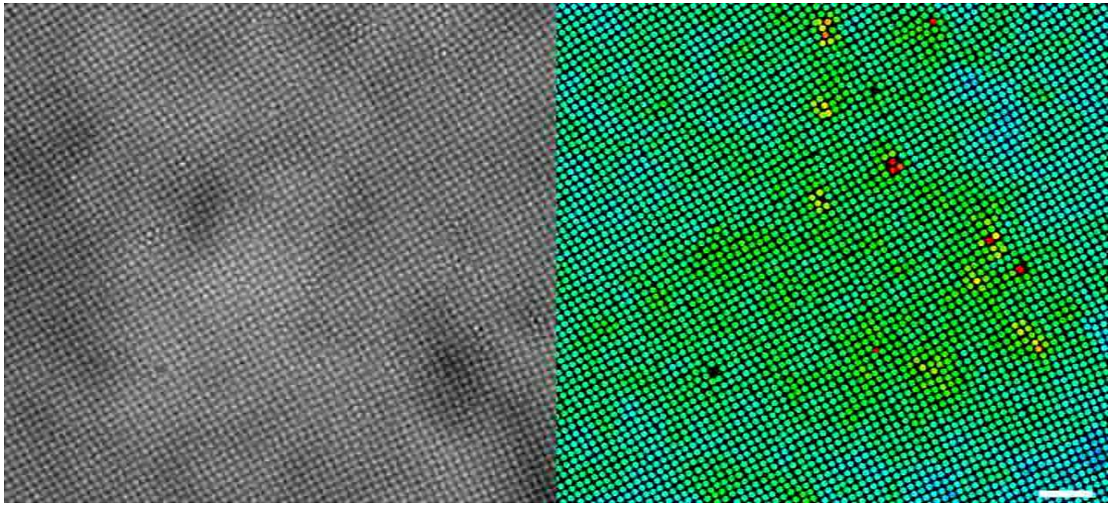
Wang et al, **Science** (2012)

Solid-solid transition

Thermodynamically stable packing configuration for hard spheres confined between two walls, switches between hexagonal and square lattices, depending on the relative height and particle size.





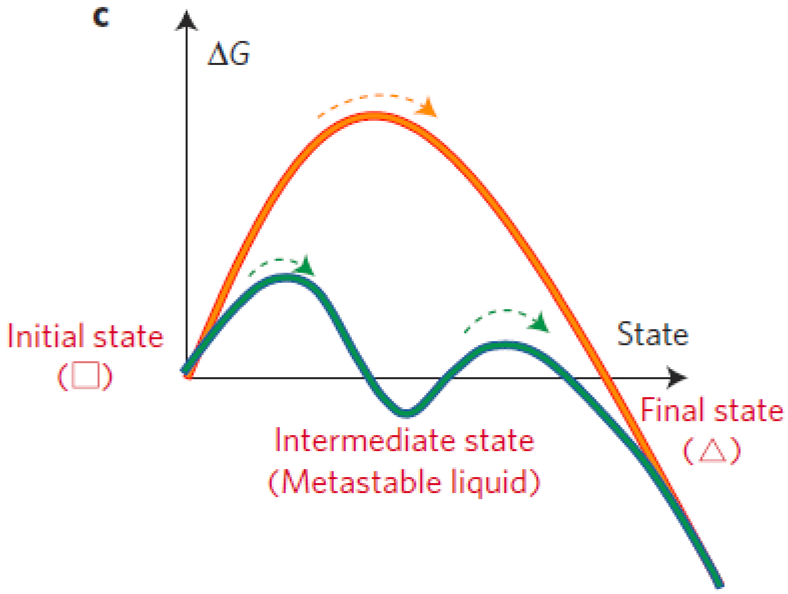


Instead of directly transiting from square to hexagonal, a metastable liquid phase was formed between the two phases

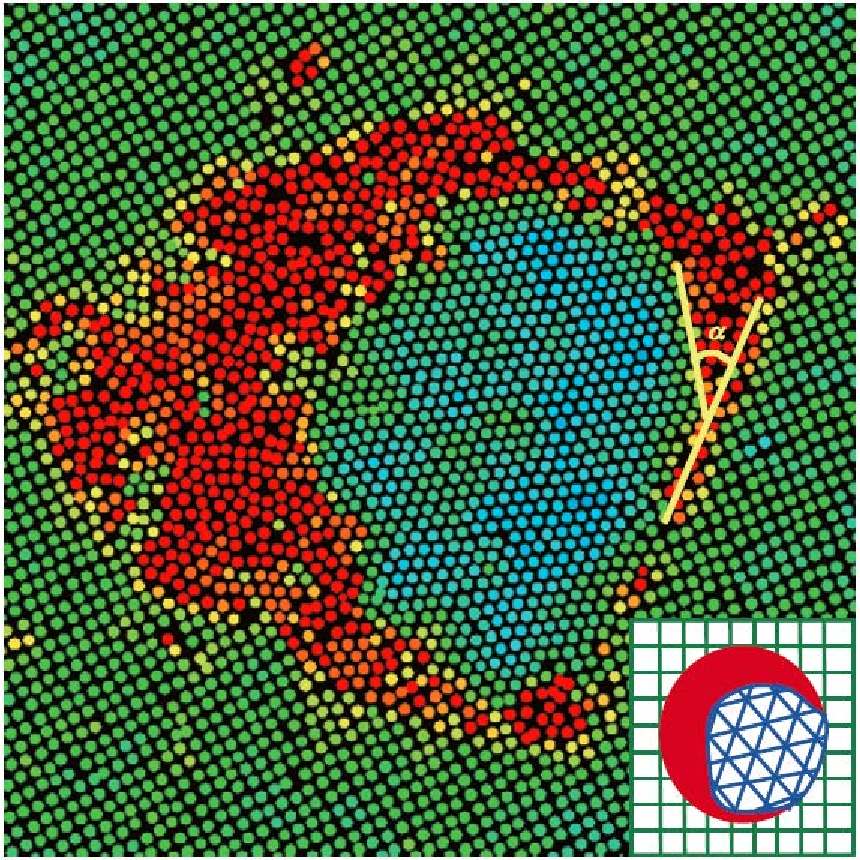
Peng et al, **Nat. Mat.** (2015)

Solid-solid transition

Instead of forming a nucleus directly from square phase, the system chooses two step nucleation, which reduces interfacial tension, thus making the process easier.



Energy barrier for nucleation



$$\gamma_{\square-L} + \cos\alpha \cdot \gamma_{L-\Delta} = \gamma_{\square-\Delta}.$$

$$\gamma_{\square-L} < \gamma_{\square-\Delta}.$$

Summary

胶体在平衡态研究中的应用

Brownian motion

Microrheology

Entropic forces and self-assembly

Phase transition in colloidal crystal

Lecture 3

Physics of Glasses

Brief review of equilibrium statistical mechanics

Glass as a material

Structure, dynamics and thermodynamics of glasses

Study glasses using colloids

Equilibrium statistical mechanics

Statistical physics aims to understand/predict the behavior of multi-body systems with a few parameters, including macroscopic parameters (pressure, temperature and volume etc.) and microscopic parameters (particle mass, radius, interaction and lattice constants).

To connect macroscopic observables to microscopic states, we employ the partition function

$$Q = \sum_r e^{-\beta E_r}$$

The partition function tells us the probability of any possible configurations under the given constrains, thus we can obtain the expected value of any observables by doing ensemble average.

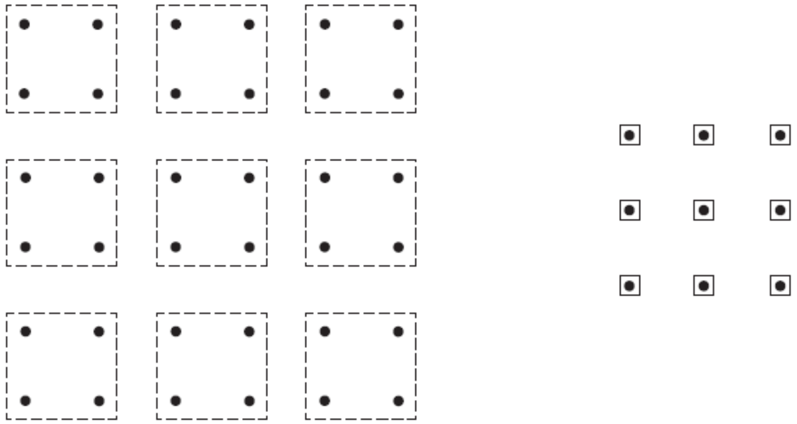
$$\bar{f} = \int f(\mathbf{x}, \mathbf{p}) \rho(\mathbf{x}, \mathbf{p}) d\mathbf{x} d\mathbf{p}$$

The operation of ensemble averaging is based on an assumption that all possible states can be reached within a reasonable amount of time, i. e. the relaxation time is relatively short - **ergodicity**. This is generally true for system near equilibrium (minimum free energy)

Equilibrium statistical mechanics

Partition functions in a many-body system with interactions are generally hard to calculate (too many integrals). If the system has certain symmetry (crystalline lattice, rotational symmetry e. g.) the evaluation of partition functions will be greatly simplified, sometimes can even be achieved precisely.

$$f(T,\phi)=\frac{1}{2}r(T)\phi^2+u(T)\phi^4+\ldots,$$



Free energy expression from Landau theory, the order parameters has f → -f symmetry

Kandanoff “block spin renormalization for spins on a square lattice

Now let’s imagine we have lost both ergodicity and symmetry, then we have a glass.

Glasses in Nature

When a liquid is rapidly cooled, it may avoid crystallization and form a glass instead.

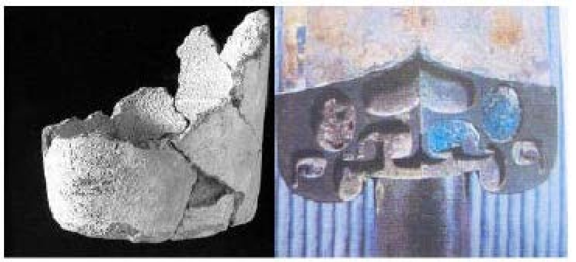
Volcanic glass

Amber

Glass formed by meteorite impact

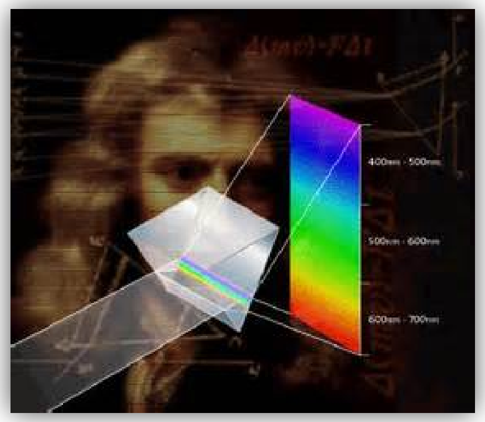
Glasses in human history

Early humans made tools and weapons from volcanic glasses



Glass cup and decorations from ancient Egypt and China

Glass artifact from ancient Greek



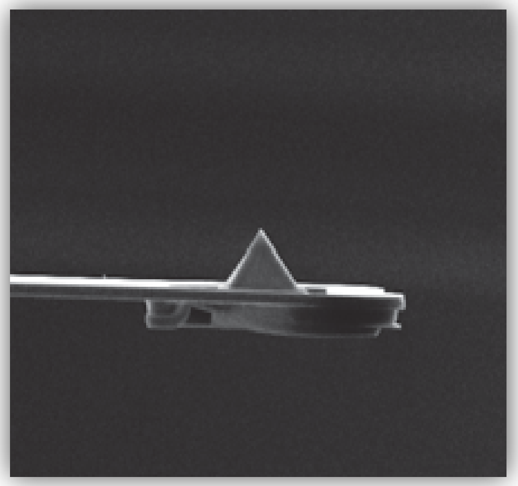
Prism and spectra

Telescope

Chemistry glassware

Modern Glasses

Plastics (polymers)



Amorphous carbon

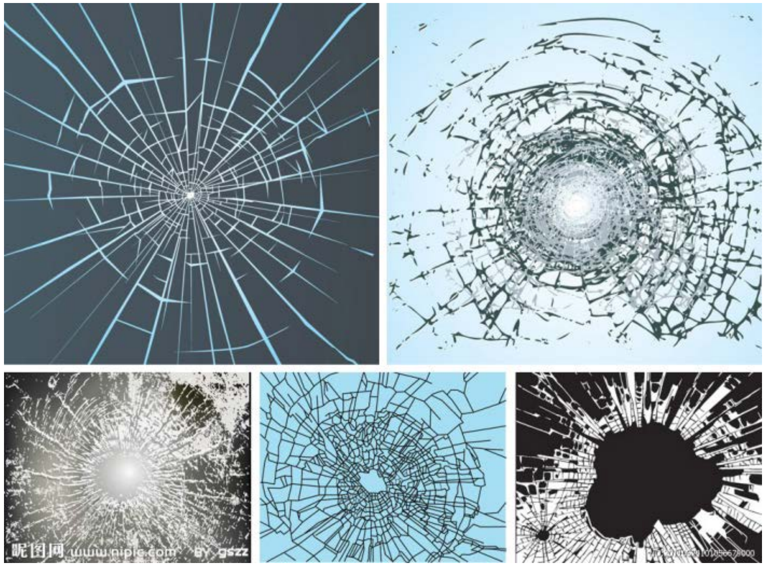
Metallic glasses

Solar cells made of amorphous silicon

Optical fibers

Problems as a material

Properties are hard to control, non-equilibrium process



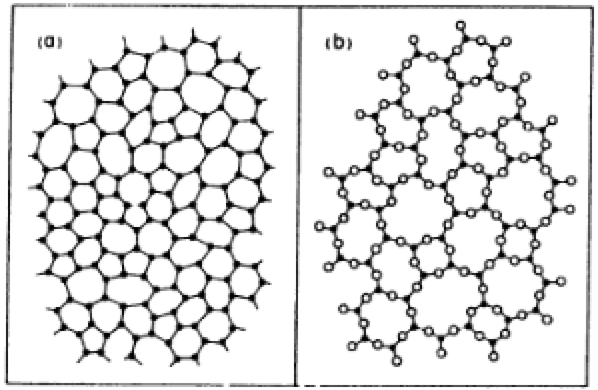
Brittleness is the Achilles' heel of all glasses

The properties of glasses evolve with time (aging)

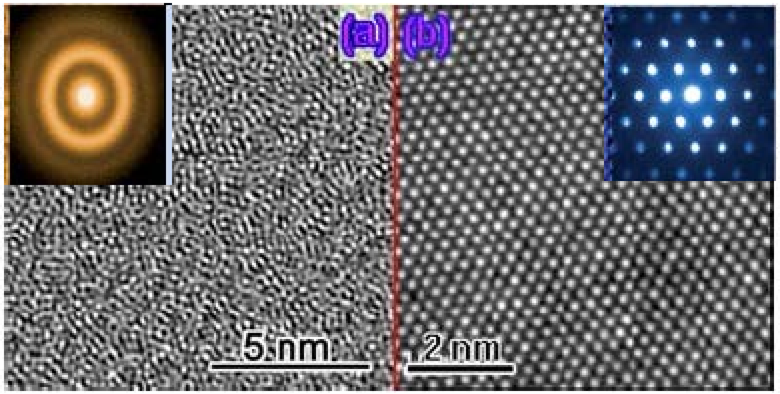
Most problems of glass materials are due to the lack of understanding of the fundamental physics of glasses.

Structure of glasses

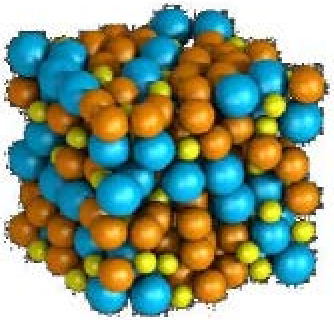
The structures of glasses are disordered.



Typical structure of a network glass (2D)



High resolution STM images of metallic glass (left) and crystalline metal, and the x-ray diffraction patterns



The structure of a binary glass by computer simulation

Due to the lack of periodicity, no tools can measure the precise arrangement of atoms in bulk glasses.

Short range order

Define a pair correlation function g(r), that measures the probability of finding another particle at distance r from a particle at the origin.

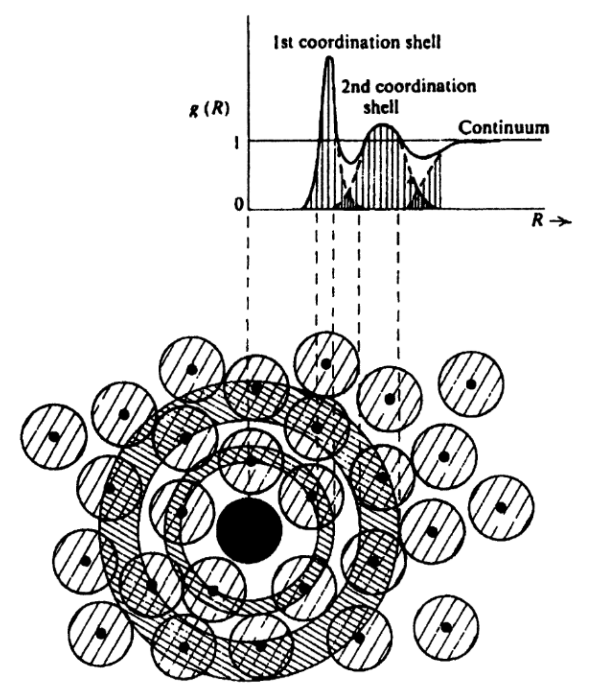


Diagram for the definition of g(r)

Experimentally, the *g(r)* can be calculated from the static structure factor *S(k)* measured in scattering experiments with equation:

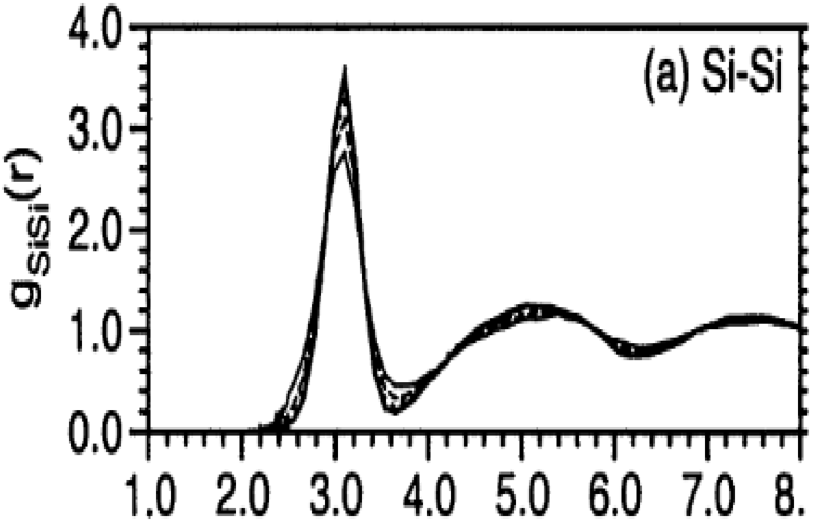
$$g(R) = 1 + \frac{1}{2\pi^2\rho}\int_0^\infty [S(k)-1]\frac{\sin kR}{kR}k^2dk$$

where S(k) is the Fourier transformation of density

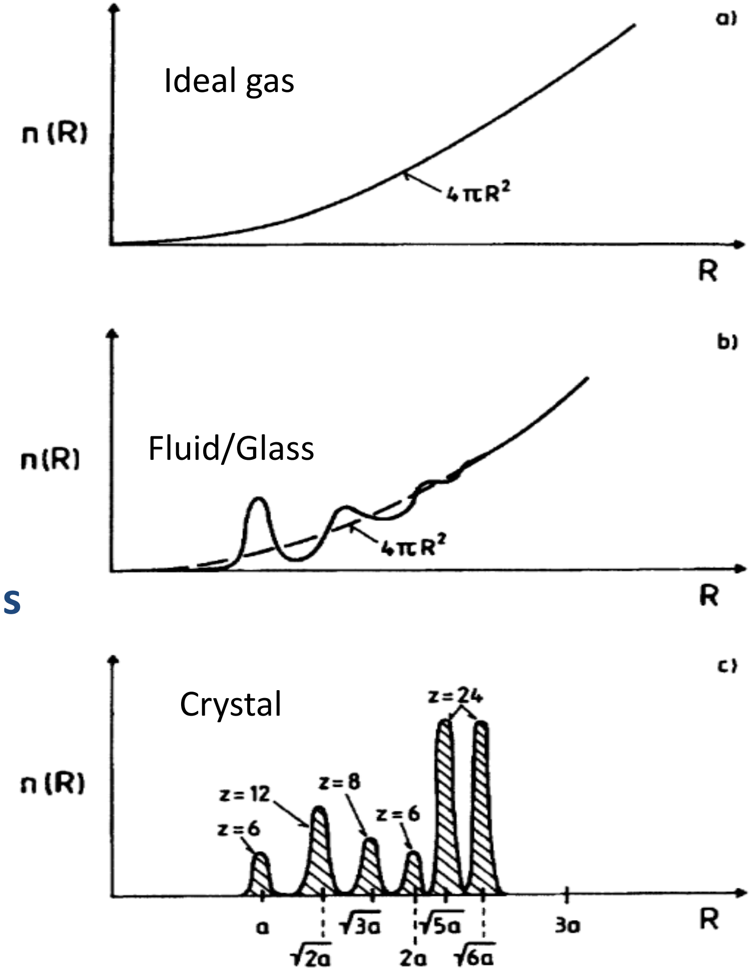
$$S(\vec{k}) = \frac{1}{N}\langle \rho_{\vec{k}}\, \rho_{-\vec{k}}\rangle = \frac{1}{N}\sum_{j=1}^{N}\sum_{l=1}\langle \exp[-i\vec{k}\cdot(\vec{r}_j - \vec{r}_l)]\rangle$$

If atoms/particles are completely randomly distributed in space, *g(R)* is a constant for all *R*s.

Short range order



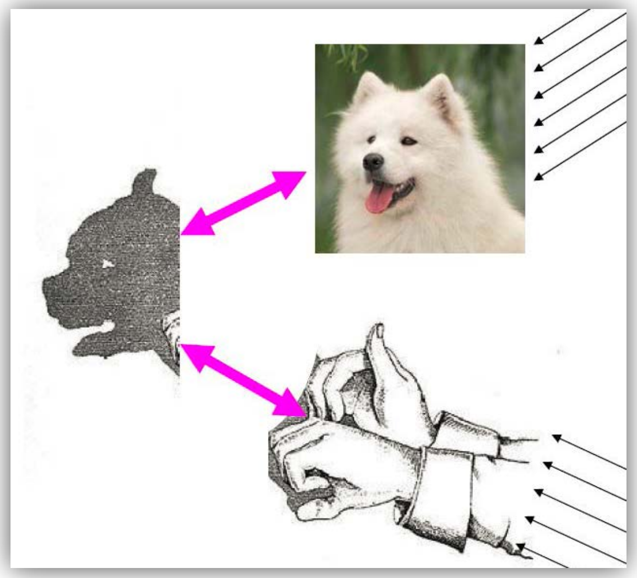
Pair correlation function between silicon atoms in silicon glass at different temperatures



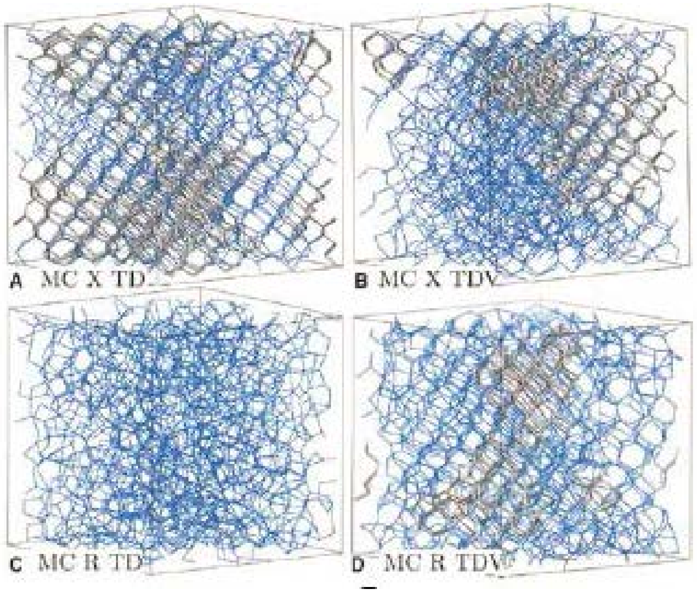
Comparison between the radial density function *$n(R) = 4\pi R^2 g(R)$* for ideal gas (completely random), glass, and crystal (regular lattice)

Pair correlation function of glasses shows that the probability of finding a particle at short distances is much higher than average, i. e. there is short range order (SRO) in glasses.

Ambiguities in g(r)

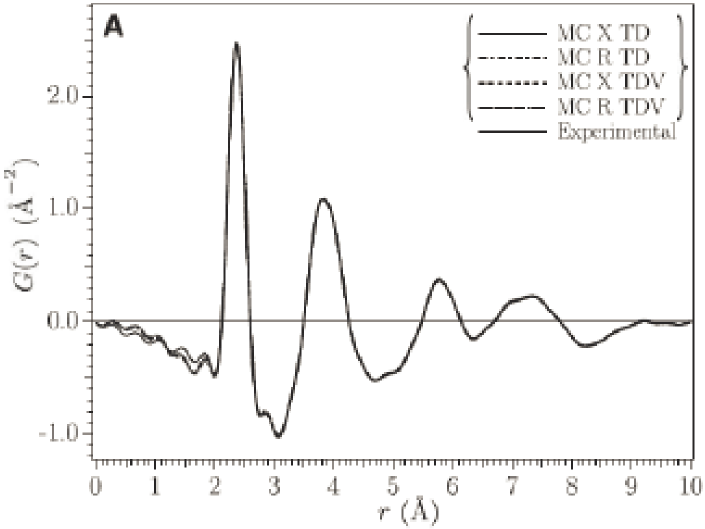


Projection to lower dimensions



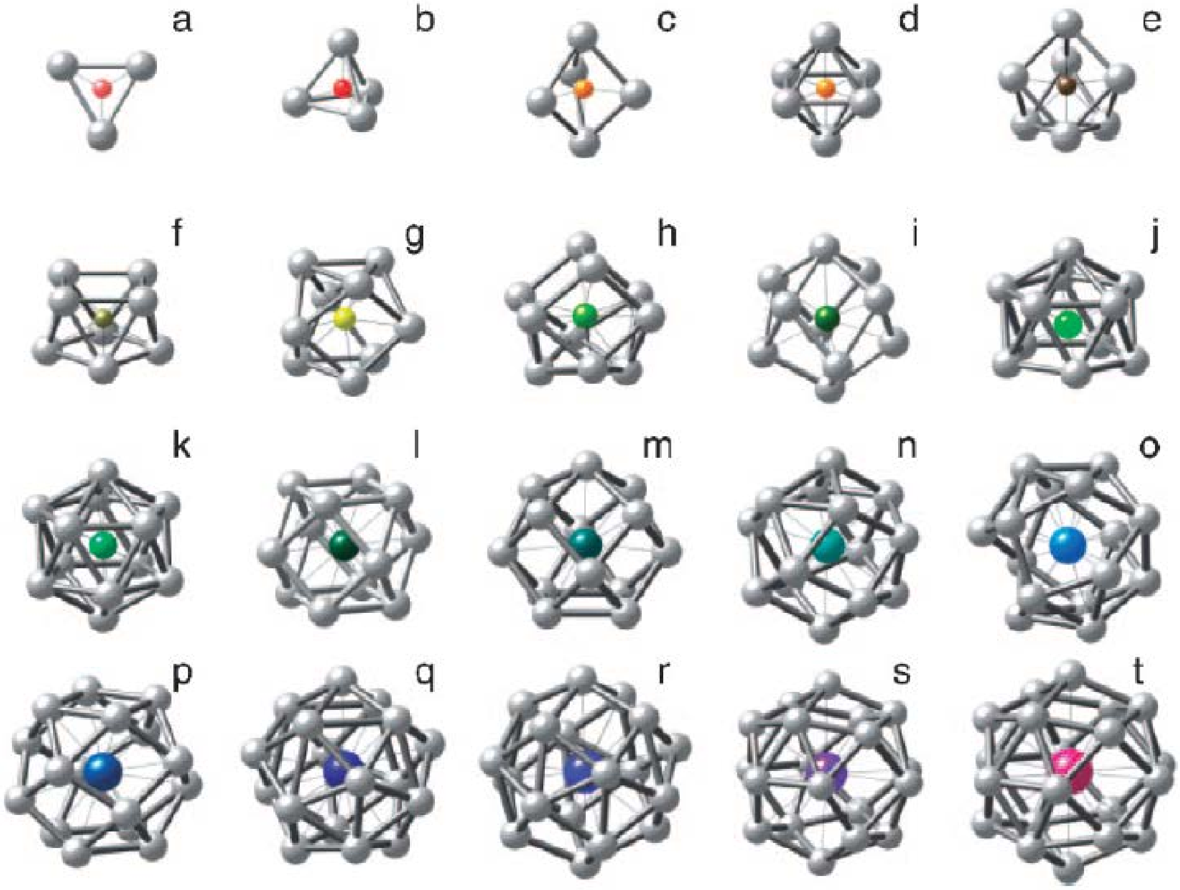
All these four different structures can result in the same g(r) curve below

Scattering information such as g(r) project the 3D structural information to a 1D curve. The g(r) can not uniquely reconstruct the 3D arrangement of atoms in glasses



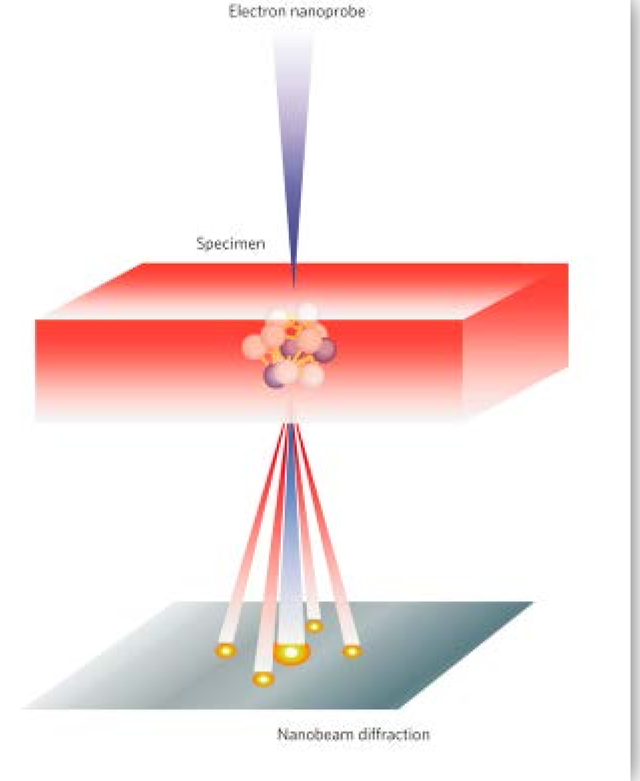
Short range order

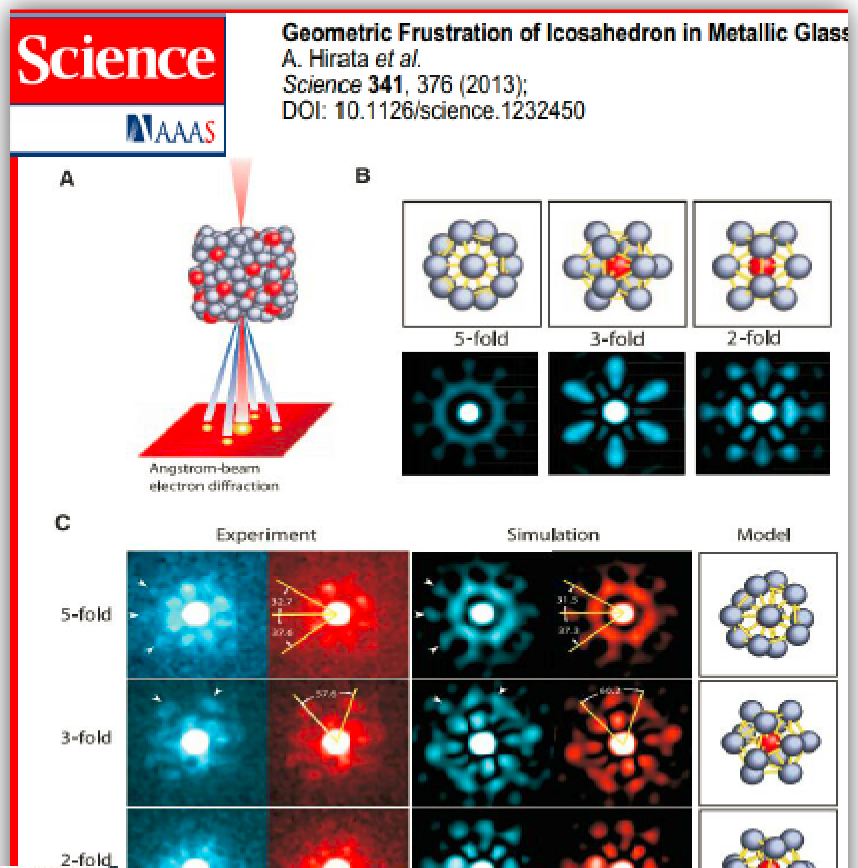
The origin of the short range order is not clear, researchers have proposed that locally atoms prefer to pack closely, which leads to SRO.



Candidate "building block" structures of closely packed atoms

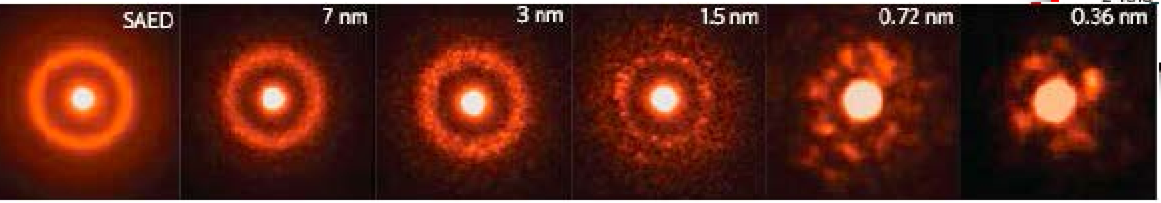
Short range order





Science AAAS

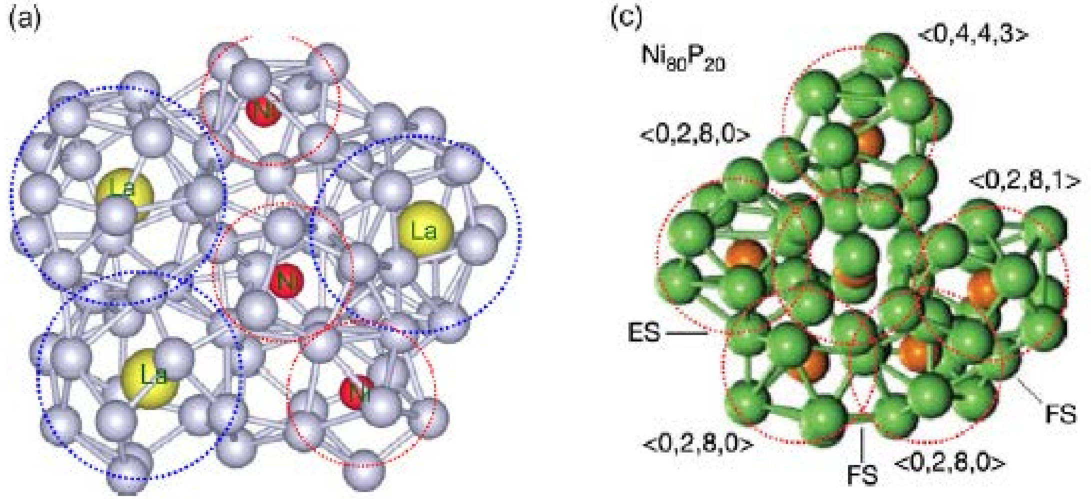
Geometric Frustration of Icosahedron in Metallic Glass
A. Hirata *et al.*
Science **341**, 376 (2013);
DOI: 10.1126/science.1232450



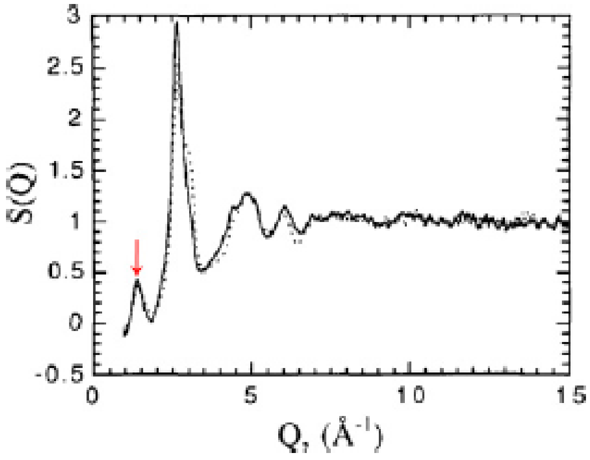
Using tightly focused electron beams, researchers are able to measure the diffraction pattern of small cluster of atoms, showing signs of short ranged order packings.

Medium range order (MRO)

If we agree that the atoms in glasses are closely packed into clusters at short range, then these clusters will continue to pack together to form medium range order.



Packing of clusters in space (simulation)

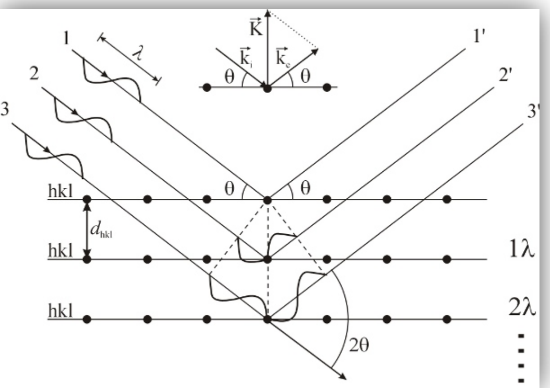


It is suggested that a small peak in the structure factor corresponds to MRO in glasses

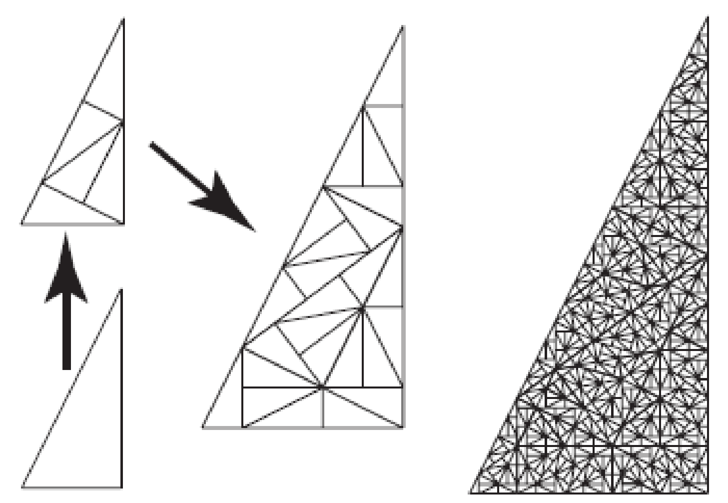
Closely packed clusters can not fill space thus will be frustrated, unable to form long range order.

Amorphous order

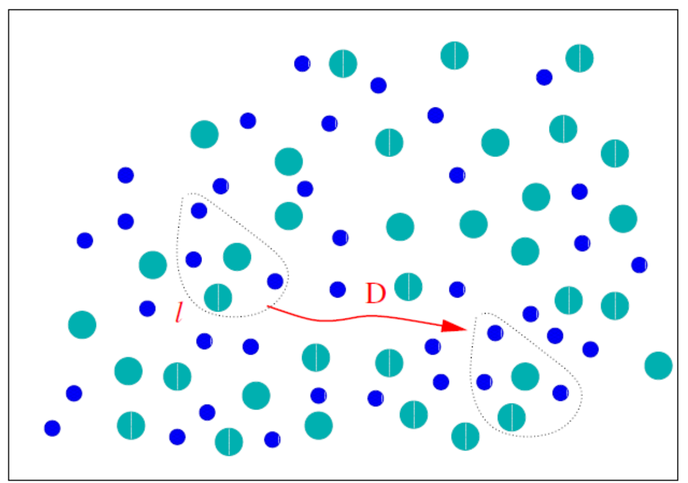
Most structure-probing techniques employs diffraction that detects "periodicity". But is it possible to have structural correlation (order) without periodicity?



Diffraction and periodicity



Long range order without periodicity



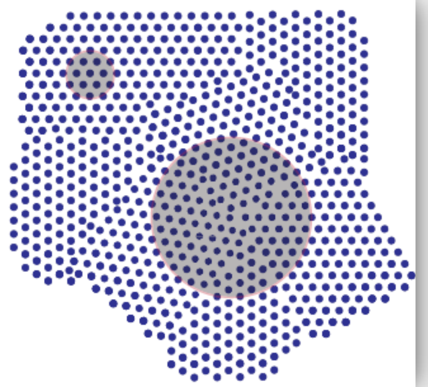
Possible order in glasses

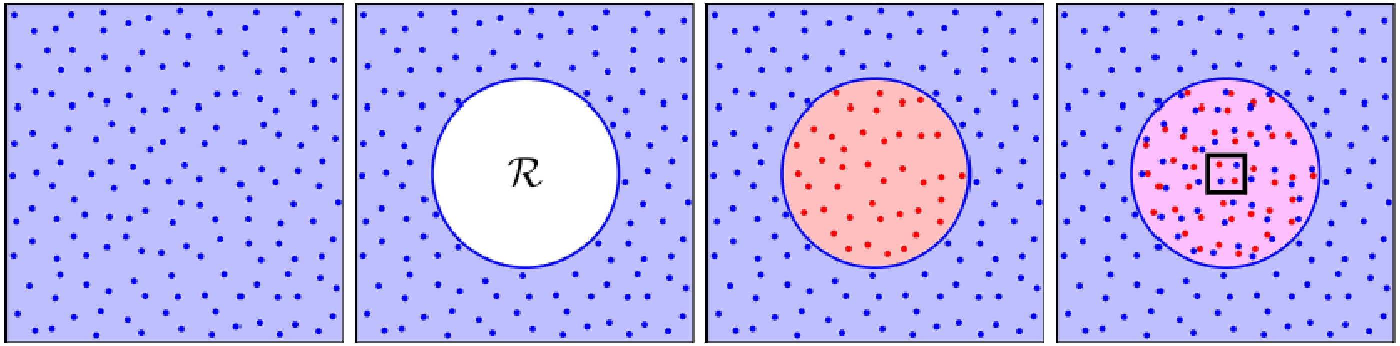
Is it possible that atoms in glasses are also arranged according to some "rules" even without the periodicity?

If allowed to fully develop, will result in structures of amorphous order.

May explain the slow down at the glass transition

Point-to-set correlations





(a) Pick an equilibrium configuration $\mathbf{X}_1$.

(b) Fix the configuration $\mathbf{X}_1^{\text{out}}$ outside a region $\mathcal{R}$.

(c) Pick a new conditional equilibrium configuration $\mathbf{X}_2$ with $\mathbf{X}_2^{\text{out}} = \mathbf{X}_1^{\text{out}}$.

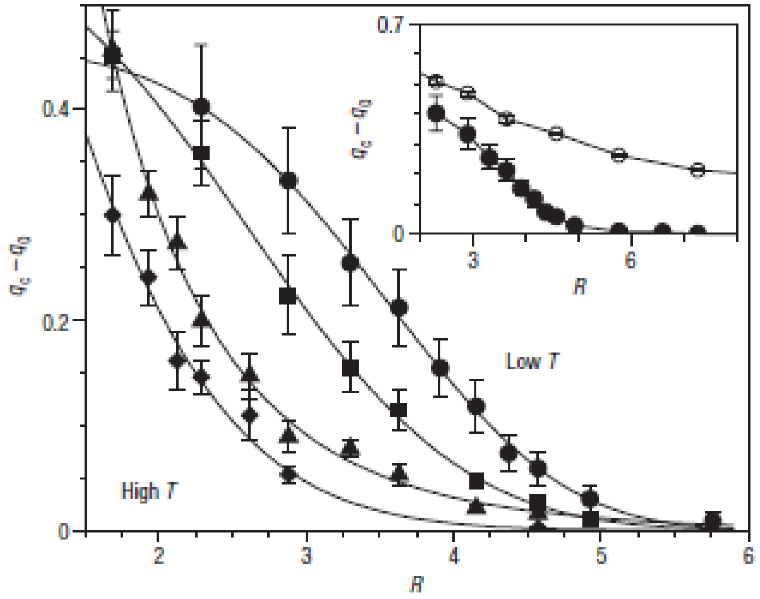
(d) Compare two configurations $\mathbf{X}_1^{\text{in}}$ and $\mathbf{X}_2^{\text{in}}$ in a cell $\mathbf{c}_*$ centered inside the region $\mathcal{R}$.

In a single crystal domain, the position of particles are uniquely determined by the spatial correlation with other particles in the same domain. For length scales greater than the domain size, such correlation decreases rapidly.

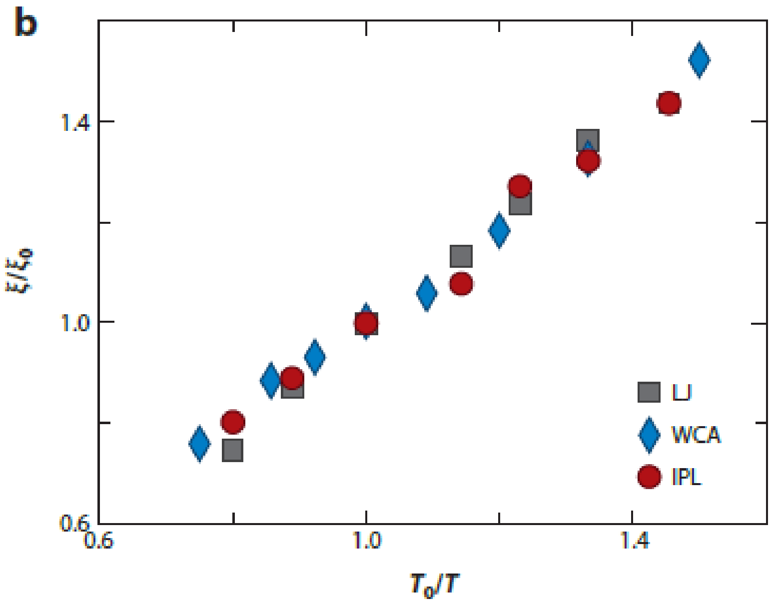
If amorphous order does exist in glasses or during glass transitions, it can be detected by examine the point-to-set correlation over a certain lengthscale.

In a supercool liquid, we first freeze particles outside of a sphere with radius R, if the structure of the particles inside and out side of the sphere are strongly correlated, then the positions of the particles inside the sphere will be uniquely determined by the boundary

Point-to-set correlations



Overlap function for different temperatures

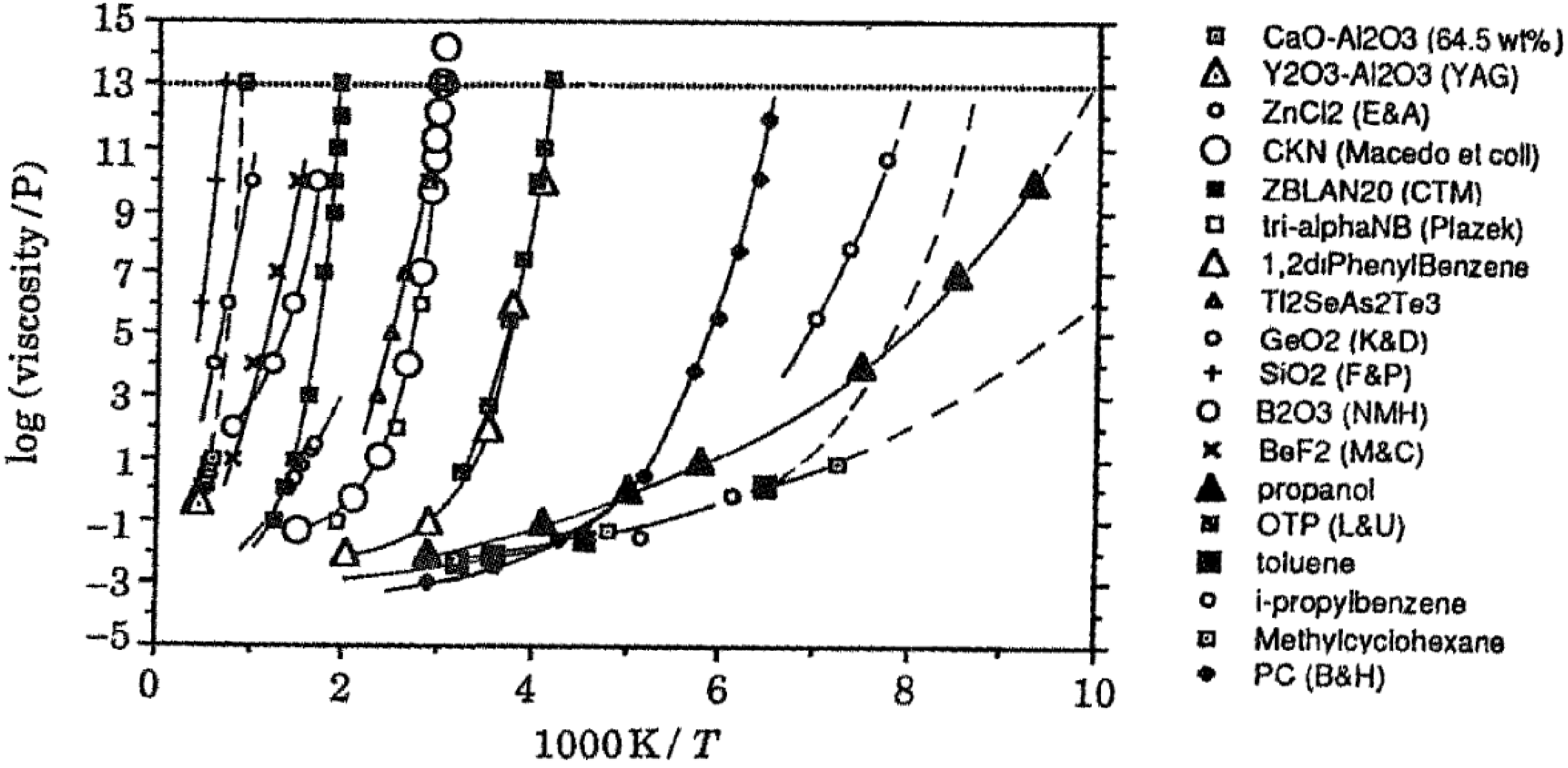


Correlation length extracted from overlap functions

Computer simulations have shown that well above the glass transition temperature, point-to-set correlations are observed, and the correlation length scale increase as the temperature is lowered.

Dynamics of glasses

The first sign of unusual physics in glasses is the relaxation time.



Relaxation time near melting point T_m ~ picoseconds.

Relaxation time near the glass transition T_g ~100 seconds.

T_g ~1/3 T_m, temperature alone can not explain.

Viscosity increases drastically $\eta = G\tau$ by 14 orders of magnitude in a small temperature window.

Pouring a cup of …

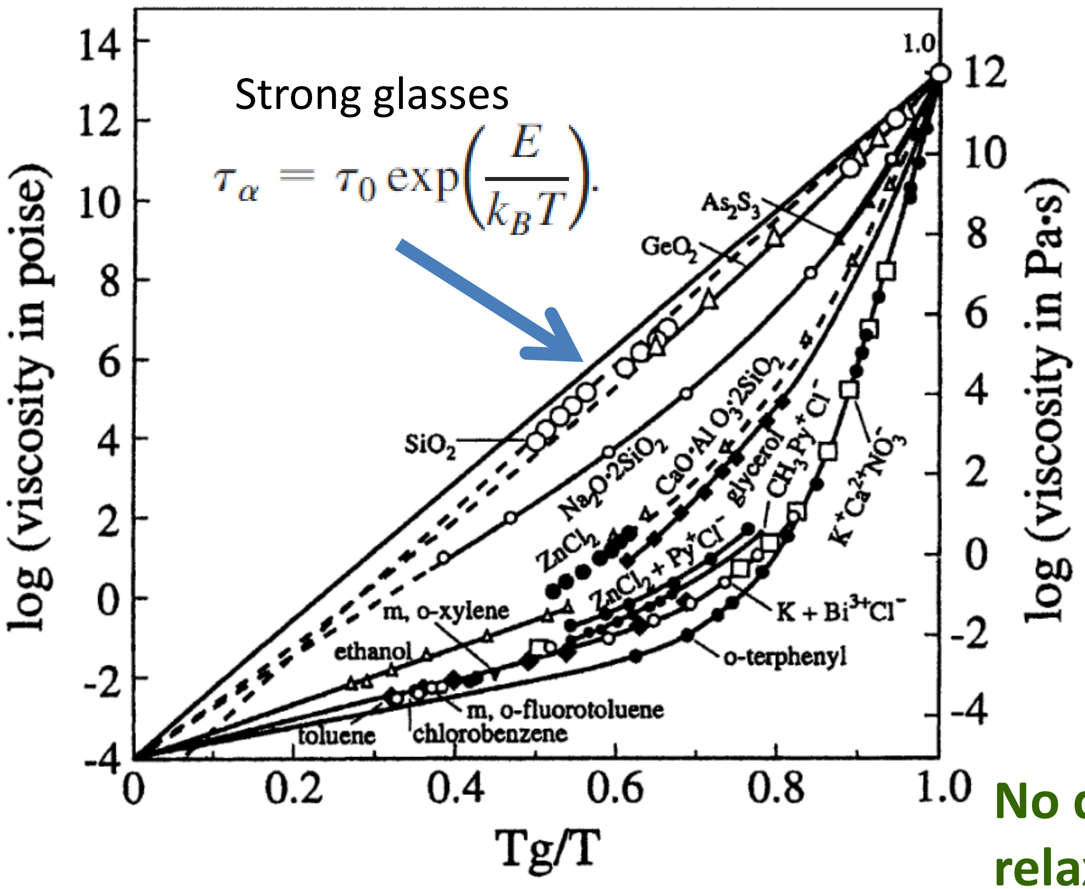
Water
Viscosity 10^{-3} Pa s
A few seconds

Honey
Viscosity 10s Pa s
~ minute

Tar
Viscosity 10^{10} Pa s
~ 100 years

Fluid at glass transition
Viscosity 10^{12} Pa s
~ 300 years

Dynamics of glasses



Strong glasses

$$\tau_\alpha = \tau_0 \exp\left(\frac{E}{k_B T}\right).$$

$$\tau_\alpha = \tau_0 \exp\left[\frac{DT_0}{(T - T_0)}\right],$$

VFT law

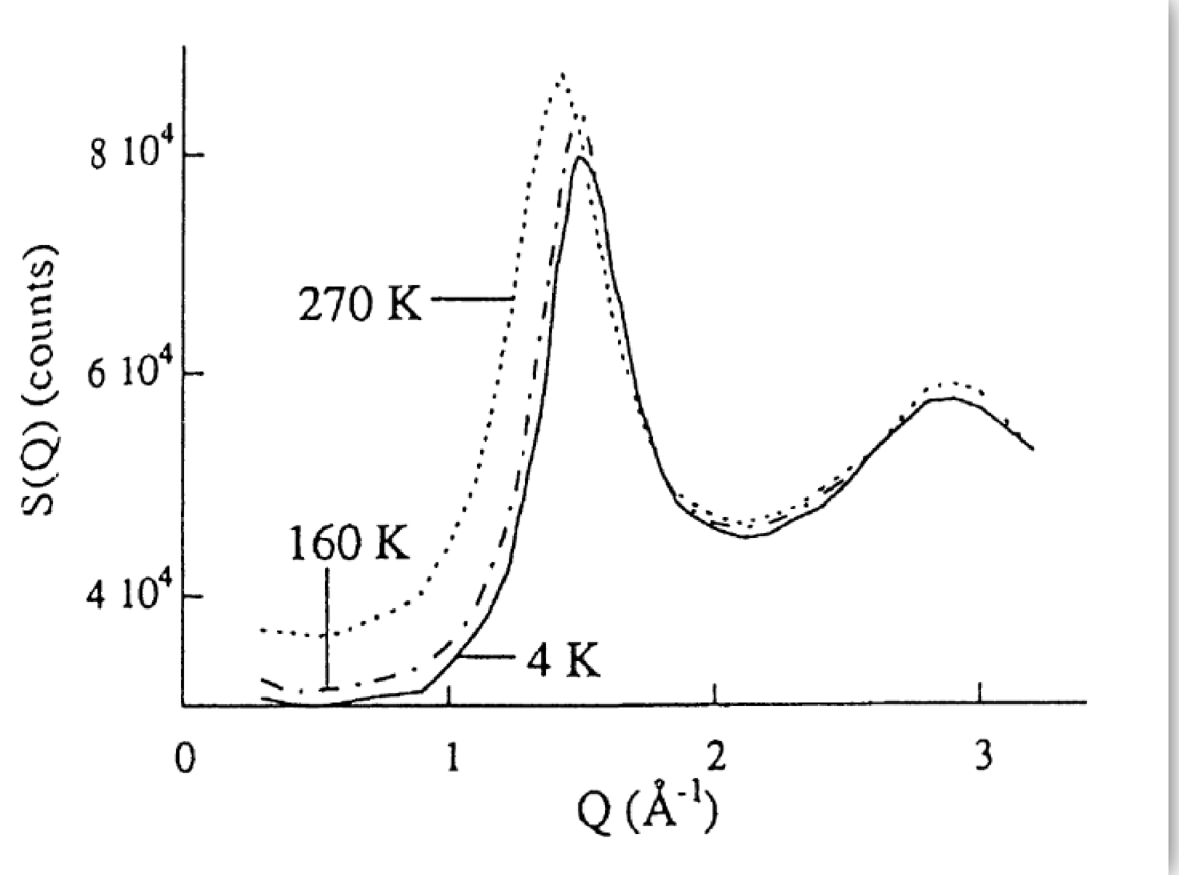
$$\tau_\alpha = \tau_0 \exp\left[K\left(\frac{T_*}{T}\right)^2\right],$$

Bassler law

No definitive answer if the relaxation time will truly diverge?

A straight line correspond to a constant activation energy, called strong glass formers.
A curved ling correspond to a progressively increasing activation energy, thus known as fragile glass formers.

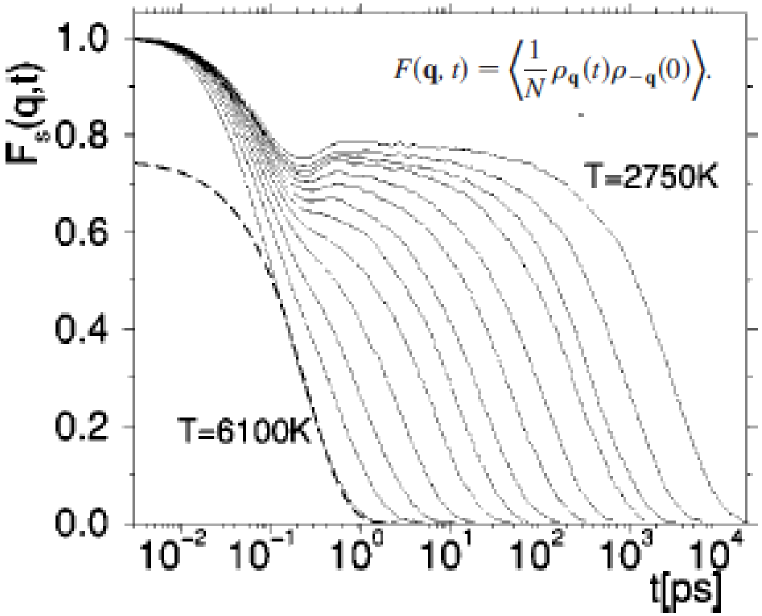
Dynamics and Structure



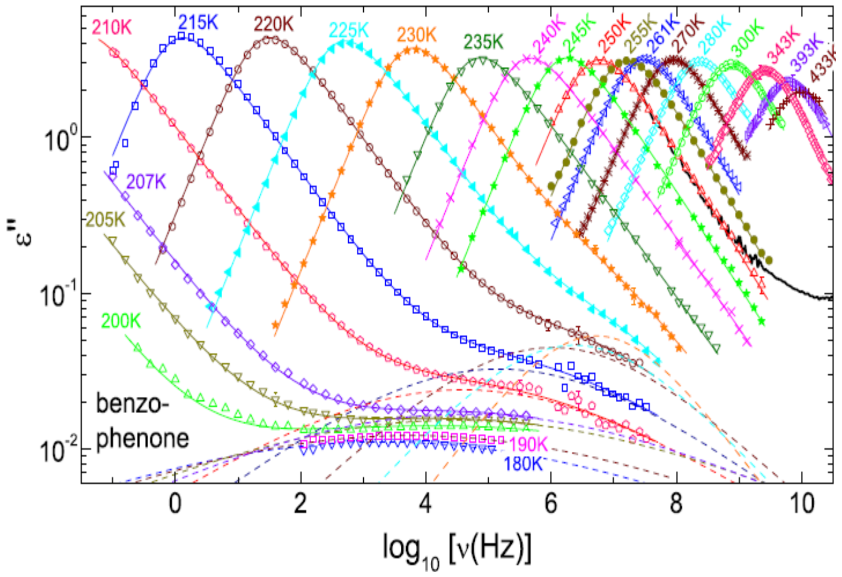
Structure factor of liquid and glassy states for polybutatdiene

As the dynamics dramatically slow down for more than 10 orders of magnitude, the structure of a glass is essentially indistinguishable from that of a fluid.

Different time scales



Intermediate scattering function in silica glass

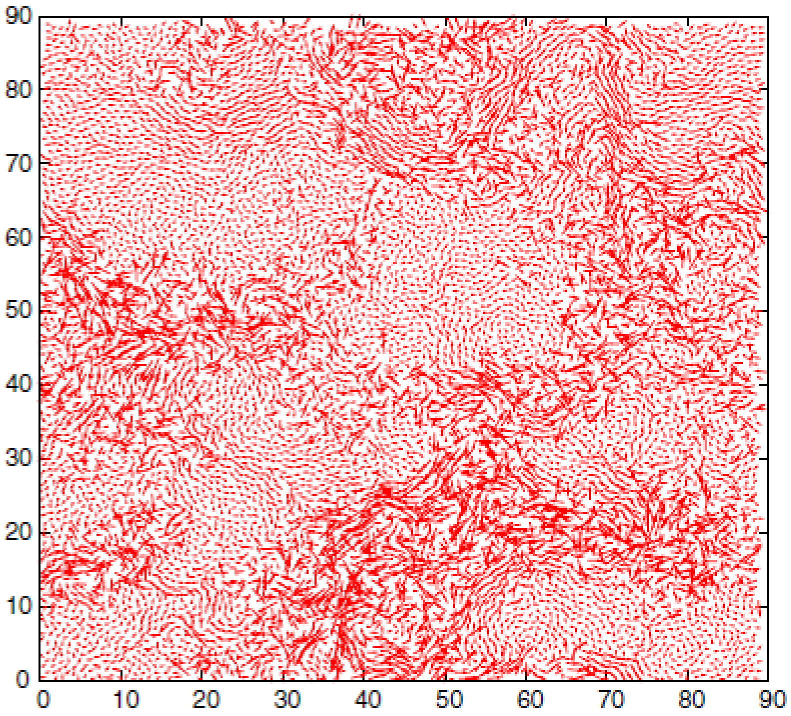


Dielectric susceptibility of benzophenone

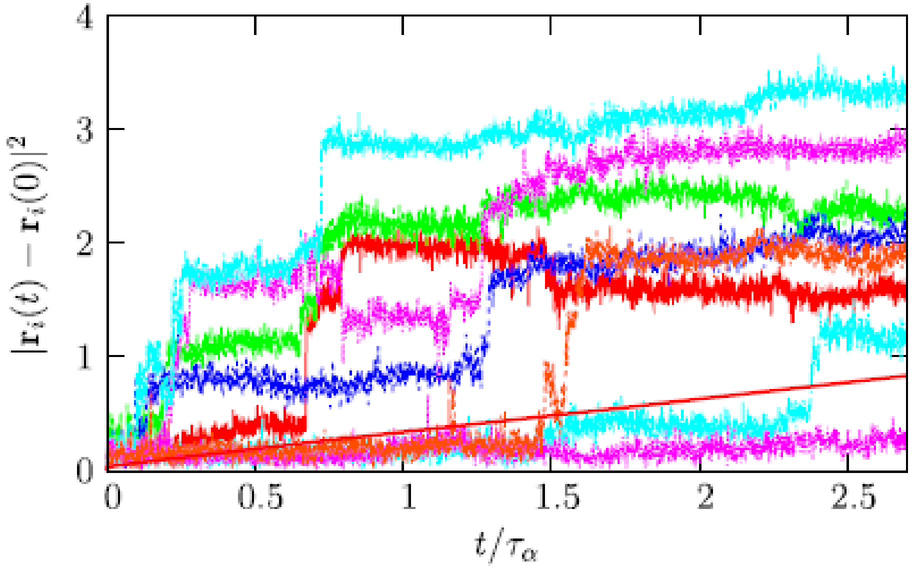
As a fluid is cooled down, two different relaxation time scales begin to appear.

The fast relaxation process are known as β-relaxation and the slower relaxation process are called α-relaxation.

Dynamical heterogeneity



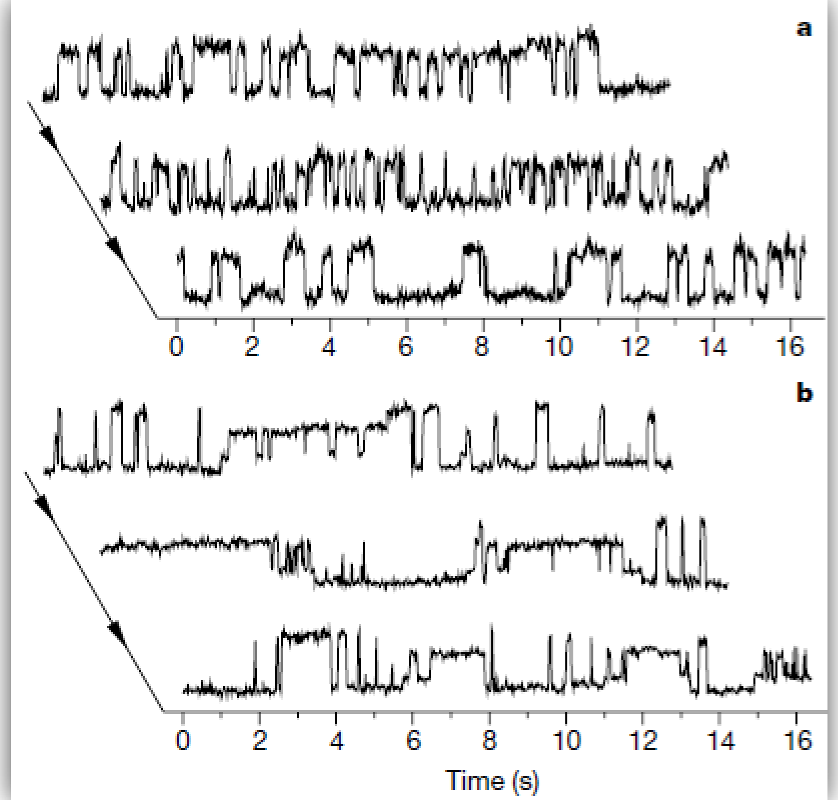
Particle displacements over a constant time interval in a 2D binary mixture.



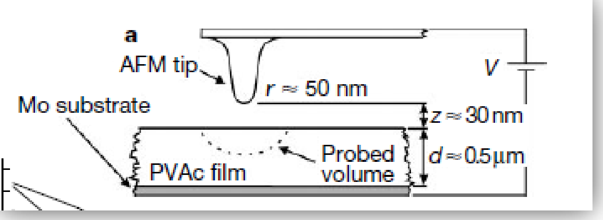
Particle displacements of individual particles over time.

Different parts of the glass/supercool liquid relax differently, some particle moves much faster than other particles. This phenomenon is known as 'dynamical heterogeneity'

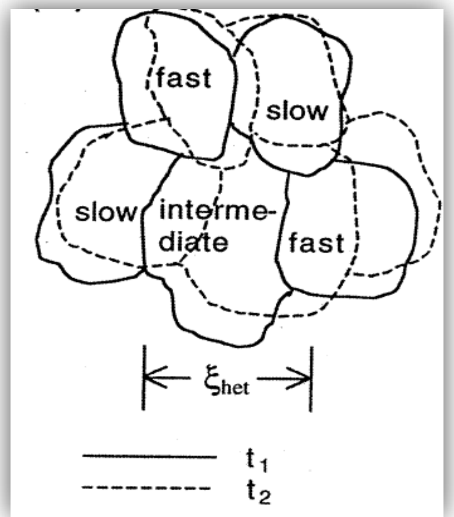
Dynamical heterogeneity



Time series of polarization at two temperatures. a) at 299 K and b) at 300 K



Probing the dielectric fluctuations of PVA on nanometer scale using AFM.



Dynamics vary with space and time

Dynamical heterogeneity is not only observed spatially, but also temporally (Vidal et al, **Nature** 2000)

Growing dynamical heterogeneity

To evaluate the dynamical correlation between two points, define a two-point correlation function.

$C_o(\mathbf{r}, t) = [o(\mathbf{x}, t = 0)o(\mathbf{x} + \mathbf{r}, t)]_{\mathbf{x}},$ where o(x,t) can be any observable in space and time

Note C(r, t) depends on the particular position x, for each point in a glass, a C(r, t) can be measured.

If dynamics is homogeneous, the C(r, t) measured at each point should be the roughly same. If the dynamics is heterogeneous, the measured C(r, t) will have significant fluctuations. Define local variance function

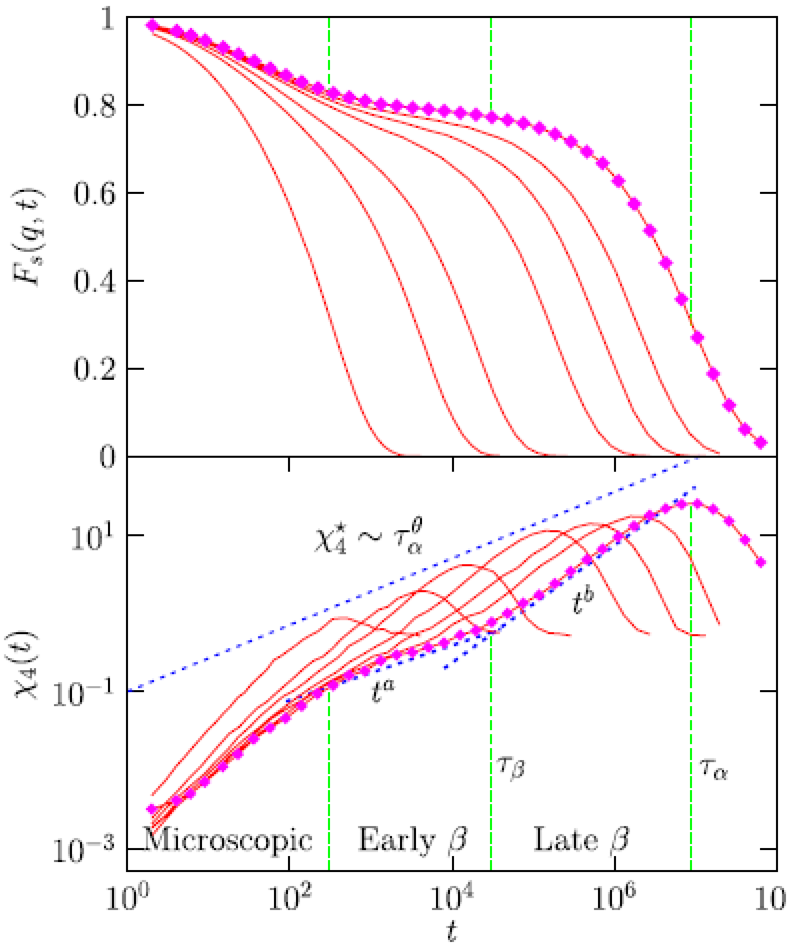
$$G_4(\mathbf{y}, t) = [o(\mathbf{x}, 0)o(\mathbf{x} + \mathbf{r}, t)o(\mathbf{x} + \mathbf{y}, 0)o(\mathbf{x} + \mathbf{y} + \mathbf{r}, t)]_{\mathbf{x}} - [o(\mathbf{x}, t = 0)o(\mathbf{x} + \mathbf{r}, t)]_{\mathbf{x}}^2, \qquad (20)$$

Its spatial integral $\Sigma_C^2 = \frac{1}{V}\int d\mathbf{y} G_4(\mathbf{y}, t),$ reflects the fluctuation within a volume of V

Set r = 0, we obtain $\chi_4(t) = N\Sigma_C^2.$

χ_4 reflects the variance of local time correlation funcition

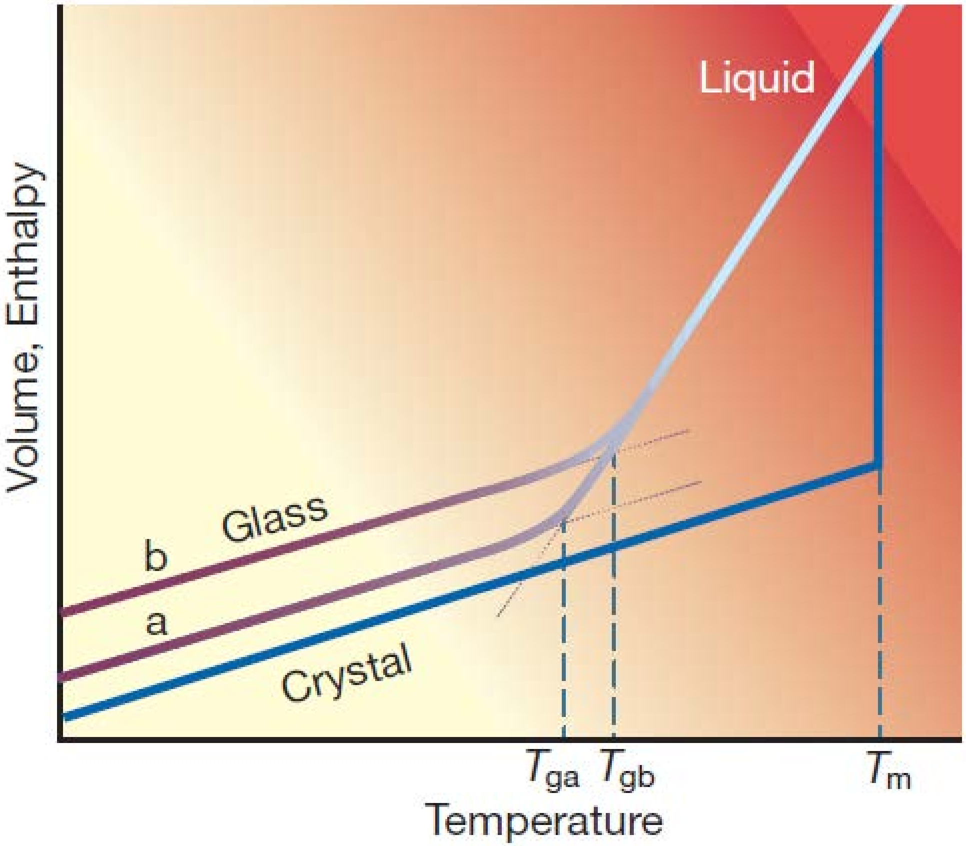
Growing dynamical heterogeneity



The peak in χ_4 indicate the time scale at which the dynamics is most heterogeneous, and the actual high of χ_4 is proportional to the number of particles whose dynamics are correlated.

As the temperature decreases, both the length scale and time scale of DH grows

Thermodynamics



Formation of glasses is a non-equilibrium process, depending on the cooling rate.
A faster cooling rate results in higher transition temperature.
The specific heat changes abruptly but continuously at T_g, no phase transition

Entropy crisis

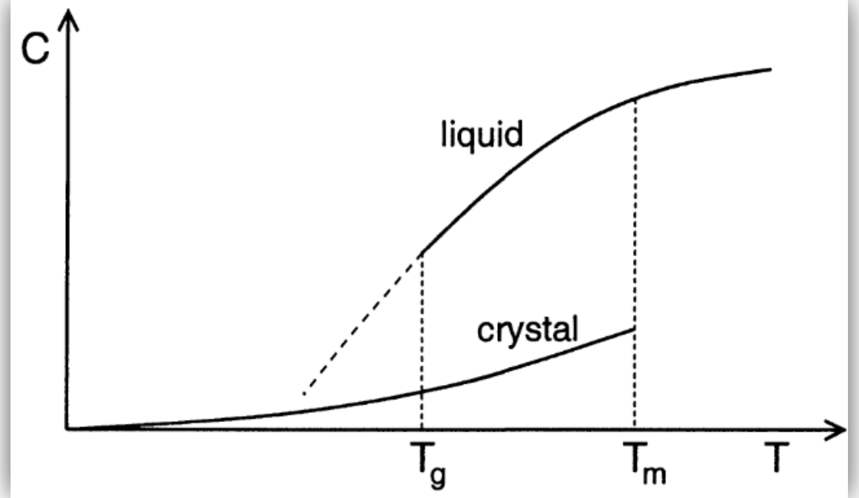
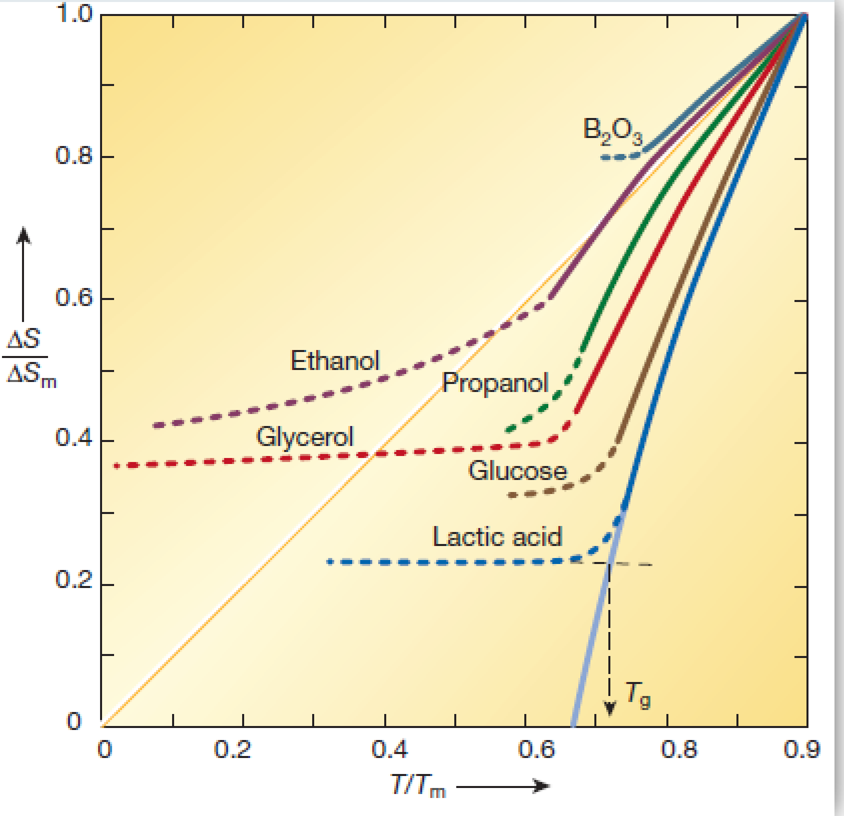


Diagram of specific heat of liquid and crystal

$$\Delta S_m = \int_{T_K}^{T_m} \frac{\Delta C_p}{T} \, dT$$

Kauzmann Temperature



Entropy difference between supercool liquid and corresponding crystal

Supercool liquid has high specific heat than crystal, if continue to cool down a supercool liquid, at some point, the entropy of the liquid (disordered)will be lower than that of a crystal (ordered). The system avoids the entropy crisis by glass transition.

Energy landscape

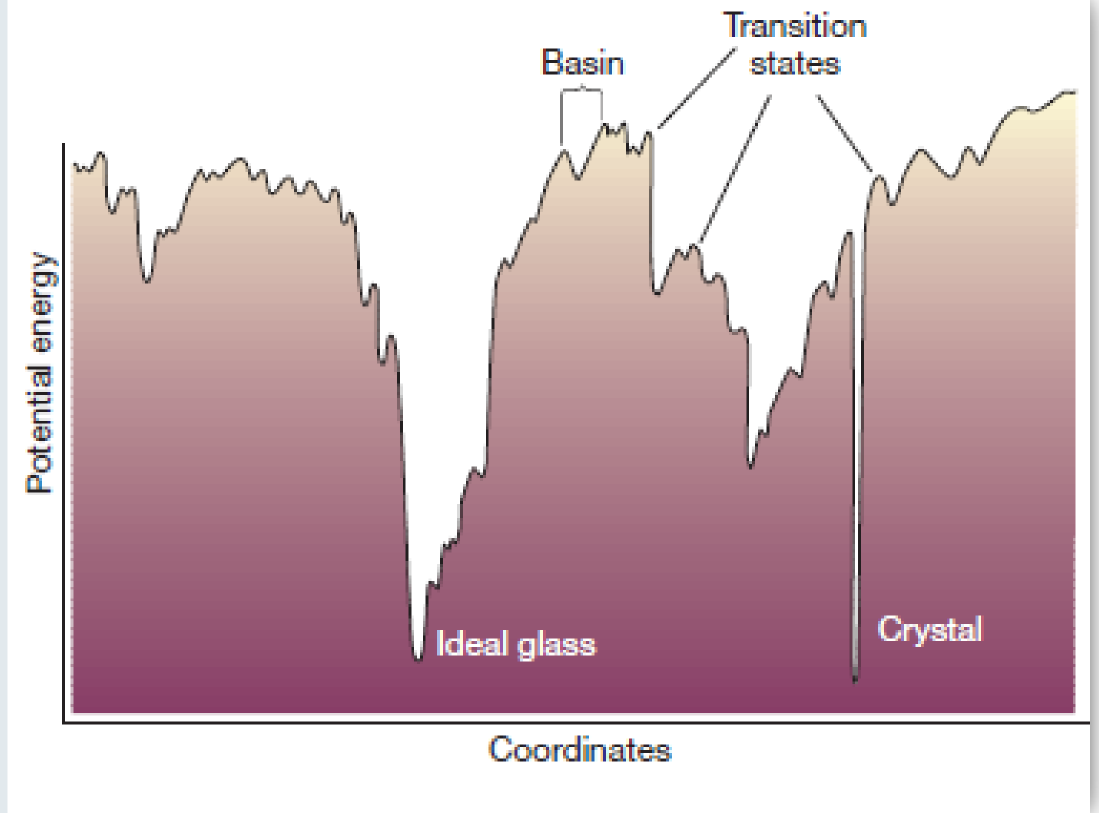
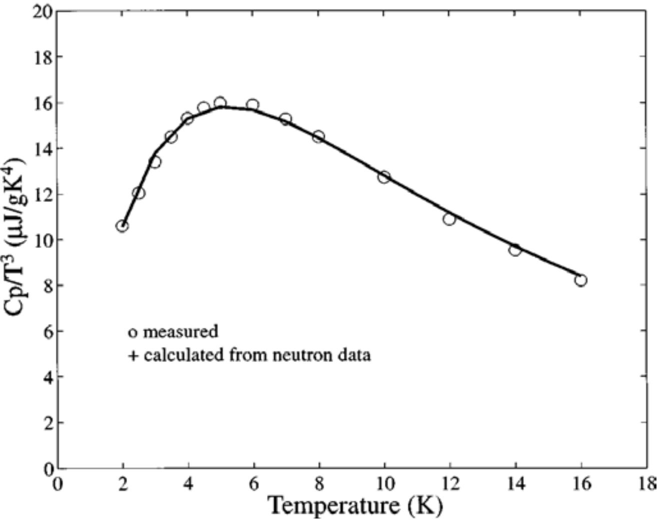


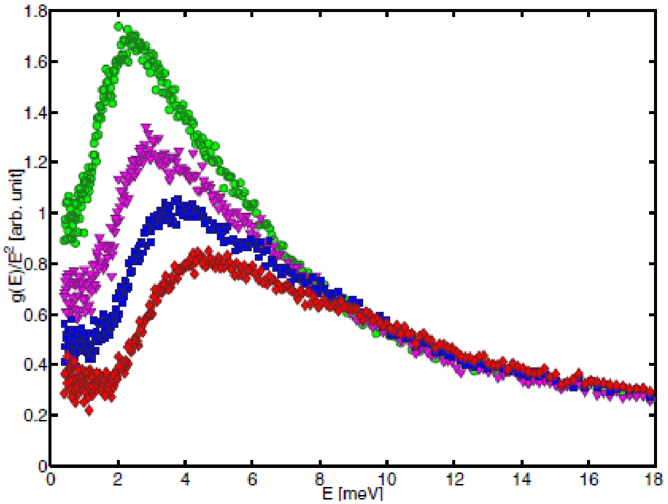
Diagram of an energy landscape

Supercool fluid has ‘rugged’ potential energy landscape corresponding to different configurations.
When slowly cooled, the system can sample all possible configurations and find the one with lowest energy. When rapidly quenched, the system is stuck at some local basin on the energy landscape.

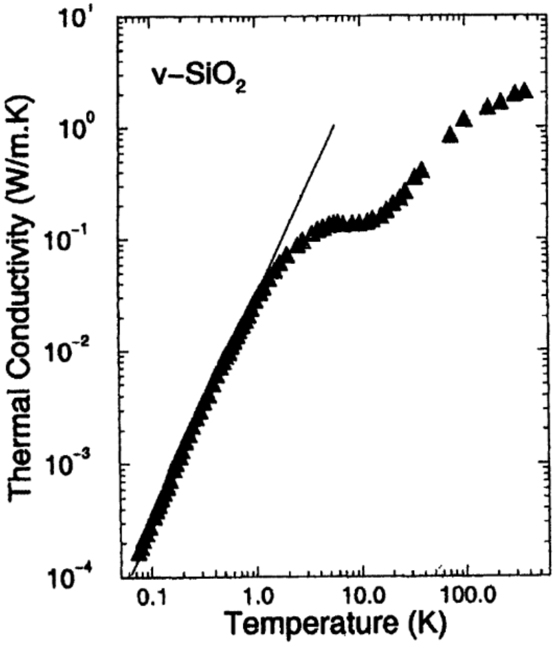
Abnormal low frequency vibrations



Specific heat



Phonon density of states

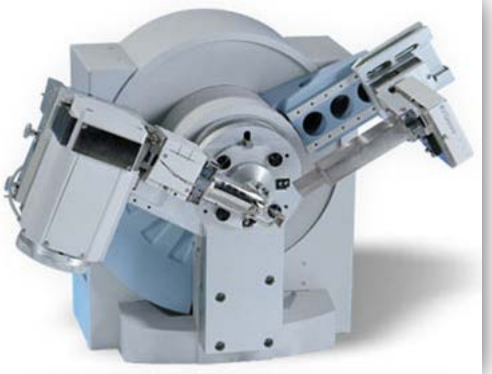


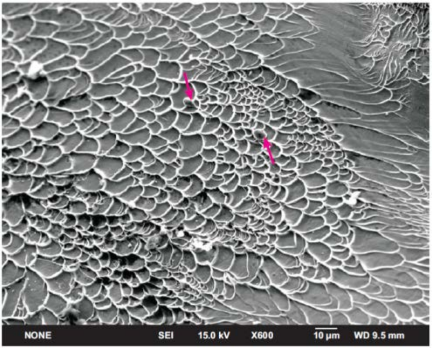
Thermal conductivity

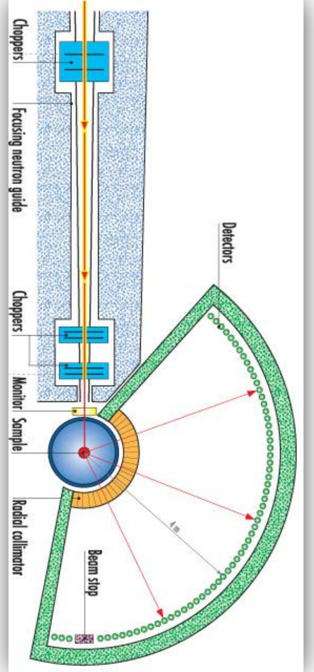
In solid state physics, Debye predicts that the phonon density of states increases with frequency with $D(\omega) \sim \omega^{d-1}$, correspondingly, the specific heat increases with temperature by T^3, and the thermal conductivity increases with temperature by T^2.

All these predictions fails at the low frequency regime of glasses, indicating unusual low frequency vibrational modes.

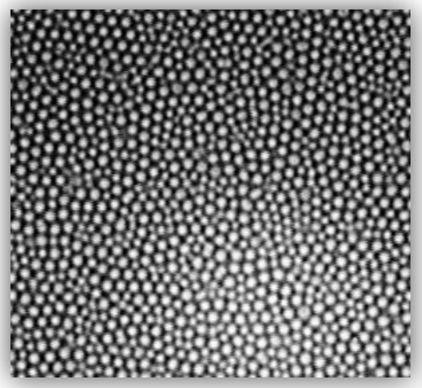
Studying glasses with colloids

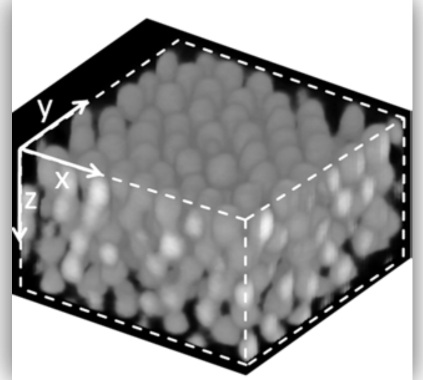


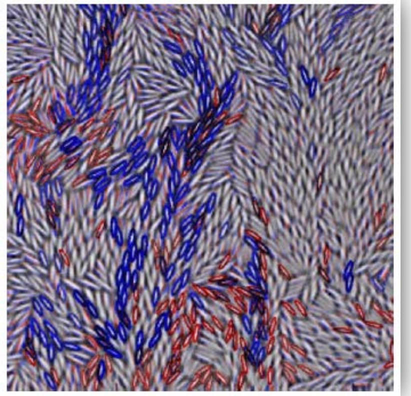


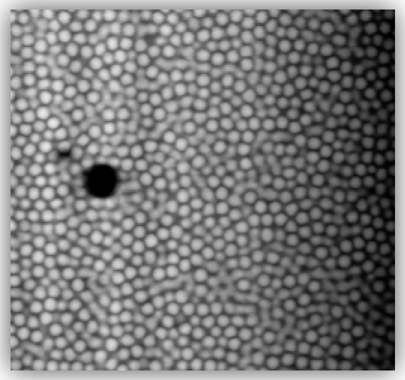


Conventional material research methods only obtain averaged results from bulk samples, even when local information is available (e. g. STM) the large picture is lost.



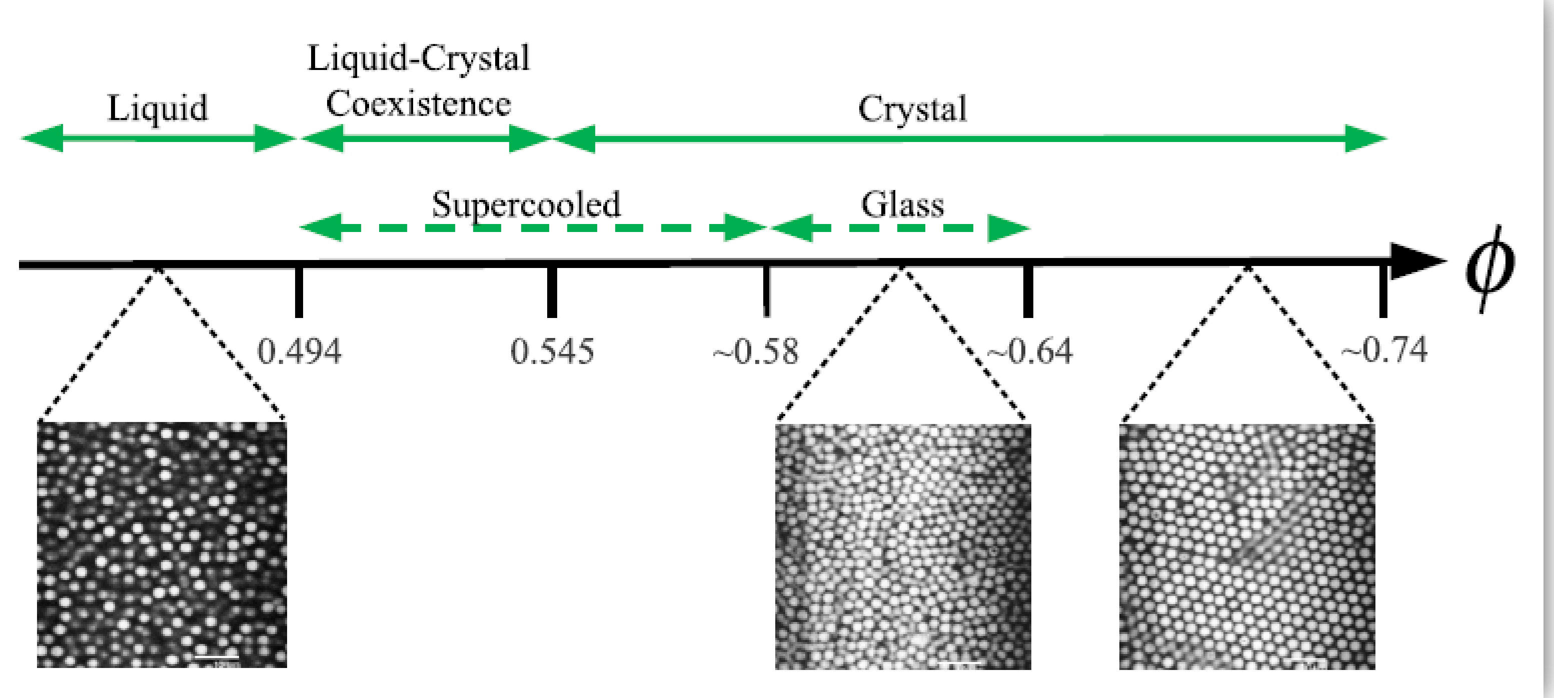






Colloids, on the other hand, offer visibility, sub-atomic structural information, statistically significant, easy to control.

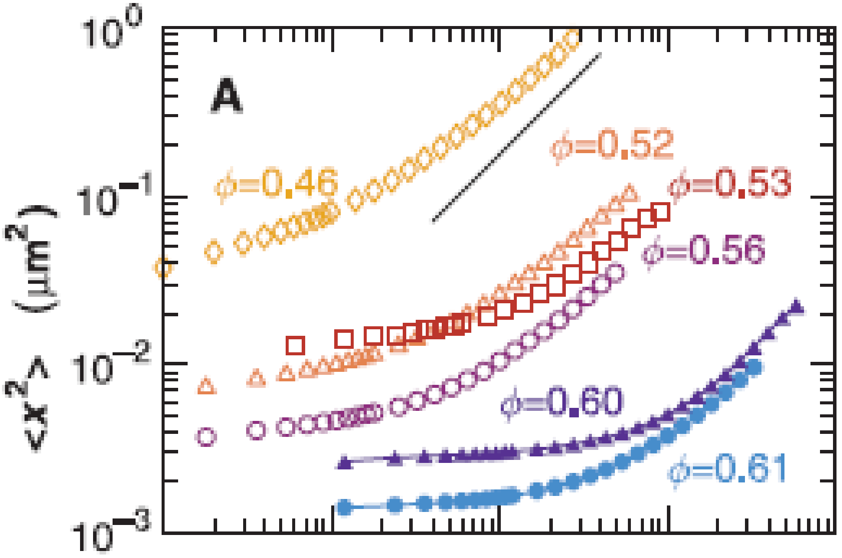
Phase diagram



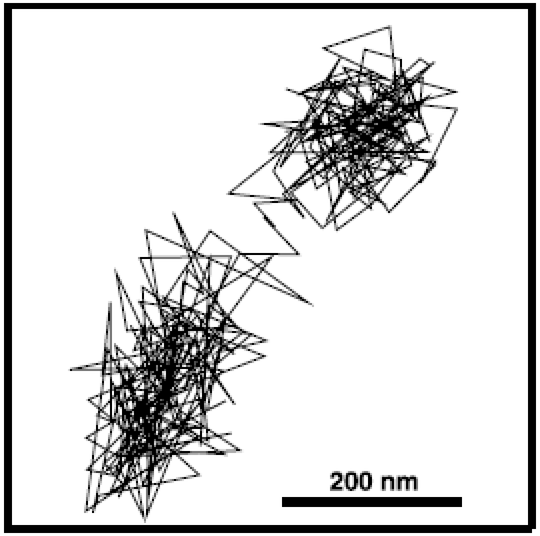
Phase diagram of monodispersed hard spheres

Volume fraction or entropy is the main driving force for phase behaviors in colloidal systems, including glass transition.

Dynamical heterogeneity



Slowing dynamics: mean square displacements for colloidal particles at different packing fractions

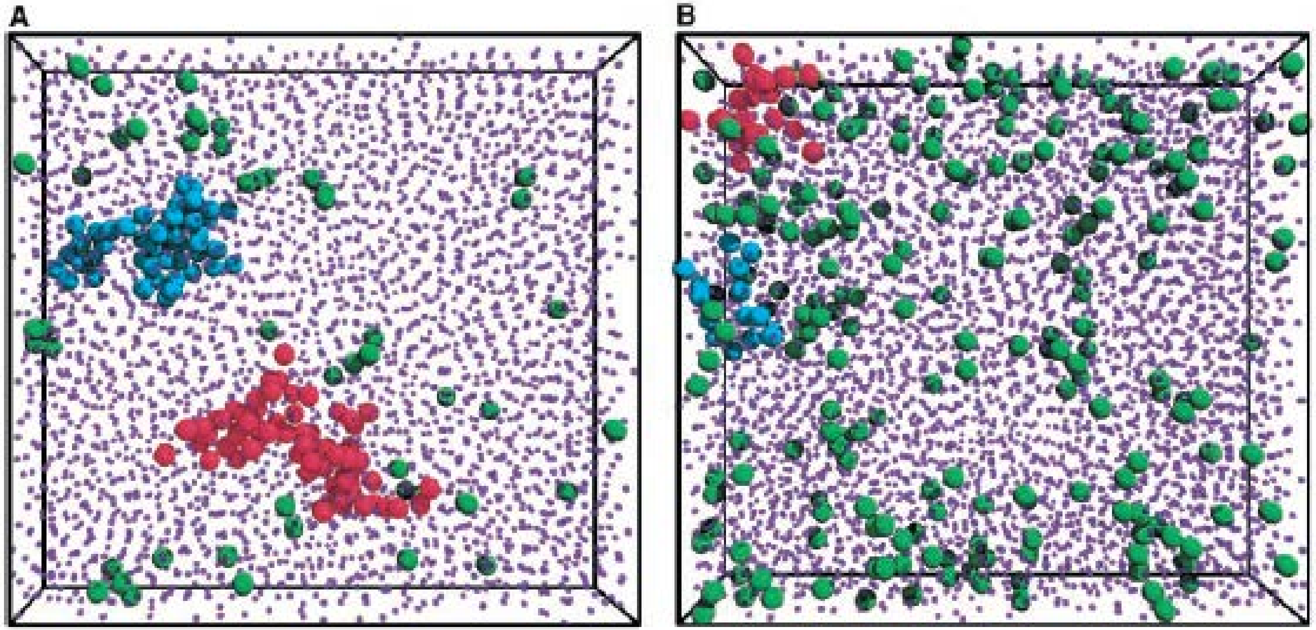


Caging effect: trajectory of a particle in a colloidal glass

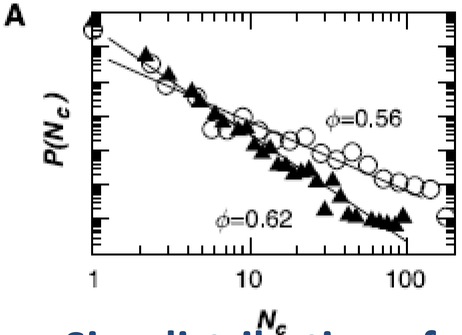
Eric Weeks et al. studied the dynamics of 3D colloidal supercool liquids and glasses using confocal microscopy.
Slow and fast dynamics correspond to the caging and jumping between cages of particles.

(Weeks et al, **Science** 2000)

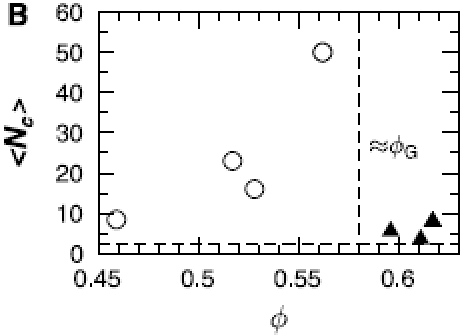
Dynamical heterogeneity



Spatial distribution of fast particles



Size distribution of dynamically correlated clusters

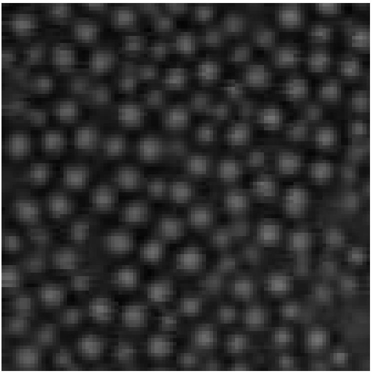


Average size of correlated clusters

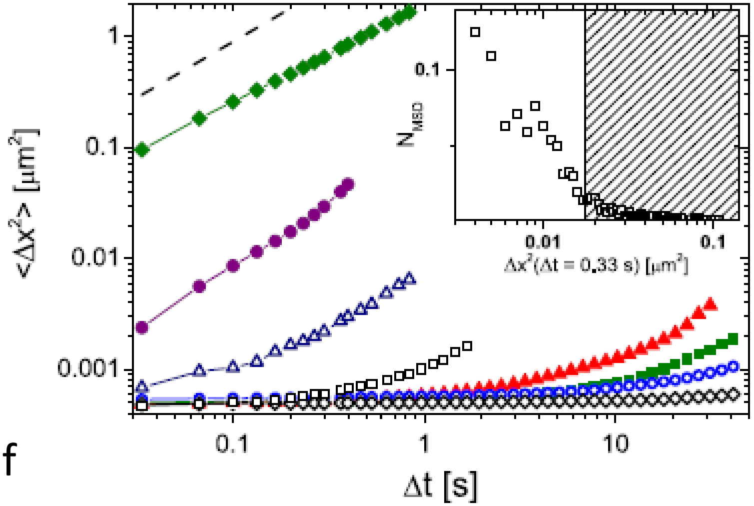
Fast particles are spatially correlated, the size of the clusters grows when approaching glass transition, and drops significantly after glass transition

Aging of glasses

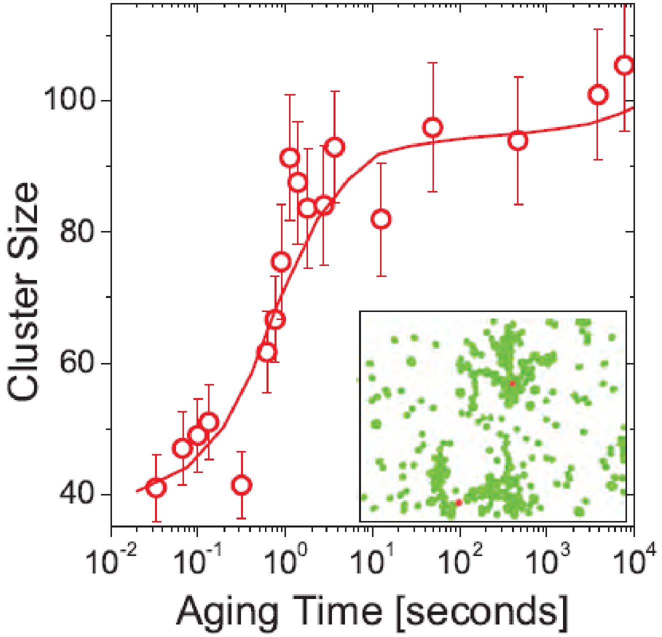
The property of a glass evolves even after completely cooled down, a phenomenon known as aging.



Rapid quenching of a colloidal glass



Mean square displacements of a glass after quenching

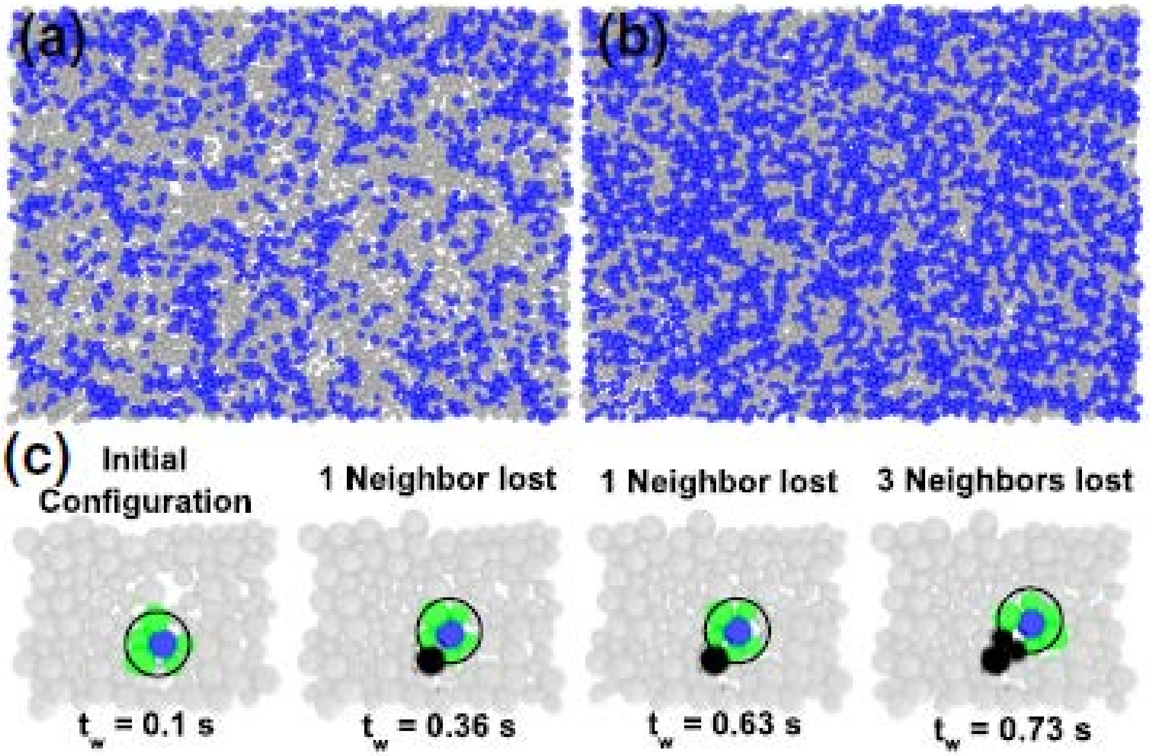


Size of dynamically correlated clusters (faster particles)

After quenching, the dynamics of colloidal glasses rapidly slows down, at the same time, the size of dynamically correlated clusters increases, which in turn makes further rearrangements more difficult.

(Yunker et al, **PRL** 2009)

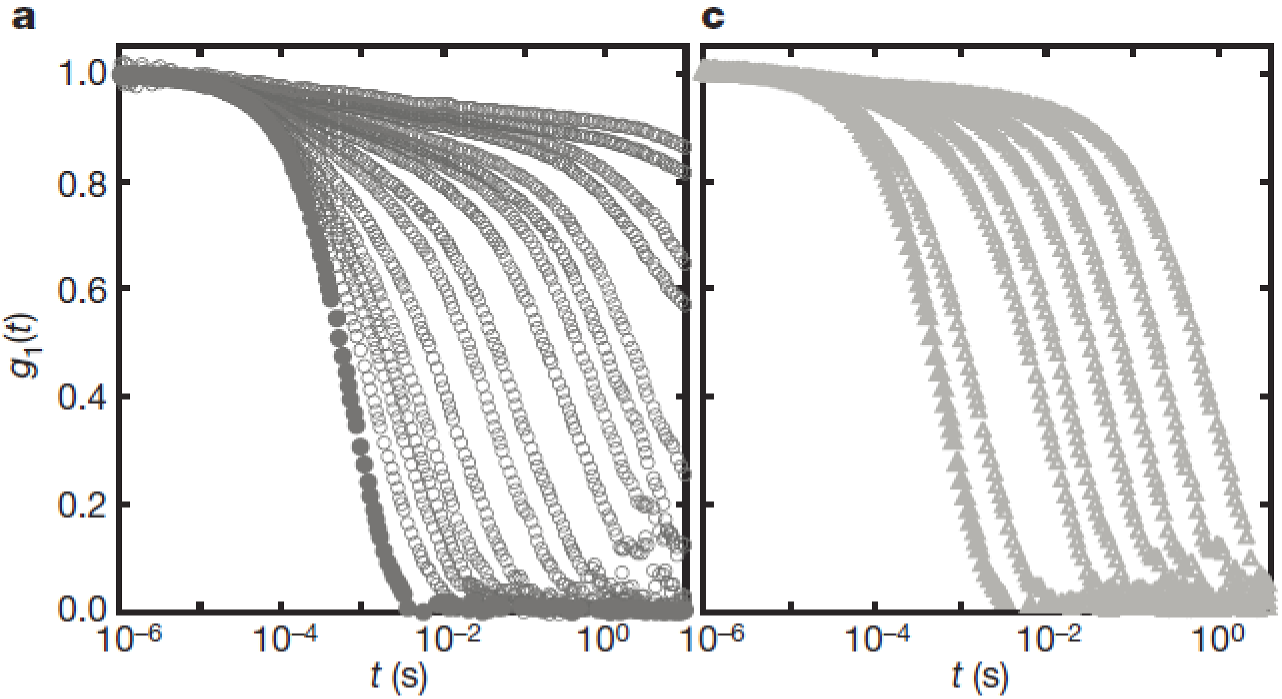
Aging of glasses



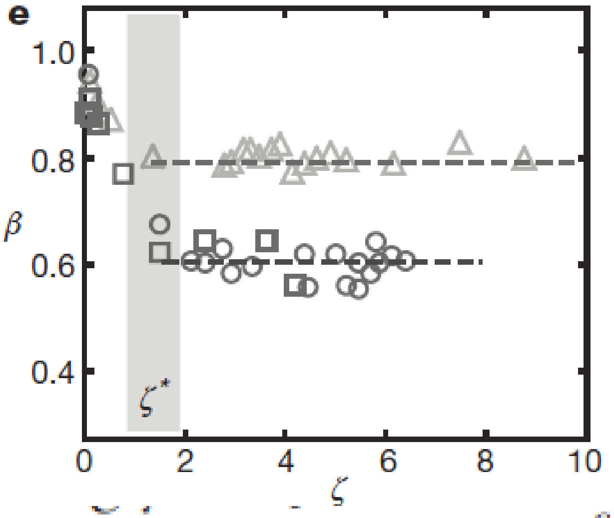
Local structure of colloidal glasses at different aging times (blue color indicate 6 neighbors) and an example of an irreversible rearrangement

The local structure of glasses becomes more ordered after aging through irreversible rearrangements.

Soft particles make strong glasses



Intermediate scattering function for particles with medium stiffness (a) and soft particles (c)



$$g_1(t) \propto \exp(-t/\tau)^{\beta}$$

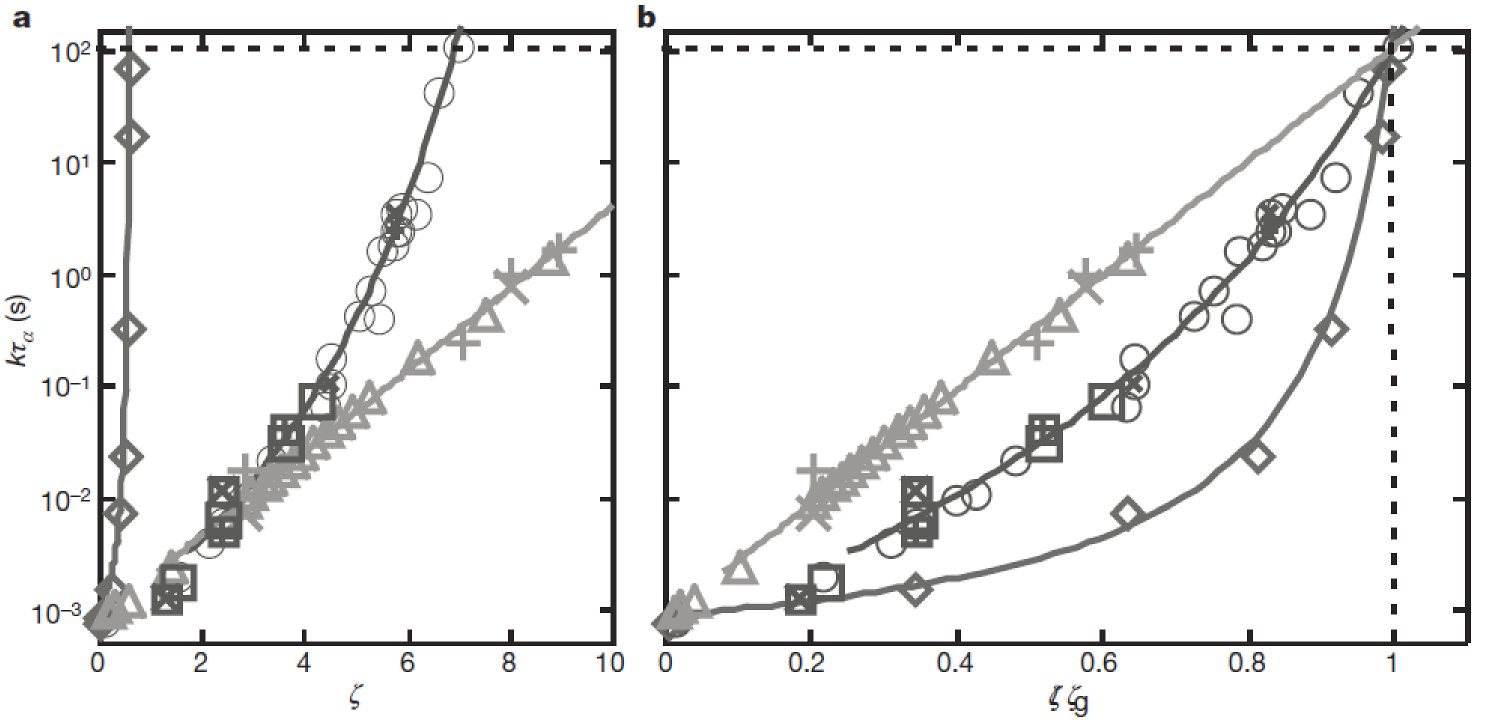
Fitted β of g(t) using an stretched exponential function

Colloidal glasses made of particles of different stiffness show different relaxation behaviors.

A β closer to 1 indicate strong glass behavior.

(Mattson et al, **Nature** 2009)

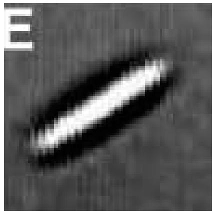
Soft particles make strong glass



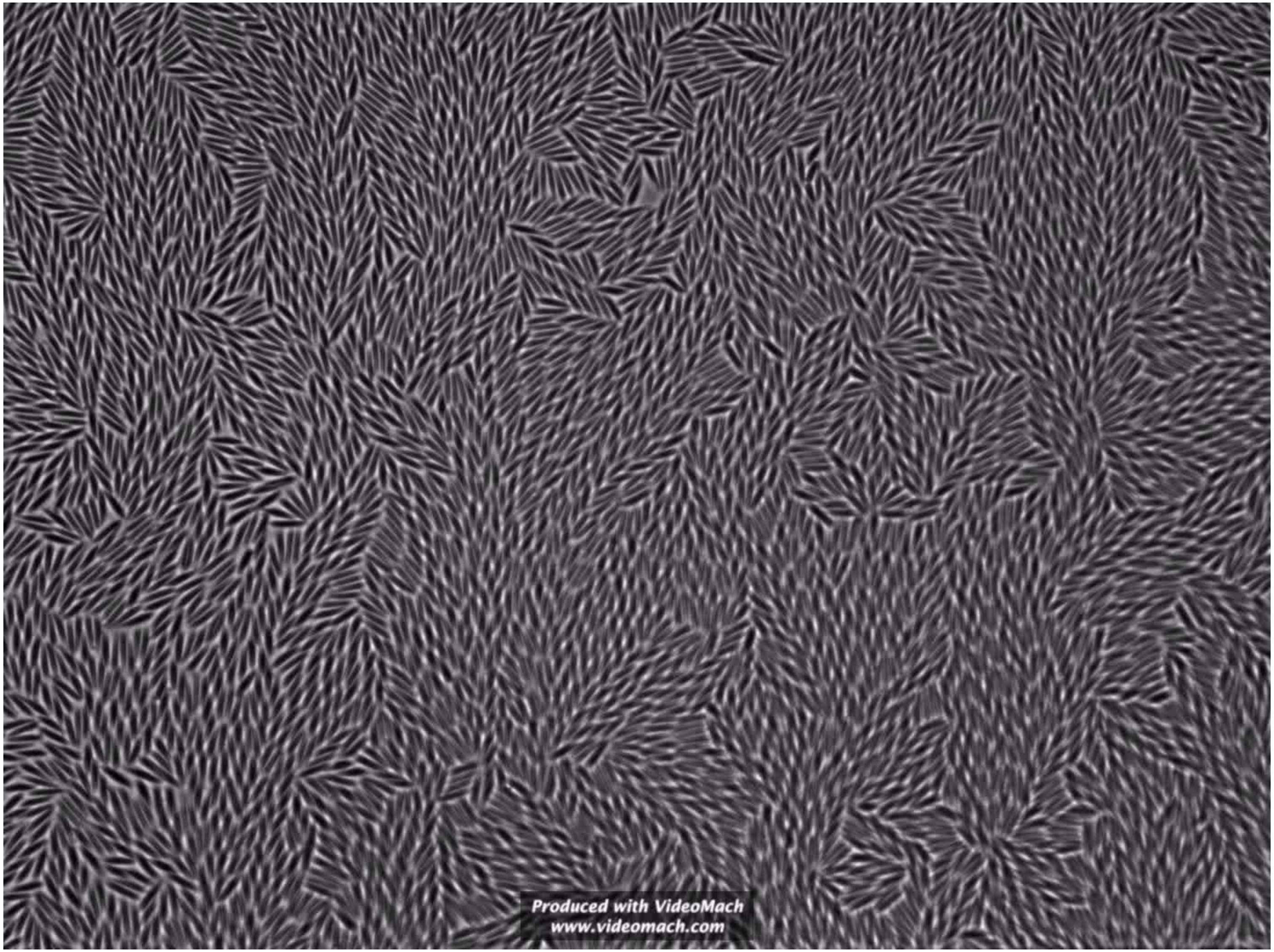
Relaxation time (a) and viscosity (b) of glasses made of different particles with hard (diamonds), medium(circles) and soft (triangles)

The relaxation time and viscosity data show that soft particles indeed form stronger glasses, probably due to their better ability to maintain stable structure than hard spheres.

Shape matters

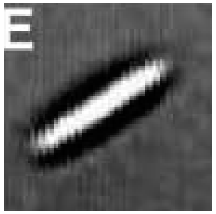


Ellipsoidal colloidal particle

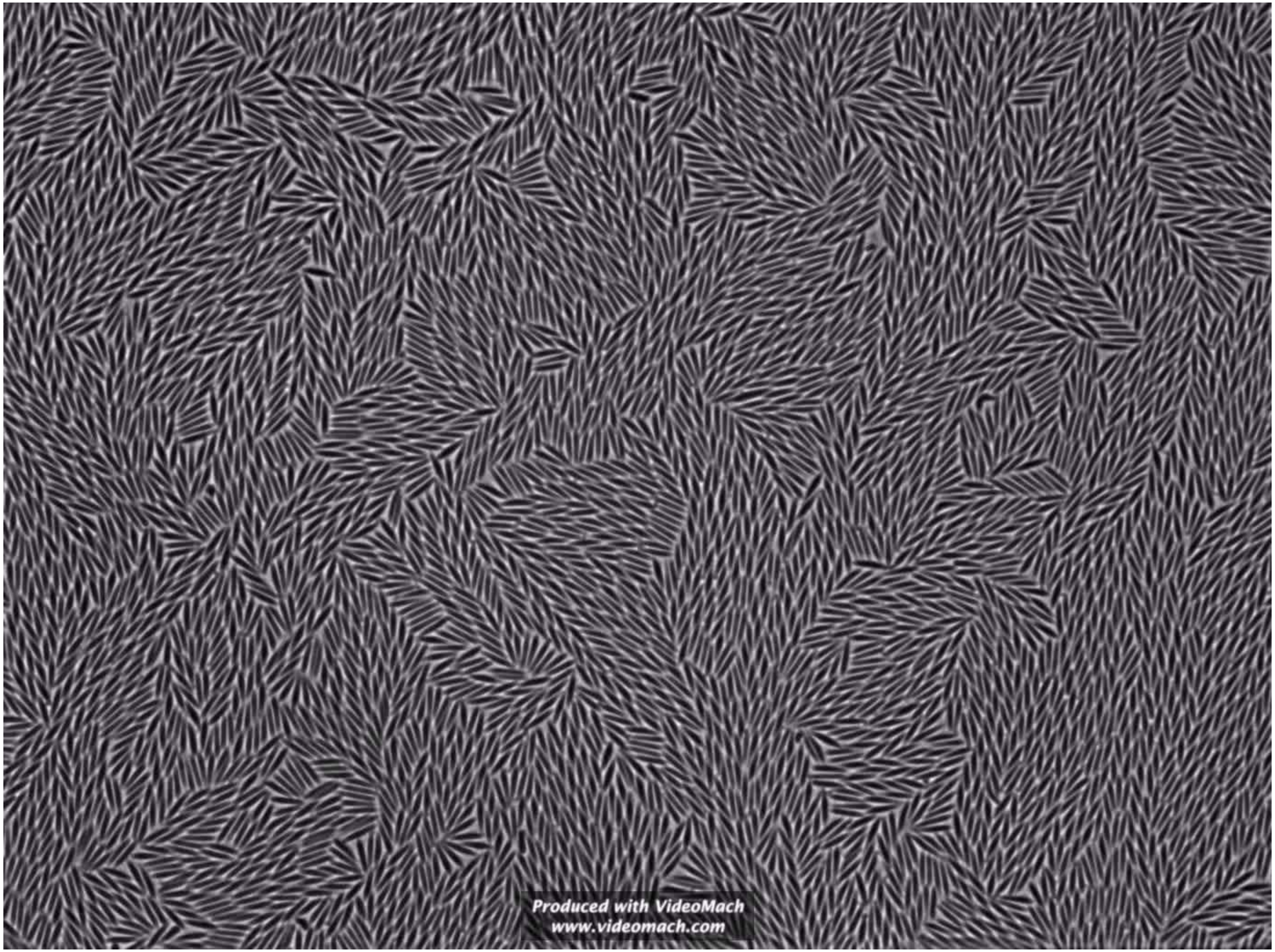


Colloidal glass made of ellipsoidal particles (area fraction 70%)

Shape matters

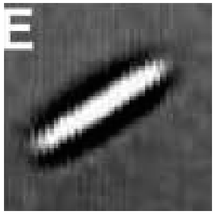


Ellipsoidal
colloidal
particle

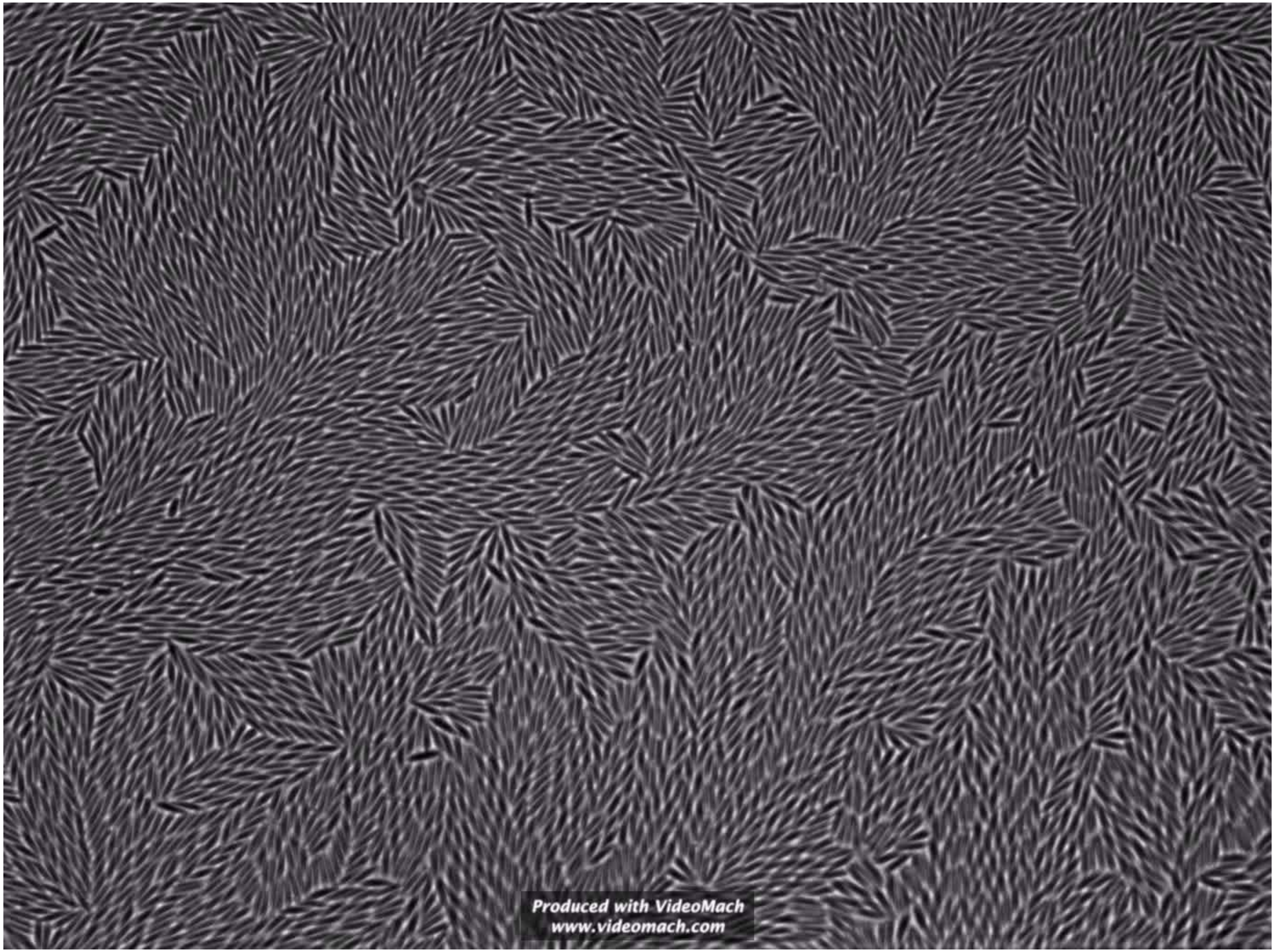


Colloidal glass made of ellipsoidal particles (area fraction 76%)

Shape matters

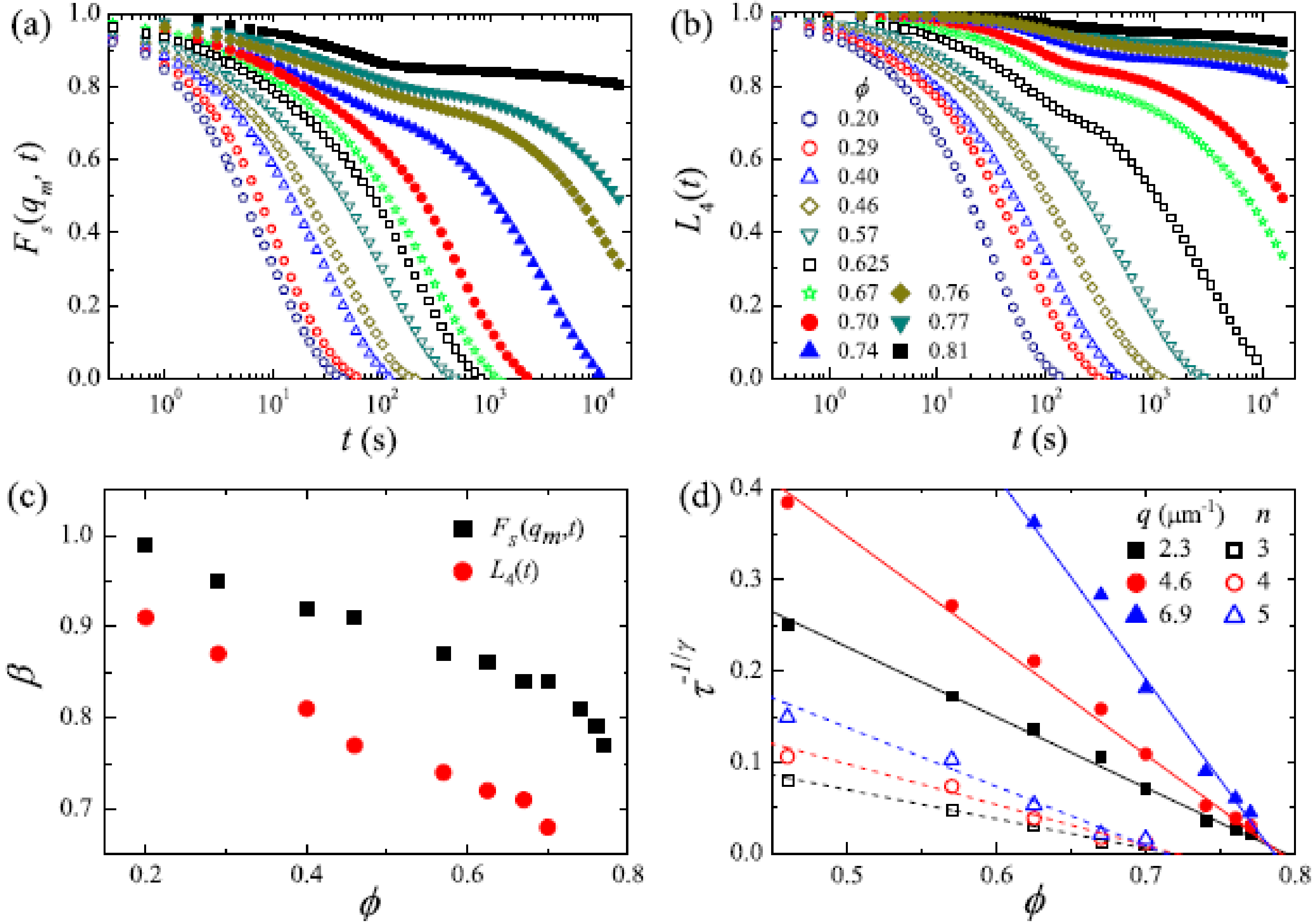


Ellipsoidal colloidal particle



Colloidal glass made of ellipsoidal particles (area fraction 81%)

Two-step glass transition



Relaxation of translational and rotational motion at different packing fractions.

The relaxation time increases differently for translational and rotational motion, with rotational dynamics arrested at a lower packing fraction.

(Zheng et al, **PRL** 2011)

Summary for glasses

The structure of glasses are disordered (not quite sure really).

The dynamics of glasses slows down significantly around glass transition (don’t know why).

Not much is known about the thermodynamics of glasses except the specific heat (which we don’t understand).

Honestly, we don’t even know when a glass is a glass!

Colloids provide a powerful tool to investigate glasses on particle levels that are hard to realize otherwise.

> ***Glass itself remains one of the deepest puzzles of physics***
>
> ***—P. W. Anderson***

Lecture notes will be available at Ms. Ji Haihong upon request