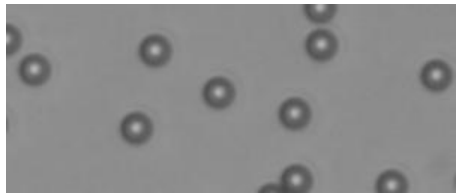
Soft Matter

Lecture 2

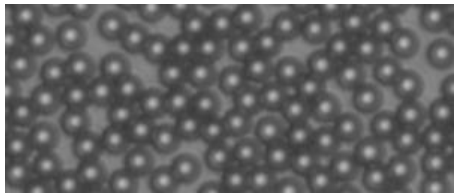
Summary lecture 1

- Colloidal systems

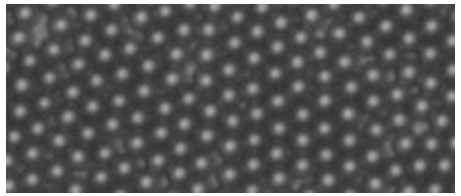
Colloidal gas



Colloidal liquid



Colloidal crystal



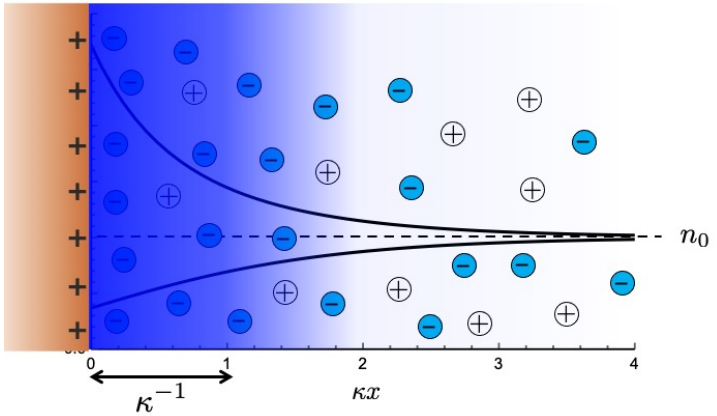
- Van der Waals interactions
  - Hamaker constant

$$U = -\frac{A_{132}}{12\pi D^2}$$

- Electrical double layer
  - Debye length

$$\Phi(x) = \Phi_0 e^{-\kappa x}$$

$$\kappa^{-1} = \sqrt{\frac{\epsilon\epsilon_0 k_B T}{2e^2 n_0 z^2}}$$



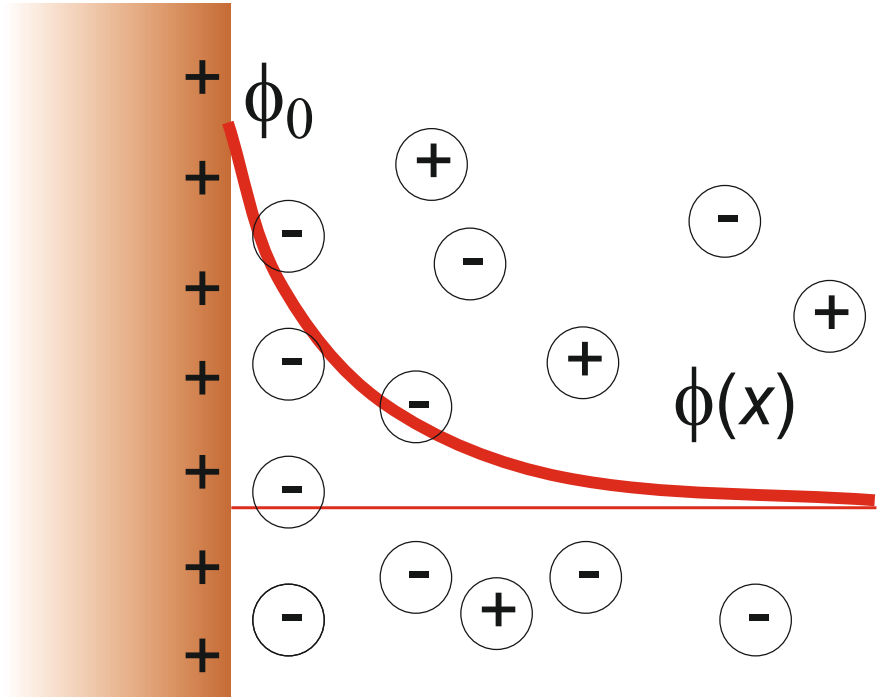
Contents of the course

- Introduction to Soft Matter
- Colloids
  - Interactions between ‘macroscopic’ objects
  - Brownian motion
  - Entropy-driven phase transitions
- Polymers
- Interfaces and surfactants
- Optical microscopy and tweezing
- Mechanical properties of soft matter
- Q & A

Today's lecture (2)

- Double layer repulsion
  - Interaction between two charged surfaces
- DLVO theory
  - Van der Waals interactions and double layer repulsion combined
- Brownian motion
  - Diffusion coefficient
  - Langevin equation
- Entropy driven phase transitions
  - Crystallisation of hard spheres
  - Liquid crystals

Last week: single charged surface



Boltzmann:

$$n_+(x) = n_0 \exp\left[-\Phi(x)\right]$$
$$n_-(x) = n_0 \exp\left[+\Phi(x)\right]$$

Poisson's Law:

$$\nabla^2\phi = -\frac{\rho}{\epsilon\epsilon_0}$$

Via (linearised) Poisson-Boltzmann equation:

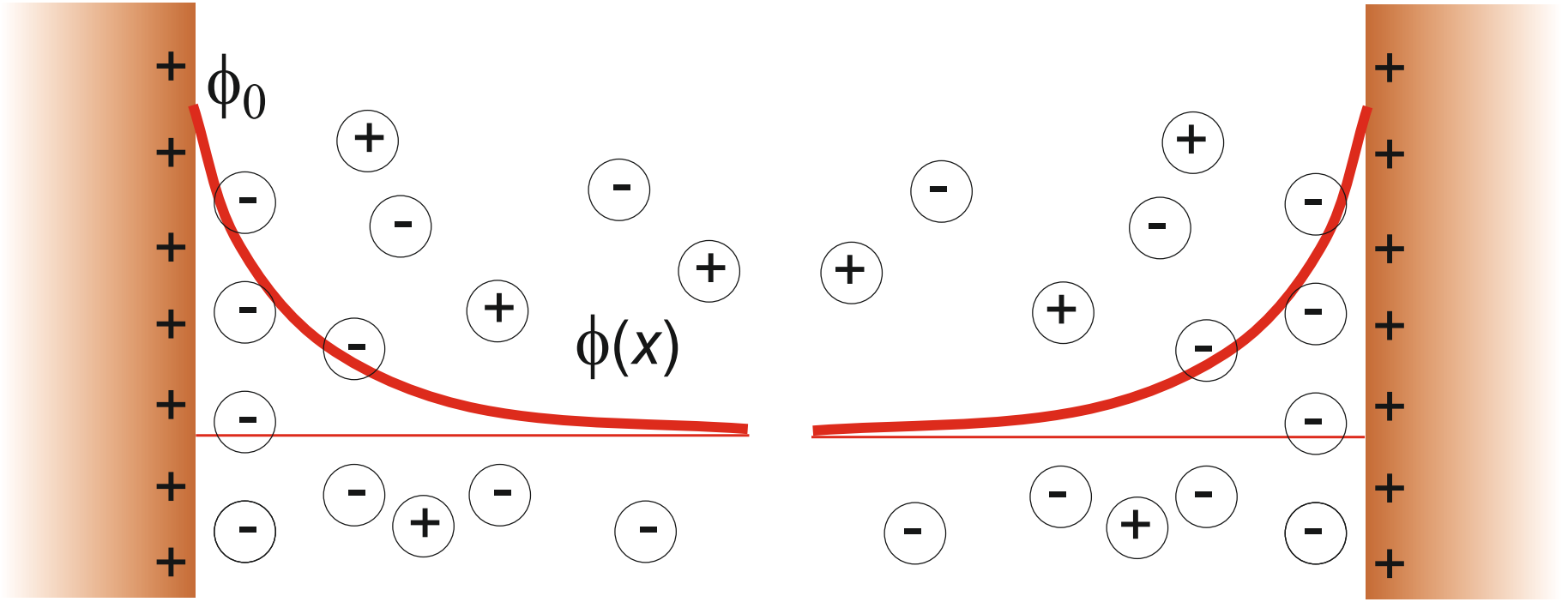
$$\Phi(x) = \Phi_0 e^{-\kappa x}$$

ϕ_0 : surface potential

$\phi(x)$: electrostatic potential

$\Phi(x) = ze\phi(x)\beta$: dimensionless electrostatic potential

What happens when two charged surfaces approach each other?

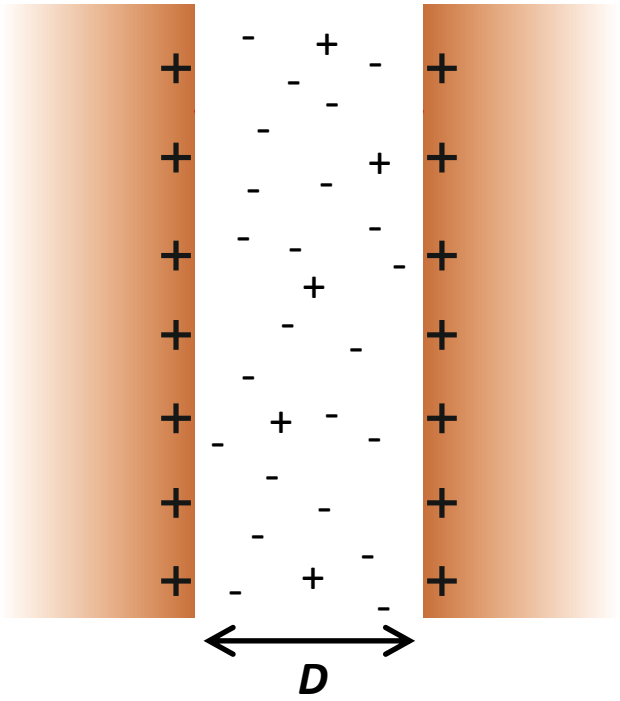


When surfaces approach, the counterions are pushed back towards the charged surfaces – this reduces the electrostatic energy, which is an **attractive** force

So why do surfaces of like charge repel each other?

osmosis

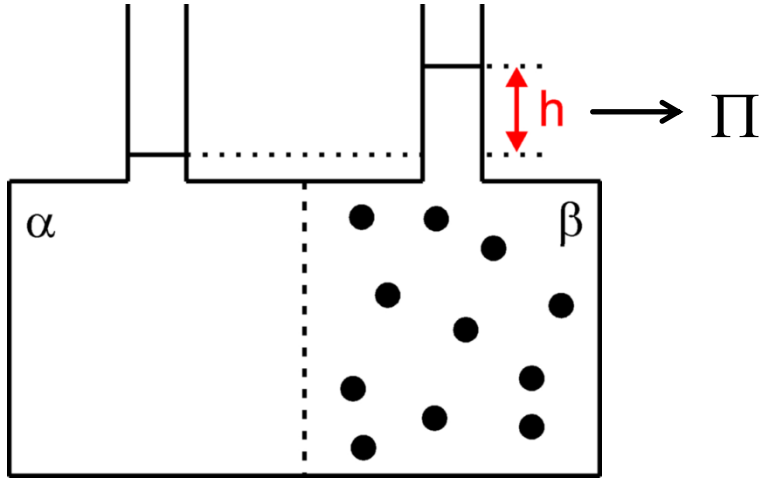
Repulsion due to osmotic pressure Π



$$\Pi = n_{\text{excess}} k_B T$$

$$n_{\text{excess}}(x) = [n_+(x) - n_0] + [n_-(x) - n_0]$$
$$= n_+(x) + n_-(x) - 2n_0$$

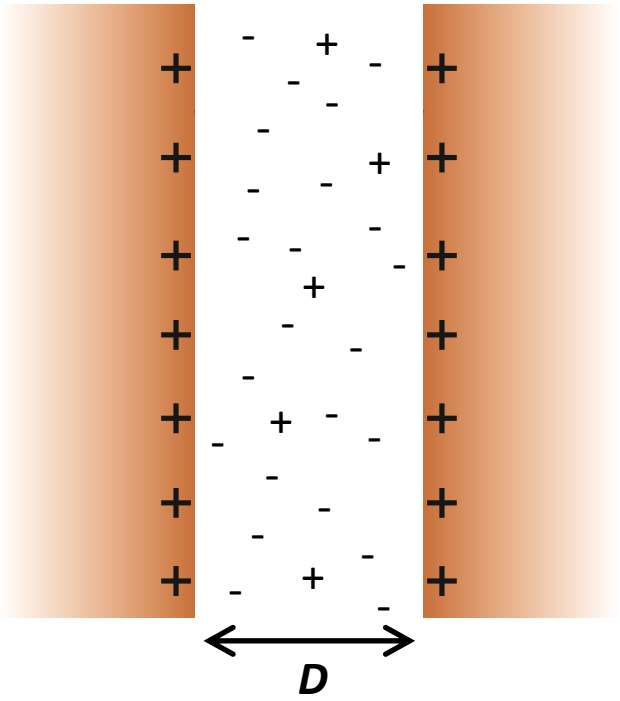
Reminder: osmotic pressure Π



Van 't Hoff's Law:

$$\Pi = n k_B T$$

Repulsion due to osmotic pressure Π



Number density distributions (between **2** charged surfaces):

$$n_+(x) = n_0 \exp\left[-\Phi_2(x)\right]$$
$$n_-(x) = n_0 \exp\left[+\Phi_2(x)\right]$$

Boltzmann

$$\nabla^2\phi(x) = -\frac{\rho(x)}{\epsilon\epsilon_0}$$

Poisson

Poisson-Boltzmann equation (for **2** charged surfaces)

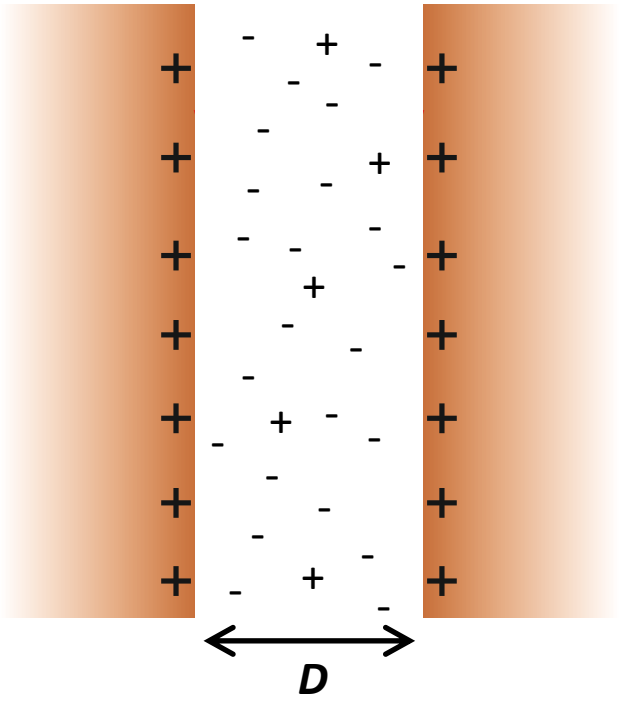
$$\Pi = n_{\text{excess}} k_B T$$

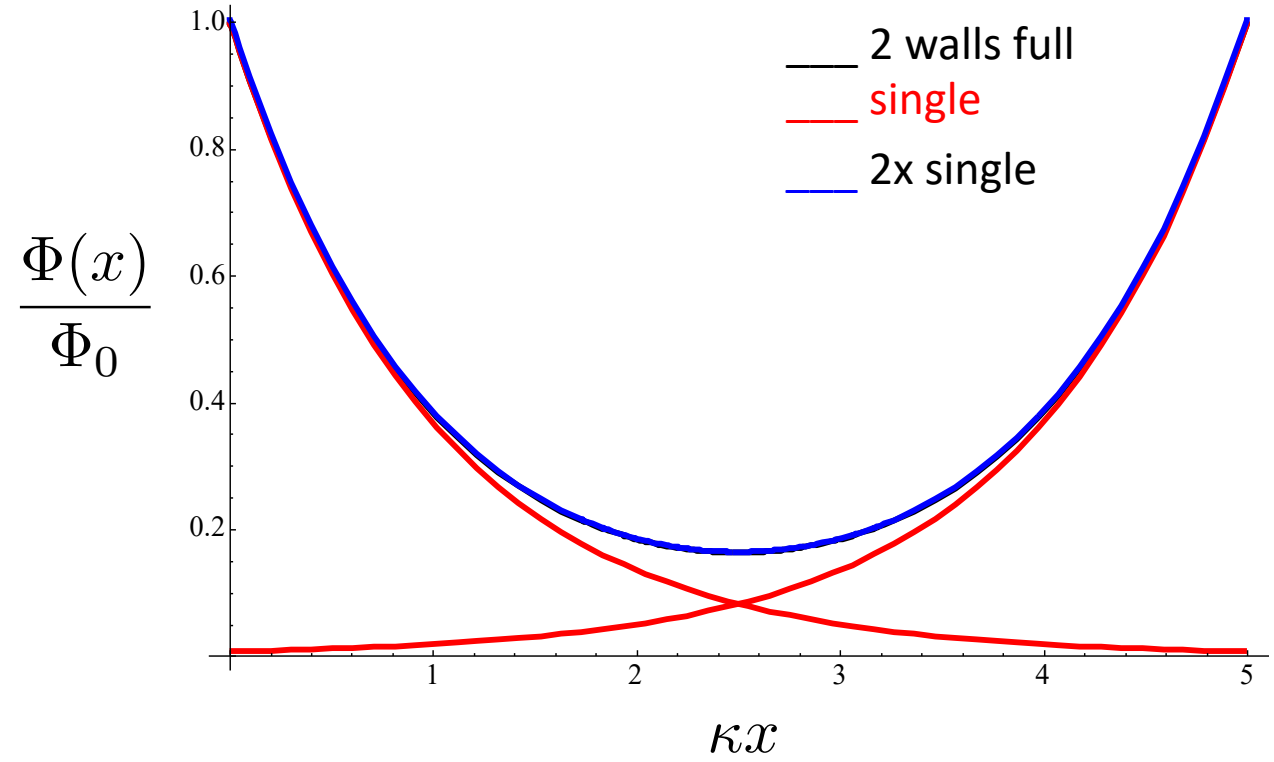
$$n_{\text{excess}}(x) = [n_+(x) - n_0] + [n_-(x) - n_0]$$
$$= n_+(x) + n_-(x) - 2n_0$$

Three options to find Φ_2:

1. Solve full Poisson-Boltzmann equation
2. Linearise PB equation and solve for Φ_2
3. **Superposition principle**

Superposition principle to find Φ_2



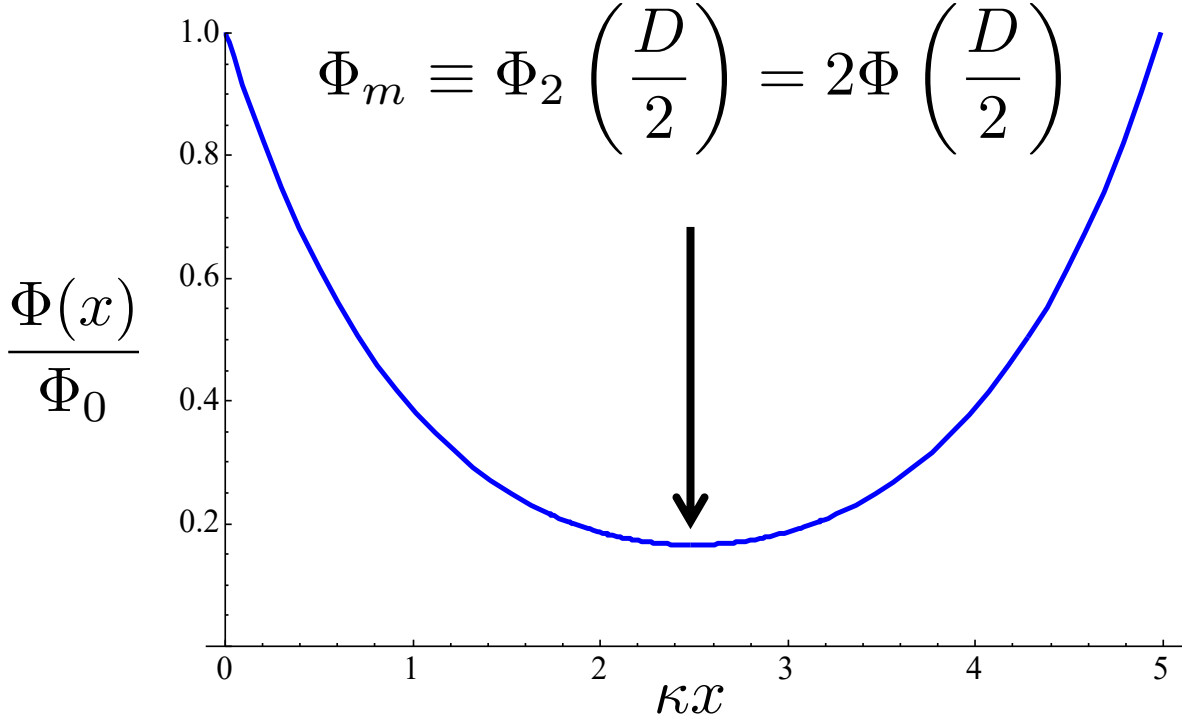


$$\Phi_2(x) = \Phi_{\text{left}}(x) + \Phi_{\text{right}}(x)$$
$$= 2\Phi(x)$$
$$= 2\Phi_0 e^{-\kappa x}$$

Evaluate osmotic pressure at the midpoint D/2

Electrostatic potential at the midpoint D/2:

$$\Phi_m \equiv \Phi_2\left(\frac{D}{2}\right) = 2\Phi\left(\frac{D}{2}\right)$$



$$[\Phi(x) = \Phi_0 e^{-\kappa x}]$$

Number densities at the midpoint D/2:

$$n_+(\tfrac{D}{2}) = n_0 \exp\left[-\Phi_m\right]$$

$$n_-(\tfrac{D}{2}) = n_0 \exp\left[+\Phi_m\right]$$

$$\Pi(D) = 4n_0 k_B T \Phi_0^2 e^{-\kappa D}$$

Double layer repulsion

$$\Pi(D) = 4n_0 k_B T \Phi_0^2 e^{-\kappa D}$$

$$\Phi_0 = \frac{ze\phi_0}{k_B T} \qquad \phi_0 = \frac{\sigma}{\epsilon\epsilon_0\kappa} \qquad \kappa^2 = \frac{2z^2e^2n_0}{\epsilon\epsilon_0 k_B T}$$

$$\Pi(D) = \frac{2\sigma^2}{\epsilon\epsilon_0} e^{-\kappa D}$$

Interaction energy: work needed to bring the two plates together

$$U(D) = -\int_{\infty}^{D} \Pi(x)dx = \frac{2\sigma^2}{\epsilon\epsilon_0\kappa} e^{-\kappa D}$$

Today's lecture (2)

- Double layer repulsion to Soft Matter
  - Interaction between two charged surfaces
- **DLVO theory**
  - **Combining Van der Waals interactions and double layer repulsion**
- Brownian motion
  - Diffusion coefficient
  - Langevin equation
- Entropy driven phase transitions
  - Crystallisation of hard spheres
  - Liquid crystals

Derjaguin-Landau-Verwey-Overbeek (DLVO) Theory

Combining the van der Waals *attraction* and the double layer *repulsion*

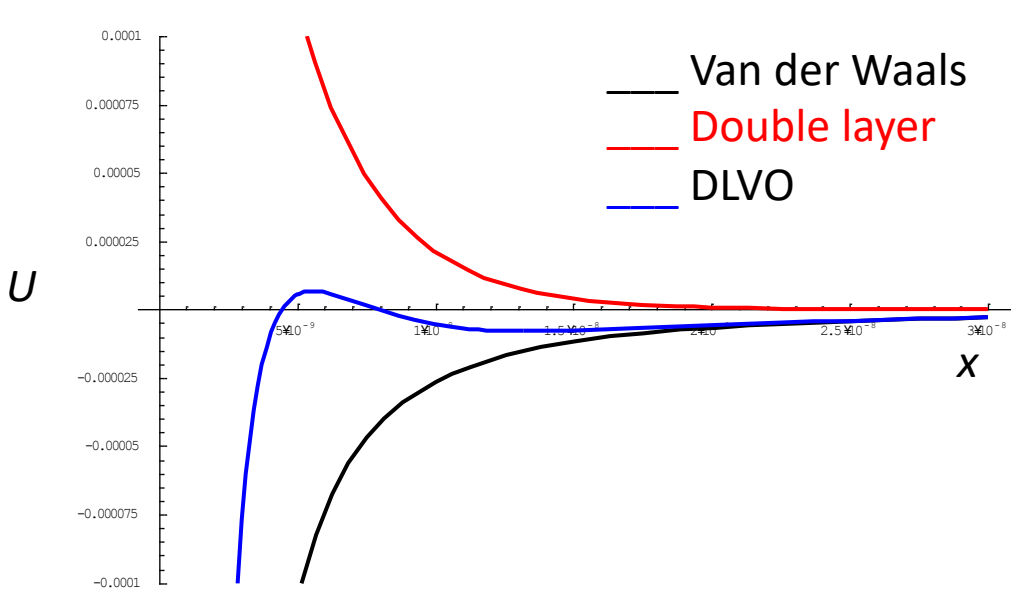
Overbeek, **D**erjaguin

Landau

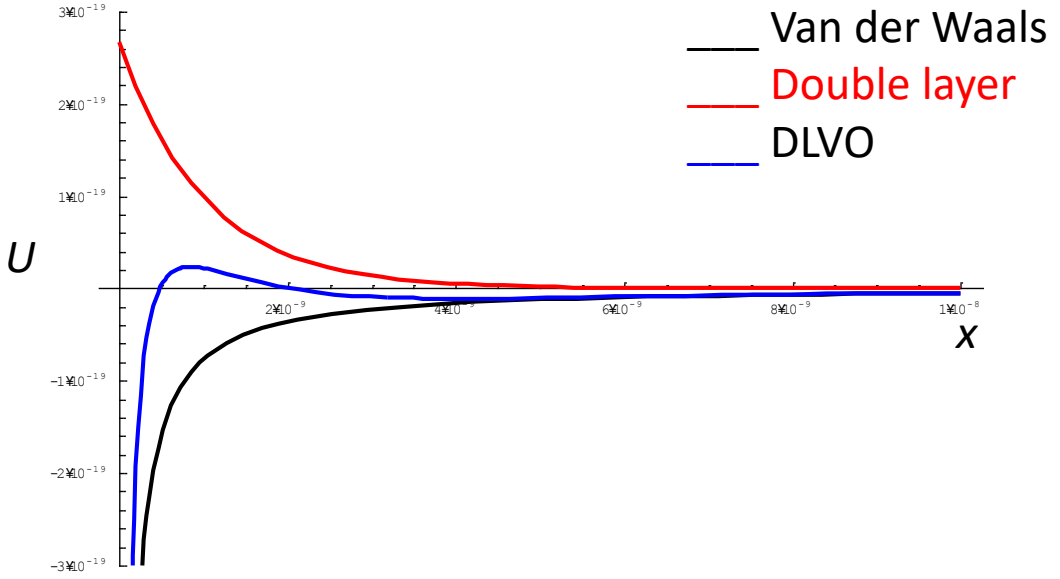
Casimir, **V**erwey, Lyklema, **O**verbeek

DLVO potential

Two plates



Two spheres *



$$U(D) = -\frac{A}{12\pi D^2} + \frac{2\sigma^2}{\epsilon\epsilon_0\kappa}e^{-\kappa D}$$

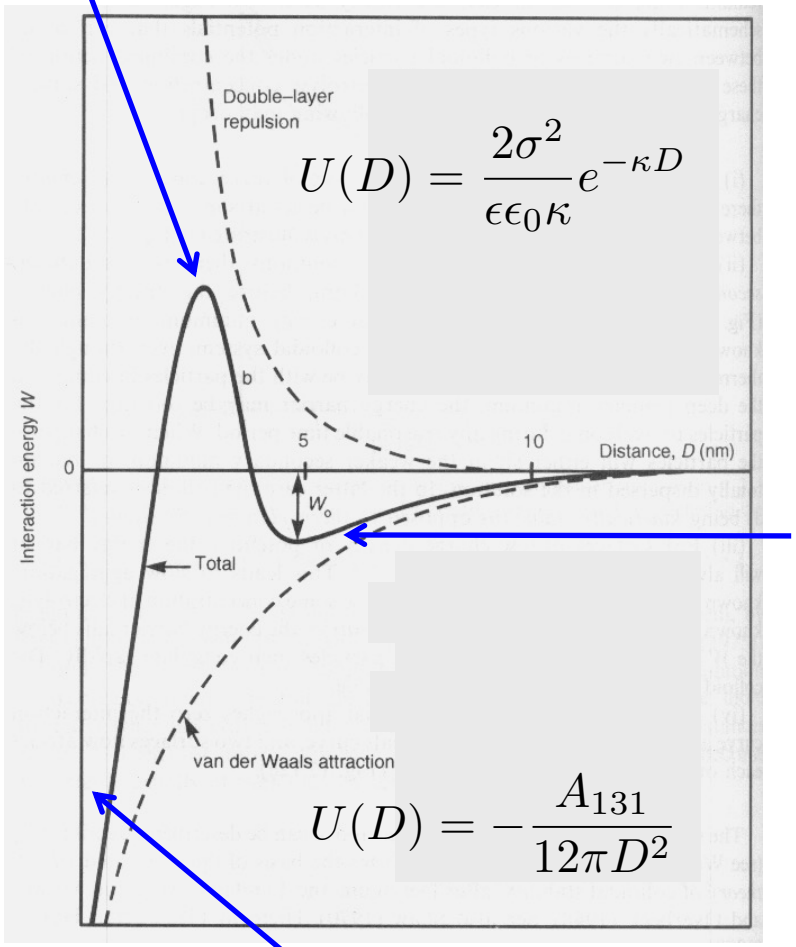
Van der Waals double layer

* Much more difficult calculation, but similar physics

DLVO theory of colloid stability

Van der Waals 'wins' at both small and large separation: Colloids are kinetically stable

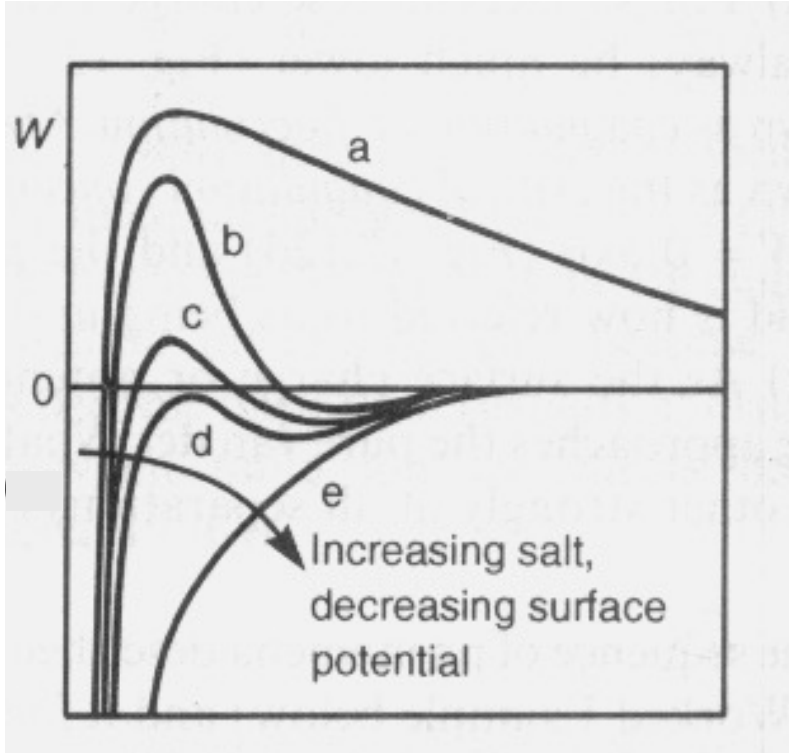
energy barrier



secondary minimum

primary minimum

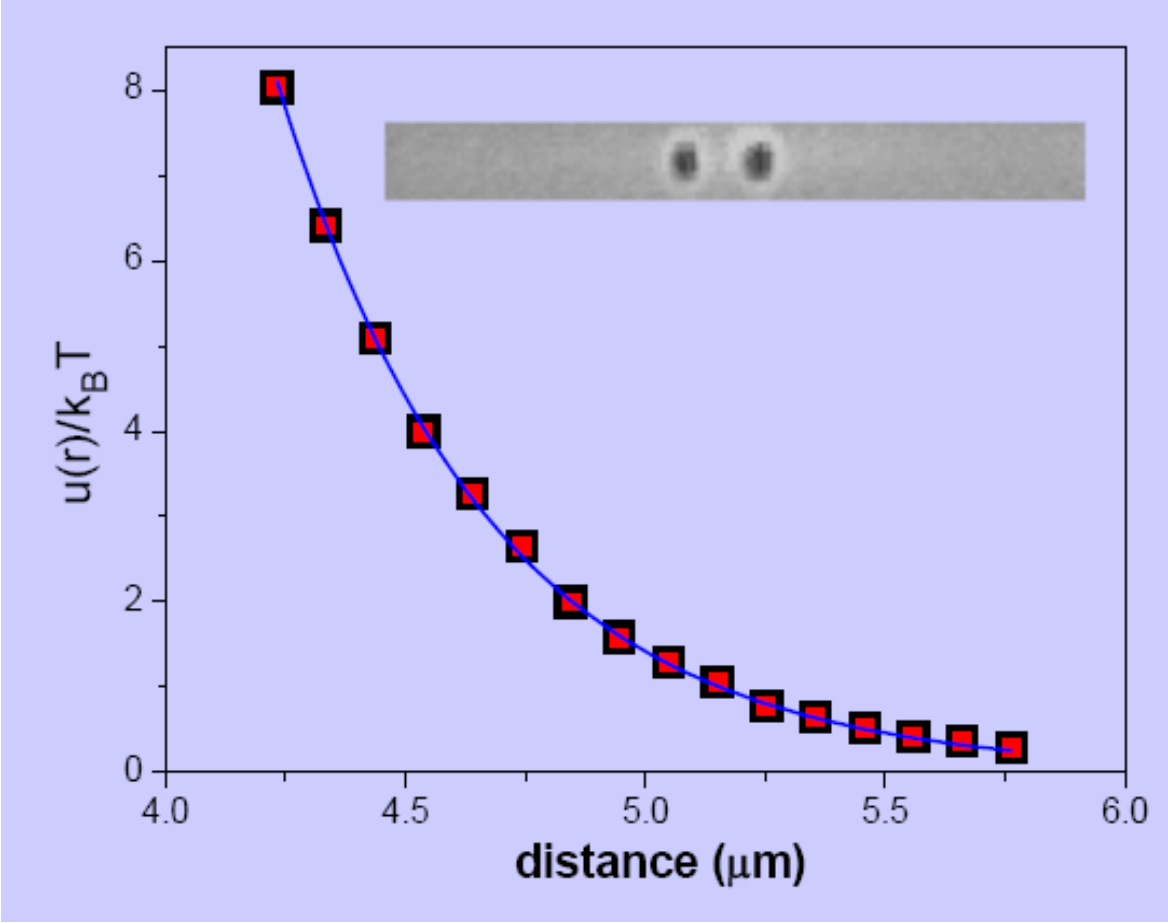
Predict effect of charge, salt, valency, temperature, pH, dielectric constant, ... on the stability of colloids



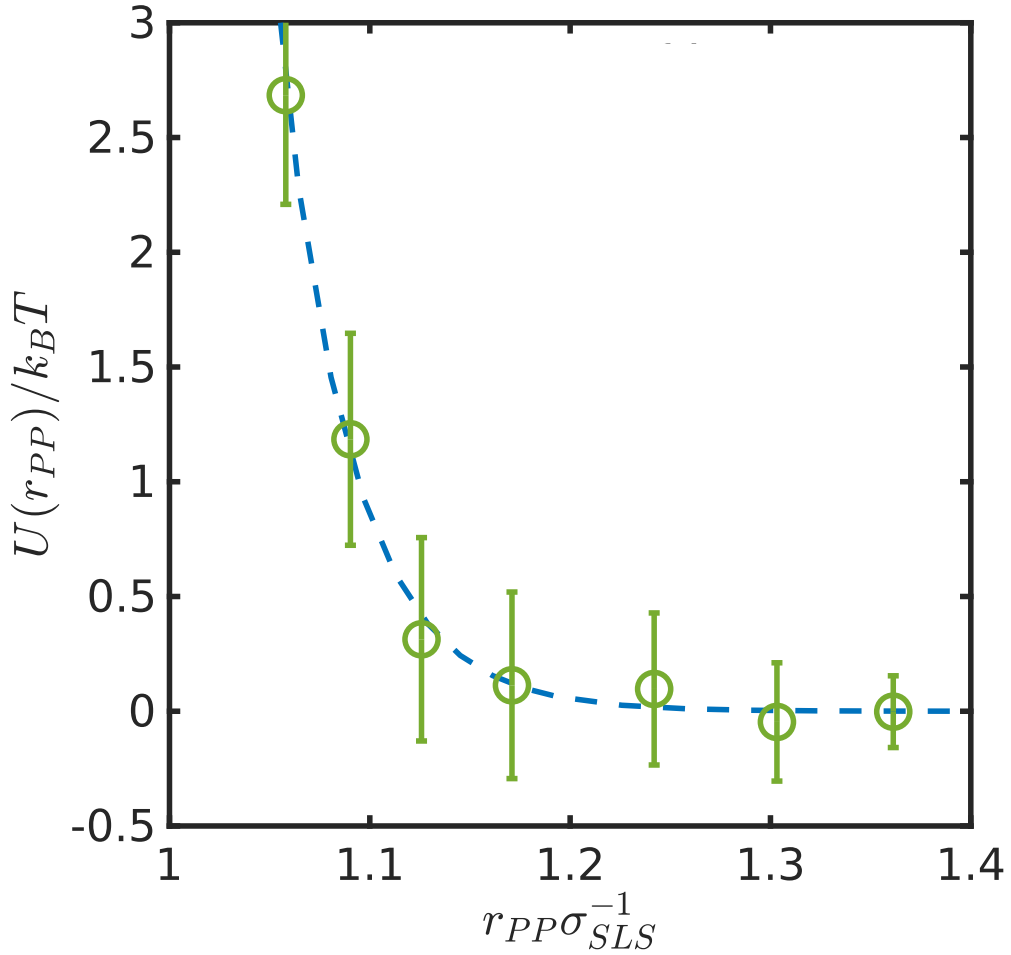
see problem set

Measurements of DLVO interactions

the repulsive double layer part



Dobnikar et al, Phys. Rev. E **69**, 031402 (2004)



Liu et al, Langmuir **35**, 7962 (2019)

(e.g.) using **optical tweezers**: more about this in lecture 5

Today's lecture (2)

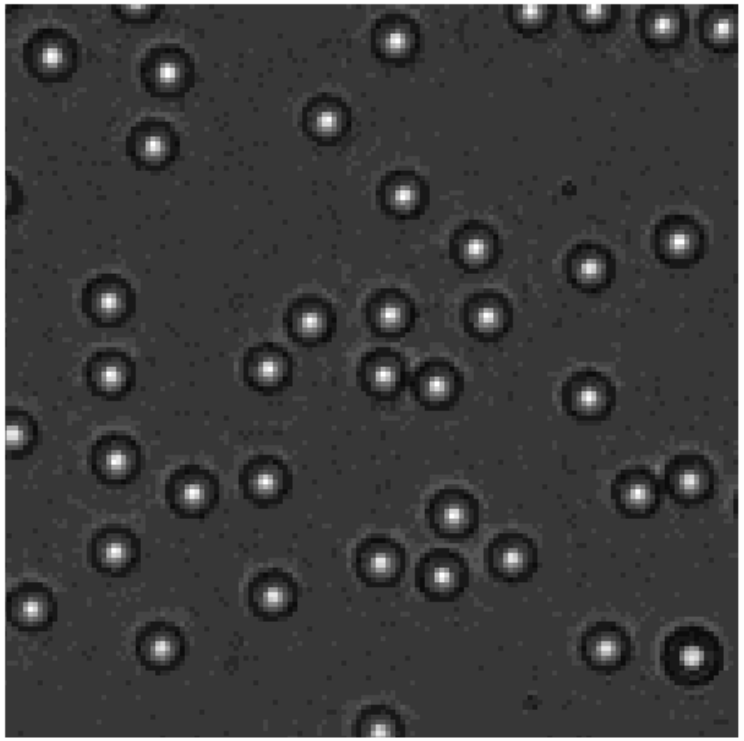
- Double layer repulsion to Soft Matter
  - Interaction between two charged surfaces
- DLVO theory
  - Van der Waals interactions and double layer repulsion combined
- **Brownian motion**
  - **Langevin equation**
  - **Diffusion coefficient**
- Entropy driven phase transitions
  - Crystallisation of hard spheres
  - Liquid crystals

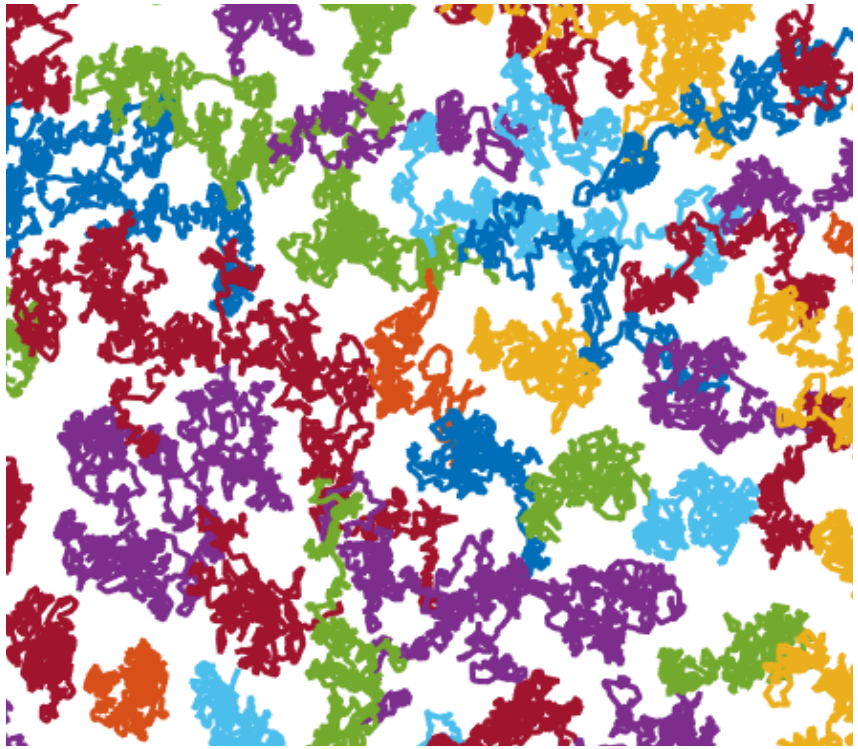
Brownian motion

Robert Brown (1773 – 1858), Scottish botanist

Discovered 'Brownian motion' in suspensions of plant pollen in 1827 (!)

Brownian motion 3 μm particles

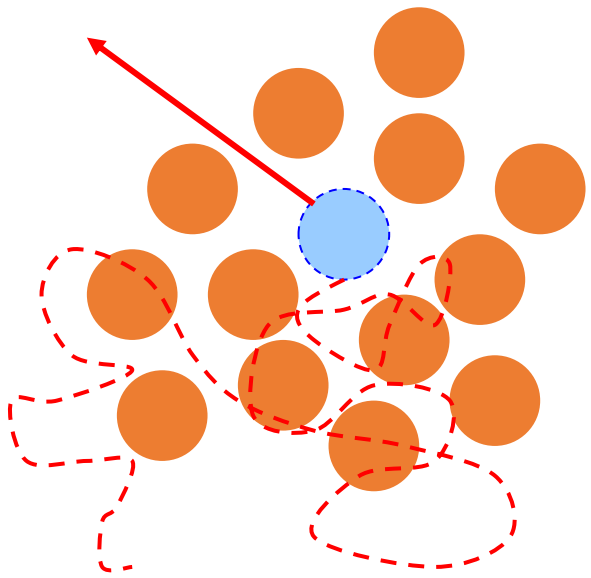




Eleanor Mackay and Alice Thorneywork (University of Oxford)

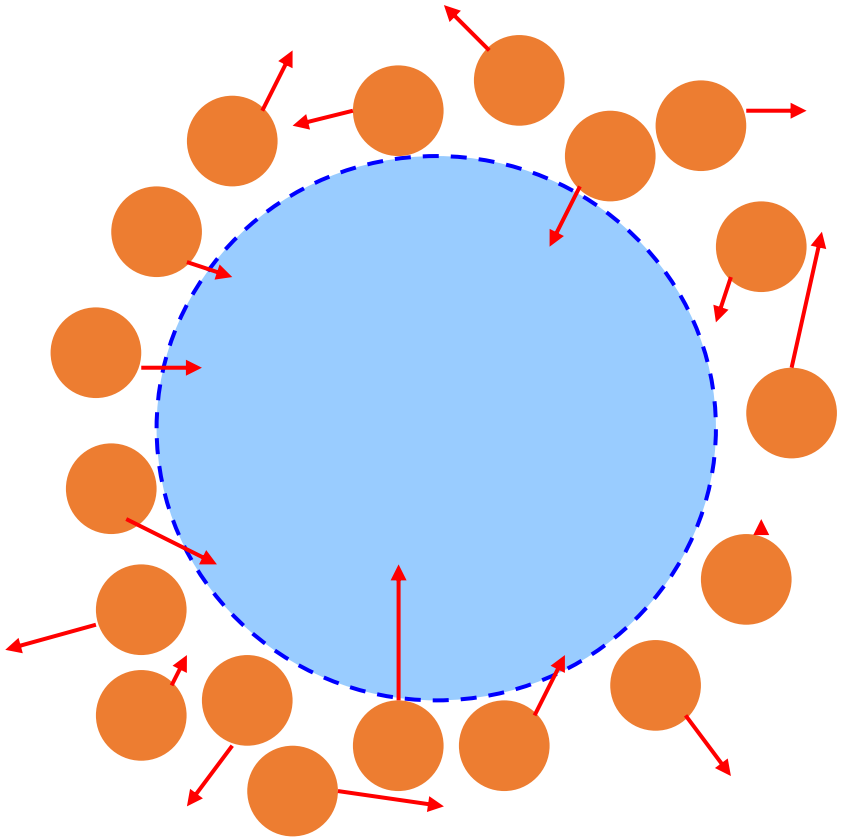
Colloidal particles in a (molecular) solvent

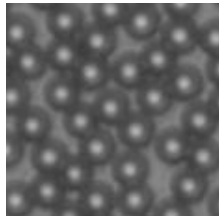
solvent molecules



Interact continuously
with other molecules

Colloidal particle and solvent molecules (*not to scale!*)





Large colloidal particles buffeted continuously by solvent molecules

Average force on particle: $\langle \mathbf{f}(t) \rangle = 0$

But instantaneous force: $\mathbf{f}(t) \neq 0$

Three key equations in Brownian motion

$$\xi = 6\pi\eta R$$

Stokes drag

$$D = \frac{k_B T}{\xi}$$

Diffusion coefficient

$$\langle r^2 \rangle = 6Dt$$

Mean squared displacement

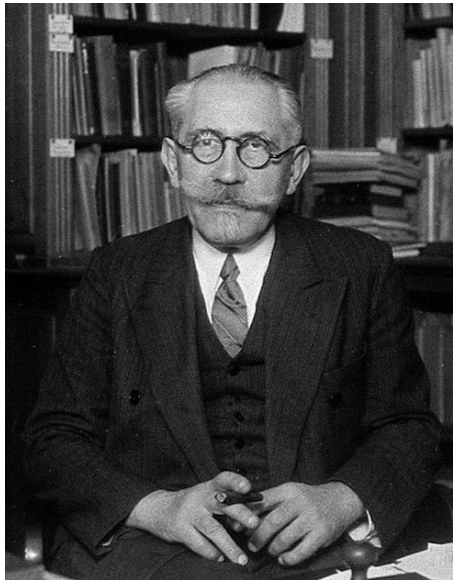
How do we understand these/where do they come from?

We start from the equation of motion:

The Langevin Equation

The Langevin Equation

… essentially F = ma …



Paul Langevin
(1872 – 1946)

acceleration

thermal force

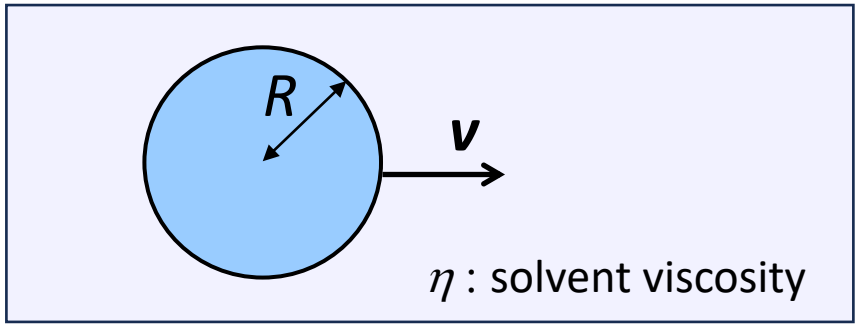
$$m\frac{d\mathbf{v}}{dt} = \mathbf{F} + \mathbf{f}(t) - \xi\mathbf{v}$$

'external' force

drag

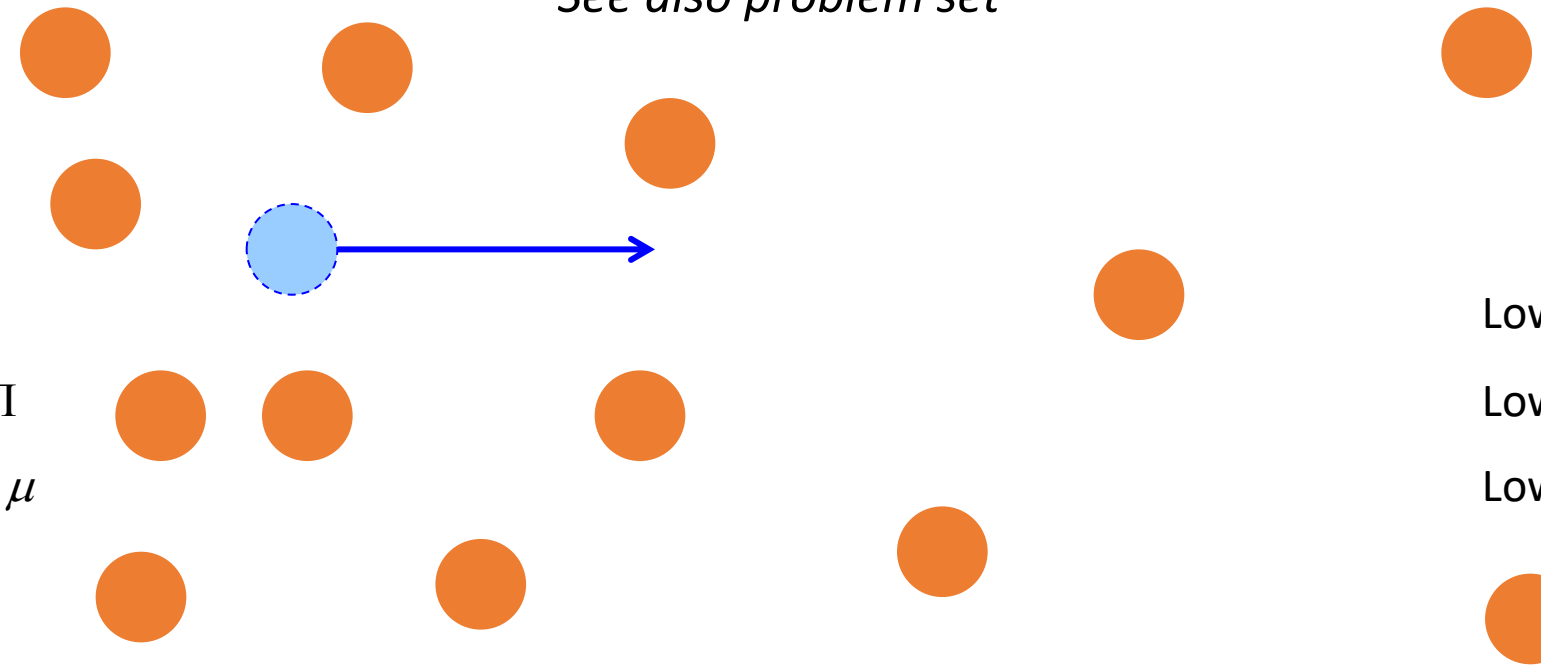
$$\xi = 6\pi\eta R$$

(Stokes Equation)



Diffusion coefficient: diffusion down a concentration gradient

See also problem set



High concentration *c*

High osmotic pressure Π

High chemical potential μ

Low concentration *c*

Low osmotic pressure Π

Low chemical potential μ

μ: work required to add one mole (or one particle)

$\Rightarrow$ Einstein-Smoluchowski Equation: $D = \dfrac{k_B T}{\xi}$ $\qquad \xi = 6\pi\eta R$

Solution to the Langevin equation

consider time scales short enough for random force not to average to zero

$$m\frac{d\mathbf{v}(t)}{dt} = \mathbf{f}(t) - \xi\mathbf{v}(t)$$

General solution for particle velocity *

$$\mathbf{v}(t) = \exp\left(-\frac{\xi}{m}t\right)\left[\mathbf{v}(0) + \int_0^t dt' \frac{\mathbf{f}(t')}{m}\exp\left(\frac{\xi}{m}t'\right)\right]$$

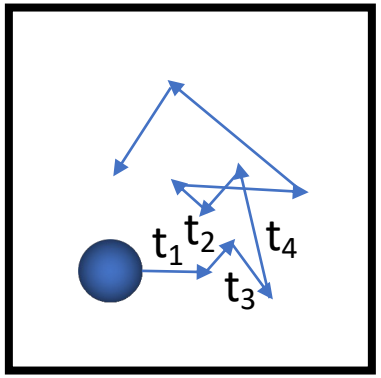
However, we can't say much about ***v***(t) as long as we don't the details of ***f***(t)

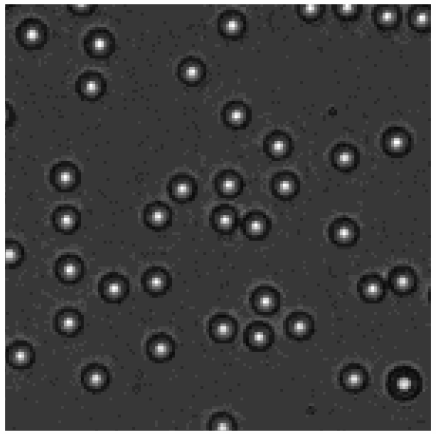
Instead look at the velocity autocorrelation function $\langle \mathbf{v}(0)\cdot\mathbf{v}(t)\rangle$

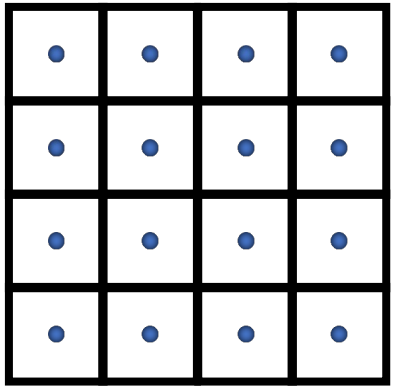
* no need to learn this

Ensemble averages and ergodicity

in equilibrium:







repeat experiment in time

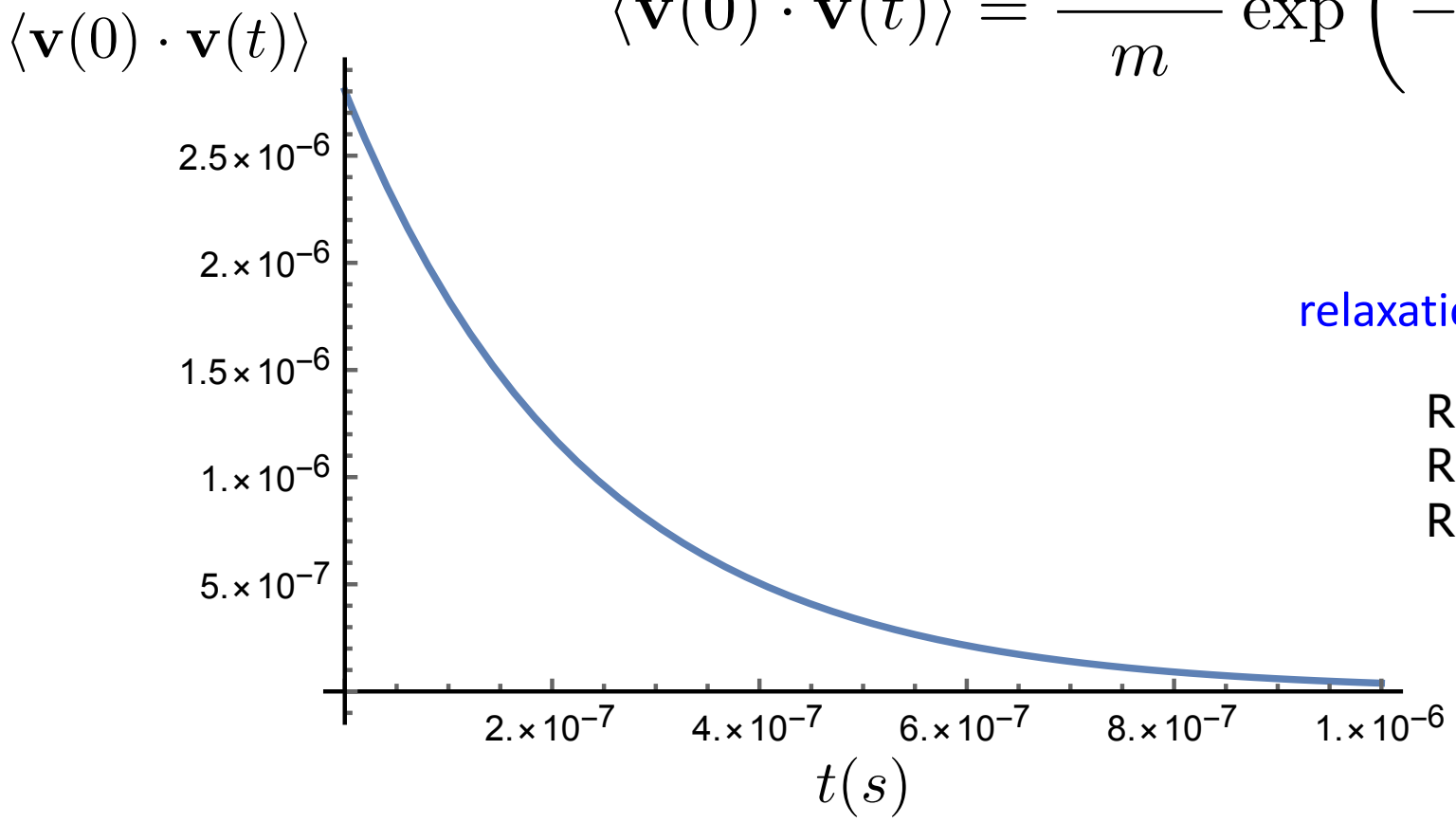
or in space

Therefore, look at ensemble averages $\langle \ldots \rangle$

Velocity autocorrelation function

How fast a Brownian particle forgets its initial velocity

$$\langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle = \frac{3k_B T}{m} \exp\left(-\frac{\xi}{m} t\right)$$



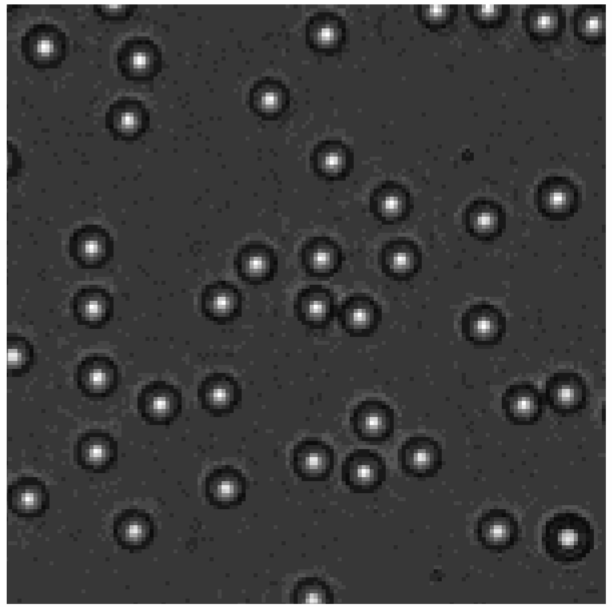
relaxation time of particle velocity $\tau = \frac{m}{\xi}$

R = 5 nm : τ = 5.8 ps
R = 100 nm : τ = 2.3 ns
R = 1 μm : τ = 0.2 μs

A colloidal particle starts moving randomly after a ***very*** short amount of time

How far does a colloidal particle move? Brownian motion as a random walk

$$\mathbf{r}(t) = \int_0^t dt' \mathbf{v}(t')$$

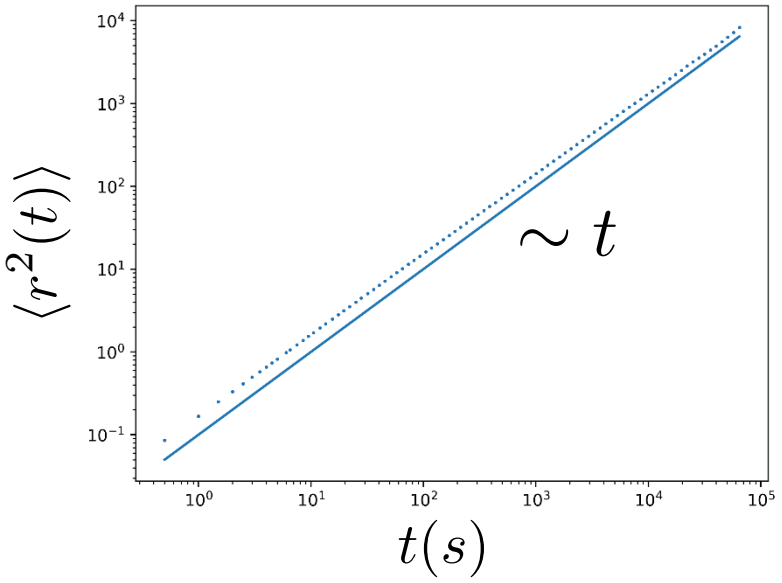


mean displacement

$$\langle \mathbf{r}(t) \rangle = 0$$

mean squared displacement:

$$\langle \mathbf{r} \cdot \mathbf{r} \rangle = \langle r^2(t) \rangle$$



Eleanor Mackay and Alice Thorneywork (University of Oxford)

How far does a colloidal particle move?

Mean squared displacement

Approach 1: work it out from (general) velocity autocorrelation function (multiple integrals)*

$$\mathbf{r}(t) = \int_0^t dt' \mathbf{v}(t')$$

$$\langle r^2(t) \rangle = \int_0^t dt' \int_0^t dt'' \langle \mathbf{v}(t') \cdot \mathbf{v}(t'') \rangle \qquad \langle \mathbf{v}(t) \cdot \mathbf{v}(t') \rangle = \frac{3k_B T}{m} \exp\left(-\frac{\xi}{m} |t - t'| \right)$$

$$\langle r^2(t) \rangle = \frac{6k_B T}{\xi} \left(t + \frac{\exp(-t/\tau) - 1}{1/\tau} \right)$$

relaxation time of particle velocity

$$\tau = \frac{m}{\xi}$$

* no need to learn this, it's a bit tricky, but very rewarding!

How far does a colloidal particle move?

Mean squared displacement

Approach 1: work it out from (general) velocity autocorrelation function (multiple integrals)

$$\langle r^2(t)\rangle = \frac{6k_BT}{\xi}\left(t + \frac{\exp(-t/\tau)-1}{1/\tau}\right)$$

relaxation time of particle velocity

$$\tau = \frac{m}{\xi}$$

Now two important regimes can be identified:

$t \ll \tau$ $\qquad \langle r^2(t)\rangle = \frac{3k_BT}{m}t^2$ Short-time **ballistic** regime

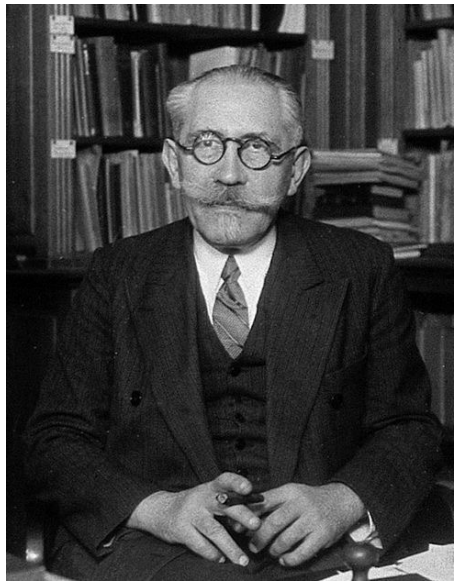
$t \gg \tau$ $\qquad \langle r^2(t)\rangle = \frac{6k_BT}{\xi}t = 6Dt$ Long-time **diffusive** regime

How far does a colloidal particle move?

Mean squared displacement

Approach 2: following Langevin himself: *see problem set*

$$\langle x^2 \rangle = 2\frac{k_B T}{\xi} t = 2Dt$$



Paul Langevin
(1872 – 1946)

MSD in *n*-dimensions: $\langle r^2 \rangle = 2nDt$

Typical time scale in colloids:

Brownian time (t_B)

How long does it take for a particle to diffuse over its own diameter (*d*)?

$$\langle r^2 \rangle = 6Dt \quad \rightarrow \quad \tau_B = \frac{d^2}{6D}$$

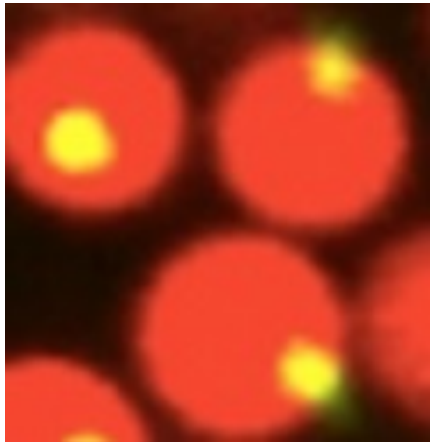
d = 10 nm τ_B = 0.3 μs

d = 200 nm τ_B = 3 ms

d = 2 μm τ_B = 3 s

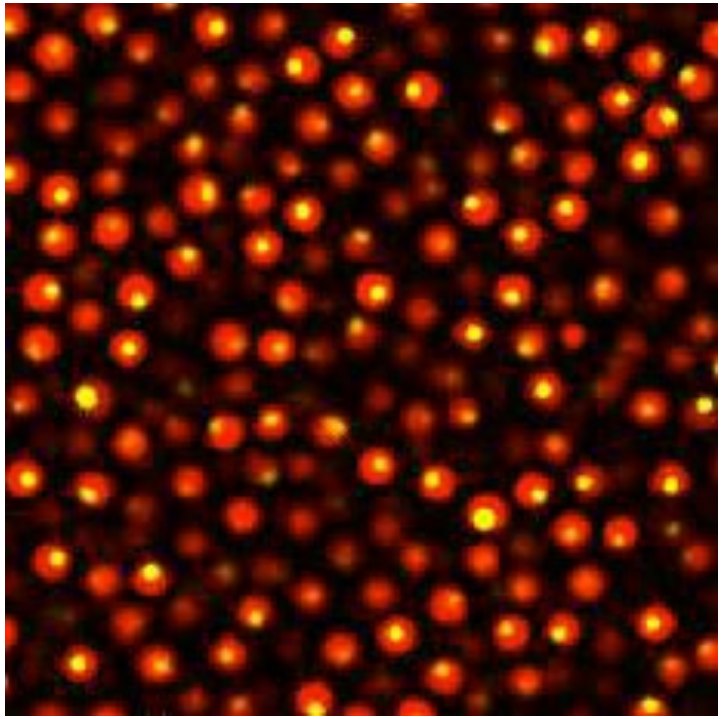
Other types of diffusion: rotational diffusion

Rotational diffusion constant of a sphere: $D_R = \frac{k_B T}{8\pi\eta R^3}$



"How can you see if a sphere rotates? Make it optically anisotropic!"

Perrin (1909)



On 11 November 1909, Einstein wrote to Perrin: "*I would not have considered a measurement of rotations as feasible. In my eyes it was only a pretty trifle*".

B.Duplantier, Brownian Motion, 'Diverse and Undulating' (2005)

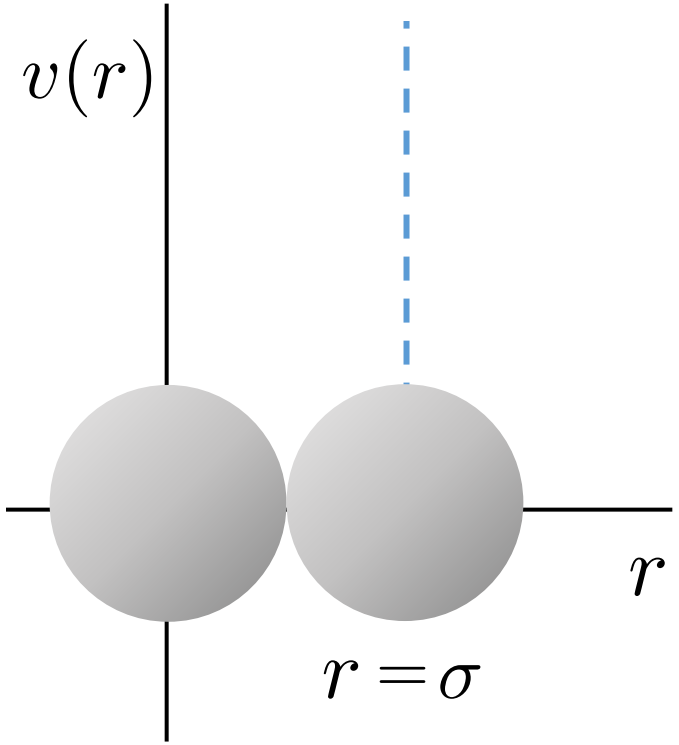
T. Yanagishima et al., Phys. Rev. X 11, 021056 (2021)

Today's lecture (2)

- Double layer repulsion to Soft Matter
  - Interaction between two charged surfaces
- DLVO theory
  - Van der Waals interactions and double layer repulsion combined
- Brownian motion
  - Diffusion coefficient
  - Langevin equation
- **Entropy driven phase transitions**
  - **Crystallisation of hard spheres**
  - **Liquid crystals**

Hard spheres

Simplest possible non-trivial interacting system

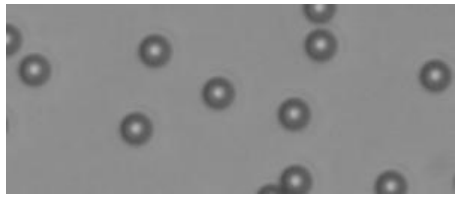


$$v(r) = \begin{cases} \infty & \text{for } r < \sigma \\ 0 & \text{for } r \geq \sigma, \end{cases}$$

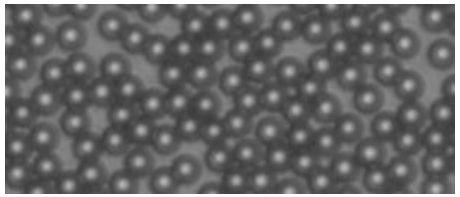
- *Temperature does not play a role in the interaction*
- *We do still have Brownian motion!*
- *Packing fraction ϕ only relevant control parameter*
- *Minimising free energy by maximising **entropy**!*

Phase behaviour of (colloidal) hard spheres

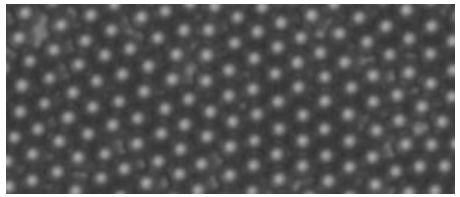
Low density fluid



High density fluid



Colloidal crystal!?



Phase Transition for a Hard Sphere System

B. J. Alder and T. E. Wainwright

University of California Radiation Laboratory, Livermore, California

(Received August 12, 1957)

Preliminary Results from a Recalculation of the Monte Carlo Equation of State of Hard Spheres*

W. W. Wood and J. D. Jacobson

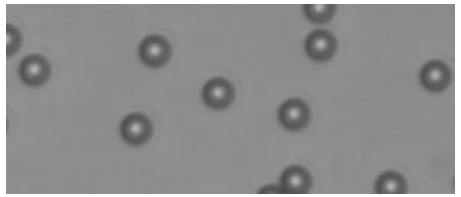
Los Alamos Scientific Laboratory, Los Alamos, New Mexico

(Received August 15, 1957)

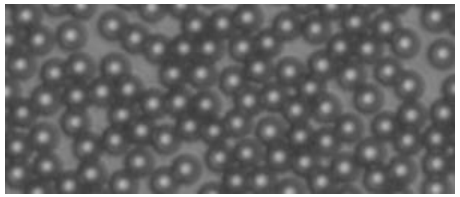
Alder, Wainwright **and** Mary Ann Mansigh

Phase behaviour of (colloidal) hard spheres

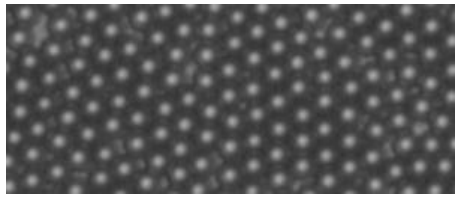
Low density fluid



High density fluid



Colloidal crystal!?



Phase Transition for a Hard Sphere System

B. J. Alder and T. E. Wainwright

University of California Radiation Laboratory, Livermore, California

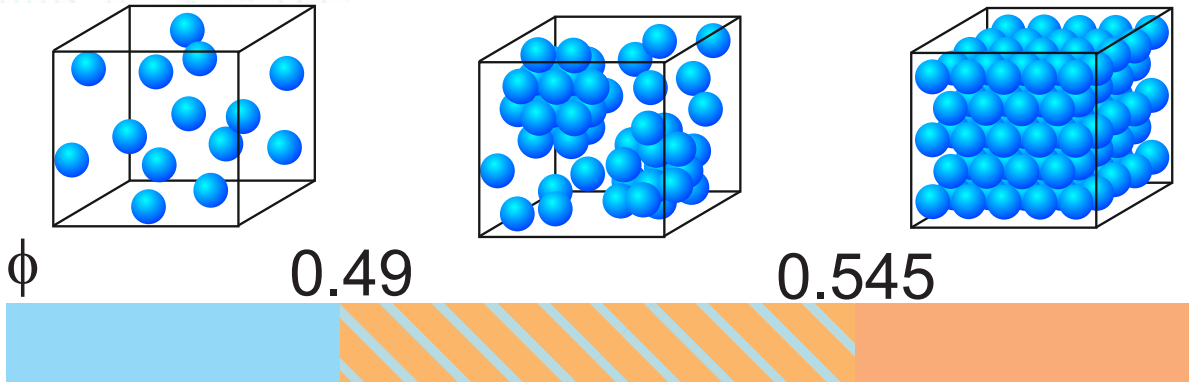
(Received August 12, 1957)

Preliminary Results from a Recalculation of the Monte Carlo Equation of State of Hard Spheres*

W. W. Wood and J. D. Jacobson

Los Alamos Scientific Laboratory, Los Alamos, New Mexico

(Received August 15, 1957)



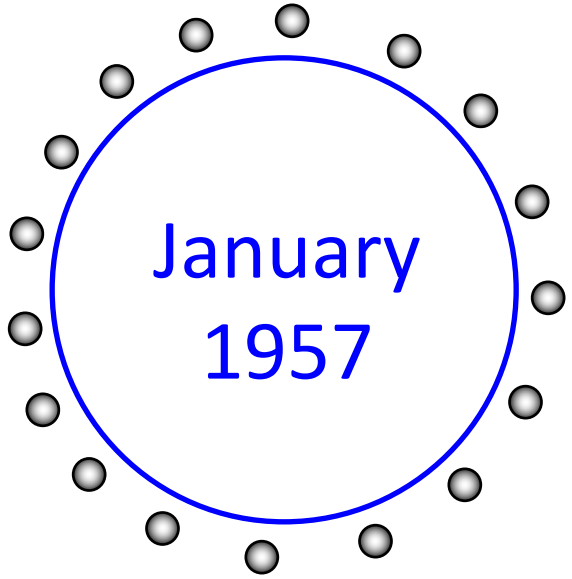
Crystallisation ...

.....with no attraction???!

No attraction, but still a phase transition: let's vote…??!

George E. Uhlenbeck
(1900-1988)

"...the transition goes a little bit against intuition; that is why so many people have difficulty with it, and surely, I am one of those."



"I think it is quite unnecessary to have an attractive force to achieve a crystalline phase and one can produce simple intuitive arguments for that."

John G. Kirkwood
(1907-1959)

The dark hand of entropy: order through entropy

Boltzmann:

$$S = k_B \ln \Omega$$

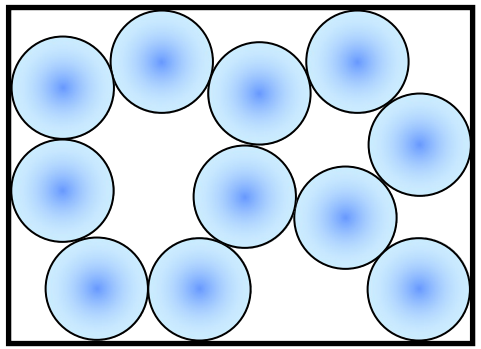
Ω = number of microstates

- *Brownian motion is crucial: "scanning" of microstates*
- *Minimising free energy by maximising **entropy**!*

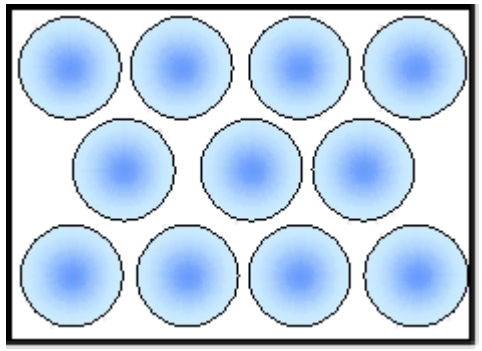
The dark hand of entropy: order through entropy

Hard sphere crystallisation

Fluid:
Disordered positions



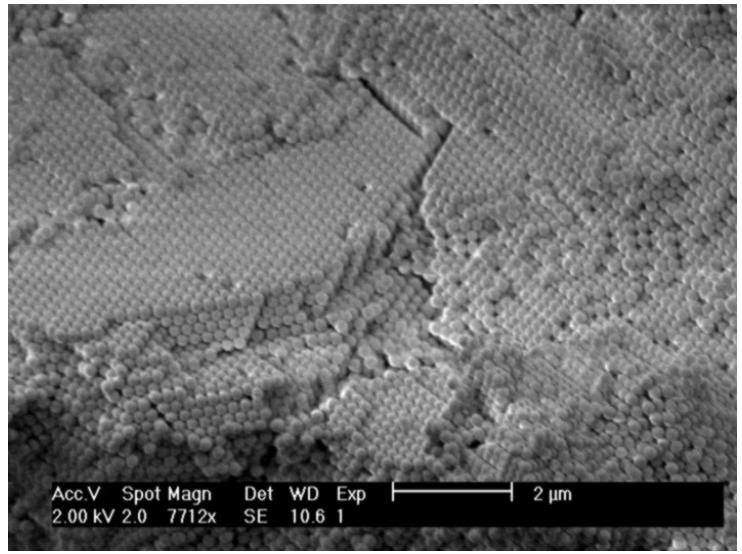
Crystal:
Ordered positions



	Fluid	**Crystal**
$S_{configurations}$	high	low
$S_{free\ volume}$	low	high

3D hard spheres: experiments

Experimental verification using a ***colloidal*** model hard spheres (1986)

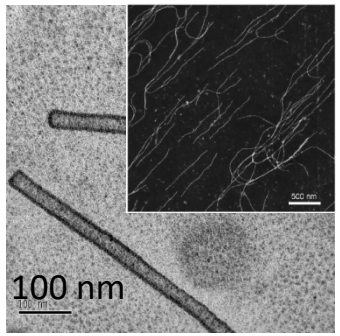


Fluid | Fluid + Crystal | Crystal | Glass

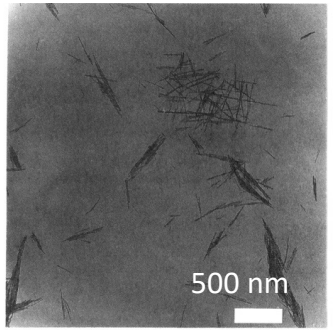
0.494 | 0.545 | ϕ

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

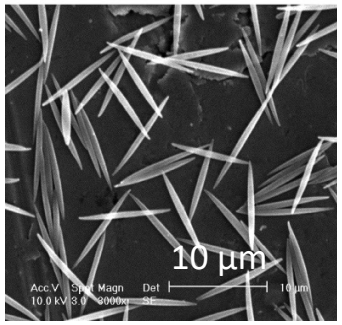
Rod-like particles: colloidal liquid crystals



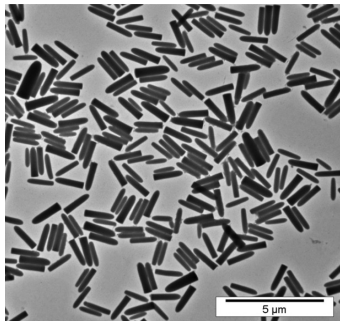
TMV/fd-virus



Boehmite rods



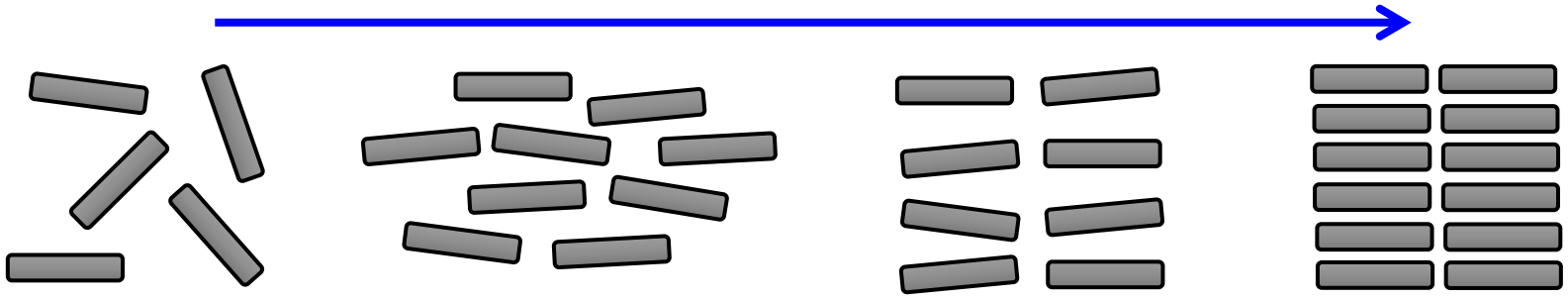
PMMA ellipsoids



Silica rods

Rods with dimensions L/D > 4: *Liquid Crystalline Phases*

Concentration



Isotropic **Nematic** **Smectic** **Crystal**

Onsager: again ordering through *entropy*

Lars Onsager (1903-1976)

Nobel prize Chemistry 1968

1. **Anisotropic Solutions of Colloids.** LARS ONSAGER, *Yale University.*—The solutions of certain colloids comprised of highly asymmetrical particles—plates or rods—are known to form anisotropic phases at remarkably low concentrations. For tobacco mosaic virus (rods), isotropic solutions containing 2–3 percent virus are in equilibrium with anisotropic phases containing 3–4.5 percent, respectively, according to the amount of electrolyte present. This phenomenon can be explained as a result of repulsive forces by the observation that the mutual co-volume of two swarms of parallel rods (or plates) is roughly proportional to the sine of the angle between their orientation, and larger than the volume of the particles by a factor which is proportional to the asymmetry. The case of rods is particularly simple in that the virial coefficients of order higher than 2 in Mayer's expansion are small, and a quantitative theory is possible. The computed ratio of concentrations at equilibrium is 1.34. The predicted osmotic pressure of the anisotropic phase is nearly proportional to the concentration, in fact, slightly greater than $3cRT/V$.

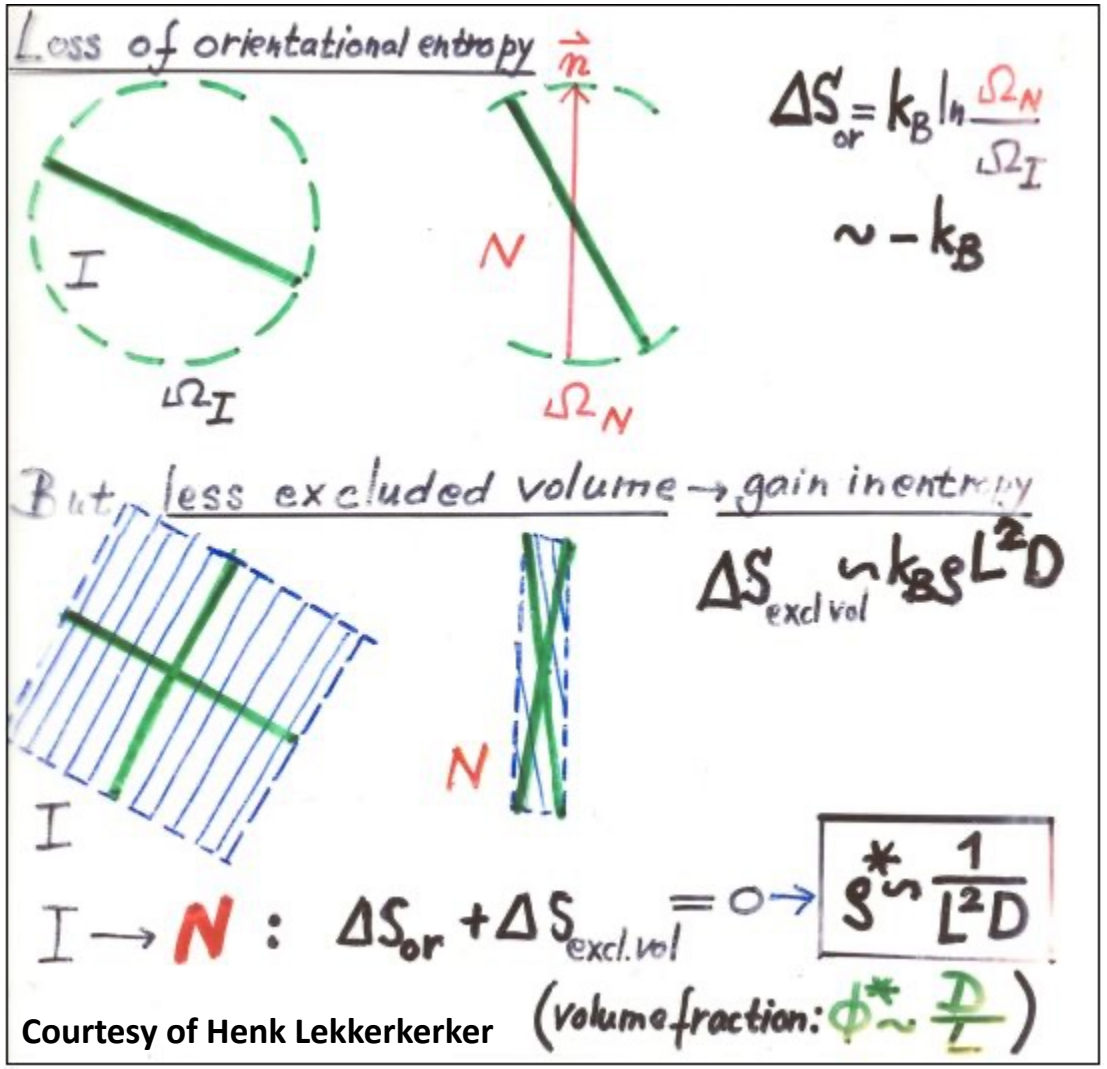
Entropy driven isotropic-nematic transition in rods

see also problem set

The isotropic-nematic transition in a suspension of rods is driven by the loss of orientation entropy and the gain of free volume entropy **Onsager (1942,1949)**

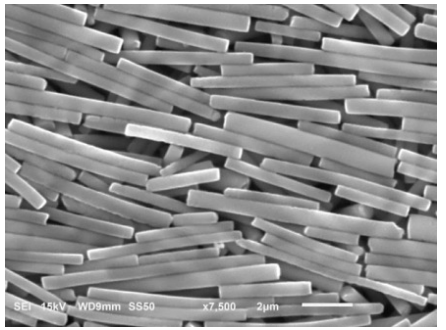
Lars Onsager (1903-1976)

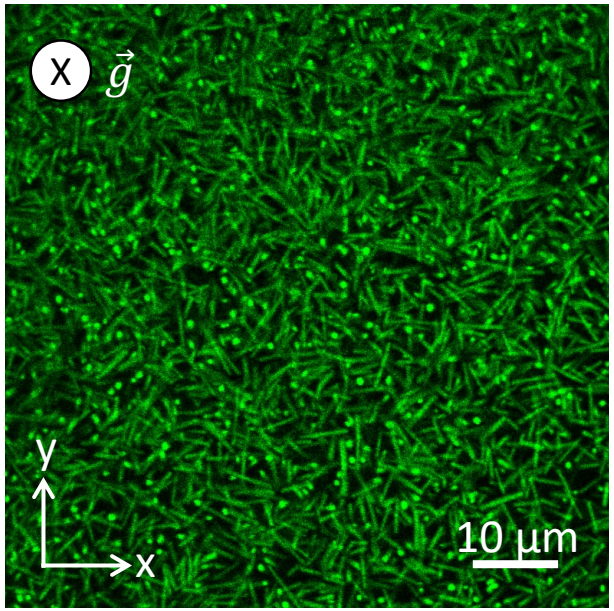
Nobel prize Chemistry 1968

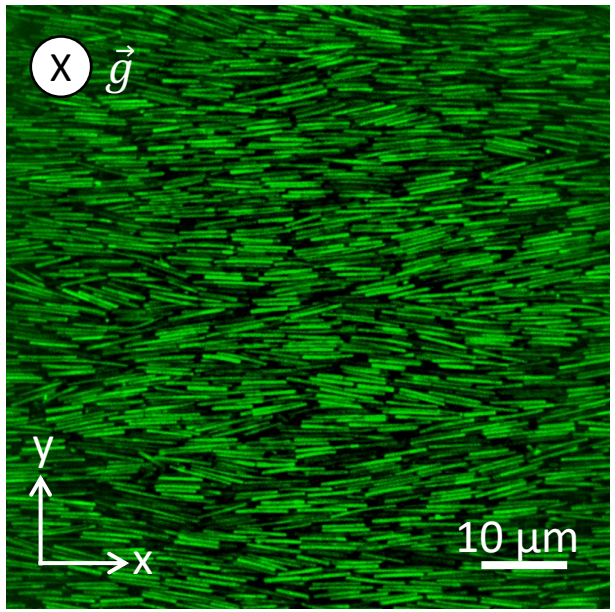


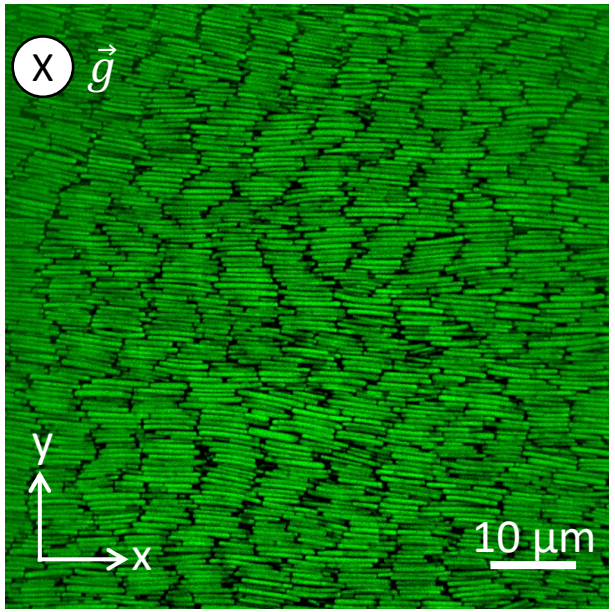
Courtesy of Henk Lekkerkerker

Colloidal SU-8 rods: colloidal liquid crystals

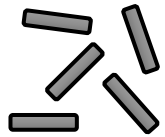




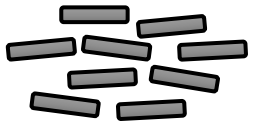




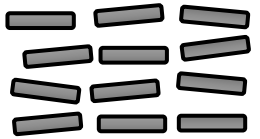
Isotropic



Nematic



Smectic-like



Fernández-Rico et. al, Adv. Mater., 1807514 (2019)

Contents of the course

- Introduction to Soft Matter
- Colloids
  - Interactions between ‘macroscopic’ objects
  - Brownian motion
  - Entropy-driven phase transitions
- **Polymers**
- **Interfaces and surfactants**
- Optical microscopy and tweezing
- Mechanical properties of soft matter
- Q & A