

Soft Condensed Matter

Keyser and Knowles
Easter 2023

Ulrich Keyser (ufk20) & Tuomas Knowles (tpjk2)

Colloids, electrolytes and charged interfaces 1
Lecture 17 27/4/23

*Upcoming lectures: Fri 28/4 10:15am, Mon 1/5 10:15am,
Tue 2/5 9am, Wed 4/5 10:15, Thu 5/5 9am*

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9. 1 Colloids

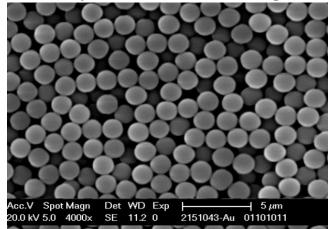
The encyclopaedia Britannica defines colloids as:

"Colloid, any substance consisting of particles substantially larger than atoms or ordinary molecules but too small to be visible to the unaided eye; more broadly, any substance, including thin films and fibres, having at least one dimension in this general size range, which encompasses about 10^{-3} to 10^{-7} cm. Colloidal systems may exist as dispersions of one substance in another - for example, smoke particles in air or as single materials, such as rubber or the membrane of a biological cell."

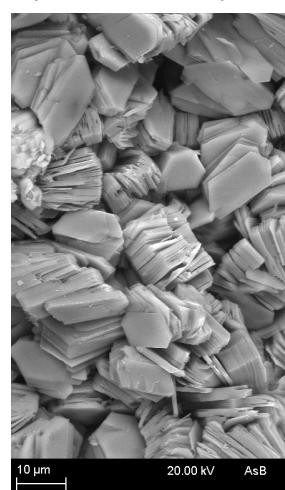
42

9.1 Examples of colloidal particles

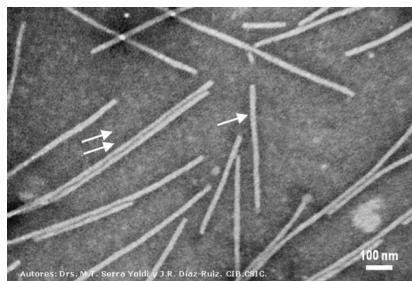
Small particles from e.g. silica or PMMA:



Soil particles like clay



Biological materials like tobacco mosaic virus:



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9.1 Characteristic energy in colloidal systems

$$k_B T$$

44

9.1 What are colloids?



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9.1 What distinguishes colloids from atoms or pebbles?

Diameter of colloidal particles spans several orders of magnitude

Distinct class of systems due to their properties

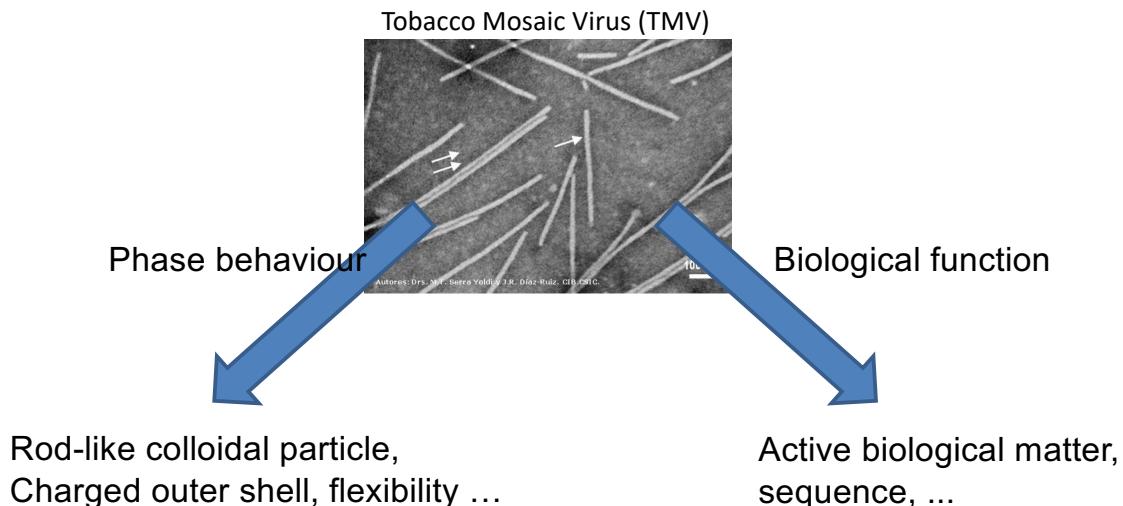
AIM:

Understand properties WITHOUT knowledge of their structure in atomic detail but by shape and surface properties

46

9.1 What distinguishes colloids from atoms or pebbles?

Some of our example particles behave like colloids in certain aspects only



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9.1 What distinguishes colloids from atoms or pebbles?

The characteristic energy in colloidal systems

has to be:

$$k_B T$$

The characteristic diffusion time in colloidal systems has to be finite:

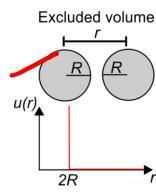
$$2Dt_{exp} = R^2$$



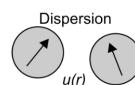
48

9.1.3 Forces of interactions between colloids

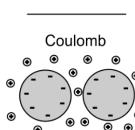
1) Excluded volume interactions



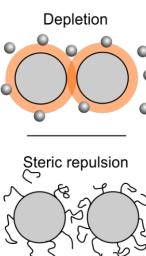
2) Dispersion interactions



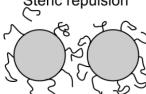
3) Coulomb interactions



4) Depletion interactions



5) Steric stabilisation



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Take home messages I: Colloids

- Colloidal systems are consisting of multiple components where one of them is particles with typical sizes around 10^{-5} to 10^{-9} m
- Gravity introduces a length scale for sedimentation in colloidal systems
- Colloidal systems can be also defined by diffusion time scale compared to experiment time
- Several forces of interactions control the stability of colloidal systems
- Five interactions: excluded volume, dispersion forces, coulomb, depletion and steric interactions

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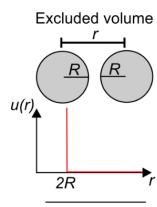
Colloids, electrolytes and charged interfaces 2 Lecture 18 28/4/23

*Upcoming lectures: Mon 1/5 10:15am, Tue 2/5 9am,
Wed 3/5 10:15, Thu 4/5 9am*

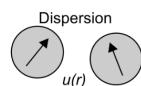
51

9.1.3 Forces of interactions between colloids

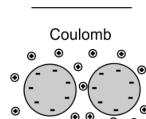
1) Excluded volume interactions



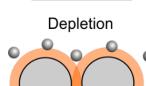
2) Dispersion interactions



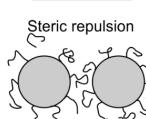
3) Coulomb interactions



4) Depletion interactions

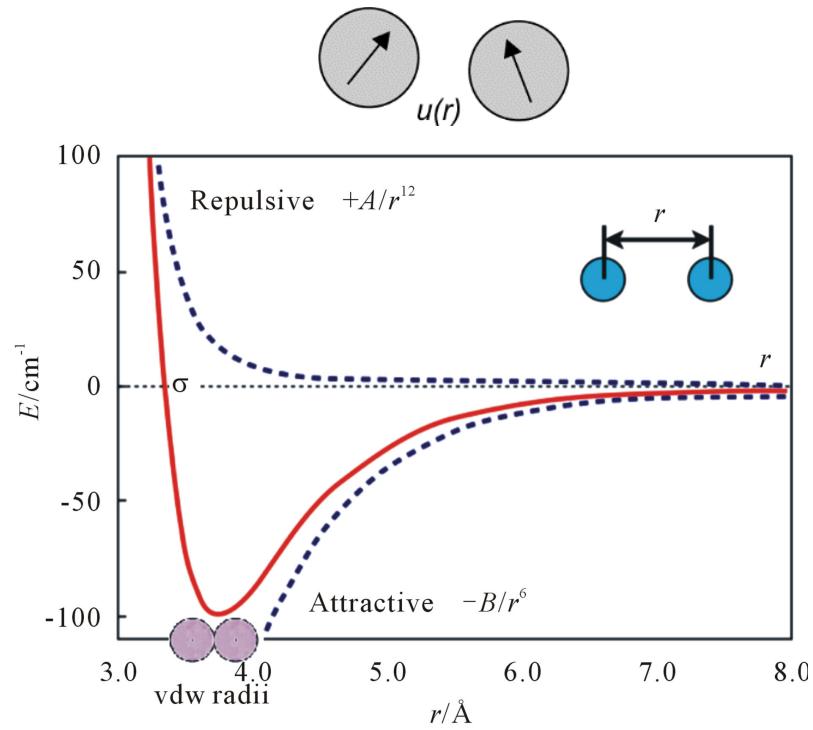


5) Steric stabilisation



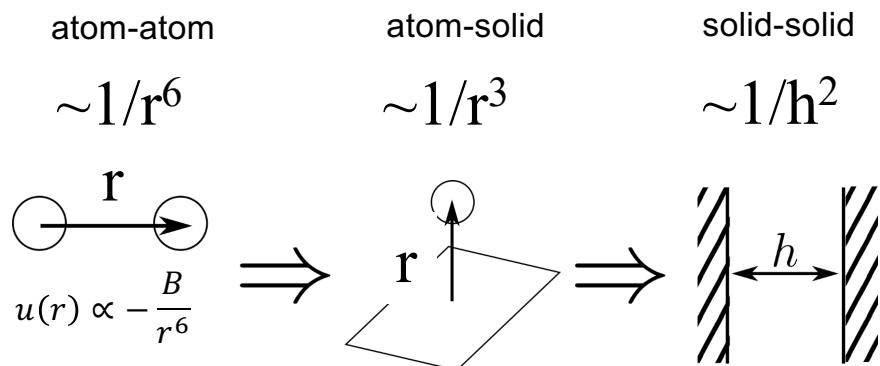
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9.3 Dispersion forces between neutral objects



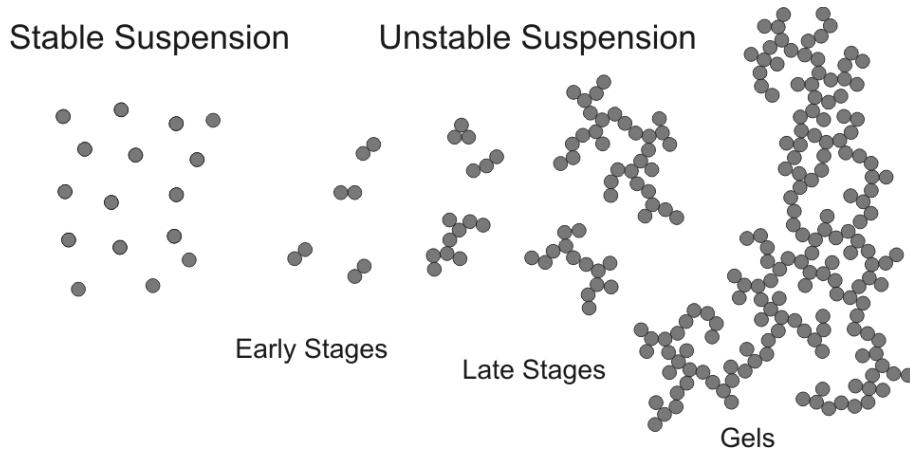
53

9.3 Range of Dispersion forces depends on geometry



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9.3.2 Dispersion forces drive aggregation in colloids

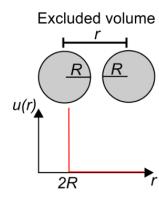


How can we prevent aggregation in colloids and stabilise particle suspensions?

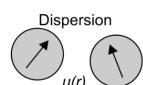
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9 Forces of interactions between colloids

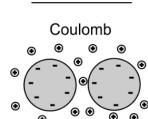
1) Excluded volume interactions



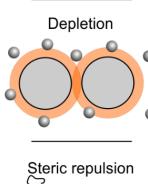
2) Dispersion interactions



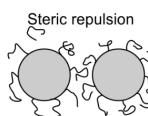
3) Coulomb interactions



4) Depletion interactions

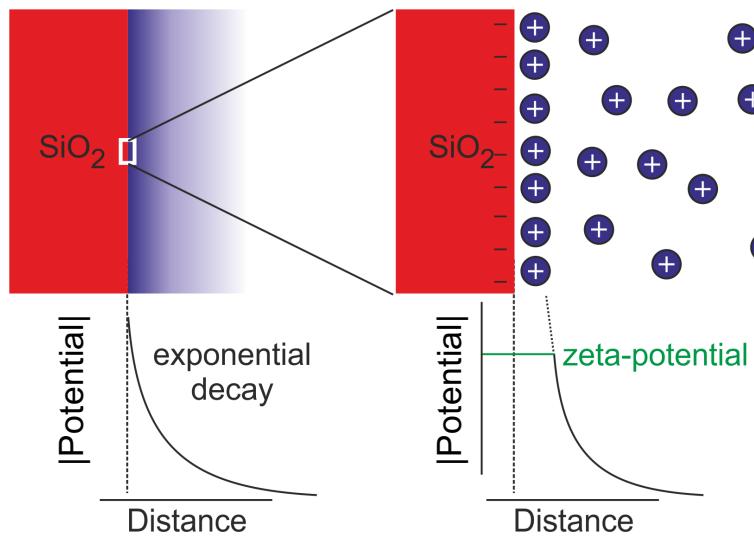


5) Steric stabilisation



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9.4.1 Charged surface in dilute electrolyte solution



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Take home messages: Charged surfaces

- Charged surfaces on solutions are screened by counter-ions
- Electric double layer (EDL) forms and distribution of ions is described by Poisson Boltzmann (PB) equation
- For small surface charges the Poisson-Boltzmann eq. can be linearized
- Distribution of counter- and co-ions on planar and spherical surfaces shows that Coulomb interactions are shorter ranged in ionic solutions

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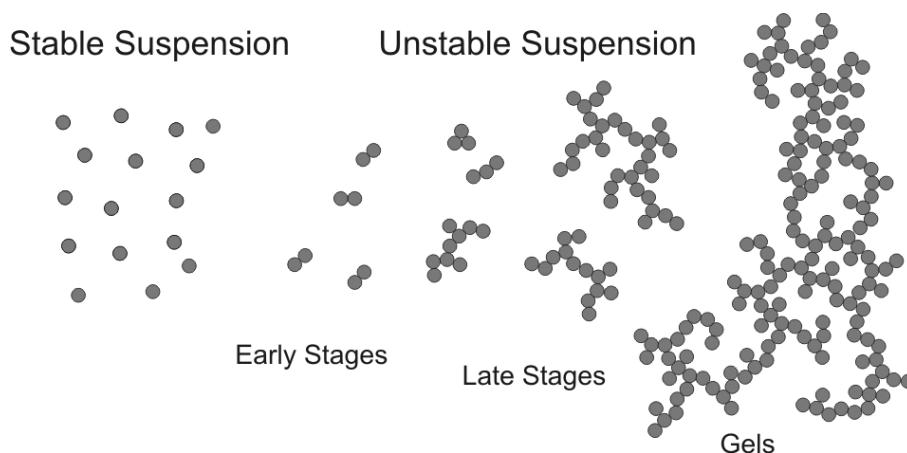
Ulrich Keyser (ufk20) & Tuomas Knowles (tpjk2)

Colloids, electrolytes and charged interfaces 3
Lecture 19 1/5/23

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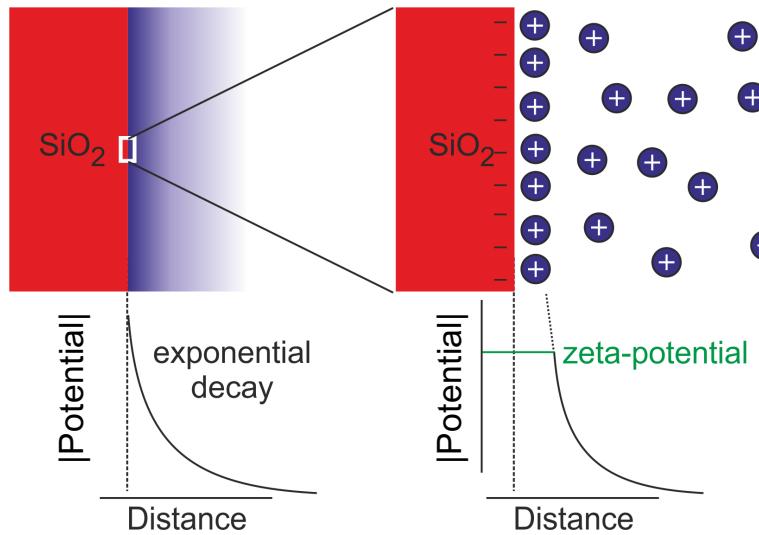
9 Dispersion forces drive aggregation in colloids



How can we prevent aggregation in colloids and stabilise particle suspensions?

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9.4.4 Charged surface in dilute electrolyte solution



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9.4.3-5 Debye length, Bjerrum length, and ionic strength

- Electrostatic interactions lead to formation of double layer around charged surfaces
- Extension of EDL is dominated by two different length scales, Debye screening length

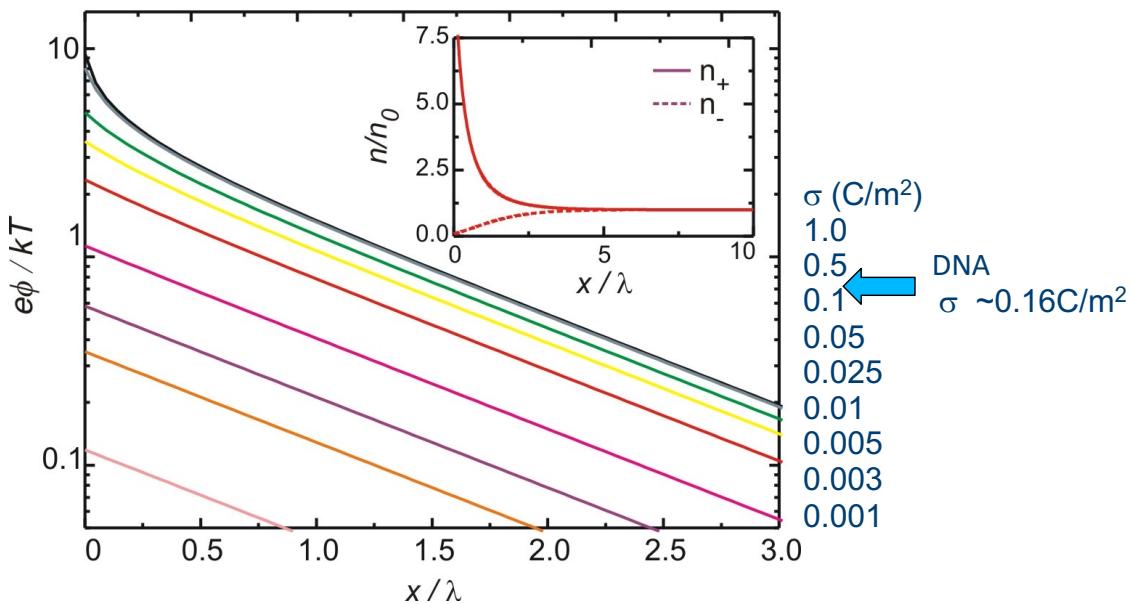
$$l_D \equiv \lambda_D = \left(\frac{e^2}{\varepsilon_0 \varepsilon k_B T} \sum_i z_i n_i \right)^{-1/2} \text{ for monovalent salts } \lambda_D = \left(\frac{\varepsilon_0 \varepsilon k_B T}{e^2 n_0} \right)^{1/2}$$

- Debye length is determined by the properties of the solution
- Bjerrum length in SI units is : $l_B \equiv \frac{e^2}{4\pi \varepsilon_0 \varepsilon k_B T}$ and thus $\lambda_D = (4\pi l_B n_0)^{-1/2}$
- At room temperature, in water, l_B is approximately 0.7 nm *
- Ionic strength I is used in the literature, I is defined by grouping the ions and their respective concentrations c_i together:

$$I \equiv \frac{1}{2} \sum_i z_i^2 n_i$$

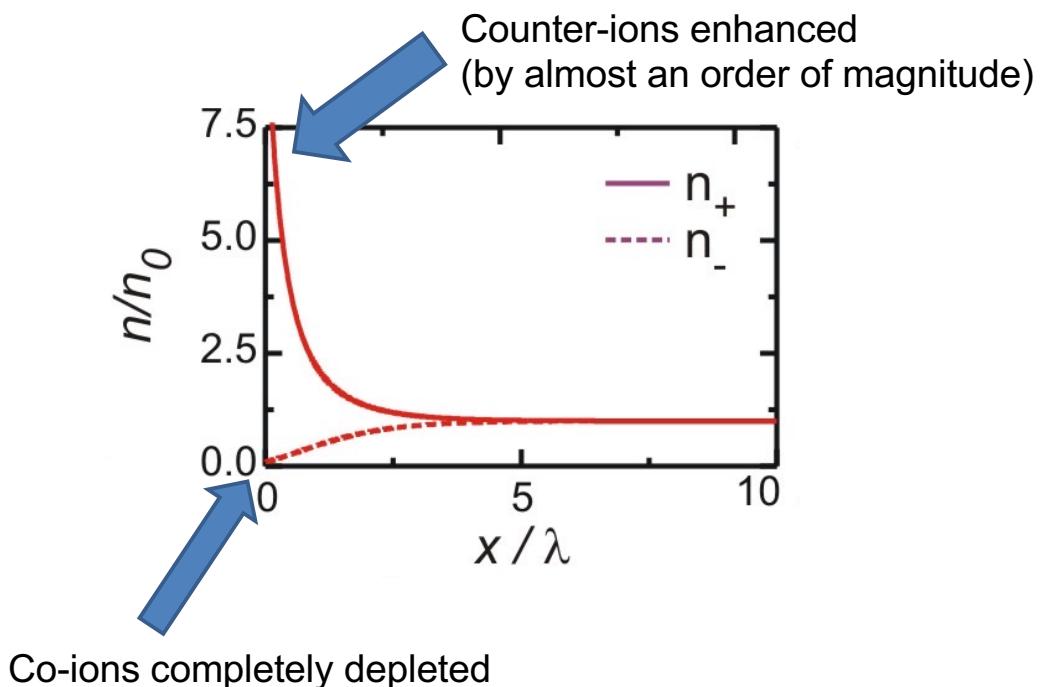
* For water l_B is not temperature dependent as the product of the relative dielectric constant and temperature εT is independent of T . 62

9.4.8 PB for highly charged systems



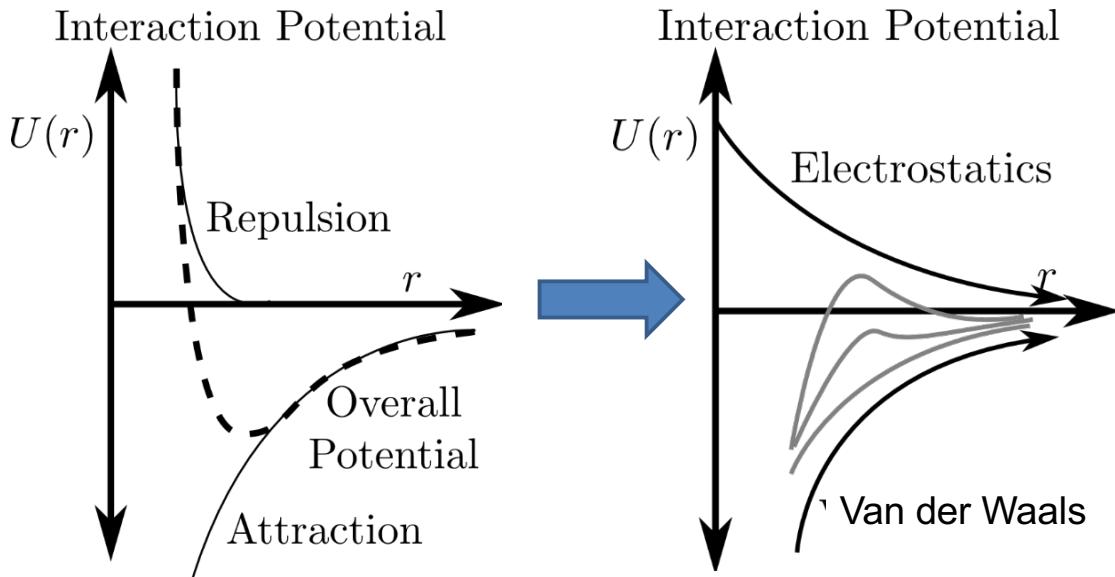
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9.4.8 Co- and counterions in non-linear PB



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9.5 DLVO for controlling aggregation



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Take home messages II: Colloids and Electrolytes

- Dispersion forces drive accumulation of colloidal particles
- Controlling interactions between colloidal particles is possible with electrostatic and steric interactions
- Coulomb interactions in (aqueous) electrolytes are screened with the Debye screening length indicating the exponential decay of the field, depending on $n^{-1/2}$
- Coulomb interactions are screened in electrolytes
- Combining dispersion forces and Coulomb repulsion leads to DLVO theory to describe interactions between particles

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Colloidal phase diagrams &
Electrokinetic phenomena 1

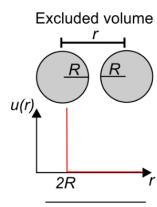
Lecture 20 3/5/23

Upcoming lectures: Wed 3/5 10:15, Thu 4/5 9am

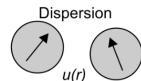
67

9 Forces of interactions between colloids

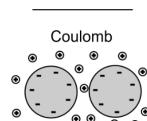
1) Excluded volume interactions



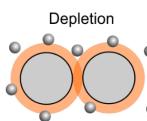
2) Dispersion interactions



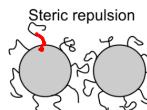
3) Coulomb interactions



4) Depletion interactions

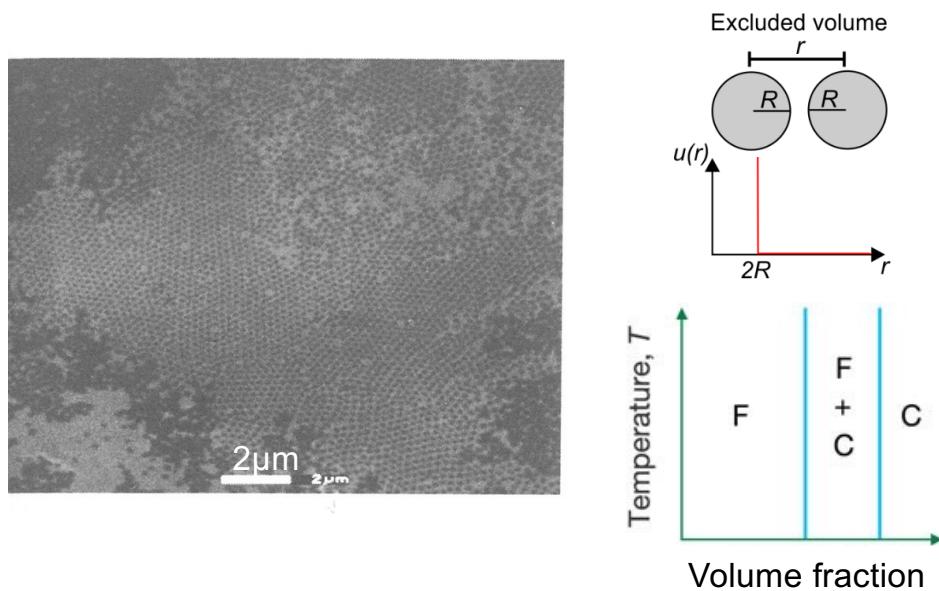


5) Steric stabilisation



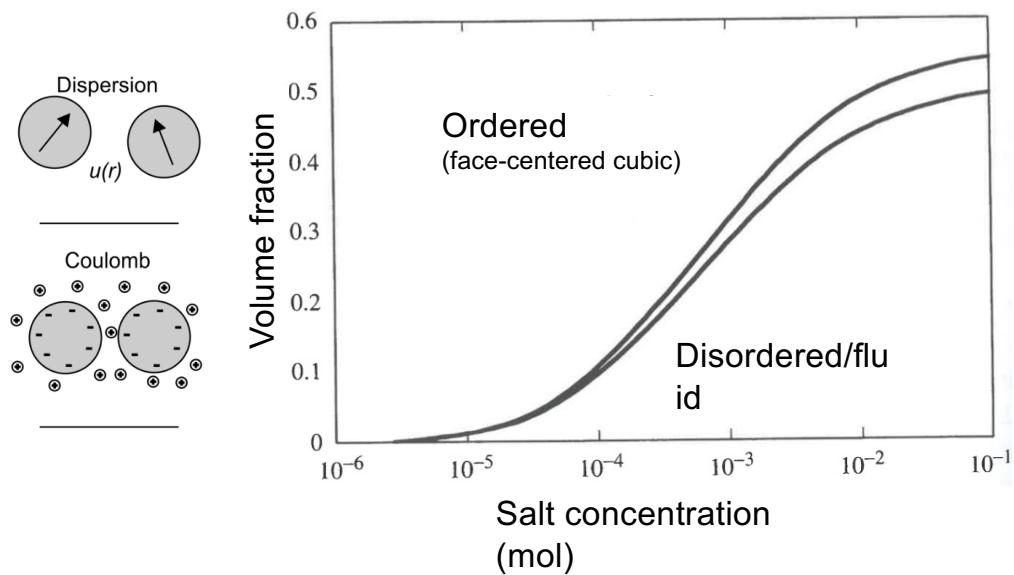
68

9.5.2 Colloidal phase diagrams



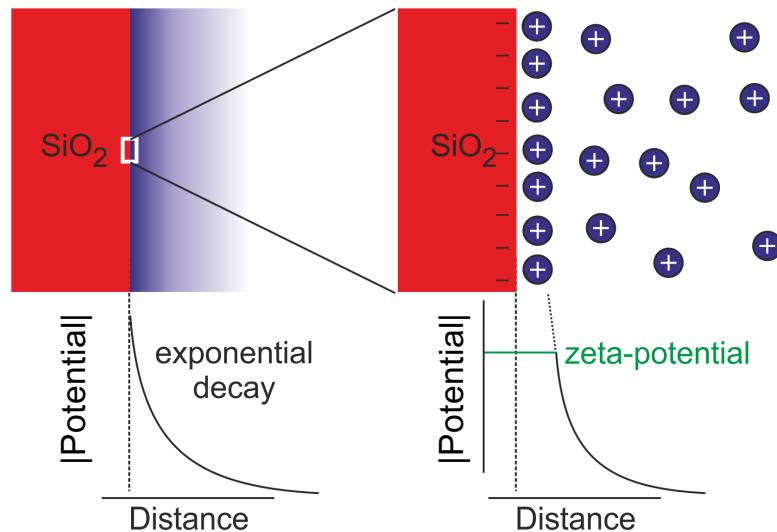
69

9.5.2 Colloidal phase diagrams



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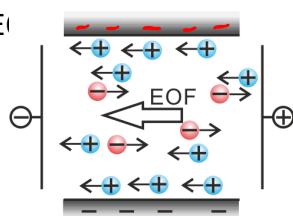
10. Charged surface in dilute electrolyte solution with electric fields (out of equilibrium)



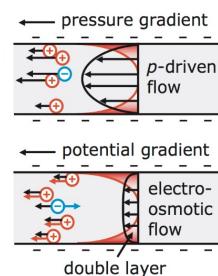
71

10.2 Electrokinetic phenomena

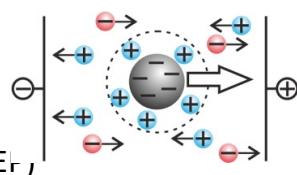
- Electro osmosis (E_O)



- Streaming potential



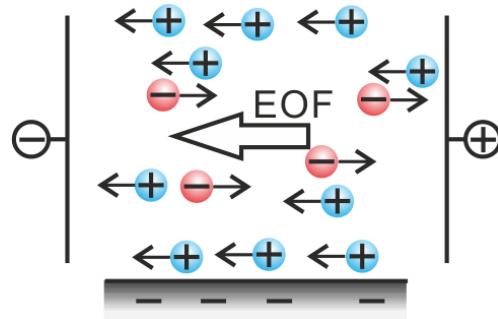
- Electrophoresis (E_F)



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10.2.1 Electrokinetic phenomena

- Electro osmosis (EO) on semi-infinite plane

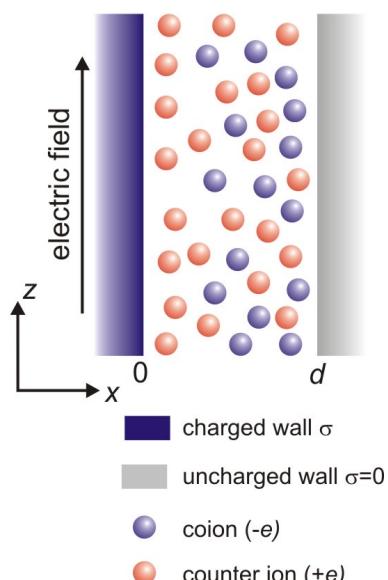


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10.2 “Symmetry” of EOF and EP in thin Debye layer limit

- Applied electric field:
two possibilities

 1. Wall can move velocity is then simply given by
 2. Wall is stationary then ions move with same velocity but opposite sign



Helmholtz Smoluchowski

$$\text{Velocity} \quad v_{eo} = -\frac{\epsilon_0 \epsilon_r}{\eta} \zeta E$$

$$v_{ep} = +\frac{\epsilon_0 \epsilon_r}{\eta} \zeta E$$

Mobility

$$\mu_{eo} = -\frac{\epsilon_0 \epsilon_r}{\eta} \zeta$$

$$\mu_{ep} = +\frac{\epsilon_0 \epsilon_r}{\eta} \zeta$$

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Electrokinetic phenomena 2

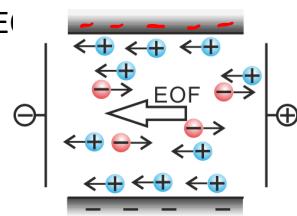
Lecture 21 3/5/23

Upcoming lectures: Thu 4/5 9am

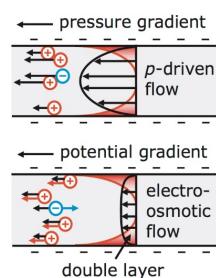
75

10.2 Electrokinetic phenomena

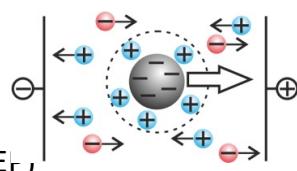
- Electro osmosis (E_O)



- Streaming potential



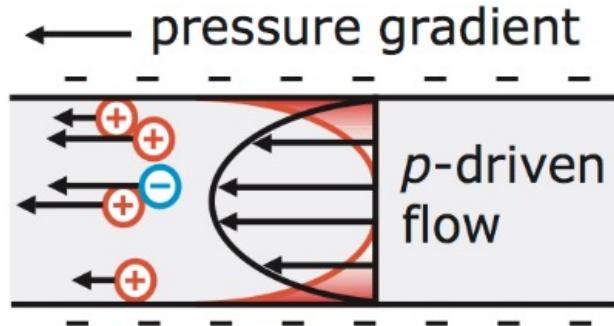
- Electrophoresis (E_F)



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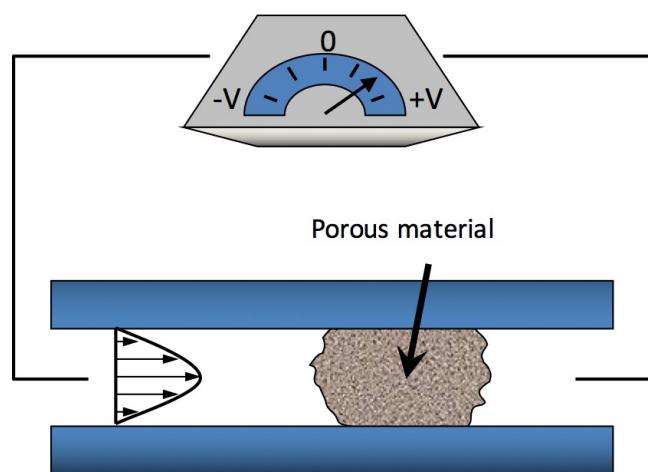
10.2.2 Streaming potential

- Streaming potential in charged channels



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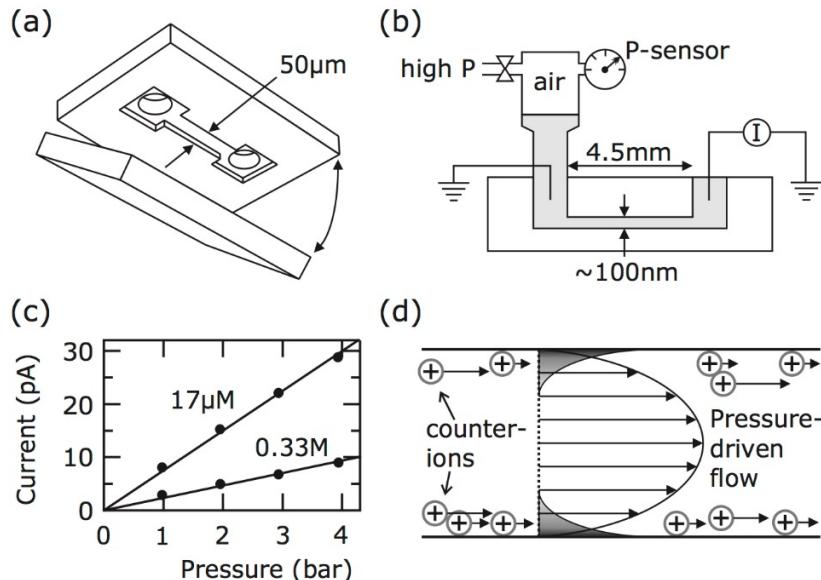
Quincke (1859) streaming potential



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10.2.2 Power generation with EKP

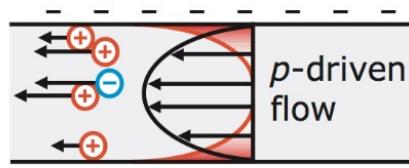
- Streaming potential



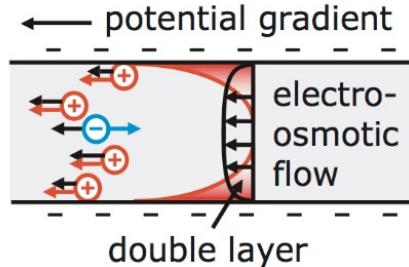
79

10.2.2 Connection of streaming potential and electro-osmosis

- Streaming potential: ← pressure gradient



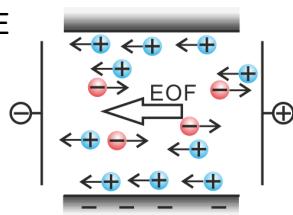
- Electro-osmotic flow: ← potential gradient



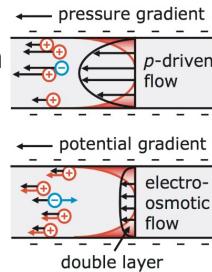
80

10.3 Electrokinetic phenomena: electrophoresis

- Electro osmosis (E)



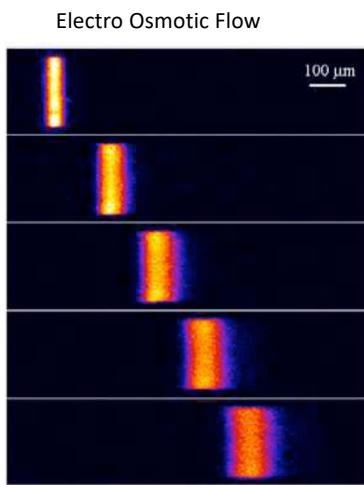
- Streaming potentialia



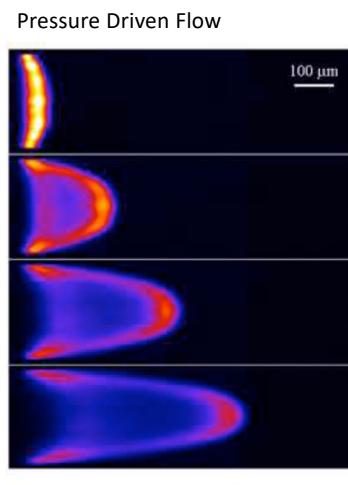
- Electrophoresis (E_r)

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Comparison EOF and pressure driven flow



(a)



(b)

Visualization performed using a molecular tagging technique (caged fluorescence visualization) and shows the reduced sample dispersion for (a) EOF in a capillary with a rectangular cross section 200 mm wide and 9 mm deep; (b) pressure-driven flow in a rectangular cross-section 250 mm wide and 70 μm deep.

<http://microfluidics.stanford.edu/Projects/Archive/caged.htm>

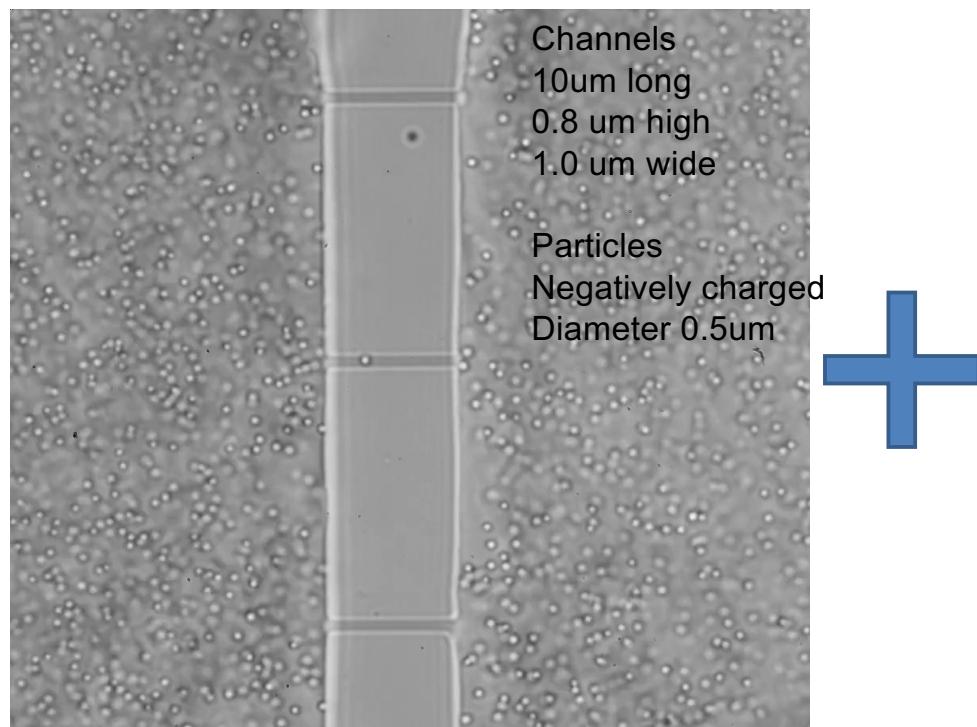
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Take home messages EDL and mobility

- Electric double layer (EDL) is the most important element for understanding electro-kinetic phenomena
- Surface or “Zeta” (ζ)-potential is a parameter that is calculated from mobility data and hence describes the electrophoretic mobility for those specific experimental conditions only
- Electrophoresis and electro-osmosis are closely related and differ only by the sign in the Helmholtz-Smoluchowski equation in the thin Debye layer limit
- Energy production is possible with streaming currents but limited by the no-slip boundary conditions in the hydrophilic channel walls

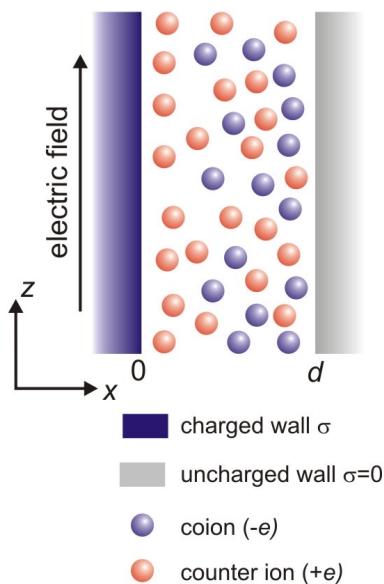
83

10.3 Electrophoresis of colloidal particles



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Velocity of ions in thin Debye layer limit



- Applied electric field:
two possibilities
 1. Wall can move velocity is then simply given by
 2. Wall is stationary then ions move with same velocity but opposite sign

Helmholtz Smoluchowski

Velocity

$$v_{eo} = -\frac{\epsilon_0 \epsilon_r}{\eta} \zeta E$$

$$v_{ep} = +\frac{\epsilon_0 \epsilon_r}{\eta} \zeta E$$

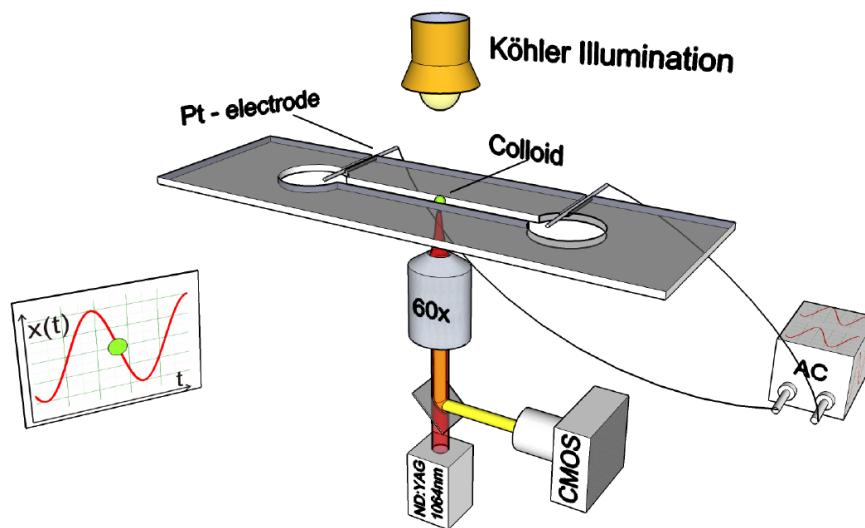
Mobility

$$\mu_{eo} = -\frac{\epsilon_0 \epsilon_r}{\eta} \zeta$$

$$\mu_{ep} = +\frac{\epsilon_0 \epsilon_r}{\eta} \zeta$$

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10.3.3 Testing Helmholtz Smoluchowski



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Optical Tweezers: Nobel Prize 2018

THE
NOBEL
PRIZE

Arthur Ashkin Facts



III. Niklas Elmehed. © Nobel Media

Arthur Ashkin
The Nobel Prize in Physics 2018

Born: 2 September 1922, New York, NY, USA

Affiliation at the time of the award: Bell Laboratories,
Holmdel, NJ, USA

Prize motivation: "for the optical tweezers and their
application to biological systems."

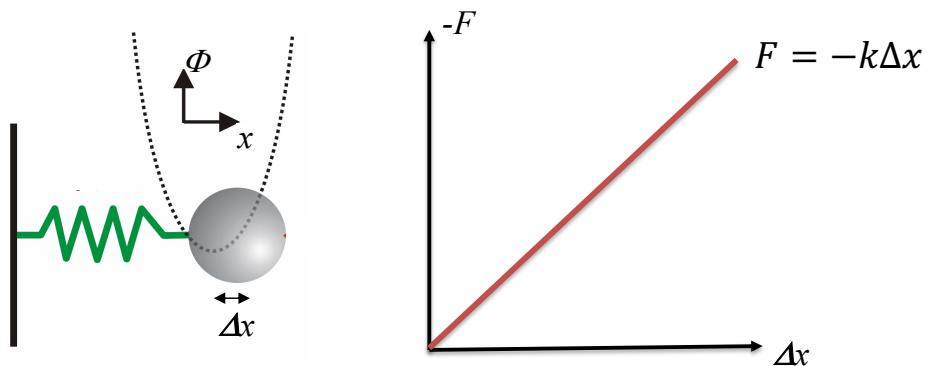
Prize share: 1/2

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Optical trap as harmonic spring

For small distances Δx between the particle centre and the laser focus one can calculate the force F as for a simple harmonic spring with force constant κ .

$$F + k\Delta x = 0$$



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10.3.3 Oscillation of charged particle in AC-field

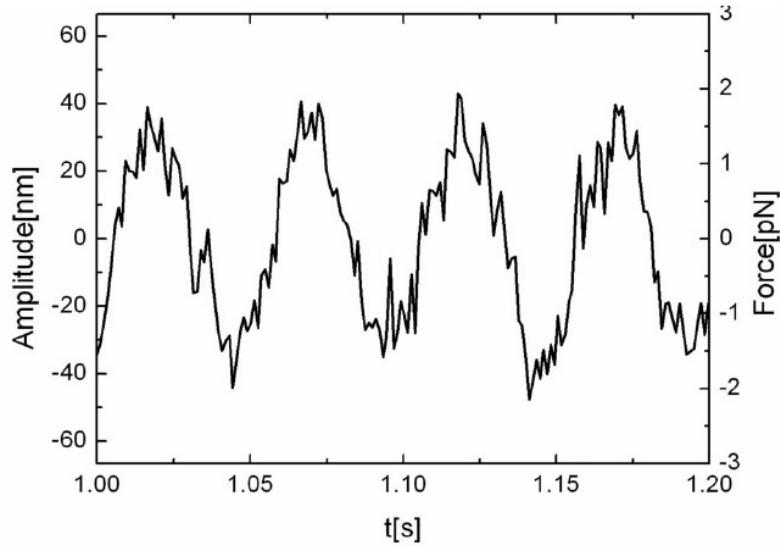
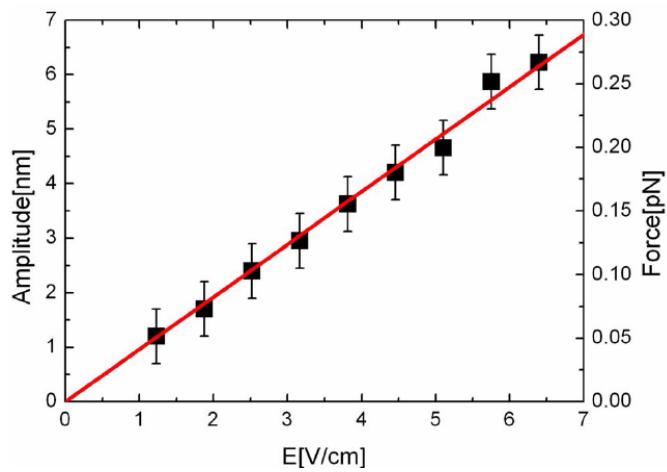


FIG. 4. Amplitude and force as a function of time of a $2.23 \mu\text{m}$ PS colloid moving in an ac field of $E=63 \text{ V/cm}$ at $f=20 \text{ Hz}$ in de-ionized water.

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10.3.3 Electrophoretic Force depends linearly on Voltage



For small extensions from the laser focus optical forces are depending linearly on the distance.

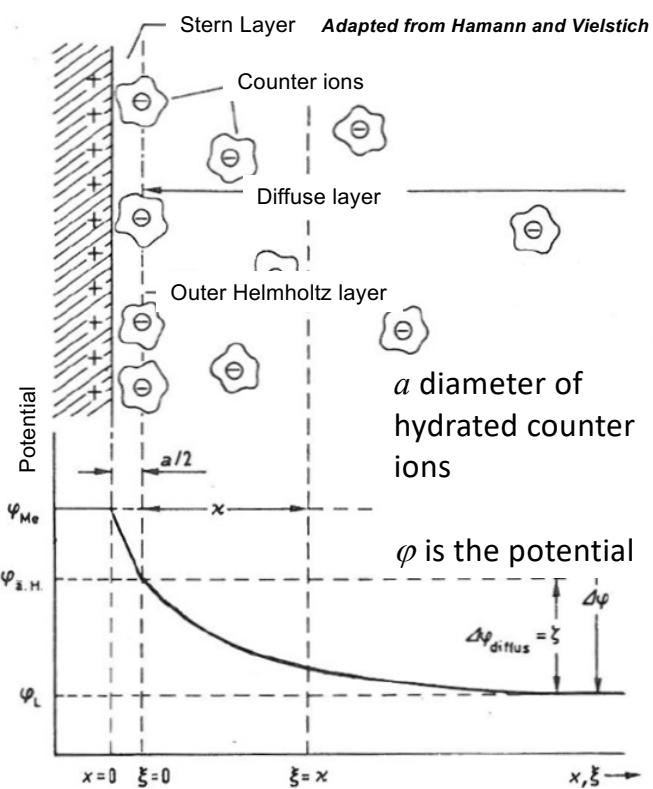
If the force constant k of the optical trap is known the force is simply $F = -kA$, where A is the amplitude of the motion of the colloidal particle in the optical trap due to the applied electric field. Experimental data on single particle confirms Helmholtz-Smoluchowski for thin Debye limit.

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Electric Double Layer

In aqueous solutions we have to deal with a situations where (usually) every surfaces is charged. Not only the constituents (proteins, molecules, DNA, metals or any other surface) but also the water molecules are carrying charge. Water dissociates into H_3O^+ and OH^- and at pH=7: there are around $10^{-7}\text{M} \leftrightarrow 10^{17}$ of both ions present in solution per litre.

Interactions - van der Waals, hydrophobic, chemical and Coulomb, give rise to a structure close to any charged surface, composed of ions and water, known as the **electric double layer (EDL)**. The EDL determines the behaviour of charged polymers or biological molecules in aqueous solutions.



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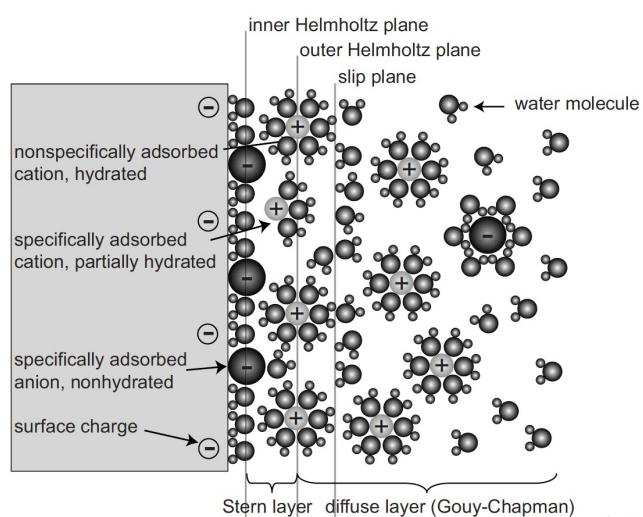
EDL: Zeta (ζ) potential

The surface/Zeta(ζ)-potential describes the potential at the plane above the charged surface where the water molecules and ions are considered as mobile on the timescales of the experiments. The layer beyond the slip length is also known as the diffuse layer as the ions and water molecules are free to move unhindered on the surface.

Zeta(ζ)-potential is a parameter that is very often used in the literature for the description of the surface charge of particles and surfaces in all of colloid sciences as well as in nanofluidic applications.

However, ζ depends on all the experimental conditions and possibly the type of measurement.

Importantly, in experiments one the mobility of particles is measured and then a model is used a to extract ζ .



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Take home messages: electro-osmosis/-phoresis

- Electric double layer is the most important element for understanding electro-kinetic phenomena
- Zeta-potential is a parameter that is calculated from mobility data and hence describes the electrophoretic mobility for those specific experimental conditions only
- Electrophoresis and electro-osmosis are closely related and differ only by the sign in the Helmholtz-Smoluchowski equation in the thin Debye layer limit
- Electro-osmotic/phoretic velocity is linearly proportional to electric field in the thin Debye layer limit

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Take home messages: Electrophoresis, Capacitance of EDL

- Helmholtz Smoluchowski equation is linear in electric field and surface potential and describe mobility of particles in thin Debye layer limit
- Measurement of the mobility allows to extract the surface potential of the particles, however the so called zeta-potential is model dependent
- EDL has a complex structure and water structure plays an important role. Full ED structure has rich substructure with many different layers in the Stern layer that indicates the location of the no-slip boundary conditions. AC measurements can be used to quantify the EDL capacitance and models with series capacitors allow extraction of changes in permittivity.

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Soft Condensed Matter

Keyser and Knowles
Easter 2023

Ulrich Keyser (ufk20) & Tuomas Knowles (tpjk2)

Gel electrophoresis
Lecture 22 4/5/23

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Structure of DNA – The Secret of Life

James Watson (1928-)



Francis Crick (1916-2006)

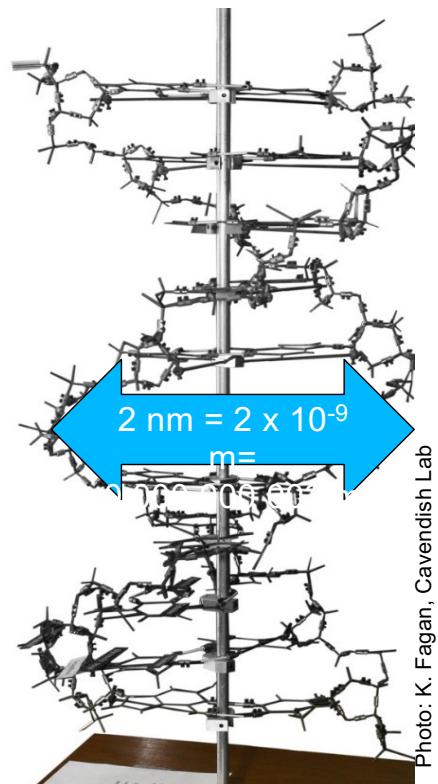
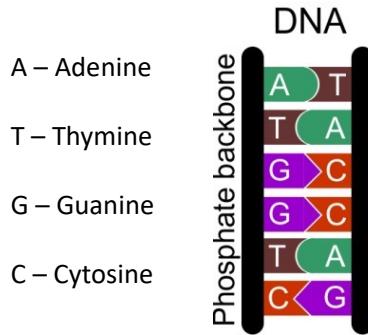
It has not escaped our notice that the specific pairing we have postulated immediately suggests a possible copying mechanism for the genetic material.

Nature 1953

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DNA and Genetic Code

- Molecule of life has four letters:



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10.5 Problem: Separate DNA molecules by length

The velocity of a charged particle (like DNA) is given by the applied electric field divided by the friction coefficient:

$$v_{ep} = -\frac{f_{el}}{\xi}$$

For a double stranded DNA molecule with N basepairs (bp) of length b the electrical force on the whole molecule in a homogenous electric field E is:

$$f_{el,DNA} = -N2eE = \frac{L}{b} 2eE$$

The friction coefficient of the DNA molecule is given by N -times the friction coefficient of each basepair ξ_{bp} :

$$\xi_{DNA} = N\xi_{bp} = \frac{L}{b}\xi_{bp}$$

And hence the electrophoretic velocity $v_{ep,DNA}$ of a DNA molecule is independent of its length:

$$v_{ep,DNA} = -\frac{\frac{L}{b} 2eE}{\frac{L}{b}\xi_{bp}} = -\frac{2eE}{\xi_{bp}}$$

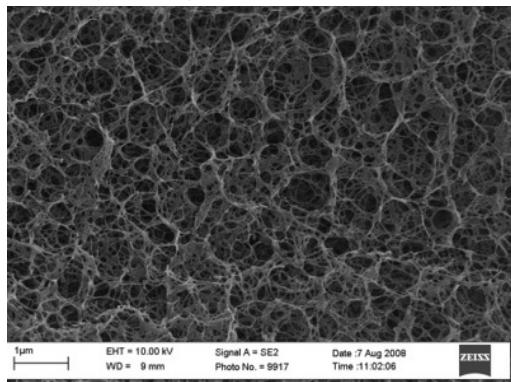
How can we separate DNA molecules by length for applications like DNA sequencing?

Introduce obstacles for molecules that lead to mobility depending on N .

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10.5.2 Gels: Maze for charged polymers for separation

Polymer gel in dried condition



Movement of charged polymers in gels enables electrophoretic sorting of polymers by their molecular mass (length). Gels can be formed for example by heating Agarose monomers to around 100°C and cooling them down to room temperature. After the cool down the polymers form a network of small pores as shown in the electron micrograph above. The density and distance of the polymers forming the mesh of pores can be tuned by the amount of agarose in the solution. **The mesh is very similar to the situation in concentrated polymer solutions and melts.**

The electrophoretic movement of polymers in this mesh is a drift-diffusion process due to the externally applied electric field. The interactions between the mesh and the DNA leads to a length-dependent mobility of the DNA molecules. Separation by length is then possible.

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10.5.2 Polymer Dynamics: Rouse

- **Rouse** – polymer is string of N beads with radius R , solvent moving freely through the chain (“free draining”)
 - Friction coefficient is given by $N\xi$ where ξ is the monomer friction coeff.
 - Rouse diffusion coefficient of polymer chain: $D_R = k_B T / N\xi$
 - Rouse time $\tau_R \Leftrightarrow$ time polymer diffuses over distance equal to its end-to-end distance R_N
 - For times smaller than τ_R , the chain exhibits viscoelastic modes, while for $t > \tau_R$ the chain is simply diffusive with $L^2 \propto t$
 - For a Rouse chain: $\tau_R \approx \frac{\xi b^2}{k_B T} N^{1+2\nu} \approx \tau_0 N^{1+2\nu}$
 - Characteristic time for monomer to diffuse over its size b $\tau_0 \approx \frac{\xi b^2}{k_B T} \Rightarrow \tau_R \approx \tau_0 N^2$ for an ideal chain with $\nu = 0.5$
 - Rouse model ignores hydrodynamic interactions, no knots in the polymer
- ...

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10.5.2 Polymer Dynamics: Zimm

- **Zimm** – similar to Rouse model but solvent moves with chain (no slip on chain), long range hydrodynamic interactions, so we have now typical size of monomers b and viscosity of solvent η . The total friction coefficient of the chain is then given by the size of the chain and depends on the fluid viscosity.
- Stokes friction (neglecting all pre-factors of order 1 as usual): $\xi \approx \eta R$
- With Stokes-Einstein we can then write down the Zimm diffusion coefficient of the full chain with radius of gyration $R = bN^\nu$:

$$D_Z = \frac{k_B T}{\xi} = \frac{k_B T}{\eta R} \approx \frac{k_B T}{\eta b N^\nu}$$

- Remember: The (Flory) exponent ν is depending on the chain, $\nu=0.5$ for ideal chain, $\nu=0.588\approx 3/5$ for self avoiding chain, $\nu=1/3$ for collapsed chains (poor solvent)

- The Zimm relaxation time τ_Z is scaling with N (ignoring pre-factors) as:

$$\tau_Z \approx \frac{R^2}{D_Z} \approx \frac{\eta}{k_B T} R^3 \approx \frac{\eta b^3}{k_B T} N^{3\nu} \approx \tau_0 N^{3\nu}$$

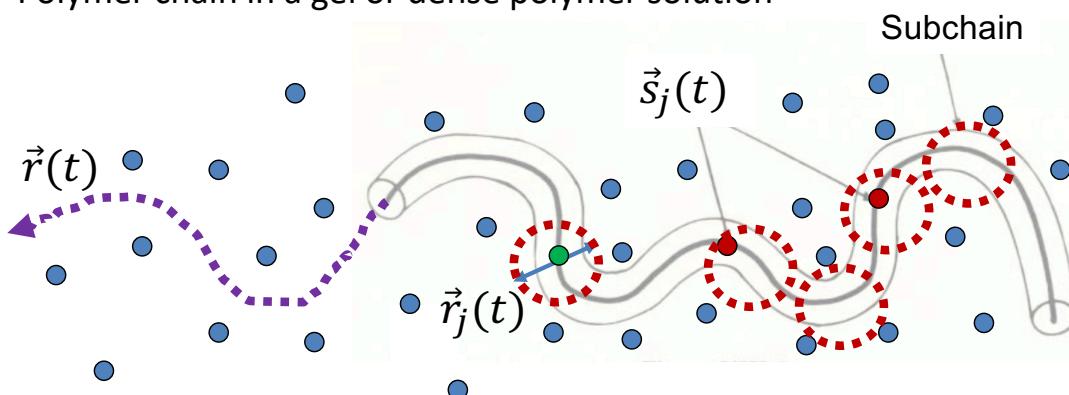
- Main difference to Rouse is the weaker dependence on N since $\nu < 1$.
- Rouse model works well in polymer melts and gels (no significant solvent flow) while Zimm is better for describing polymers in dilute solution (solvent can move).

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10.5.2 Polymer Dynamics in gels and melts: Subchains

Zimm and Rouse models assume that the chain is free to move. In a gel (or polymer melt) the chain cannot move freely and is entangled with gel fibres or other polymers. The chain cannot cross the gel fibres or polymers.

Polymer chain in a gel or dense polymer solution



Three vectors and timescales:

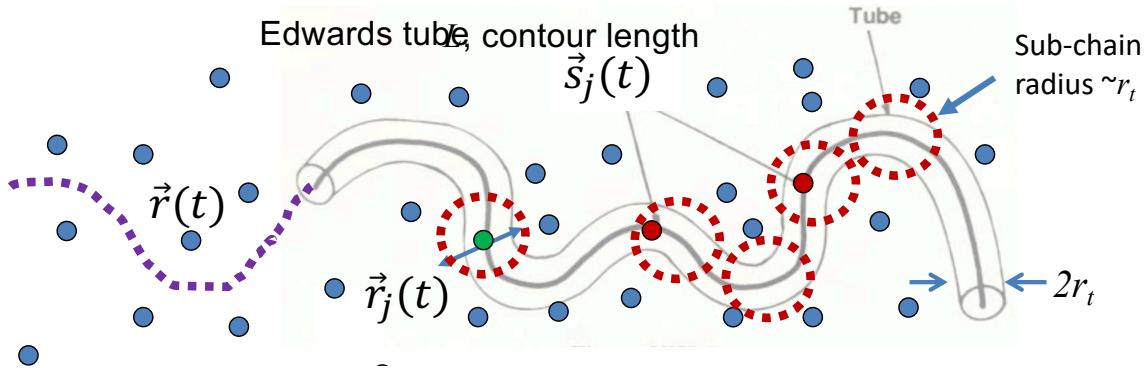
- (i) $\vec{r}_j(t)$ describes the position of monomer j in chain and position in subchain
- (ii) $\vec{s}_j(t)$ describes the motion of a monomer along the reputation tube
- (iii) $\vec{r}(t)$ describes the random walk of the chain through the fibres

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10.5.2 Polymer dynamics in entanglements: Reptation

- Idea (Sir Sam Edwards):
 - chains are confined in a ‘tube’ made of the fibres, tube has radius known as entanglement length r_t is given by $r_t \approx b\sqrt{N_e}$
 - N_e is number of monomers per entanglement

- ‘Coarse grained’ chain length is $R_0 \approx r_t \sqrt{\frac{N}{N_e}} \approx b\sqrt{N}$
- ‘Coarse grained’ contour length: $\langle L \rangle \approx r_t \frac{N}{N_e} \approx \frac{b^2 N}{r_t} \approx \frac{b N}{\sqrt{N_e}}$



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10.5.2 Diffusion along Edwards Tube: “Reptation”

The diffusion coefficient in the tube is just given by the Rouse model since the gel screens hydrodynamic interactions:

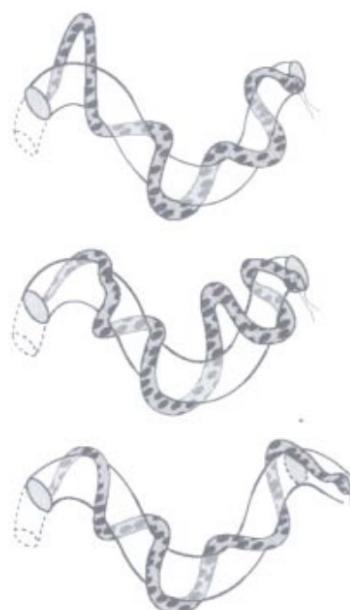
$$D_R = D_C = k_B T / N \xi.$$

The reptation time is the time to diffuse along the complete tube length

$$\tau_{\text{rep}} \approx \frac{\langle L \rangle^2}{D_c} \approx \frac{\xi r^2 N^3}{k_B T N_e} = \frac{\xi b^2}{k_B T} N_e^2 \left(\frac{N}{N_e} \right)^3$$

The lower time limit for reptation is given for the Rouse mode with $N=N_e$

$$\tau_e \approx \frac{\xi b^2}{k_B T} N_e^2$$



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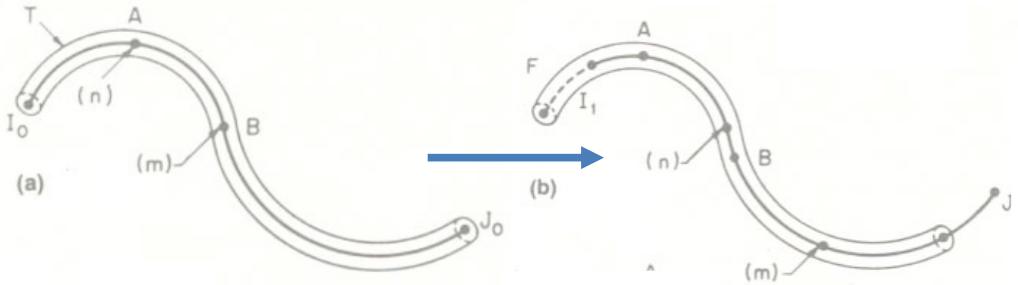
10.5.2 Timescales in Entanglement

1. For $t < \tau_e$, sub diffusion: $\langle |\mathbf{r}_j(t) - \mathbf{r}_j(0)|^2 \rangle \approx b^2 \left(\frac{t}{\tau_0}\right)^{\frac{1}{2}}$
2. For $\tau_e < t < \tau_R$, motion confined in tube \Leftrightarrow displacement only along the tube, this is slower than unrestricted Rouse motion

$$\langle |s_j(t) - s_j(0)|^2 \rangle \approx b^2 \left(\frac{t}{\tau_0}\right)^{\frac{1}{2}} \approx r_t^2 \left(\frac{t}{\tau_e}\right)^{\frac{1}{2}}$$

The tube itself is a random walk with step length $\sim r_t$

$$\langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle \approx r_t \sqrt{\langle |s_j(t) - s_j(0)|^2 \rangle} \approx r_t^2 \left(\frac{t}{\tau_e}\right)^{\frac{1}{4}}$$

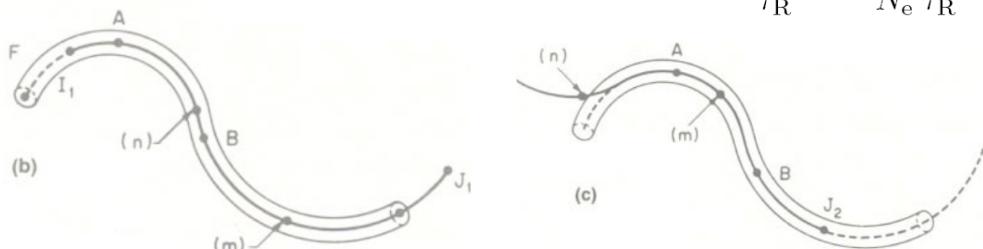


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10.5.2 Timescales in Gels

3. For $\tau_R < t < \tau_{rep}$, motion of all segments is correlated, polymer diffuses along the tube

$$\langle |s(t) - s(0)|^2 \rangle \approx D_c t \approx b^2 N \frac{t}{\tau_R} \approx r_t^2 \frac{N}{N_e} \frac{t}{\tau_R}$$



Random walk of tube is now

$$\langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle \approx r_t \sqrt{\langle |s_j(t) - s_j(0)|^2 \rangle} \approx r_t^2 \left(\frac{N}{N_e}\right)^{\frac{1}{2}} \left(\frac{t}{\tau_R}\right)^{\frac{1}{2}}$$

4. For times much longer than the reptation time $t > \tau_{rep}$, free diffusion is recovered with the diffusion coefficient D_g in the gel

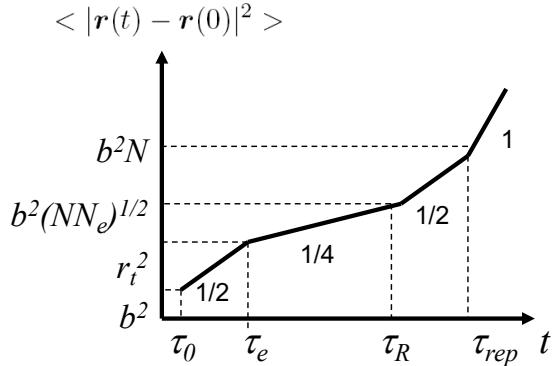
$$\langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle = 6D_g t$$

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10.5.2 Timescales in entanglement

Four different regimes

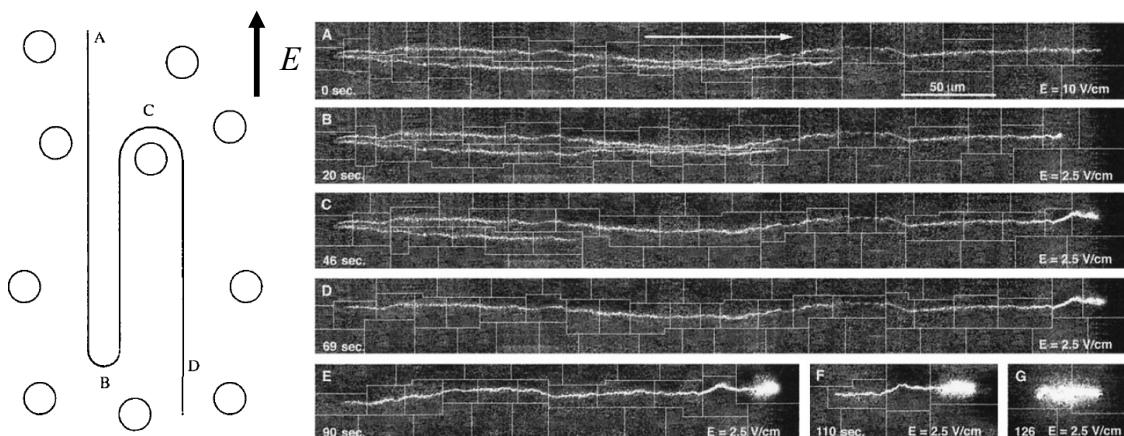
1. For $\tau_0 < t < \tau_e$ $\langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle \sim t^{\frac{1}{2}}$
2. For $\tau_e < t < \tau_R$ $\langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle \sim t^{\frac{1}{4}}$
3. For $\tau_R < t < \tau_{rep}$ $\langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle \sim t^{\frac{1}{2}}$
4. For $t > \tau_{rep}$ $\langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle \sim t^1$



Polymers behave like colloids with a diffusion coefficient and MSD scaling of t^1 only when probed on time scales much larger than the reptation time. On very short timescales polymer dynamics is slowed because of the connectivity of the chain segments (Rouse, Zimm), on intermediate time scales the slow-down arises from the entangled nature of the chains (reptation tube disengagement). For long time scales the diffusion coefficient depends on the length of the chain N , which allows for separation of polymers by their length.

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10.5.2 Imaging DNA in the Edwards (reptation) tube



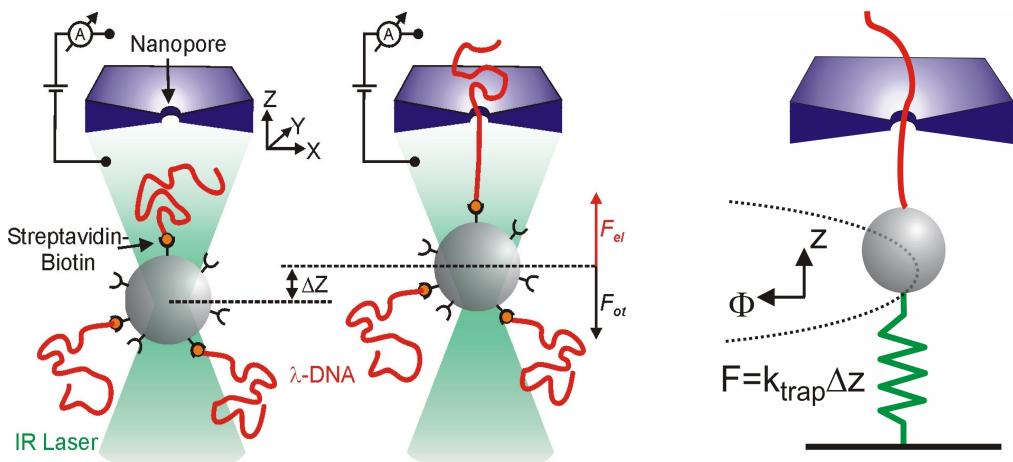
DNA can get trapped around gel fibres. Especially for very long DNA this can lead to fully stretched molecules. By labelling the DNA molecule with fluorescent dyes the reptation (Edwards) tube can be visualised in gel electrophoresis.

Molecule can get trapped in the gel by either being wrapped around a gel fibre or by forming an entropic coil in a larger void.

Measurements show that the molecule follows its reptation tube until relaxation in a void in the gel.

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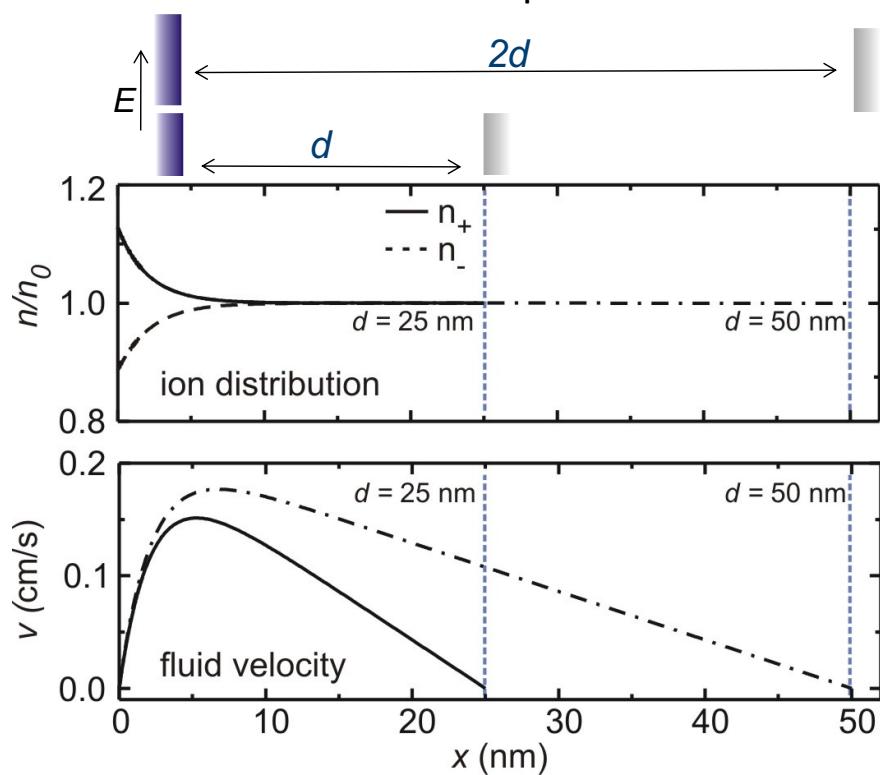
10.5.3 Forces in gel electrophoresis



DNA is moving through pores in the gels. In experiments we can use optical tweezers to measure the force on a single DNA molecule in a small nanochannel resembling a pore in gel electrophoresis. We will use electrophoresis and osmosis to explain the forces acting on the molecule.

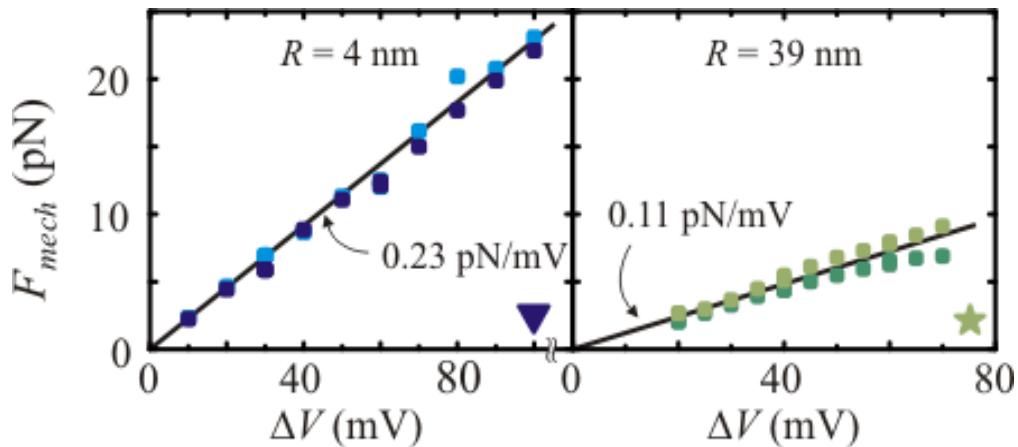
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10.5.3 Electroosmotic flow depends on boundaries



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10.5.4 Force Dependence on Nanopore Radius



- Force is proportional to voltage as expected
- For larger nanopore force is roughly halved
- Hydrodynamic coupling between molecule and nanopore leads to geometry dependence

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Summary

- SCM is an exciting and rapidly developing area since it requires understanding of many different phenomena that work together. Complexity in SCM stems from the many different forces of interaction working together at the same time.
- Example: Quantitative understanding of Gel electrophoresis requires Poisson-Boltzmann, Polymer dynamics, Fick diffusion, Ion Dynamics, Electroosmosis and -phoresis to describe the polymer behaviour
- In general, solve a problem in Soft Condensed Matter by identifying which time scales, forces or energies are dominant in the system - always consider effects with respect to thermal energy $k_B T$ and think about the length scales, forces, and related energies.

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