Soft Matter

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Acknowledgements

- Alice Thorneywork (Oxford)
- Dirk Aarts (Oxford)

Lectures and problem classes

- Lectures
  - Tuesdays 08:30 – 10:15 (HG00.622)

- Problem classes
  - Thursdays 15:30 – 17:15 (HG00.308)

... this is where you practice, so this is where you learn it all ...

... and the problems are representative for the exam!

Problems for problem classes (& study guide & answers)

http://www.dullenslab.com/teaching/softmatter and Brightspace (recorded lectures)

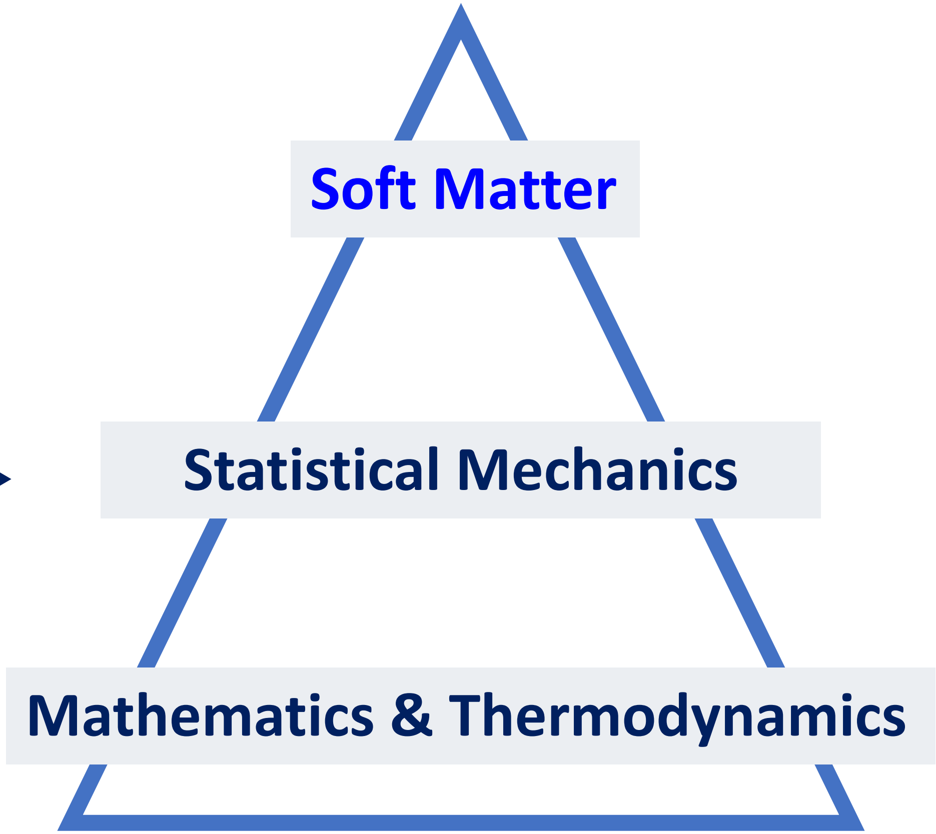
Recommended literature

- Soft Matter Physics by M. Doi, Oxford University Press (2013)
- Soft Matter, concepts, phenomena and applications by W. van Saarloos, V. Vitelli and Z. Zeravcic, Princeton University Press, (2023)
- Molecular Driving Forces by K. A. Dill and S. Bromberg, (referred to as D & B)
- Intermolecular and Surface Forces by J. Israelachvili,
- The Colloidal Domain by D. Fennell Evans & H. Wennerström,
- Theory of the stability of lyophobic colloids, E. J. W. Verwey and J. Th. G. Overbeek
- ...

Required tools

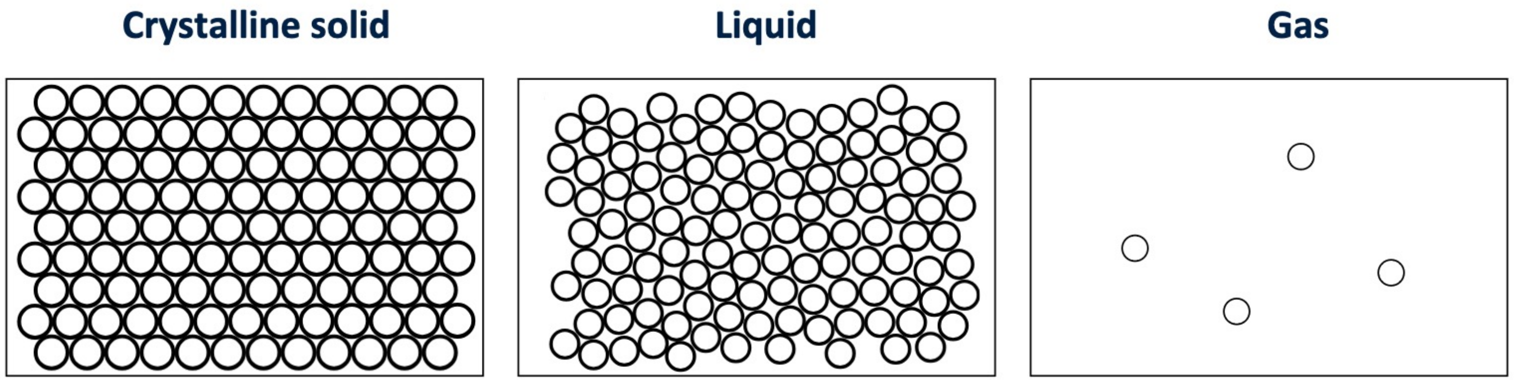
- **Mathematics**
- **Thermodynamics**
- **Statistical Mechanics**
- Your brain
- Practise (lots of it)

What Soft Matter
is built onto



What is Soft Matter?

States of Matter:



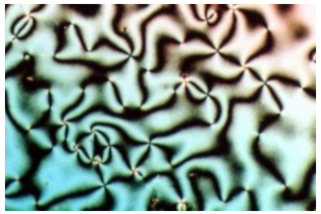
Soft Matter:

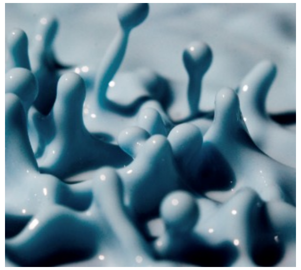
Anything that is not a gas, simple liquid or hard solid…

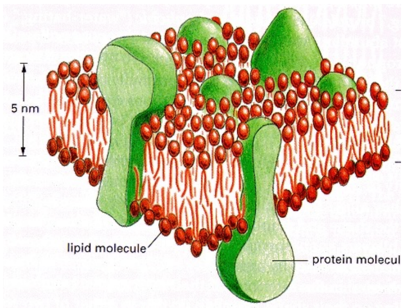
What is Soft Matter?

Anything that is not a gas, simple liquid or hard solid

- Gels
- Foams
- Elastomers
- Biological macromolecules
- Complex fluids (e.g. polymer/surfactant solutions)
- Liquid crystals
- Membranes and monolayers
- Colloids (paint, blood, ice-cream, chocolate, …)
- Granular matter (sand, salt, nuts, ...)







What do these systems have in common?

Textbook definition of Soft Matter

Chemical bonds not important

Way too difficult for QM

"Soft condensed matter is characterised by the weak interactions between polyatomic constituents, by important thermal fluctuation effects, by mechanical softness and by a rich range of behaviours".

$k_B T$ instead of $h\nu$

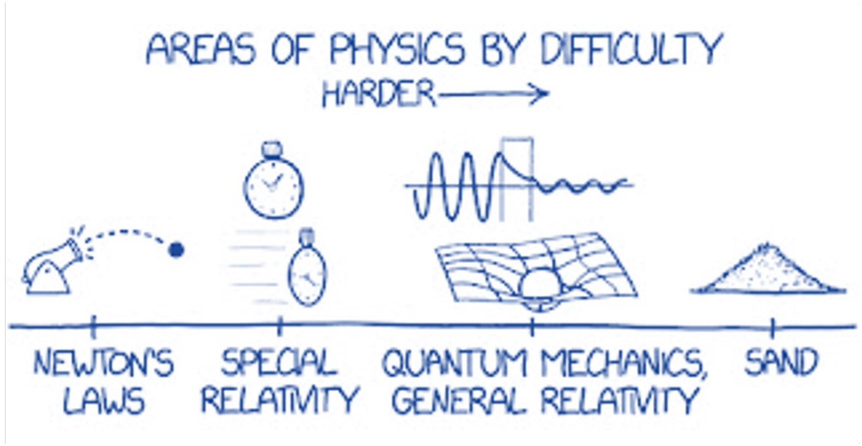
Easily deformable

That's why it's interesting!

Phase Transition in Soft Condensed Matter, ed. T. Riste & D. Sherrington, Plenum Press, 1989 (New York)

Key characteristics of Soft Matter

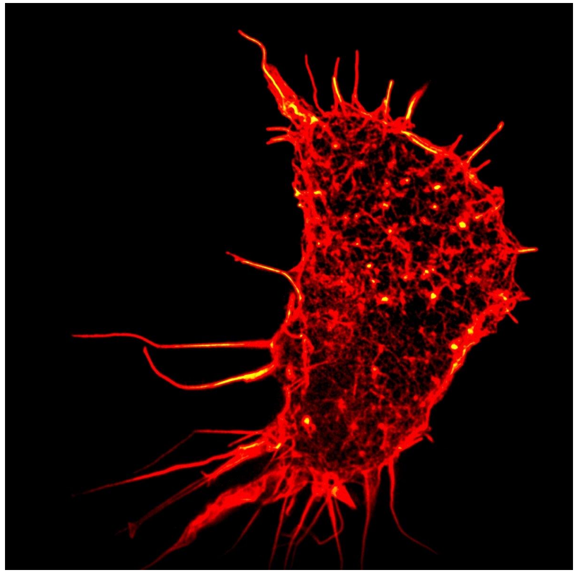
- Multiple weak interactions
  - Electrostatics (esp. charge-charge, also dipole-dipole)
  - H-bonding
  - Dispersion forces
- Entropy is *really* important
  - Fluctuations
  - Osmotic pressure
- Multiple length scales
  - Hierarchical structures & self assembly
- Multiple time scales



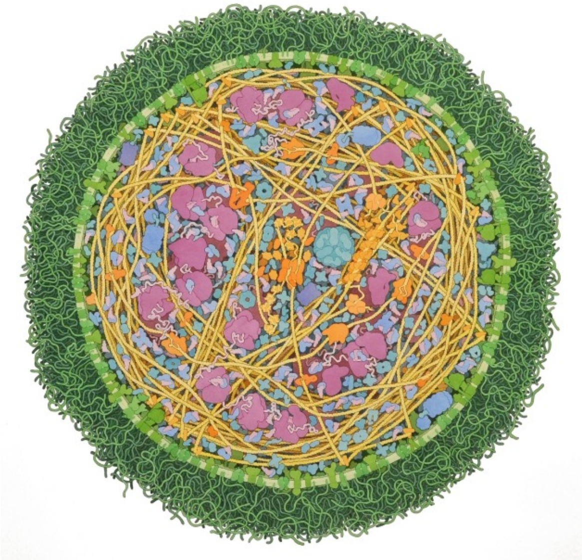
Randall Munroe, “What Makes Sand Soft?” in The New York Times (Nov 9, 2020)

Biology: soft matter come alive

... a living cell ...



Dr Alison Dun, ESRIC (UK)



Prof David S. Goodsell , Scripps Research Institute (US)

Mainly soft matter, but very complex! What should we do?

'wave your hands ...'

Building (simple) physical models that capture key behaviour

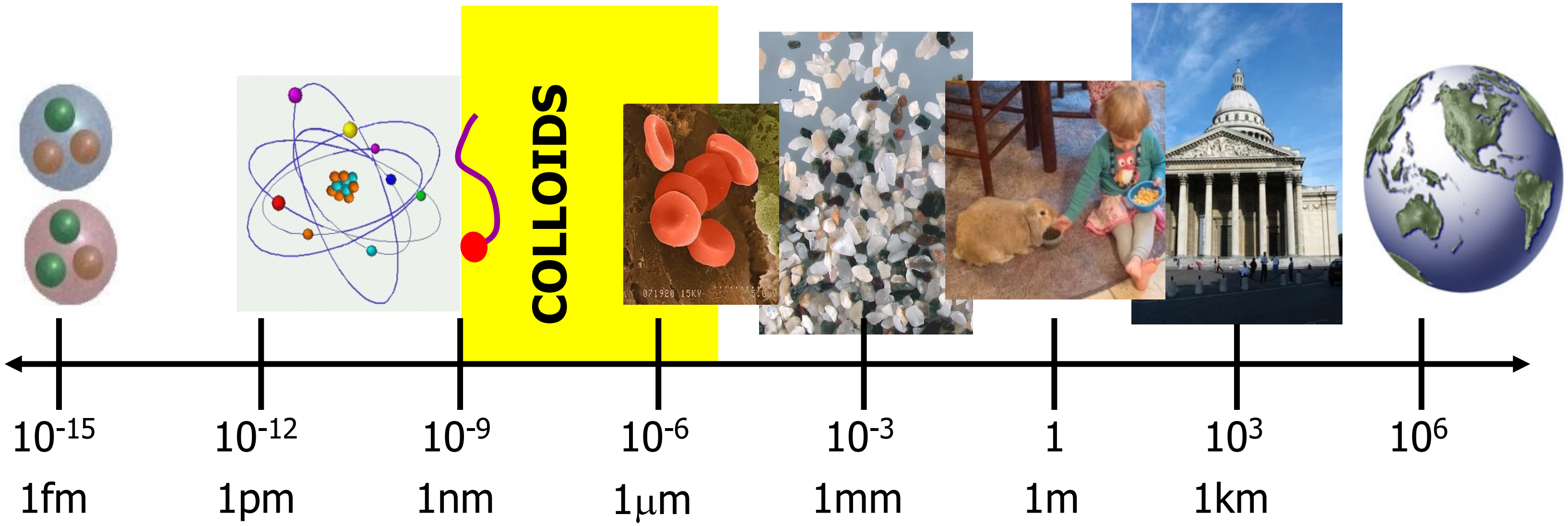
Contents of the course

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

What are colloids?

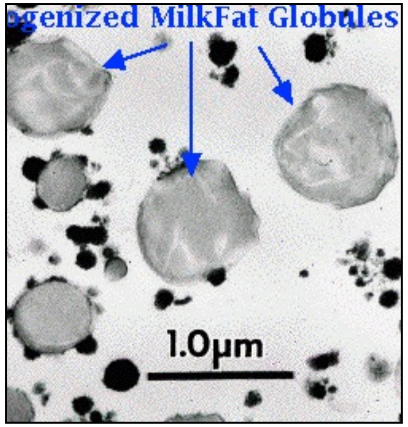
<u>International Union of Pure and Applied Chemistry</u>

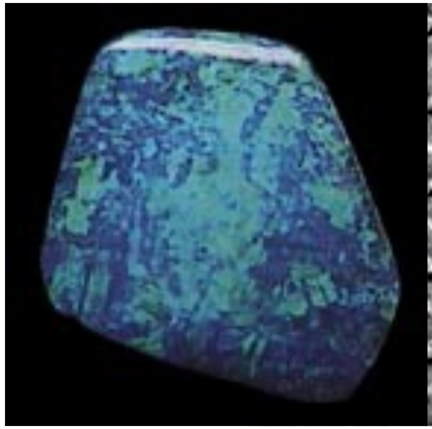
"The term colloidal refers to a state of subdivision, implying that the molecules or polymolecular particles dispersed in a medium have at least in one direction a dimension roughly between 1 nm and 1 μm."

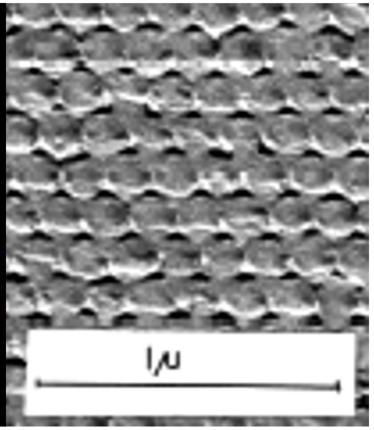


Colloids in daily life

milk

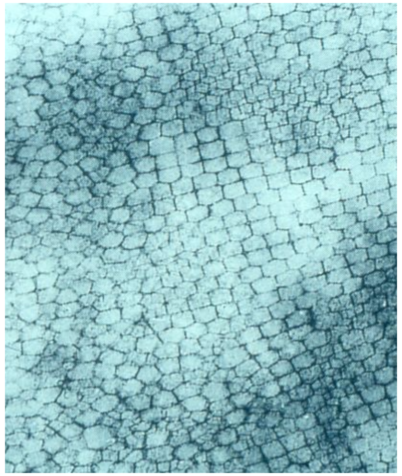


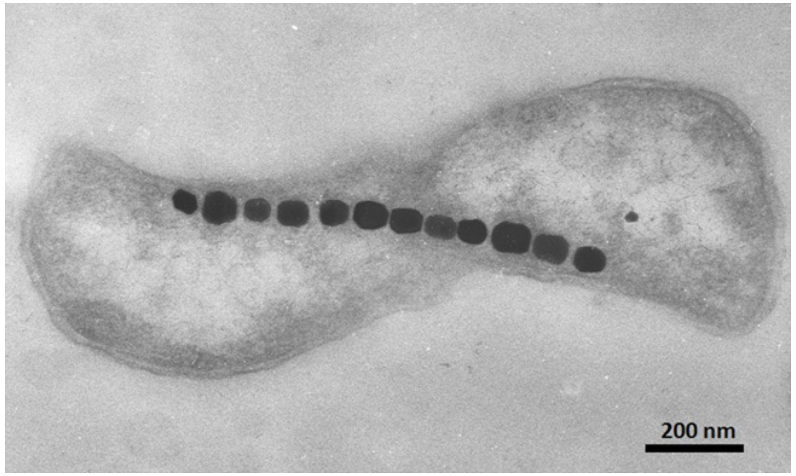




opals

paint





bacteria

Colloidal particles as 'big atoms'

Albert Einstein
(1879-1955)

5. *Über die von der molekularkinetischen Theorie der Wärme geforderte Bewegung von in ruhenden Flüssigkeiten suspendierten Teilchen;*
von A. Einstein.

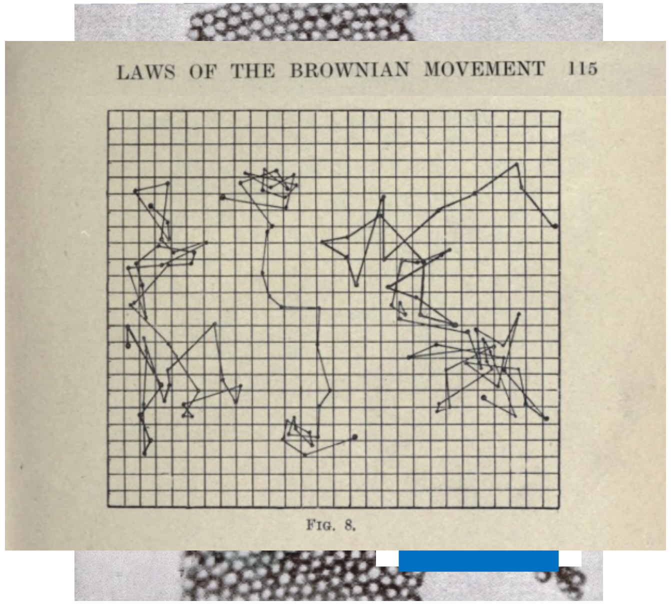
Vom Standpunkte der molekularkinetischen Wärmetheorie aus kommt man aber zu einer anderen Auffassung. Nach dieser Theorie unterscheidet sich eingelöstes Molekül von einem suspendierten Körper *lediglich* durch die Größe, und man sieht nicht ein, warum einer Anzahl suspendierter Körper nicht derselbe osmotische Druck entsprechen sollte, wie der nämlichen Anzahl gelöster Moleküle. Man wird anzunehmen haben, daß

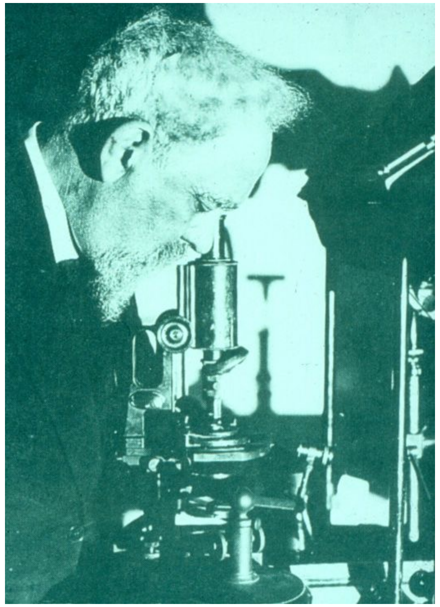
Ann. d. Physik, 17, 549 (1905)

According to this theory **a dissolved molecule is differentiated from a suspended body *solely* by its dimensions**, and it is not apparent why a number of suspended particles should not produce the same osmotic pressure as the same number of molecules.

Colloidal particles as 'big atoms'

Albert Einstein
(1879-1955)

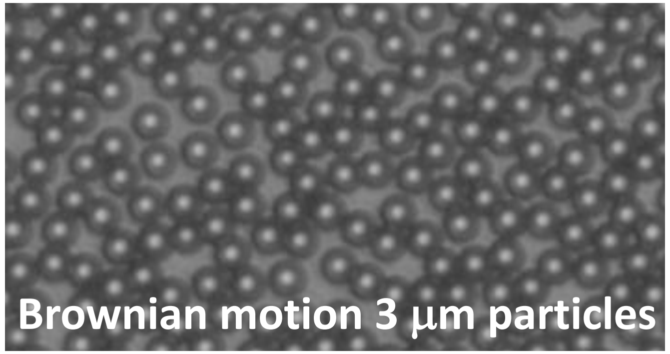


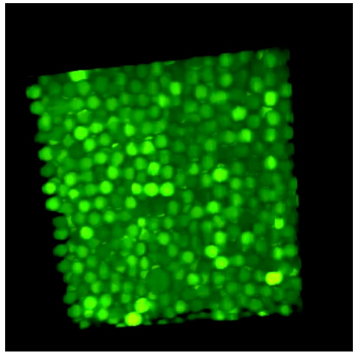


Jean Perrin
(1870-1942)

You can see them (with a microscope) ...

... and follow them: Brownian motion*



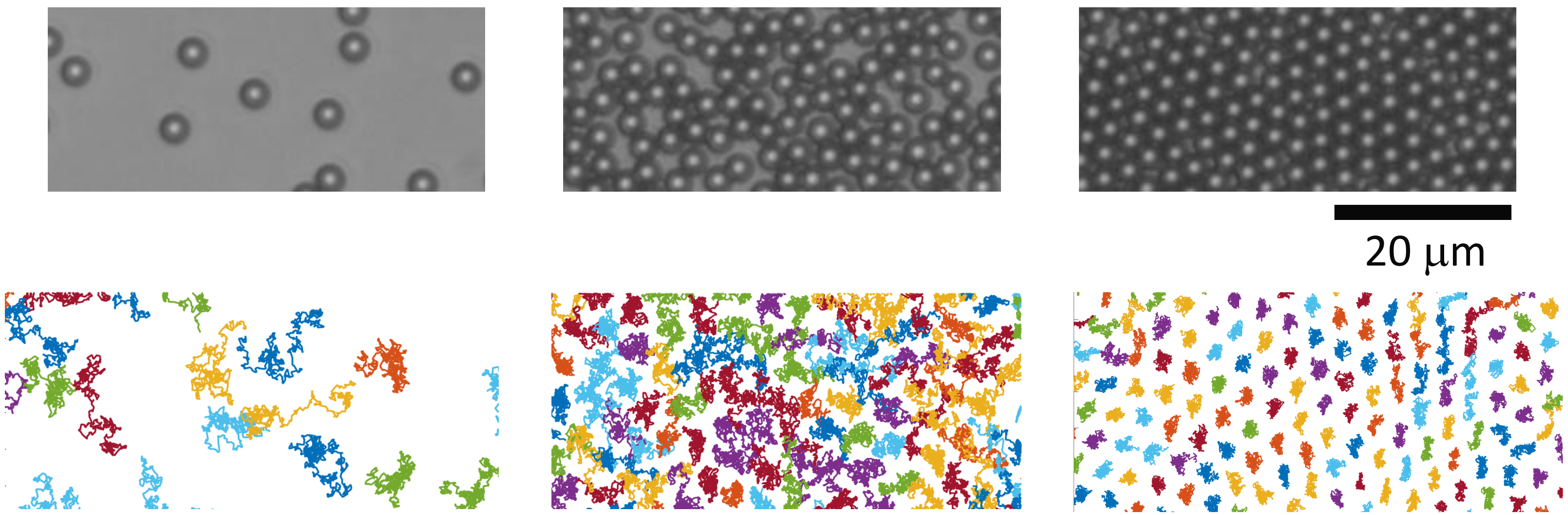


also in 3D (lecture 5)

* Thermal fluctuations is a general property of soft matter

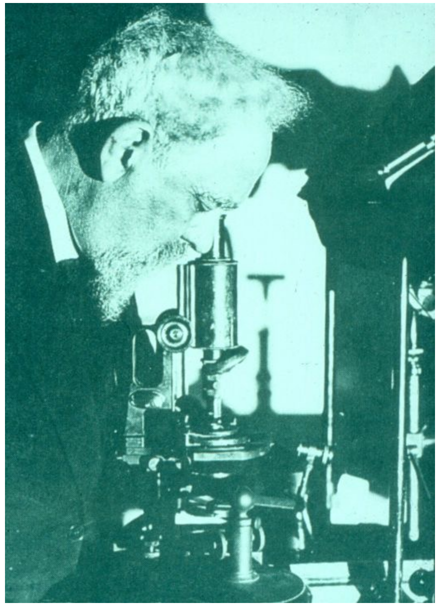
Structure and dynamics of colloidal gas, liquid and crystal

Colloidal gas | Colloidal liquid | Colloidal crystal



Brownian motion & entropy-driven phase transitions *(lecture 2)*

From colloids to the existence of atoms

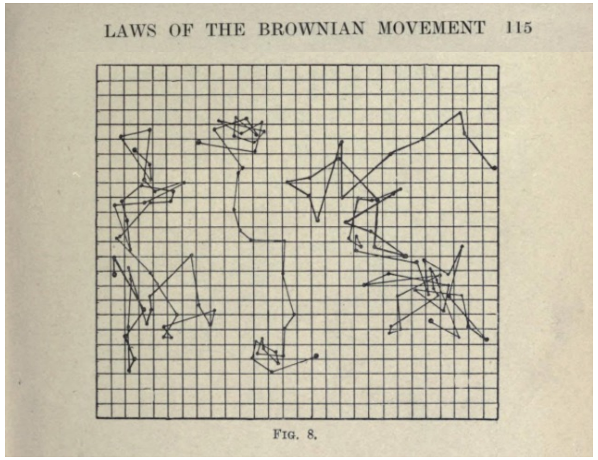


Jean Perrin
(1870-1942)

Nobel Prize Physics 1926

*"For his work on the **discontinuous structure of matter**, ..."*

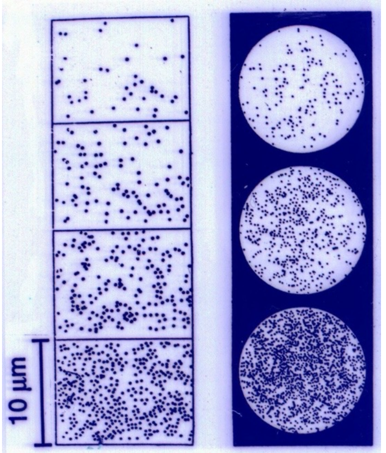
Brownian motion[1]



LAWS OF THE BROWNIAN MOVEMENT 115

FIG. 8.

Sedimentation-equilibrium[2]



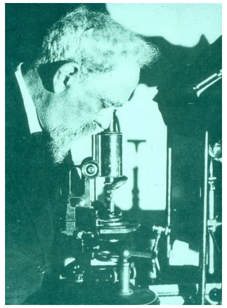
Experimental determination of Avogadro's number!

$$k_B = \frac{R}{N_{AV}}$$

[1] 3rd year soft matter practical: 'Cooking, Looking and Tweezing'

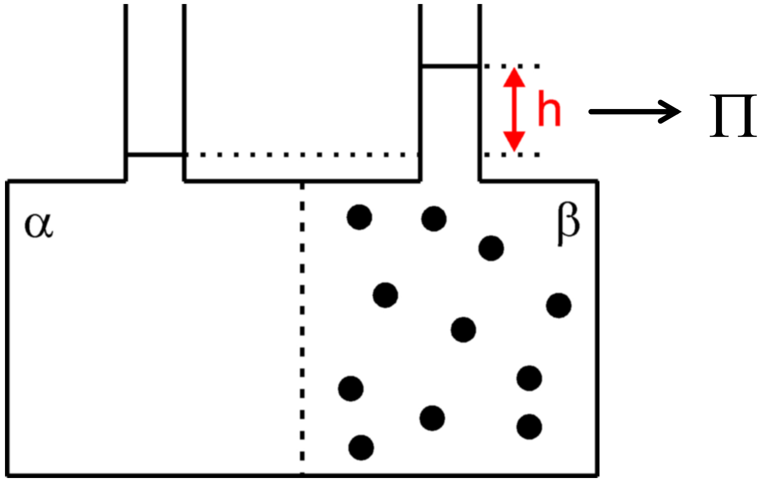
[2] Barometric height distribution: see problem set

Sedimentation equilibrium: (osmotic) pressure



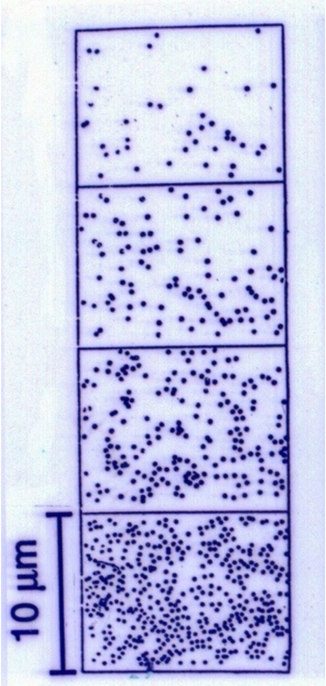
According to this theory **a dissolved molecule is differentiated from a suspended body *solely* by its dimensions**, and it is not apparent why a number of suspended particles should not produce the same osmotic pressure as the same number of molecules.

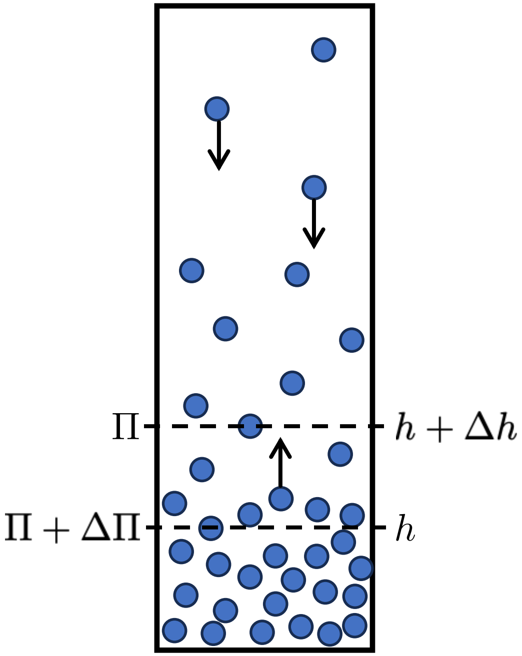
Reminder: osmotic pressure Π



Van 't Hoff's Law:

$$\Pi = n k_B T$$





Force balance

$$F_{down} = F_g$$
$$= m^* g$$

$$\lim_{\Delta h \to 0} F_{up} = -\frac{1}{n(h)} \frac{d\Pi}{dh}$$

$$n(h) = n(0) \exp\left(\frac{-\Delta \rho V g h}{k_B T} \right)$$

Barometric height distribution: see problem set

What determines behaviour of colloids?

- Interactions between 'macroscopic' objects (lectures 1 & 2)
  - Attractive (van der Waals) forces (1)
  - Repulsive double layer forces (1 & 2)
  - DLVO potential (2)

- Brownian motion (lecture 2)
  - Entropy and phase transitions

IMPORTANT

In this course we consider interactions and Brownian motion for colloids

BUT

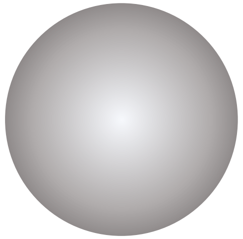
these concepts apply to Soft Matter systems in general!

Today’s lecture (1)

- Introduction to Soft Matter
- Colloids
  - **Van der Waals interactions**
    - Hamaker constant
  - Double layer repulsion
    - Poisson-Boltzmann equation
    - Debye length and electrical double layer

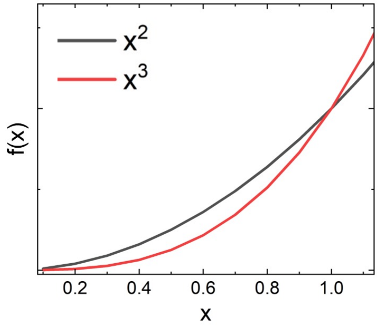
How about interactions between colloidal particles?

We have to consider surface interactions!

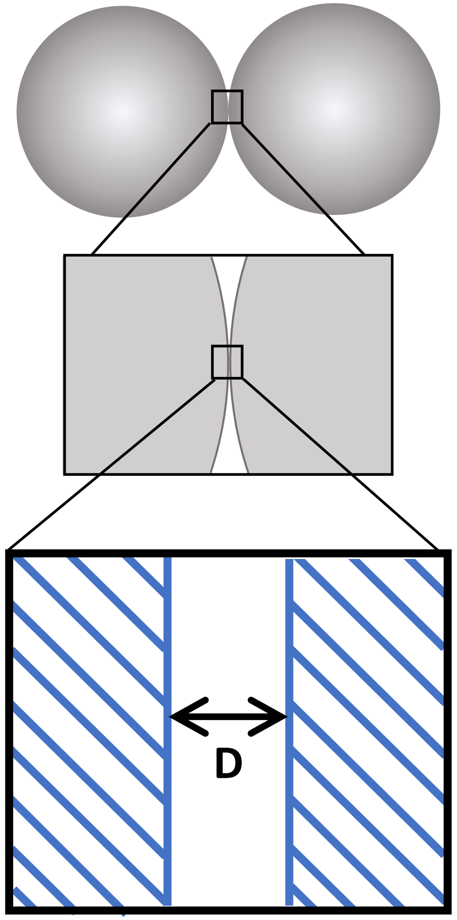


$$V \sim L^3$$

$$A \sim L^2$$

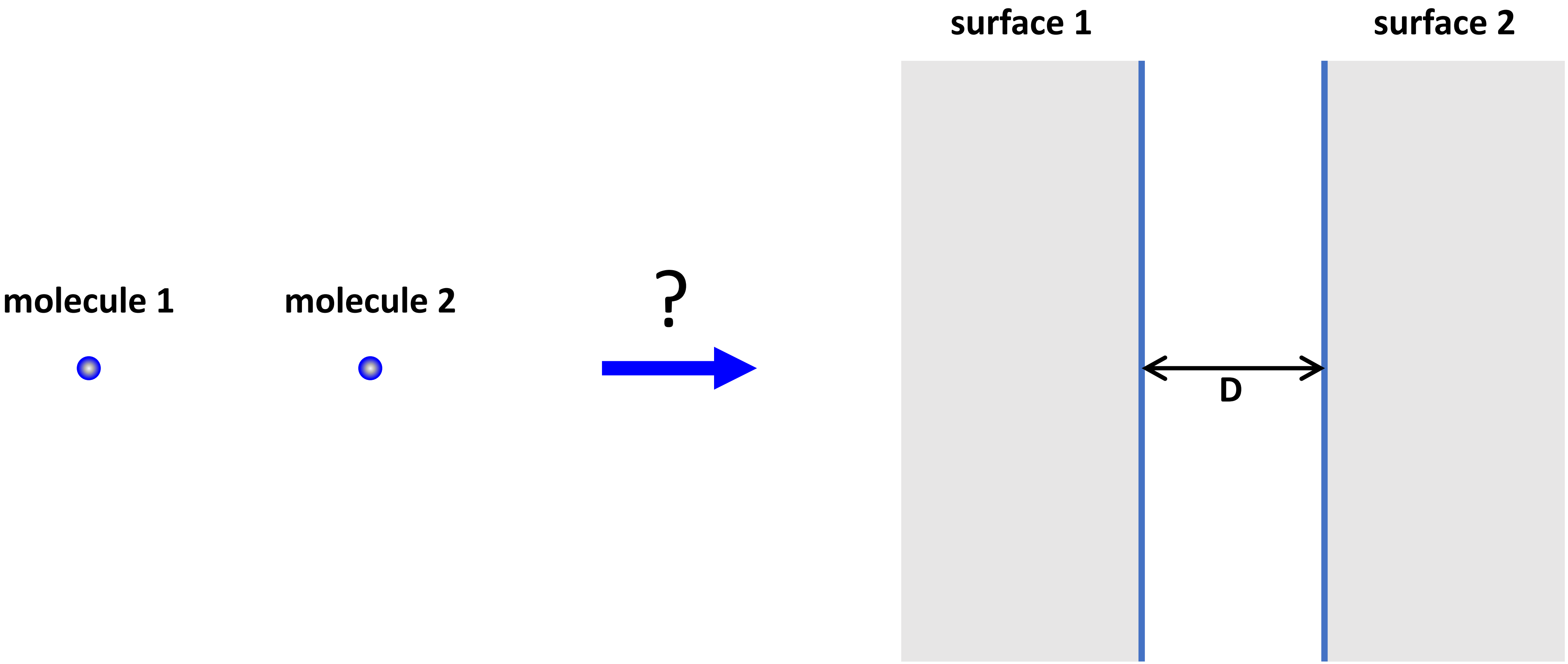


Surfaces are important at small length scales



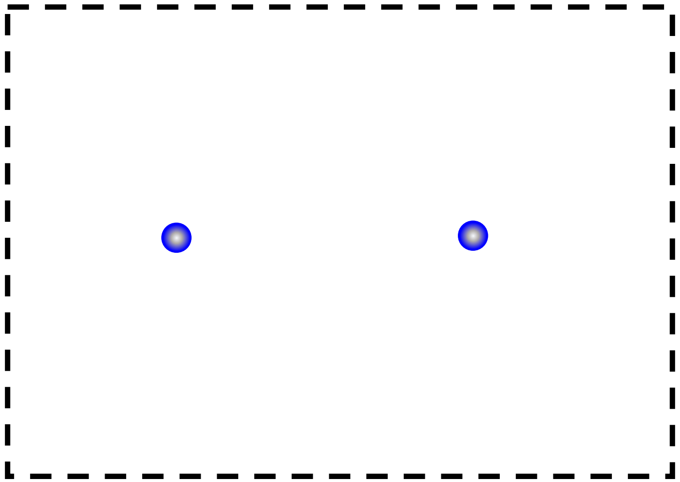
- Determines **interactions** between between **'macroscopic' objects**
  - Colloidal particles, cells, grains of sand, ...
- Note: 'surface' denotes a 'thick surface', i.e. not a monolayer

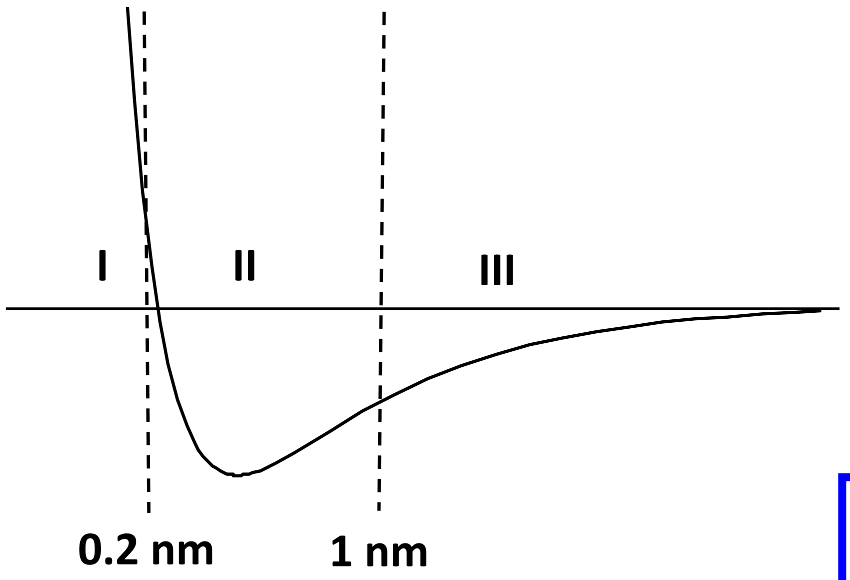
From molecular interactions to interactions between two 'macroscopic' surfaces?



Approach: Just add up interactions ...

First: two (neutral) molecules in vacuum…





$$\boxed{U_{att} = -\frac{C}{r^6}}$$

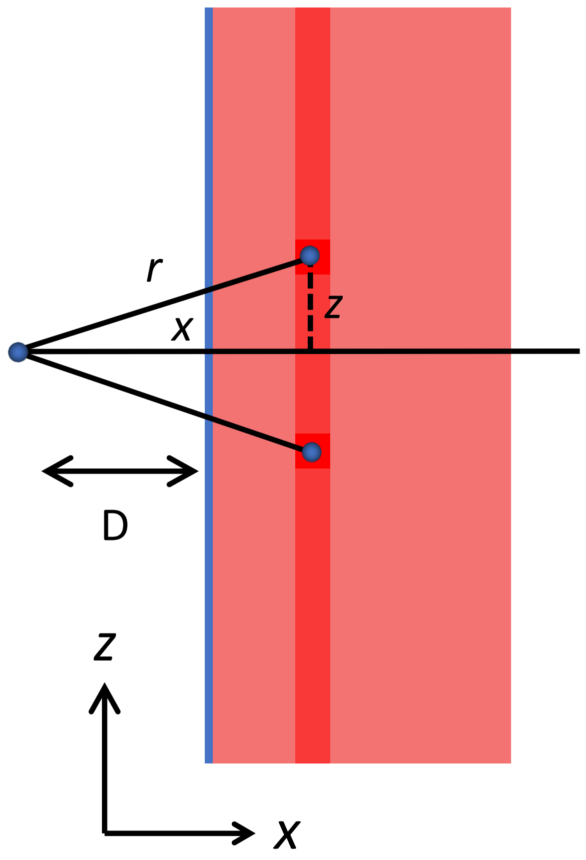
I: Strong repulsion – Pauli principle

II: Difficult – overlap between electron clouds

III: Attractions due to:

- dipole – dipole $\quad U_{dip} \propto -\frac{(\mu_A \mu_B)^2}{T}\frac{1}{r^6} \quad C_{dip} \sim 10^{-77}\ \mathrm{J/m^6}$
- dipole – induced dipole $\quad U_{ind} \propto -\alpha_B\,(\mu_A)^2\,\frac{1}{r^6} \quad C_{ind} \sim 10^{-78}\ \mathrm{J/m^6}$
- induced dipole – induced dipole $\quad U_{disp} \propto -\alpha_A \alpha_B \frac{I_A I_B}{I_A + A_B}\frac{1}{r^6} \quad C_{disp} \sim 10^{-77}\ \mathrm{J/m^6}$

Next: 1 molecule and a half-space



1. molecule-molecule interaction

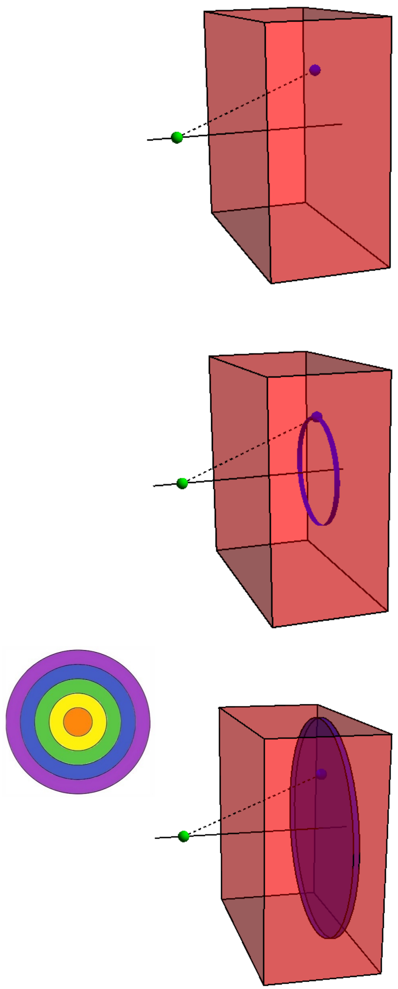
$$-\frac{C}{r^6}$$

2. sum over all molecules in a ring at distance *r*

$$-\frac{C}{\left(x^2+z^2\right)^3}\rho 2\pi z dz dx$$

3. integrate over *z (lots of different ring sizes)*

$$-C\rho 2\pi dx \int_0^\infty dz \frac{z}{\left(x^2+z^2\right)^3} = -C\rho 2\pi dx \frac{1}{4x^4}$$

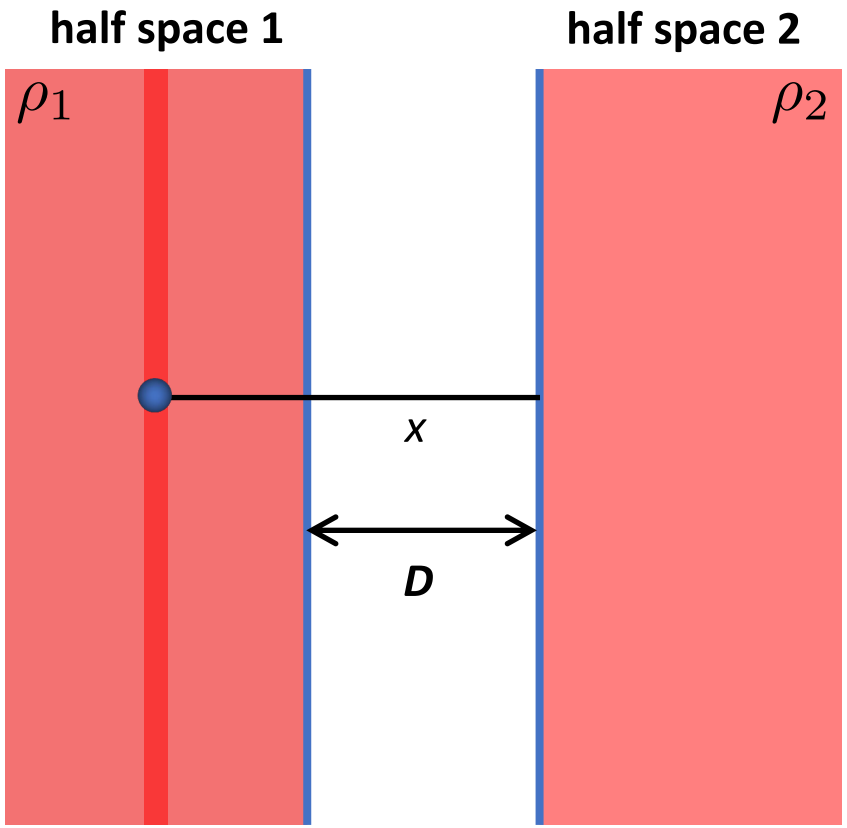


4. integrate over *x*

$$-\frac{\pi C\rho}{6D^3}$$

... range of attractive interaction has increased ...

Finally: 2 half-spaces



1. sum over all molecules in a slab at distance x in half-space 1

$$-\frac{\pi C \rho_2}{6x^3} \longrightarrow -\frac{\pi C \rho_2}{6x^3}\rho_1 dx$$ per unit area

2. integrate over *x*

$$-\frac{\pi C \rho_1 \rho_2}{6}\int_D^\infty \frac{1}{x^3}dx = \frac{\pi C \rho_1 \rho_2}{12 D^2} = -\frac{A}{12\pi D^2}$$

Hamaker constant: $A_{12} = \pi^2 C \rho_1 \rho_2$

Hamaker constant quantifies the magnitude of the interaction

$$A_{12} = \pi^2 C \rho_1 \rho_2$$

Magnitude of A_{11} in 10^{-20} J

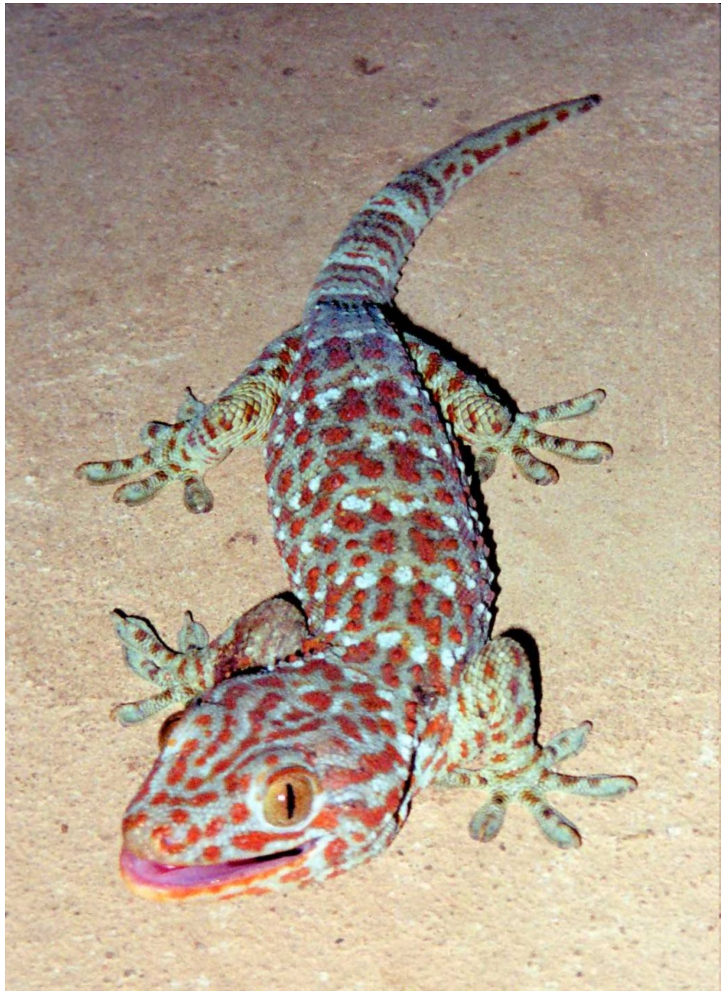
- Water 4
- Pentane 3.8
- Mica 10
- Metals 30-50

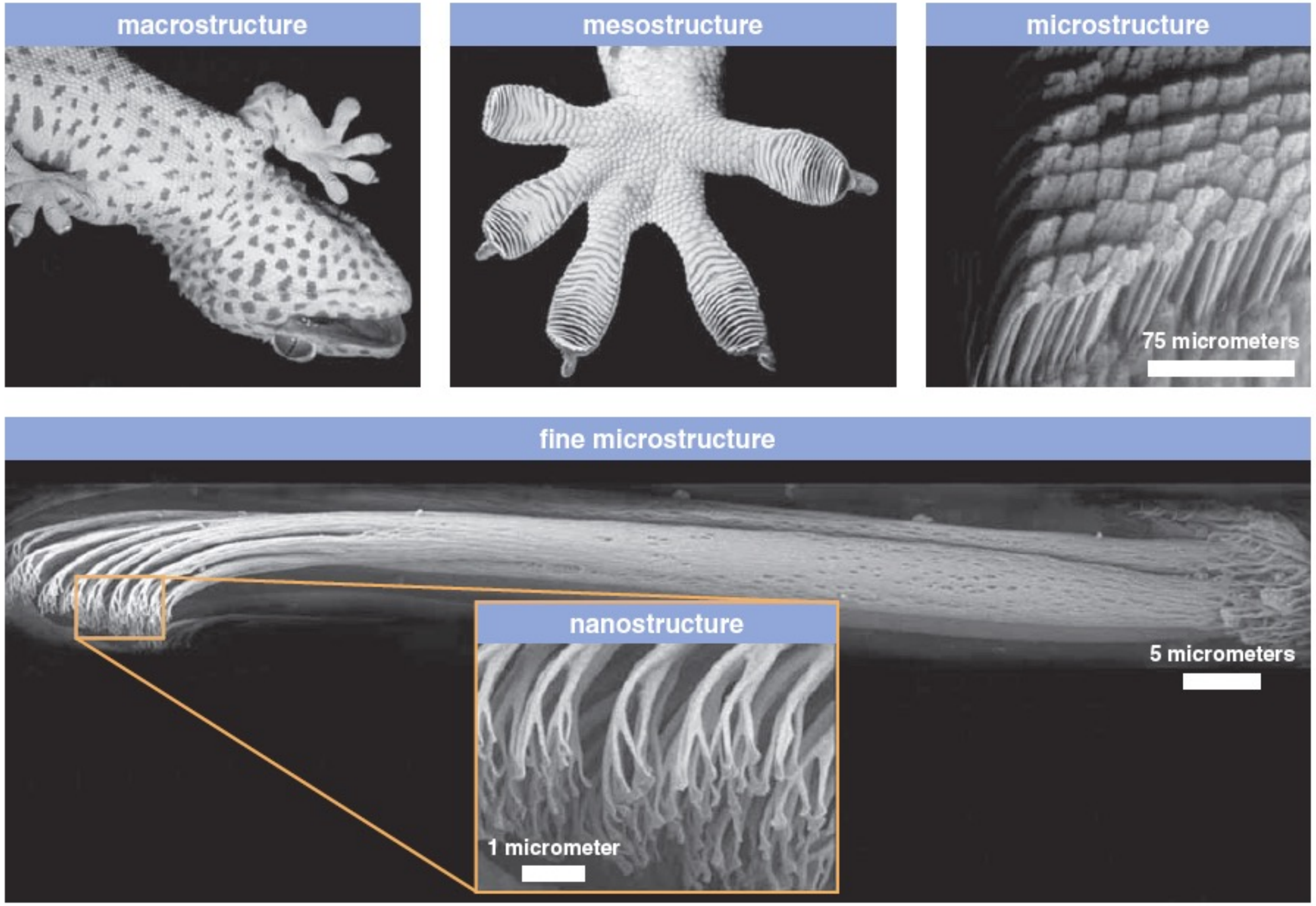
Remember: 1 $k_B T$ equals $0.4 \cdot 10^{-20}$ J

If materials 1 and 2 are not too dissimilar (or actually, have similar ionisation potentials), then

$$A_{12} \cong \sqrt{A_{11} A_{22}}$$

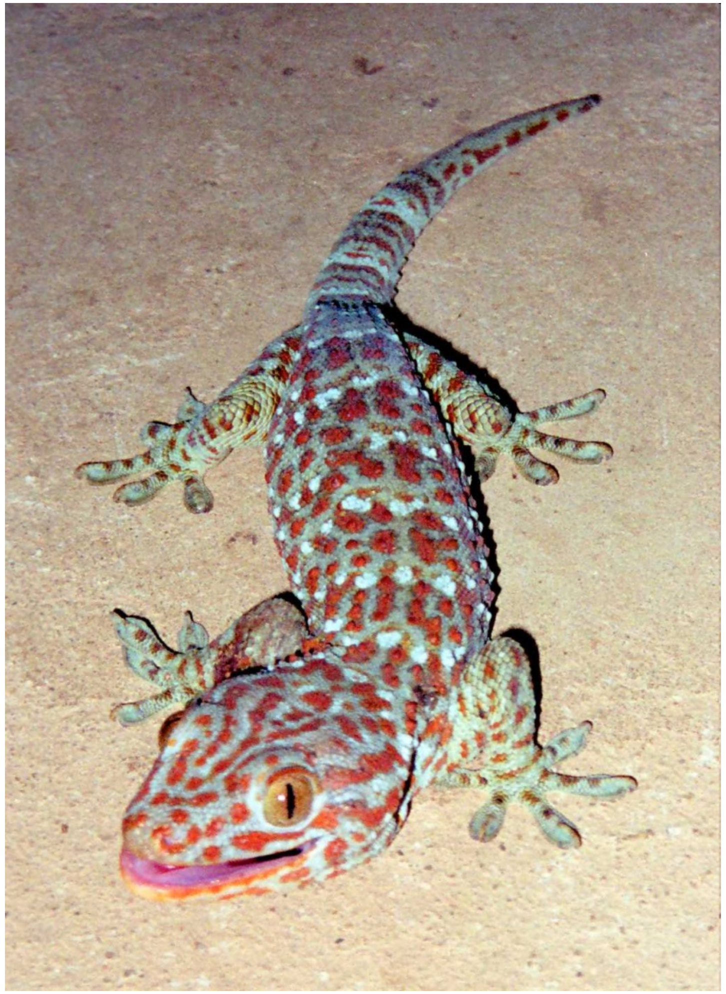
Van der Waals forces are strong! the GECKO

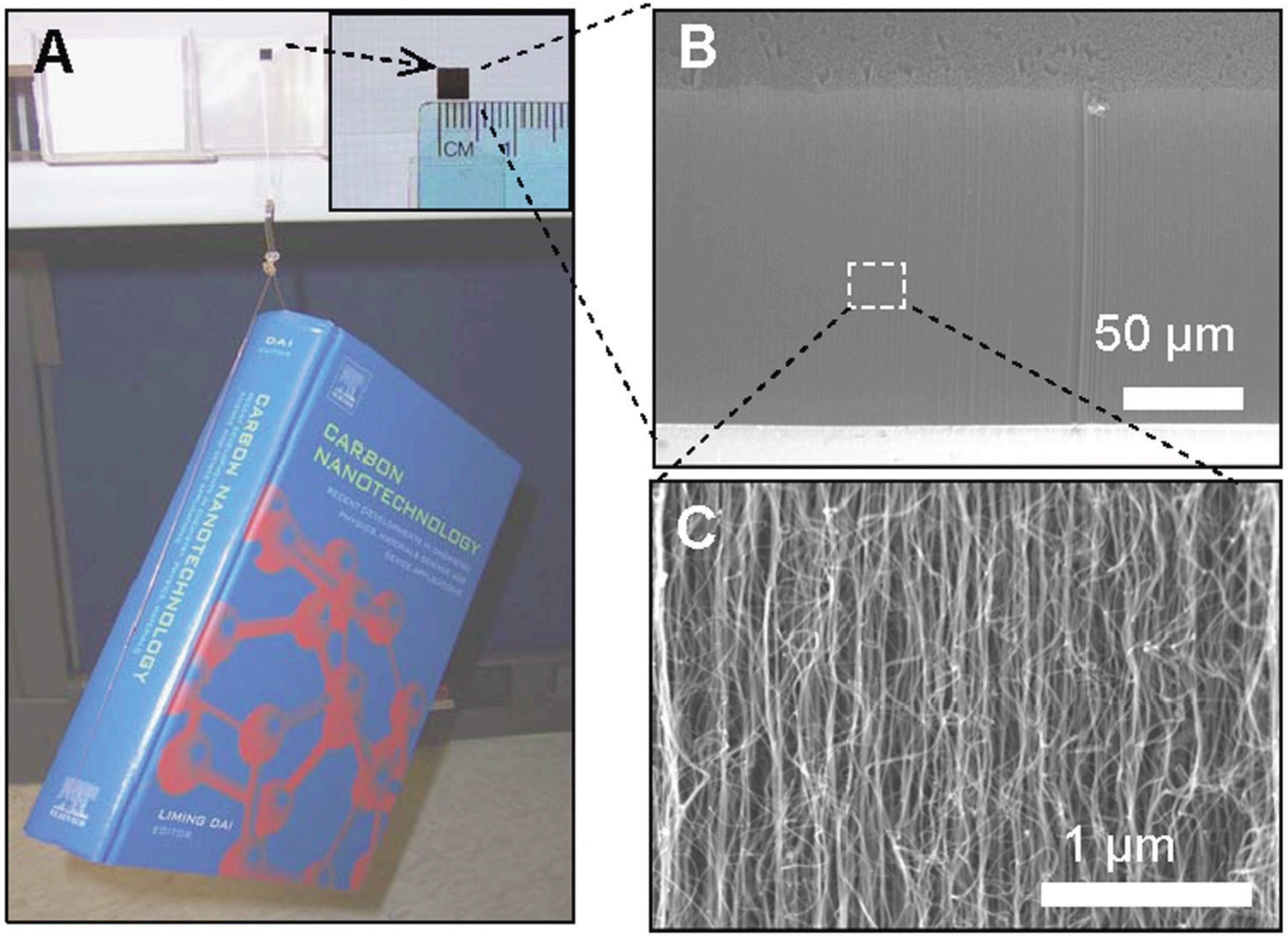




Autumn, K. (2006). How gecko toes stick. American Scientist 94, 124-132.

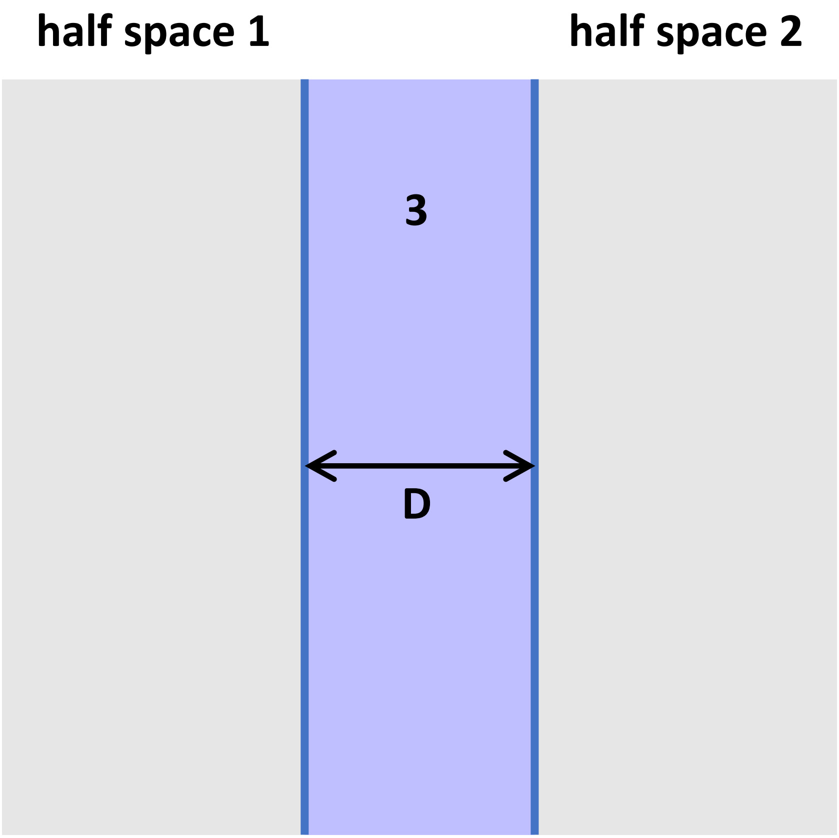
Nature inspired gecko-adhesives



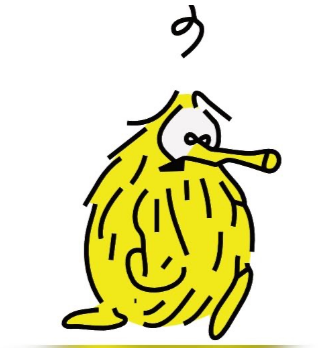


Qu et al, *Carbon Nanotube Arrays with Strong Shear Binding-On and Easy Normal Lifting-Off,* Science **322**, 238 (2008)

Two objects in a medium (3)

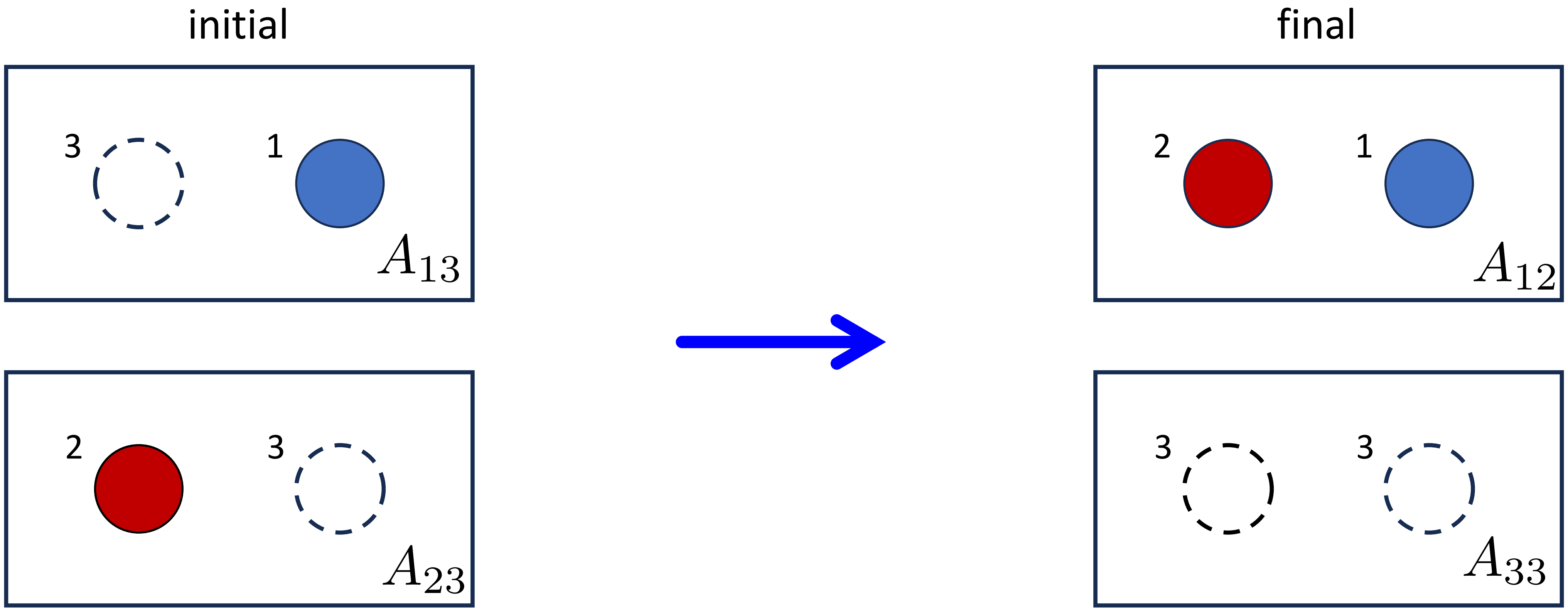


$$U = -\frac{A_{132}}{12\pi D^2}$$



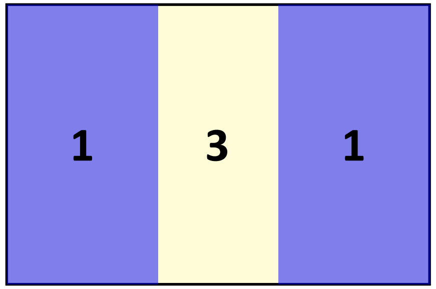
A_{132} ??

Hamaker constant objects 1 and 2 in medium 3



$$A_{132} = A_{12} + A_{33} - A_{13} - A_{23}$$

Interactions between 'like' objects



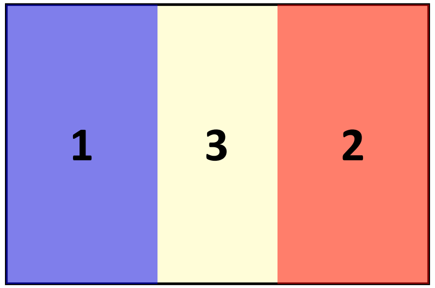
$$U = -\frac{A_{131}}{12\pi D^2}$$

$$A_{132} = A_{12} + A_{33} - A_{13} - A_{23}$$

$$\begin{aligned} A_{131} &= A_{11} + A_{33} - 2A_{13} \\ &\cong A_{11} + A_{33} - 2\sqrt{A_{11}A_{33}} \\ &= \left(\sqrt{A_{11}} - \sqrt{A_{33}}\right)^2 > 0 \end{aligned}$$

- *Interaction between like objects is* ***always attractive***
- *Interaction between 131 is equal to 313*

Interactions between ‘unlike’ objects



$$\boxed{A_{132} = A_{12} + A_{33} - A_{13} - A_{23}}$$

A_{132} may be larger or smaller than 0

attractive

repulsive

Typical values for Hamaker constants

Like objects: A_{131} in 10^{-20} J

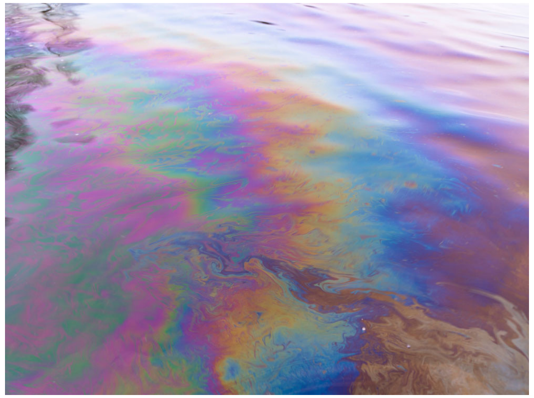
	vacuum	**across water (3)**
	$\mathbf{A_{11}}$	$\mathbf{A_{131}}$
• Cyclohexane	5.2	0.34
• Mica	10	2
• Metals	30-50	30-40

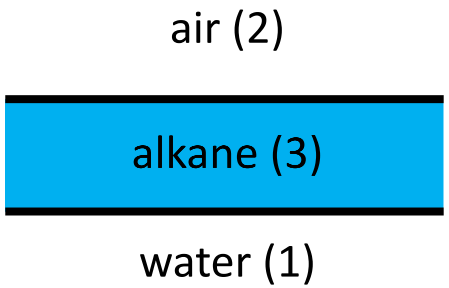
Unlike objects: A_{132} in 10^{-20} J

	$\mathbf{A_{132}}$
• water – pentane – air	0.11
• octane – water – air	-0.20
• quartz – water – air	-1.0

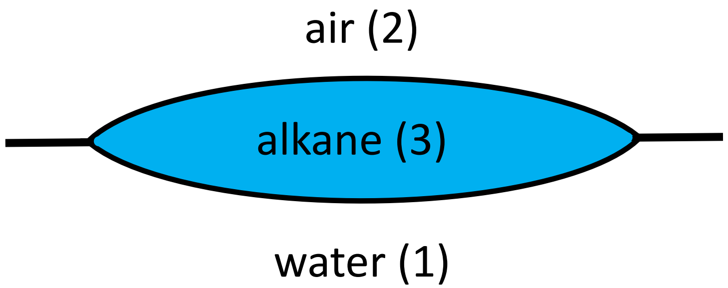
Remember: 1 k_BT equals $0.4 \cdot 10^{-20}$ J

Does oil spread on water? Alkanes on water





?
or



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

Very important in the field of wetting

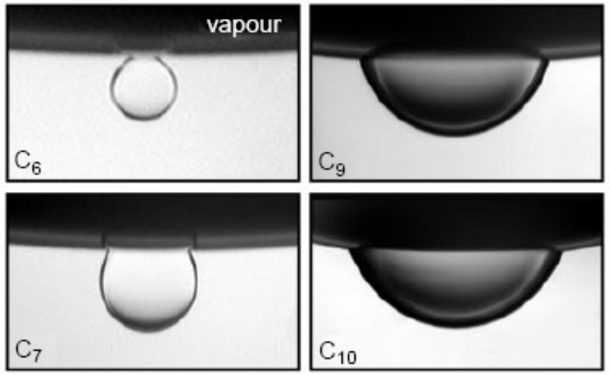


Figure 1 Photographs of methanol droplets at the liquid–vapour interfaces of the different *n*-alkanes at $T \approx 20$°C (for C_6, $T \approx 3$°C, as the wetting transition has already taken place at room temperature). The different *n*-alkanes, C_nH_{2n+2}, are

Look up Hamaker constants:

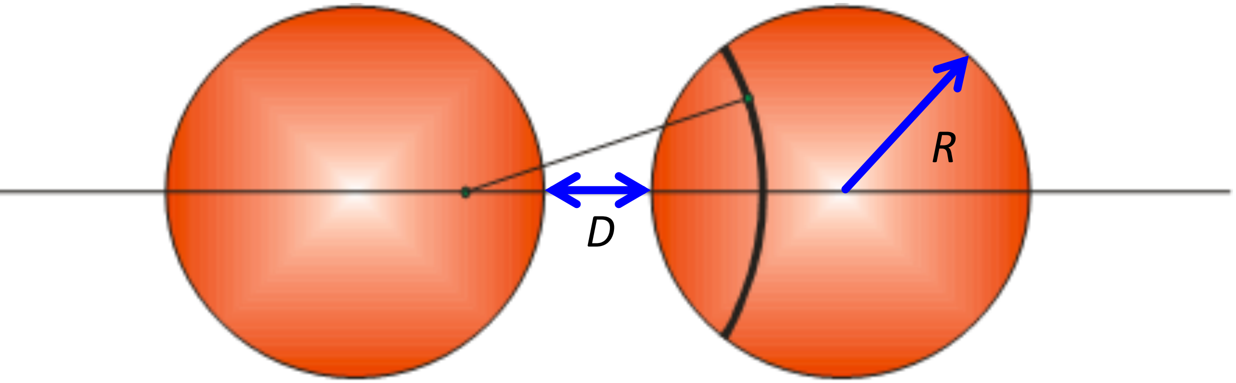
$A_{\text{water – octane – air}}$ = 0.51 10^{-20} J/m^2

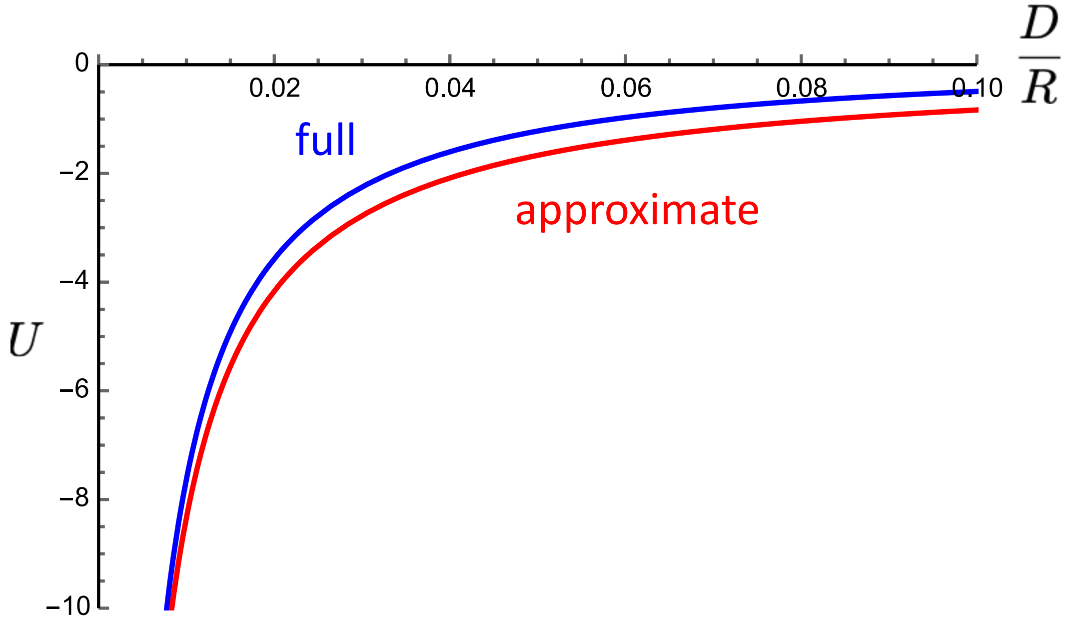
$A_{\text{water – tetradecane – air}}$ = 5 10^{-20} J/m^2

Ross et al, *Observation of short-range critical wetting*, Nature **400**, 737 (1999)

Van der Waals attraction between two spheres

Same idea but more difficult geometry





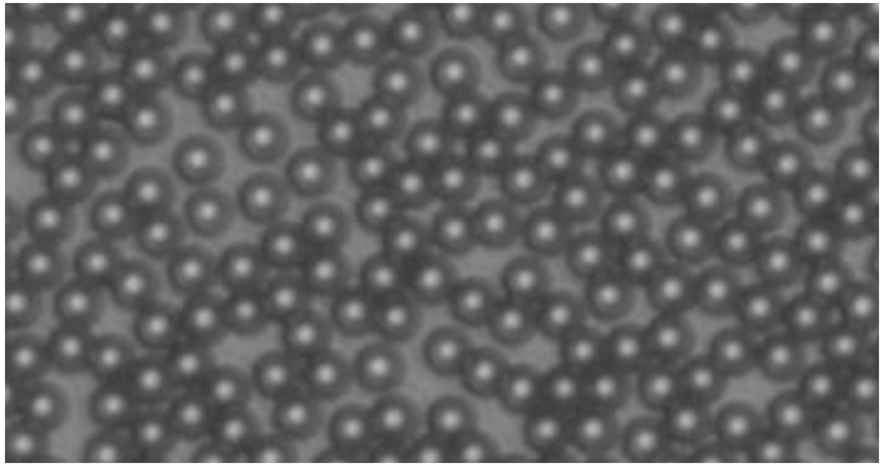
$$U = -\frac{A}{6}\left[\frac{2R^2}{D(D+4R)} + \frac{2R^2}{(D+2R)^2} + \ln\left(1 - \frac{4R^2}{(D+2R)^2}\right)\right]$$

$$\text{For } D \ll R \qquad \rightarrow \qquad U \approx -\frac{A_{12}R}{12D}$$

Van der Waals attractions and colloids

Interactions between 'like' objects are always attractive

Why is a suspension of colloids/nanoparticles stable?



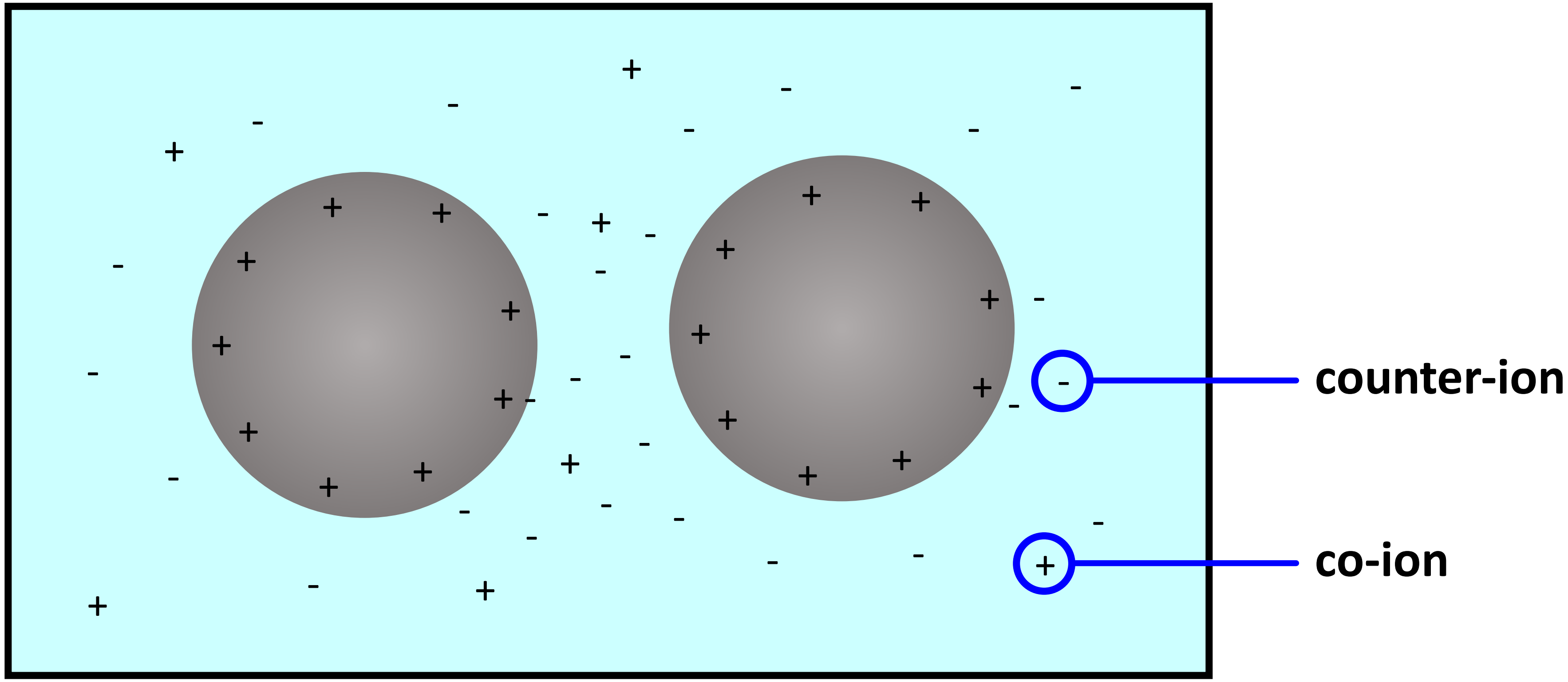
Answer: presence of repulsive interactions

1. Double layer repulsion (charge stabilisation)
2. Polymer adsorption (steric stabilisation)

Today’s lecture (1)

- Introduction to Soft Matter
- Colloids
  - Van der Waals interactions
    - Hamaker constant
  - **Double layer repulsion**
    - Poisson-Boltzmann equation
    - Debye length and electrical double layer

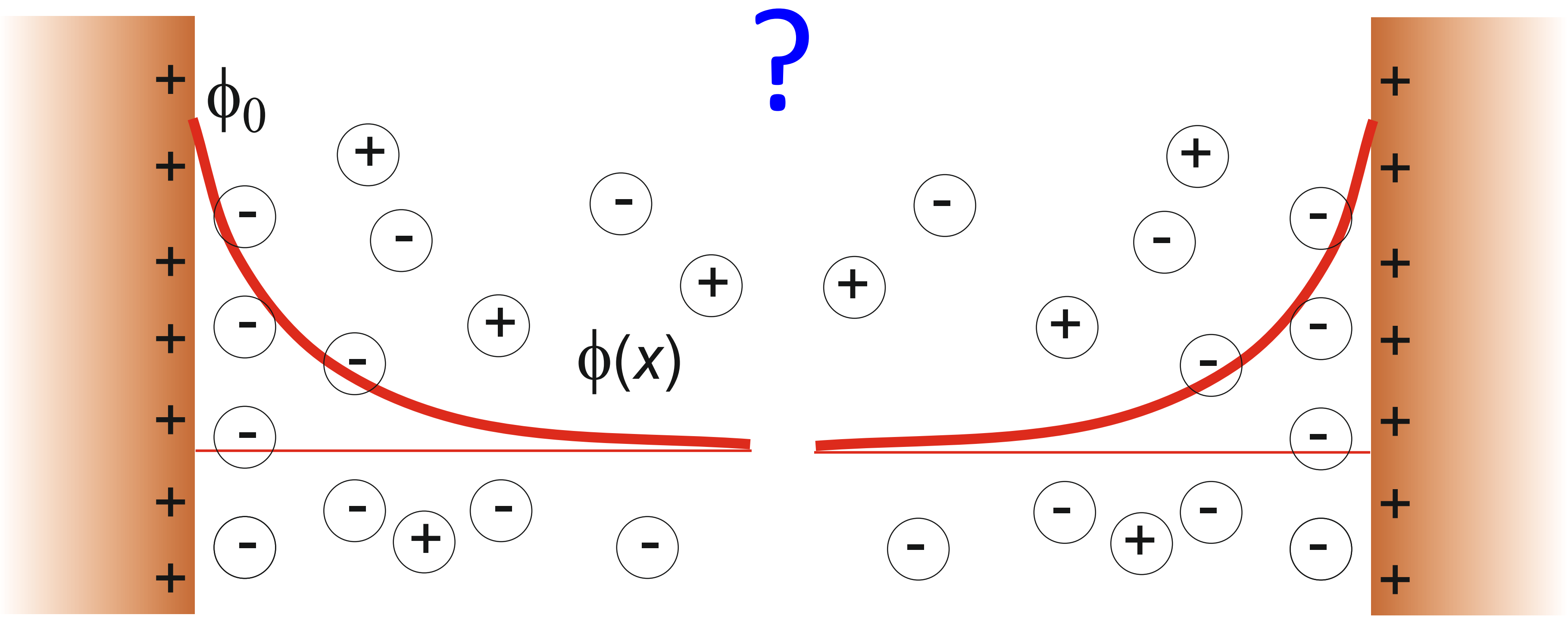
Charge stabilisation



Why do surface charges prevent 'particles' from sticking together?

Entropy is behind this effect! (not just 'like-charges' repelling …)

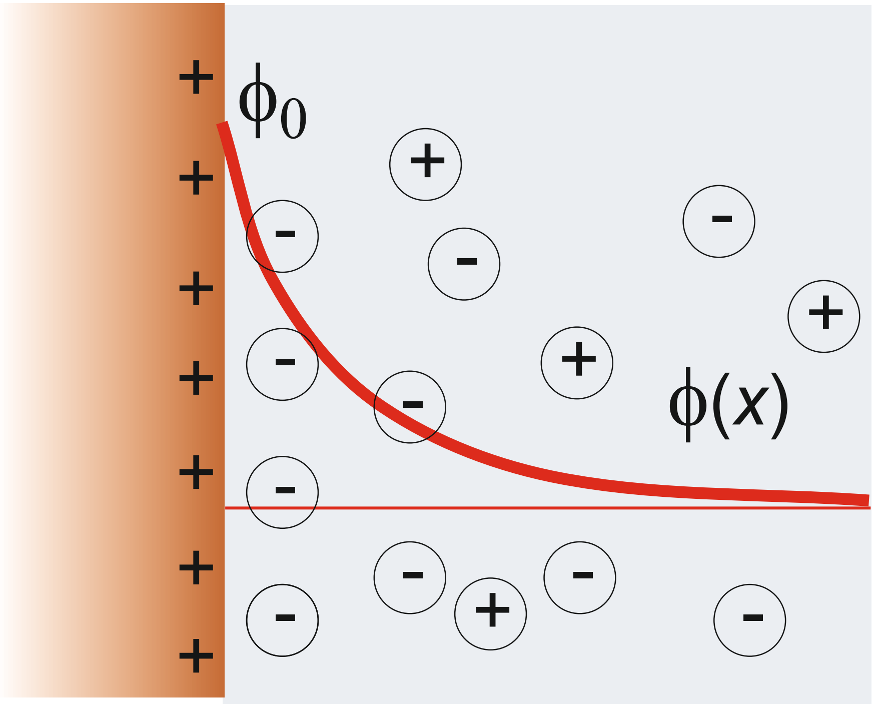
Interaction between charged surfaces



Objective:

Find expression for the repulsive interaction between two charged surfaces

Interactions between charged surfaces



ϕ_0 : surface potential

$\phi(x)$: electrostatic potential

Method:

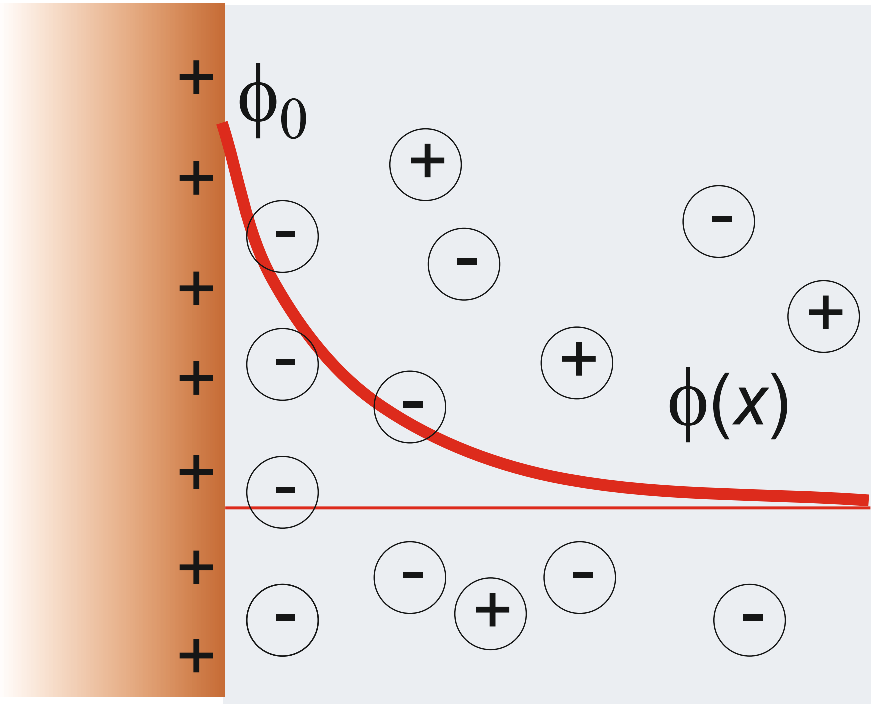
1. Calculate the number density distribution of ions and charge density near a charged surface
2. Determine the electrostatic potential near a charged surface
3. Calculate the repulsion between two charged surfaces*

Assumptions (same as in Debye-Hückel theory):

- Ions are point charges (± *ze* of a 1:1 salt)
- Ions feel average potential due to all other ions
- Solvent is continuous uniform dielectric medium with relative permittivity ε

* Lecture 2

Number and charge density distributions



ϕ_0 : surface potential

$\phi(x)$: electrostatic potential

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

Number density near a charged surface:

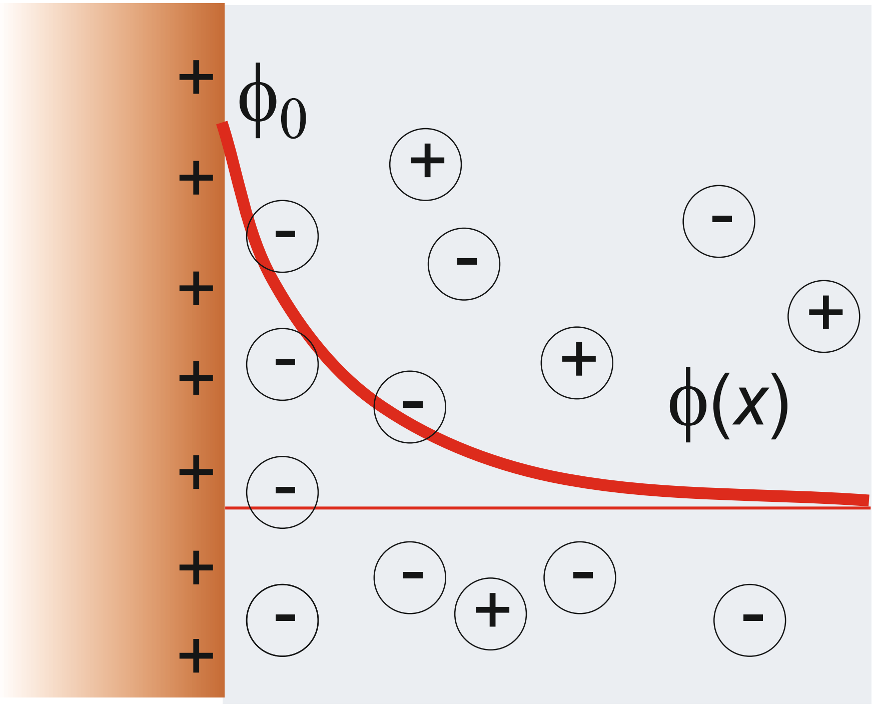
$$n_+(x) = n_0 \exp\left[-\Phi(x)\right]$$

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

Charge density near a charged surface:

$$\rho(x) = -2zen_0 \sinh\left[\Phi(x)\right]$$

Charge density distribution and Poisson's law



ϕ_0 : surface potential

$\phi(x)$: electrostatic potential

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

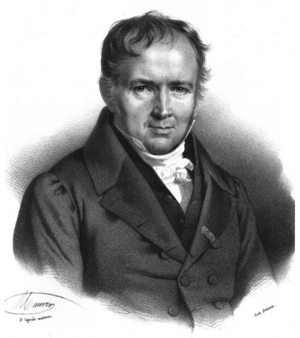
Charge density near a charged surface:

$$\rho(x) = -2zen_0 \sinh\left[\Phi(x)\right]$$

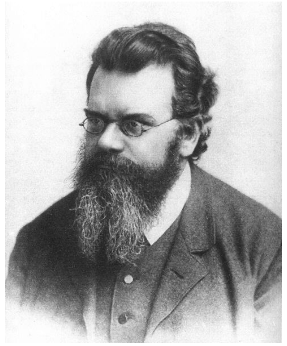
Poisson's Law:

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

permitivity of free space $\epsilon_0 = 8.85 \cdot 10^{-12}\ \frac{\mathrm{C}^2}{\mathrm{N\ m}^2}$



Poisson-Boltzmann equation (1D)



$$\frac{\mathrm{d}^2\Phi(x)}{\mathrm{d}x^2} = \kappa^2 \sinh\left[\Phi(x)\right]$$

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

Exact solution for planar surface: Gouy-Chapman equation*

Approximation for small potentials:

$$\frac{\mathrm{d}^2\Phi(x)}{\mathrm{d}x^2} = \kappa^2 \Phi(x)$$ **linearised Poisson-Boltzmann Eq.**

$$\downarrow$$

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

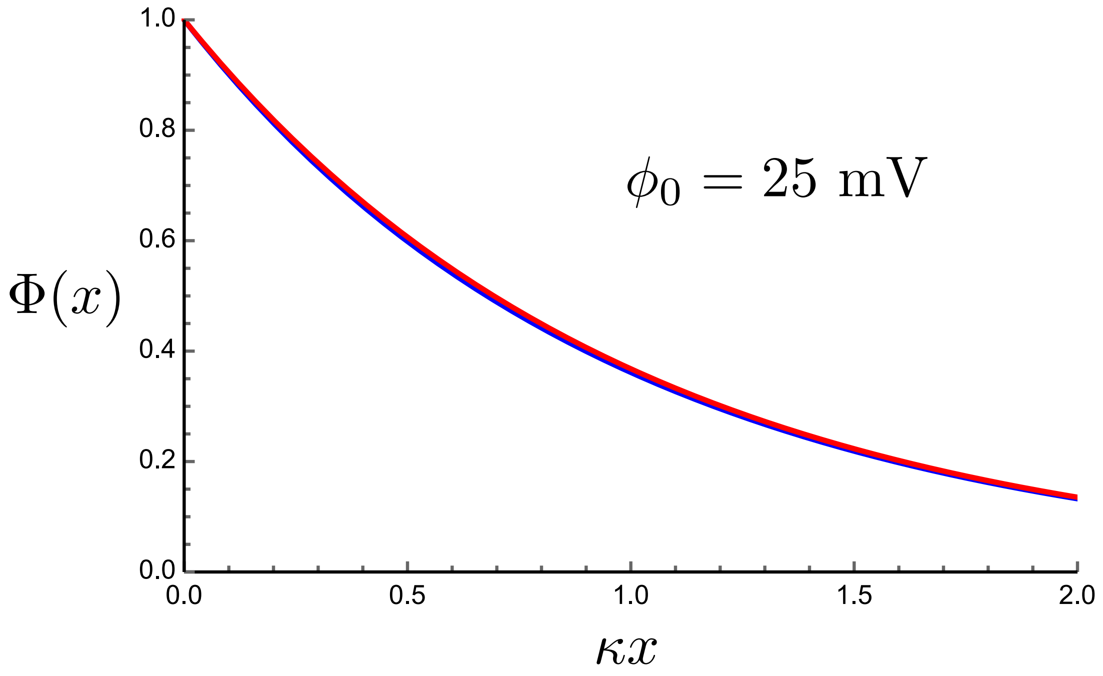
$$\left[\lim_{x\to\infty} \Phi(x) = 0\right]$$

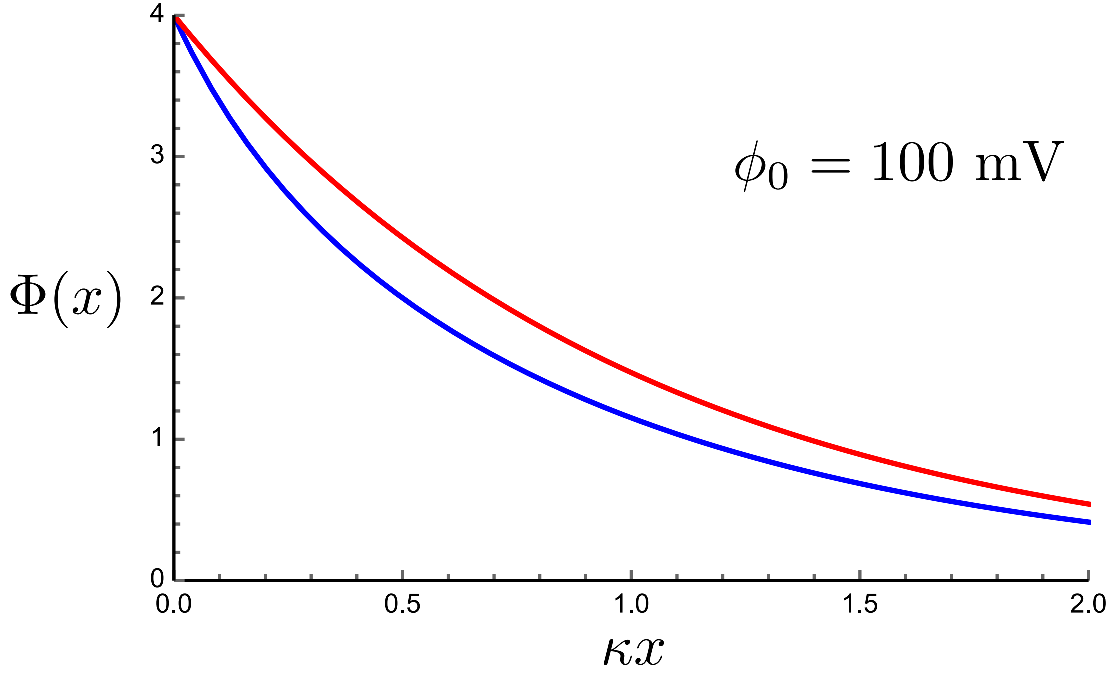
* Not derived here

How well does the linearization work?

Exact Poisson-Boltzmann equation (Gouy-Chapman*) $$\Phi(x) = 2\ln\left[\frac{1+\tanh(\Phi_0/4)e^{-\kappa x}}{1-\tanh(\Phi_0/4)e^{-\kappa x}}\right]$$

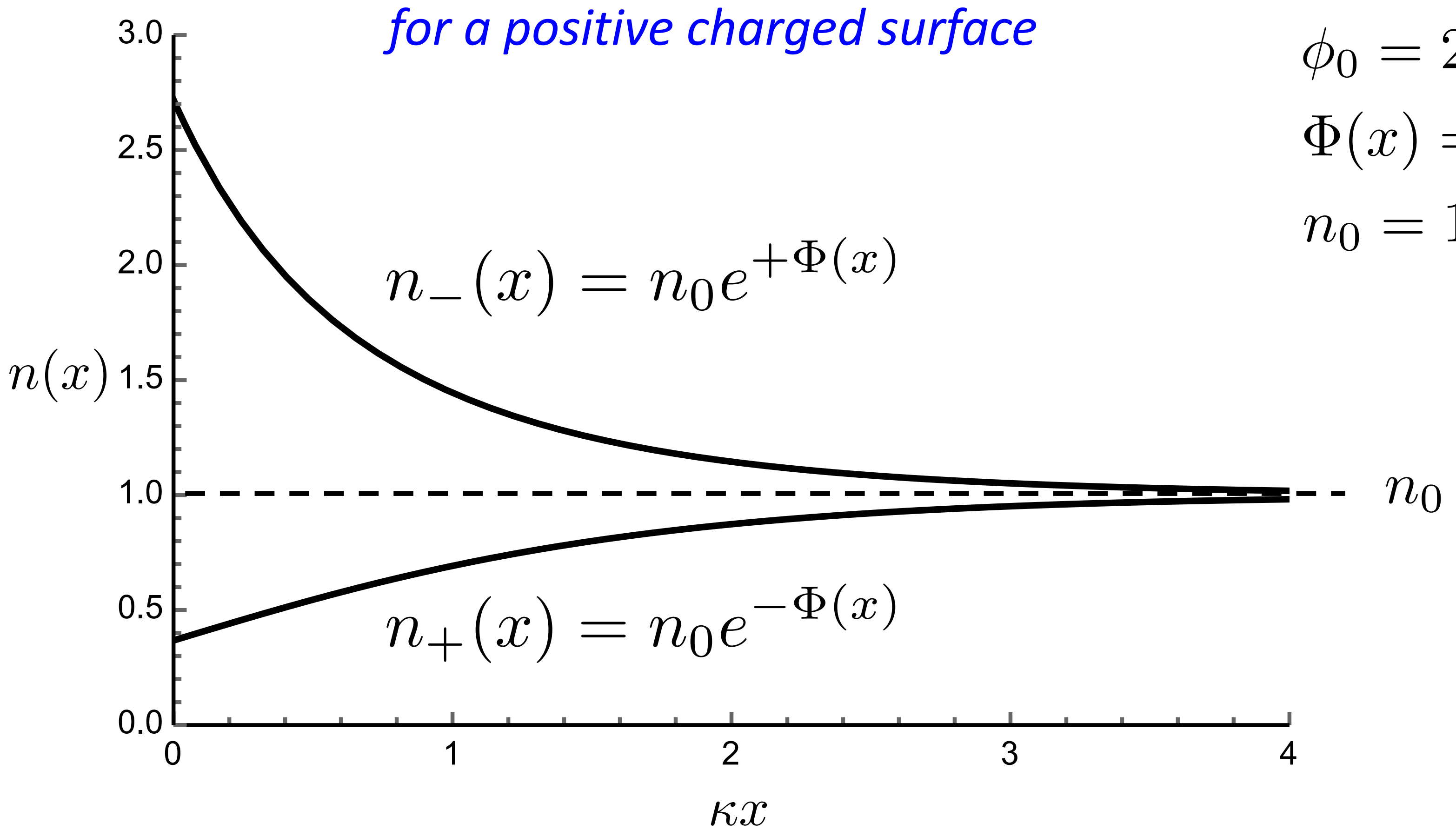
Linearised Poisson-Boltzmann equation: $$\Phi(x) = \Phi_0 e^{-\kappa x}$$





* Please don't learn this!

Ion distributions calculated from potentials



$\phi_0 = 25 \text{ mV}$

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

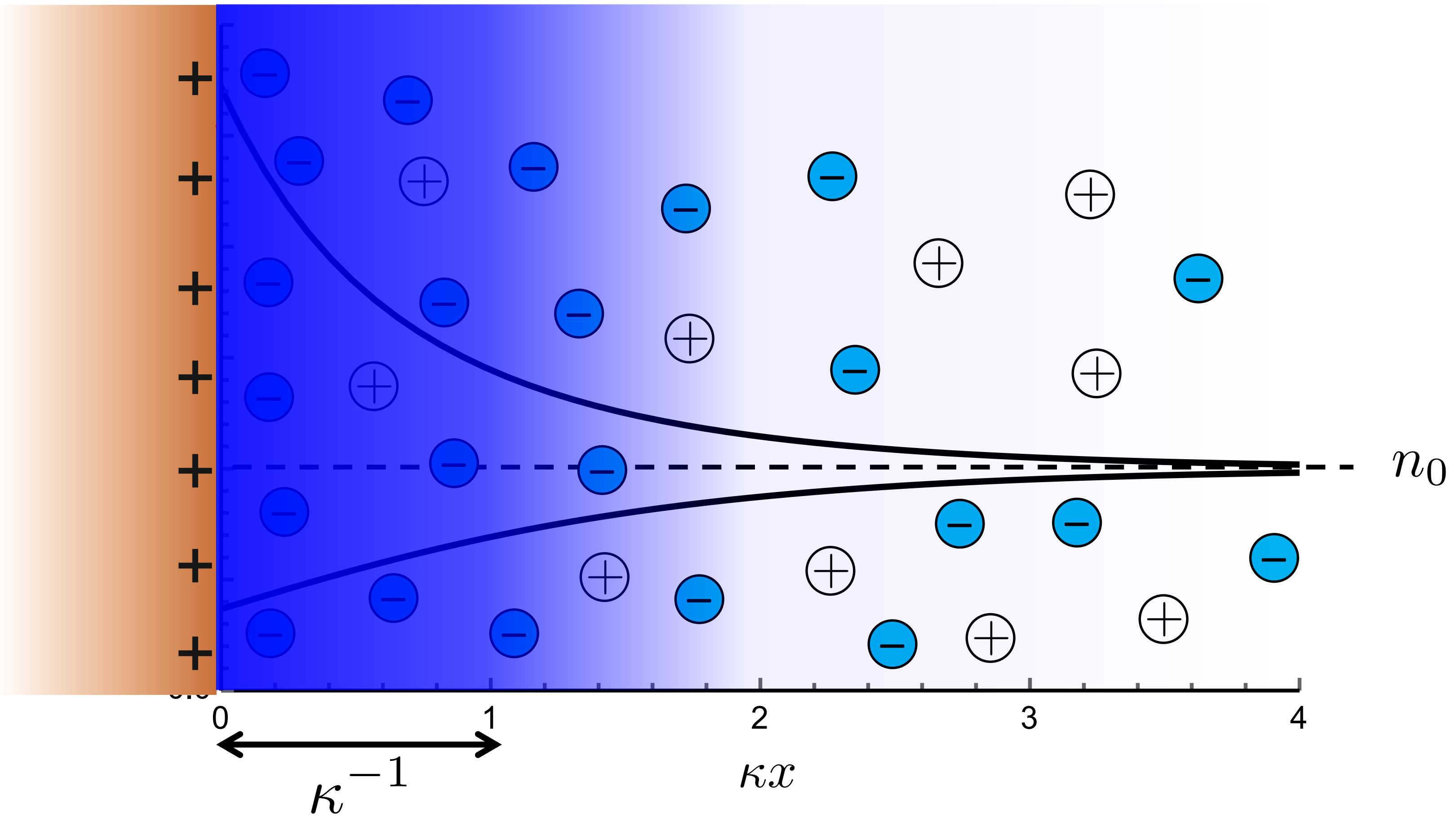
$n_0 = 1$

Close to surface:

- Excess of negative counter-ions
- Depletion of positive co-ions

$\Big\}$ ***electrical double layer***

The electrical double layer and Debye length



For $x \gg \kappa^{-1}$:

- $n_-(x)$ and $n_+(x)$ become equal and approach n_0
- κ^{-1} is a measure for the size of the electrical double layer

Relation surface potential ϕ_0 and surface charge density σ

Electro–neutrality:

Surface charge density must be exactly matched by the integrated charge density in the solution

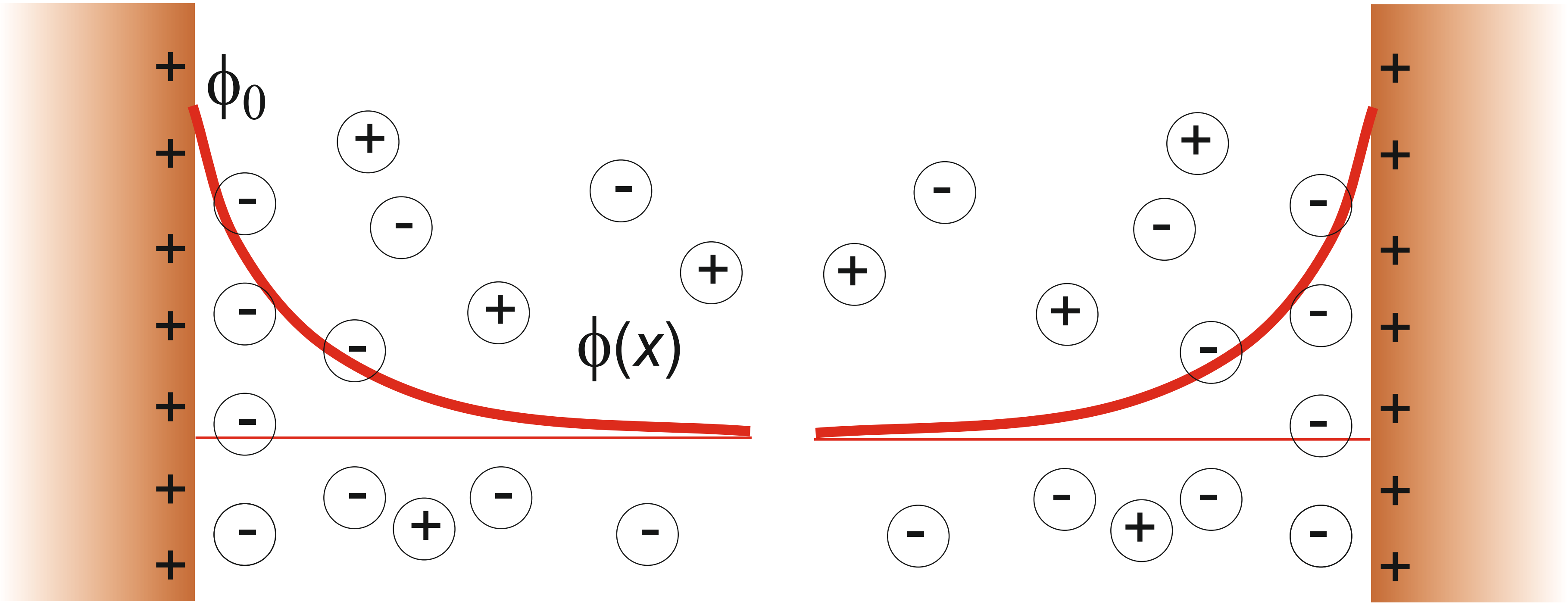
$$\sigma = -\int_0^\infty \rho(x)dx = \epsilon\epsilon_0\kappa\phi_0$$

problem set

$$\boxed{\rho(x) \approx -2zen_0\Phi(x)}$$

Is the linear Poisson-Boltzmann equation any good for colloids?

What happens when two charged surfaces approach each other?



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Lecture 2!