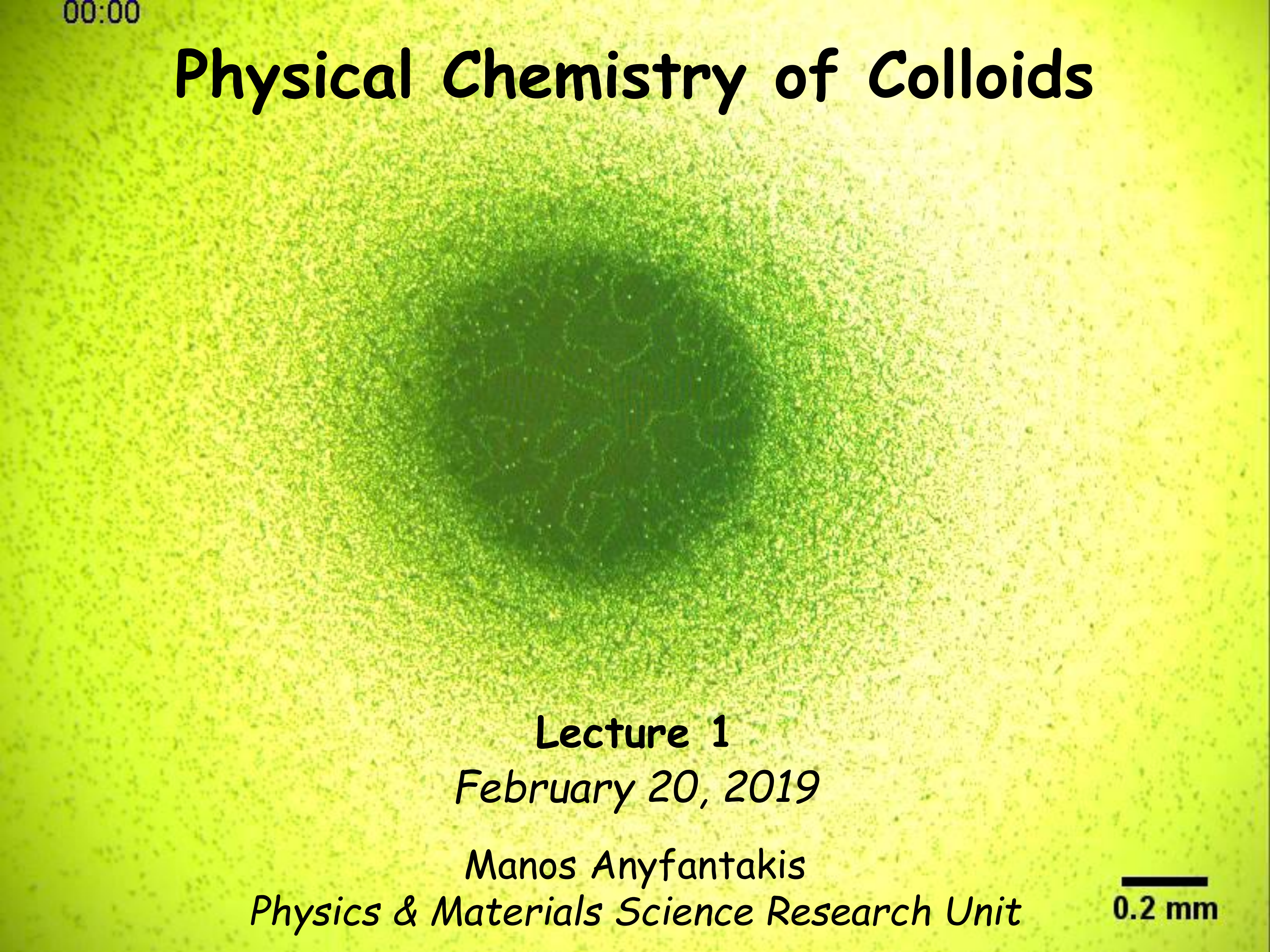


Physical Chemistry of Colloids

Lecture 1

February 20, 2019

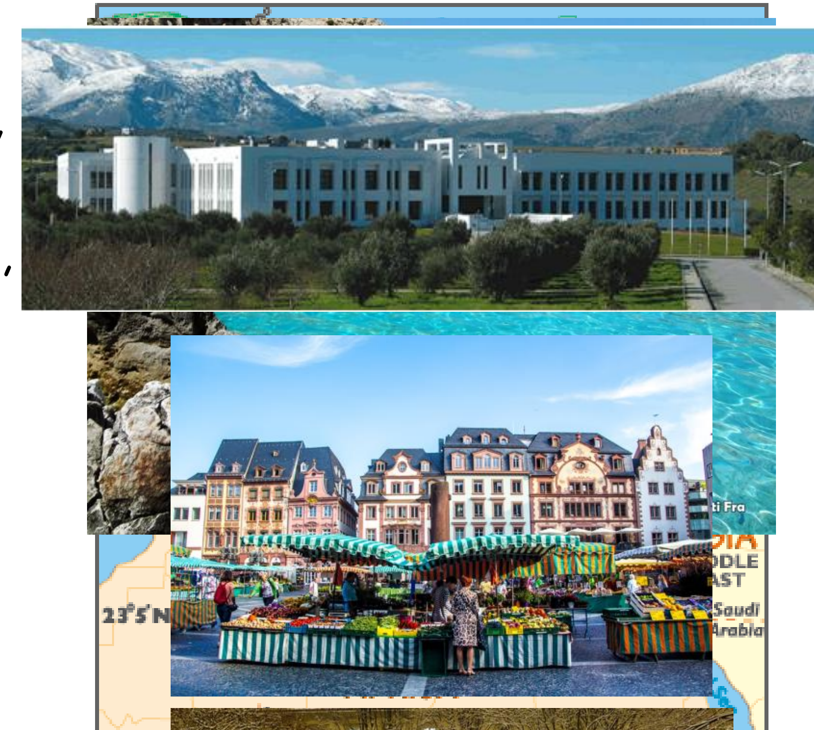
Manos Anyfantakis
Physics & Materials Science Research Unit

Who am I?

Born in Heraklion, Crete, GR (1984)

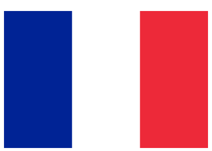
BSc, Materials Science & Technology, *Univ. of Crete*, GR (2005)

MSc, Applied Molecular Spectroscopy, *UoC*, GR (2007)

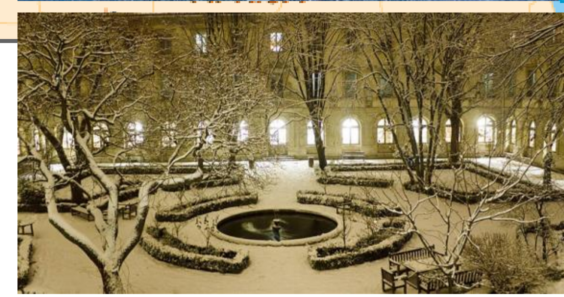


PhD, (Physical) Chemistry, *UoC* (GR) & *Max Planck Institute for Polymer research* (DE)

PostDoc @ MPIP, DE (2011-2013)



PostDoc @ *Ecole Normale Supérieure*, FR (2013-2017)



PostDoc @ *UniLu*, LU (2017-now)

How can you reach me?

E-mail

anyfas.com@gmail.com

emmanouil.anyfantakis@uni.lu

Office

BS 1.08 (Limpertsberg)

Phone

(+352) 46 66 44 6058

Web

www.anyfas.com

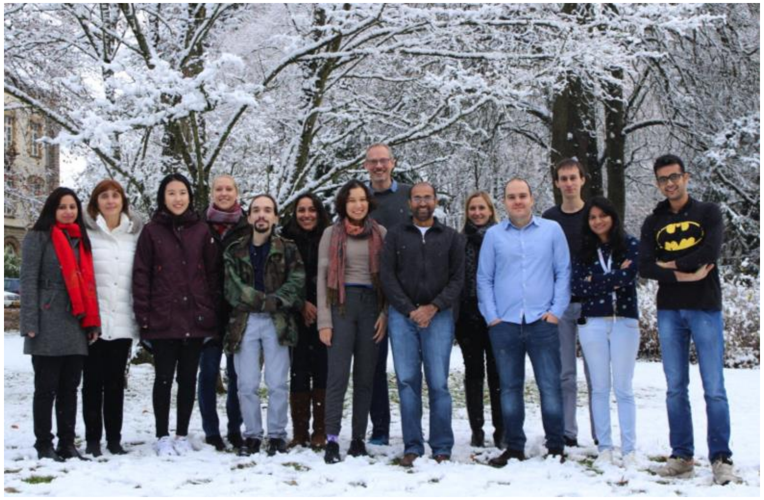
the course slides will be available here

The ESMP team & my research interests (I)

I belong to the **ESMP** team
led by **Prof. Jan Lagerwall**

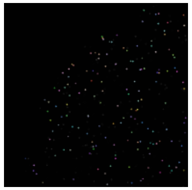
ESMP
EXPERIMENTAL SOFT MATTER PHYSICS

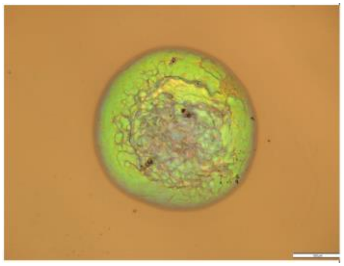
http://www.lcsoftmatter.com



My research interests @ ESMP

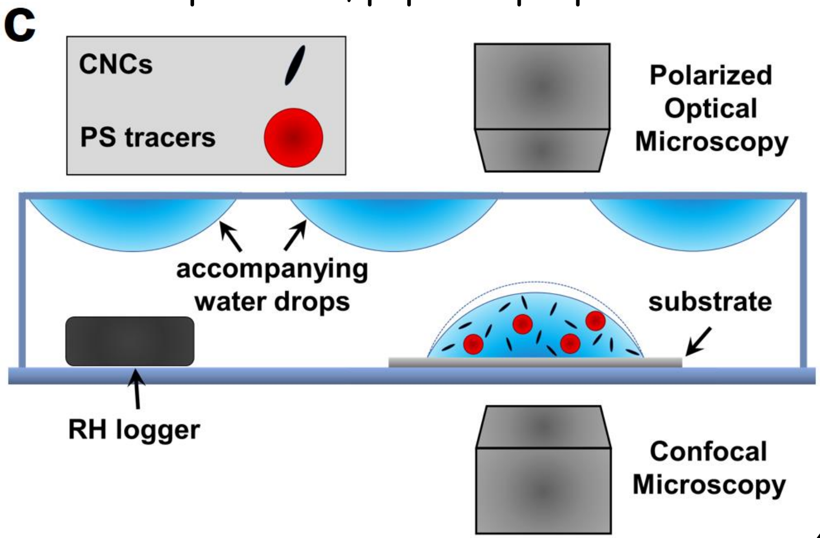
A. Formation of iridescent films from drying drops of cellulose nanocrystal suspensions





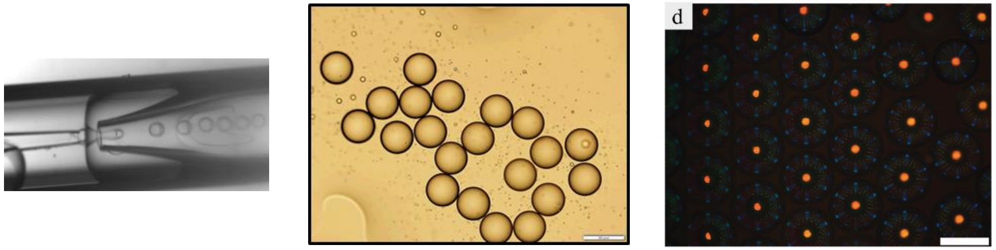
Lionel FRU, Master thesis 2019

Dupas *et* al., paper in preparation



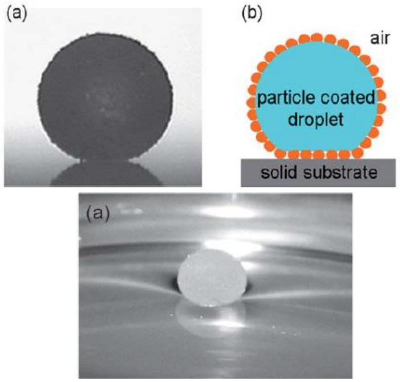
The ESMP group & my research interests (II)

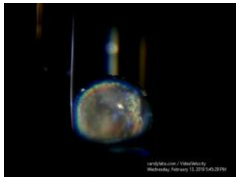
Β. Production of cellulose-based cholesteric liquid crystal shells for security applications



Adv. Mater. **2018**, *30*, 1707382

Γ. Formation of cellulose-based liquid marbles with tunable structural color

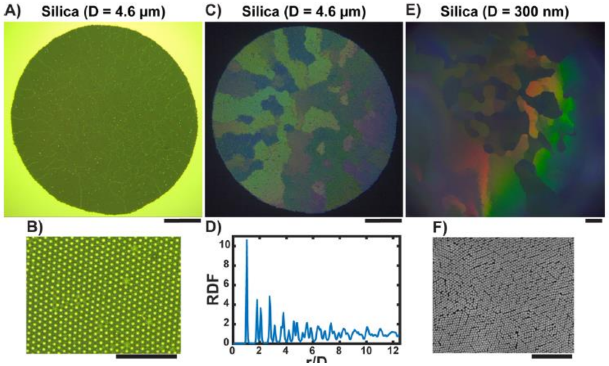


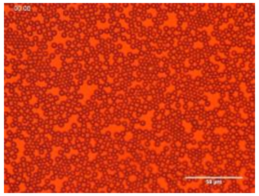


Soft Matter **2011**, *7*, 5473

Δ. Light-driven colloidal organization @ interfaces: responsive 2D crystals

Langmuir **2018**, 34, 15526





Our course-practical aspects

Room

BS 3.04 (Limpertsberg)

Date & time

every Wednesday, 2.5 hours

Organization

my proposal:

10.30-11.15	exercises
11.30-12.10	lecture, 1st part
12.20-13.00	lecture, 2nd part

Problematic dates

March 27, April 3, May 8
two possibilites: i) rescheduling, ii) replacement

Language

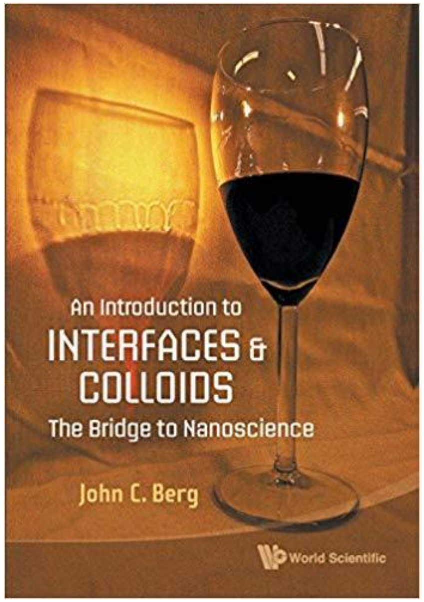
English; no impact on grade

Lecture slides

large part adapted from Prof. Lagerwall's slides
they will be available to you

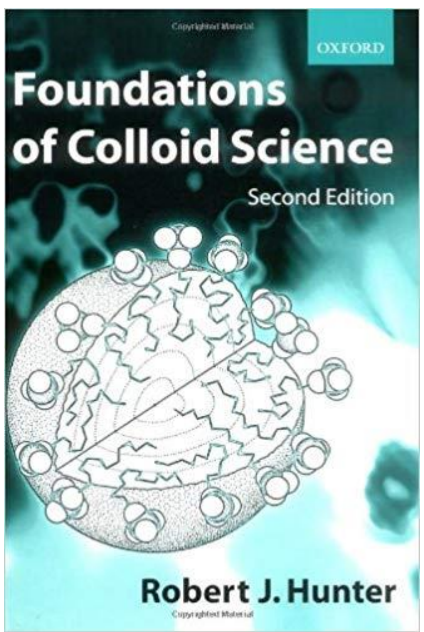
Who are you?

Recommended literature



main textbook for this course

https://www.worldscientific.com/worldscibooks/10.1142/7579



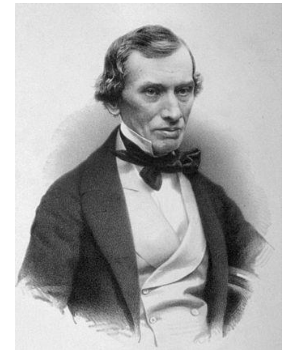
secondary textbook for this course

https://global.oup.com/academic/product/foundations-of-colloid-science-9780198505020?cc=lu&lang=en&

Colloid & interface science: key concepts (I)

Colloid: dispersion of particles (S), droplets (L) or bubbles (G) in a continuous medium (S, L, or G); the former are much larger than the molecules of the latter (***κόλλα***: glue)

Thomas Graham in 1856

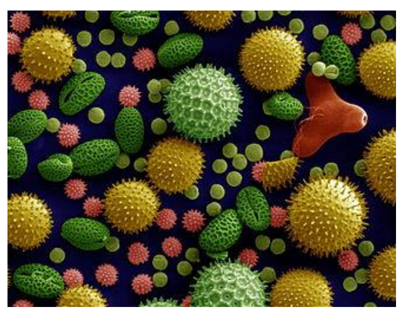


Disperse phase: the particles, droplets or bubbles; often referred to as the colloids, which is wrong; size ~ 1 nm to ~ 10 μm (Latin ***dispergere***: spread out)

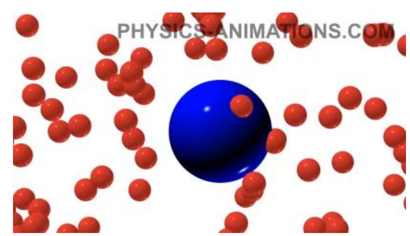
Continuous phase: the surrounding phase; commonly referred to as the solvent; size ~ 1 nm

Brownian motion: the random motion of particles suspended in a fluid driven by their collision with the fast-moving fluid molecules

Robert Brown in 1855



pollen grains



youtube.com/watch?v=6VdMp46ZIL8

Colloid & interface science: key concepts (II)

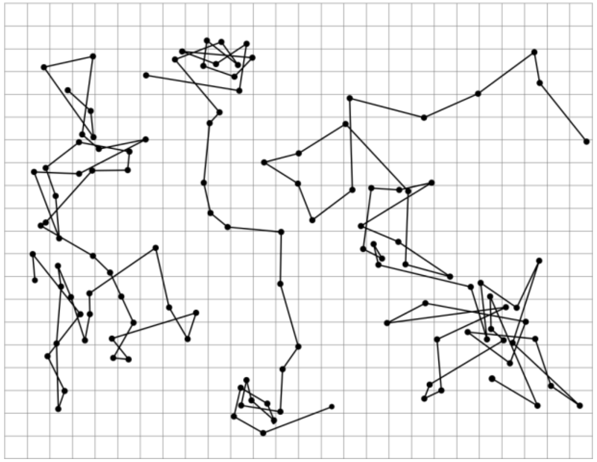
Diffusion: macroscopic manifestation of thermal motion of molecules/particles
→ *media of non-uniform composition move toward uniform composition with t*

Fick's law

$$J_A = -D_{AB}\left(\frac{\partial C_A}{\partial x}\right)$$

Einstein-Smoluchowski

$$D = \frac{\langle l^2 \rangle}{2t}$$



J_A: flux of moles of A across a surface normal to x
D_{AB}: diffusivity of A in B C_A: concentration of A
$\langle l^2 \rangle$: mean square displacement

Example
PS spheres, 2R= 1 μm
dispersed in water (η= 8.9 x 10^{-4} Pa.s)
T= 20 °C

Stokes-Einstein-Sutherland

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

random walk in 3D

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

Time scale (Brownian motion): t = 0.86 ms   microscopic systems: ~ 10^{-12} – 10^{-10} s

Length scale: 1 μm ~ λ of visible light   microscopicc systems: ~ 10^{-10} – 10^{-9} m

Colloids belong to the class of ***mesoscopic systems*** (typical for Soft Matter)

Colloid & interface science: key concepts (III)

Interface: a thin boundary region separating macroscopic chunks of matter from their surroundings or from one another (more general term than 'surface')

imgcop.com

dreamstime.com

Example
100 mL of olive oil in 1L of water:
i) macroscopic phase separation
ii) emulsion in a beaker with 2R= 10 cm

Calculate the total interfacial area A_{int} in these two cases

$A_{int,\,i} = 7.85\times10^{-3}\ m^2$ $A_{int,\,ii} = 6.03\times10^{2}\ m^2$

Colloids and Interfaces are two concepts that are interrelated !

Lyophobic (solvophobic): phobic from ***φόβος*** meaning **fear**; therefore ***solvent-fearing***

Lyophilic (solvophilic): philic from ***φίλος***, meaning **friend**; therefore ***solvent-loving***

When the solvent is water (***ύδωρ***): **hydrophobic**/**hydrophilic**

Sol: dispersion of particles or droplets in a fluid (G or L) continuous phase

IUPAC terminology

Colloids/Colloidal Systems/Colloidal Dispersions

Sols
fluid continuous phase

Lyophobic
thermodynamically unstable, not spontaneous

- **Suspensions** – solid in liquid
- **Emulsions** – liquid in liquid
- **Aerosols** – solid/liquid in gas
- **Fluid foams** – gas in liquid

Lyophilic
solutions,
stable,
spontaneous

- **Association colloids**
- **Macromolecular colloids**

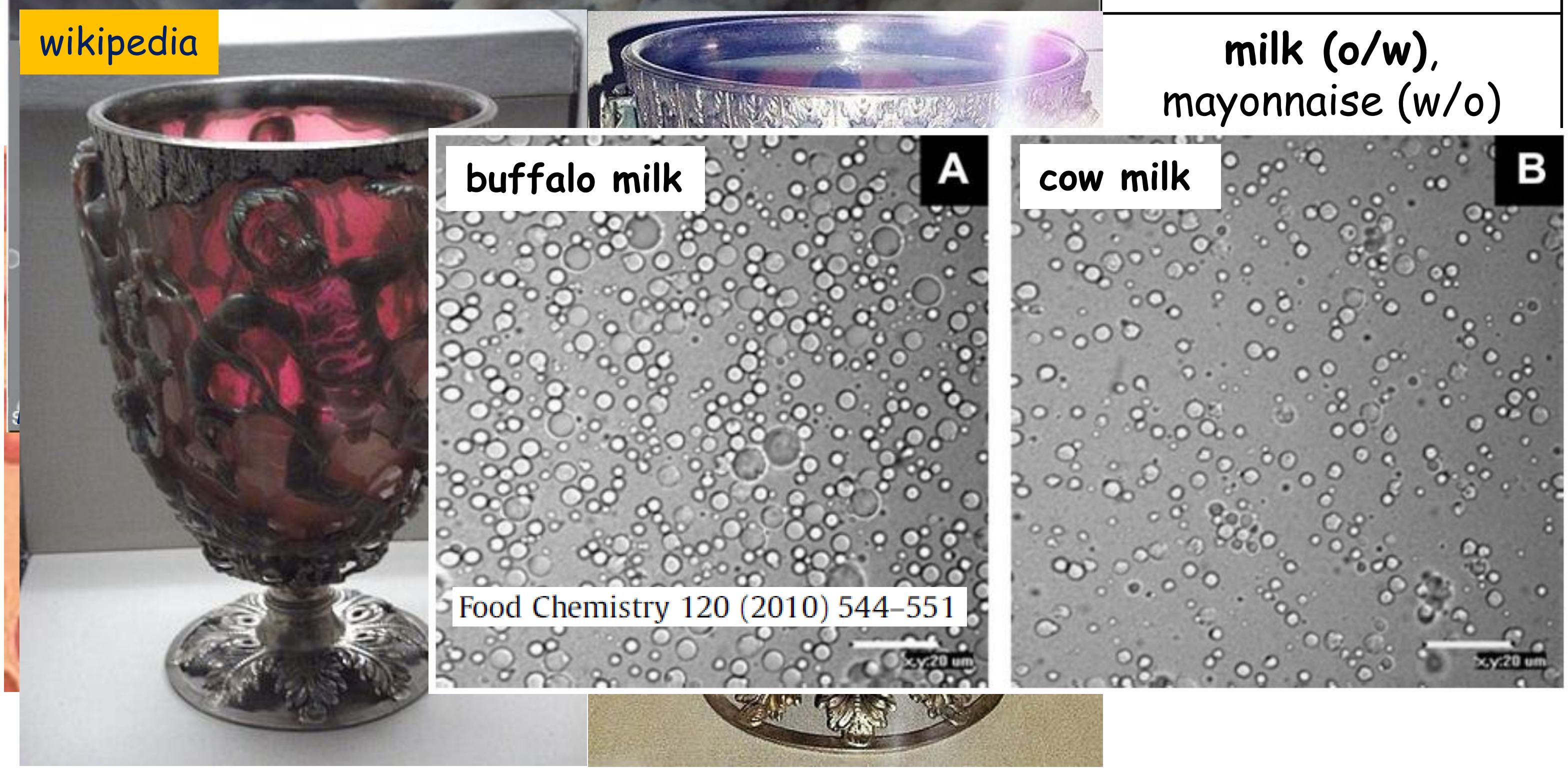
Solid colloids
solid continuous phase

insulating foam, styrofoam…

IUPAC: International Union of Pure & Applied Chemistry

Examples of colloids

disperse phase	continuous phase	type	thermodyn. state	examples
				conc. soap solution, **blood plasma**
				blood cells, paint, ink
				milk (o/w), mayonnaise (w/o)



Dimensions of colloidal systems

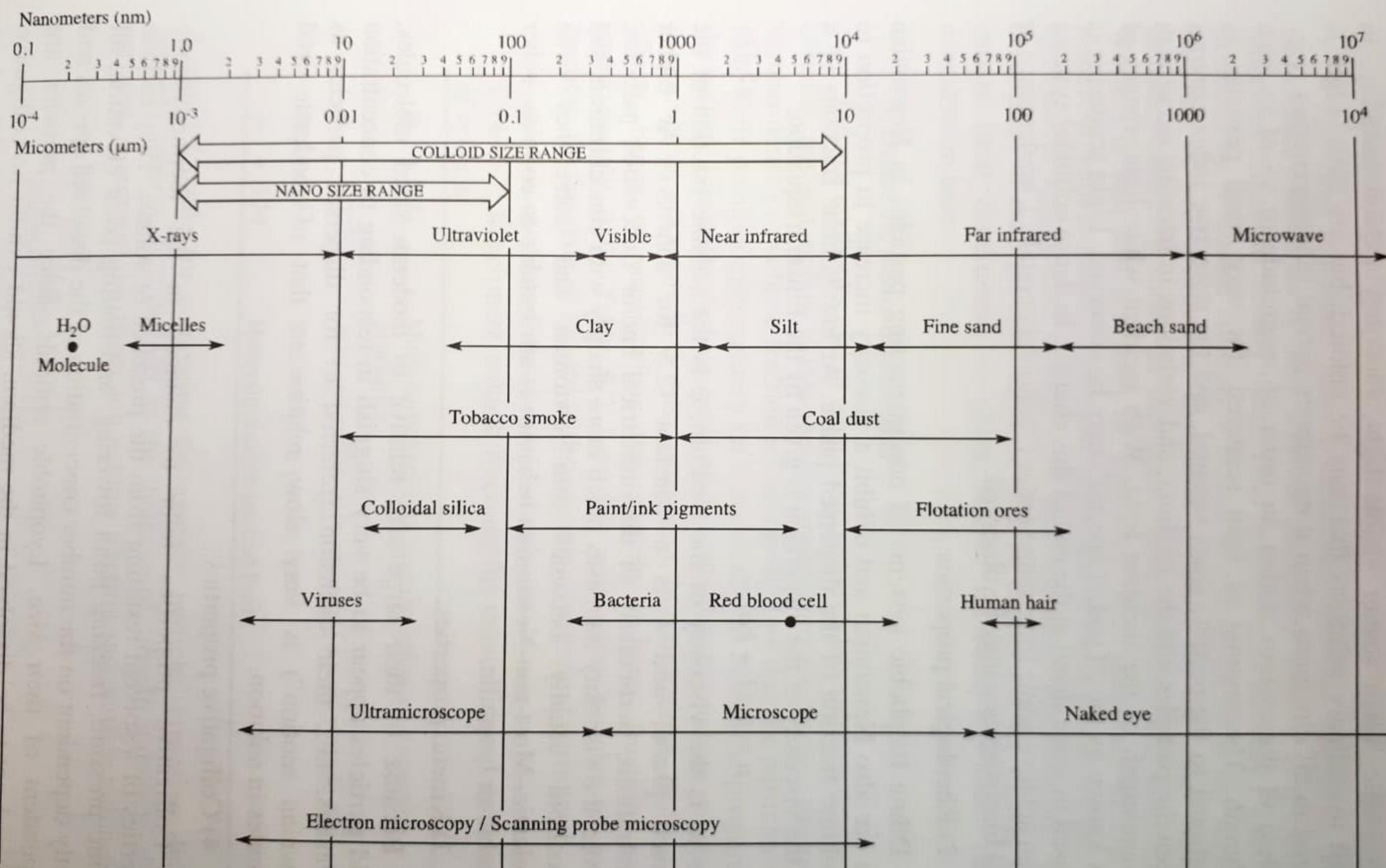


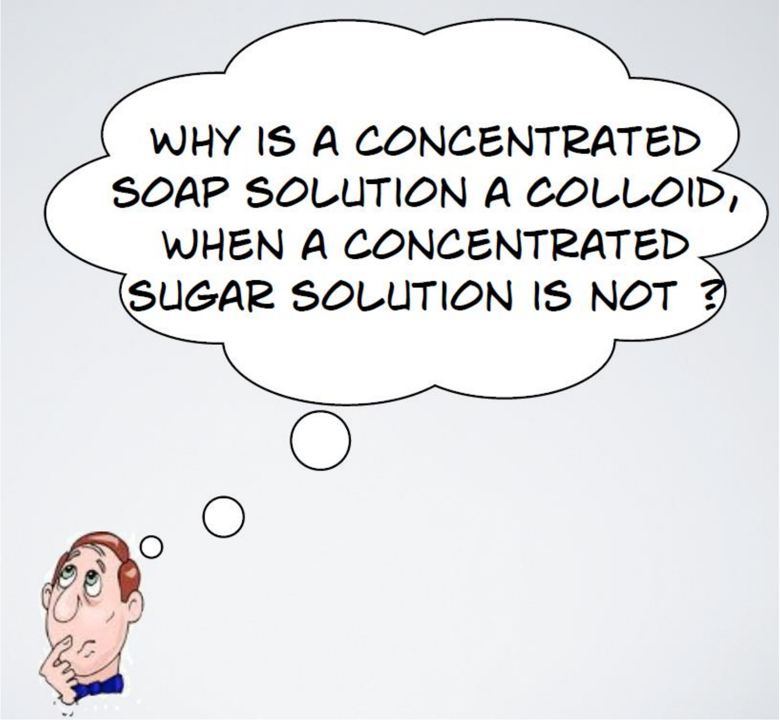
Fig. 5-2: Colloidal system dimensions.

Coffee break

pinterest.com

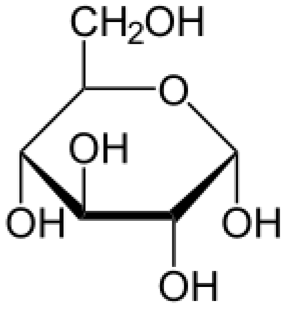
Do you recognize any colloids in flat white?

"Food for thought"



alpha-D-glucopyranose
(Haworth projection)

wikipedia.com



Stability of lyophobic colloids (I)

When talking about 'colloidal stability', we must ask:
stability against what?

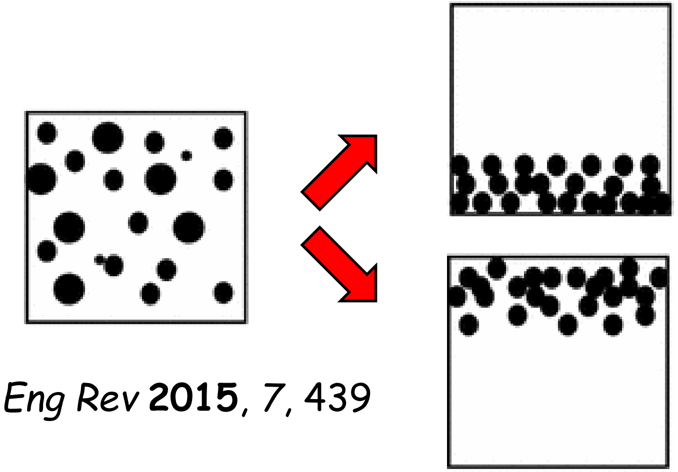
Stability against phase segregation

-refers to the spatial distribution of particles that make up the disperse phase

-particles are (generally) affected by gravity (& other external fields)

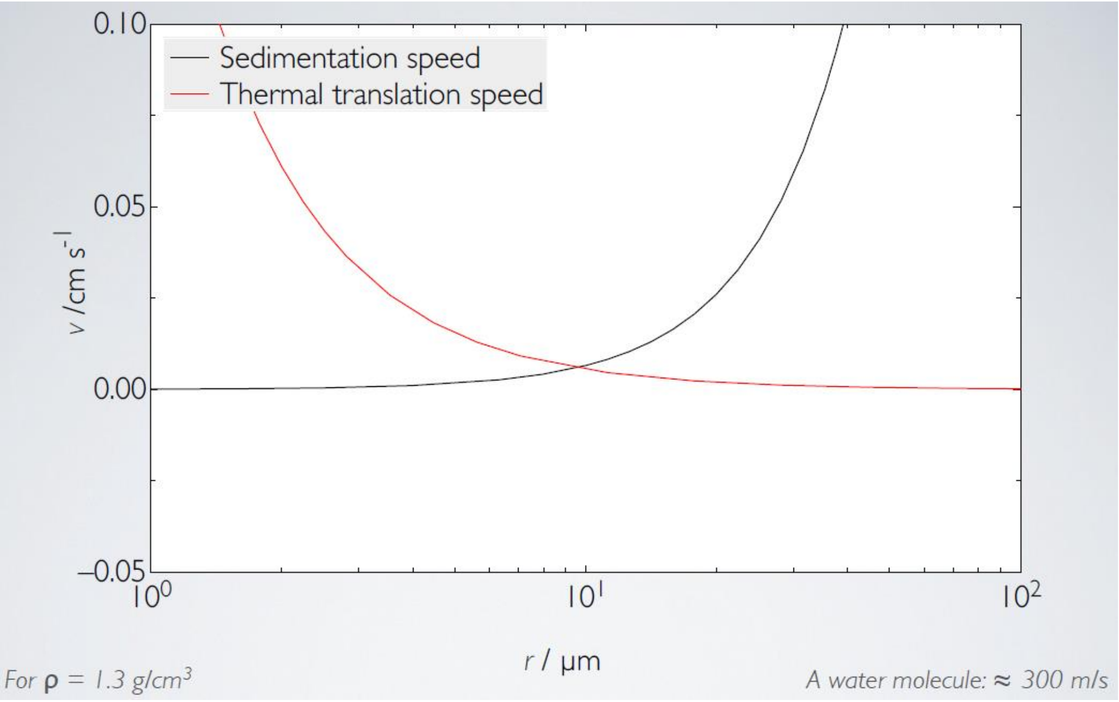
$\Delta\rho = \rho_{part} - \rho_{sol}$ important

$\Delta\rho > 0$, ***sedimentation***



Food Eng Rev **2015**, *7*, 439

$\Delta\rho < 0$, ***creaming***



Stability of lyophobic colloids (II)

Thermodynamic criteria for stability

-contrarily to sedimentation/creaming, other processes *irreversibly* change colloids

-these processes can be conveniently described using ***thermodynamics***

-requirement: **G(ξ)** must be known

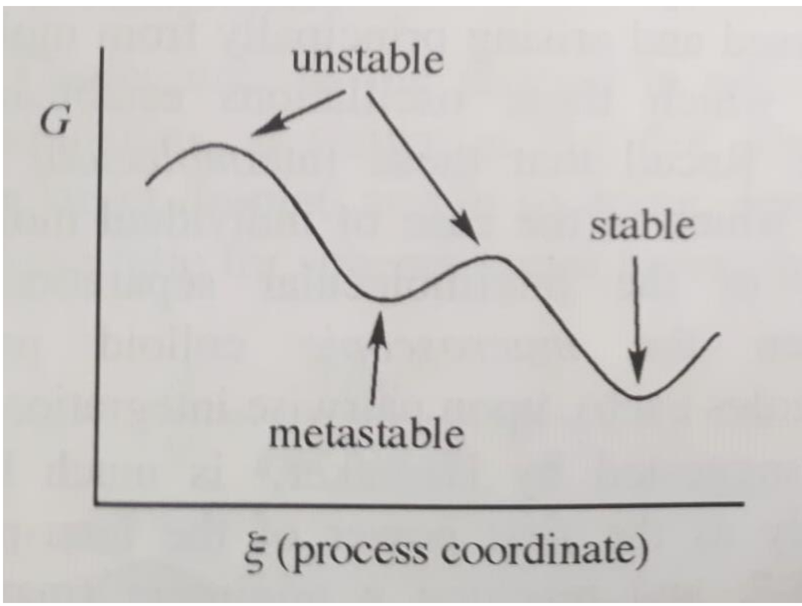


Fig. 5-5: General conditions for thermodynamic equilibrium: ($dG = 0$) and stability ($dG = 0$ *and* $d^2G > 0$).

equilibrium with respect to the process represented by ξ requires:

dG= 0 → min, max, or inflection point in G(ξ)

stability requires: local min. in G: $d^2G > 0$ → min

Stability of lyophobic colloids (III)

Aggregation

-dispersed particles stick together

-aggregation can be either reversible (flocculation) or irreversible (coagulation)

-particles approach each other → attraction

-process variable ξ for aggregation: S_0
(process: $S_0 \rightarrow 0$)

$$G = G_0 + \Phi(\xi) = G_0 + \Phi(S_0)$$

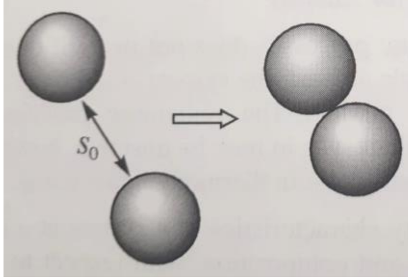
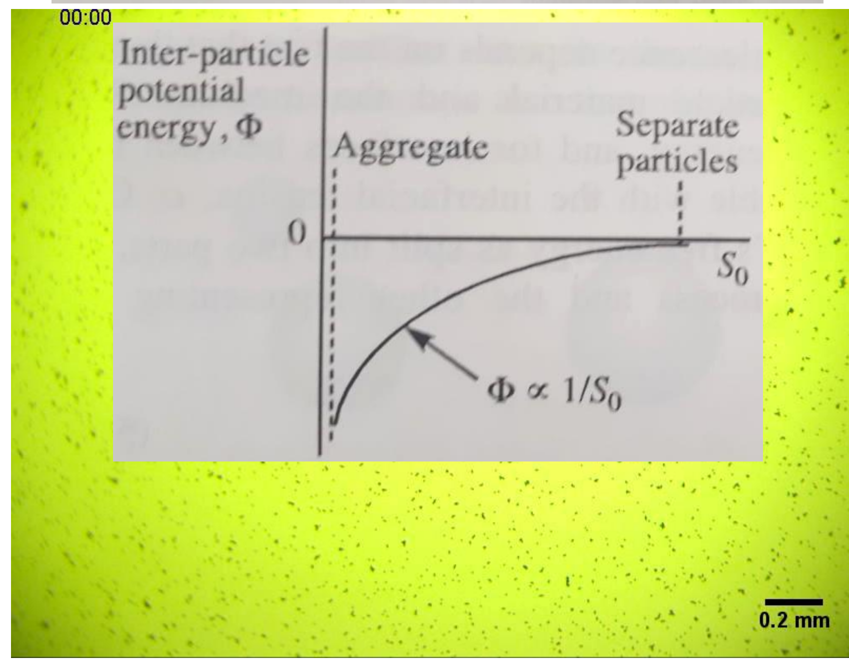
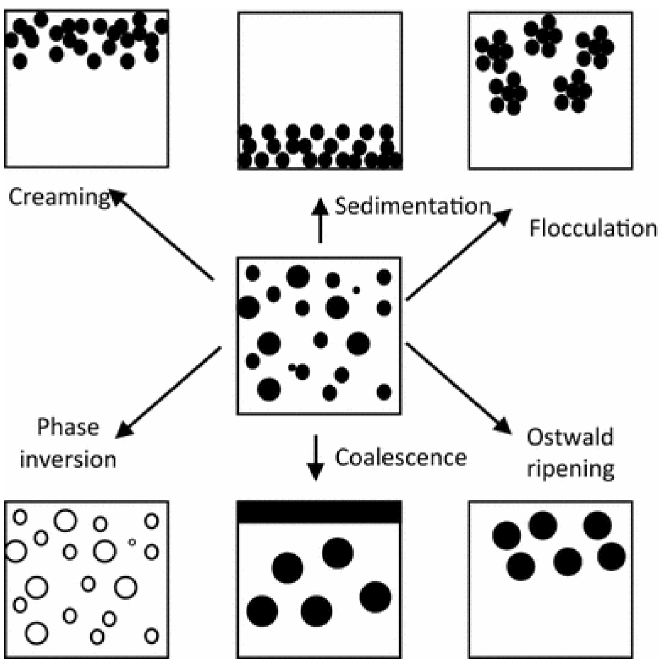


Fig. 5-6: Aggregation of two primary particles to form a doublet.





'Clumping' processes are ***spontaneous*** because they reduce the free energy of the system

Key interactions in colloids

ENTHALPIC

Ionic interactions

electrostatic interactions involving *permanent electric charges* (e.g. ion-ion)

can be *attractive* or *repulsive*

van der Waals interactions

forces involving permanent or induced electric dipoles

usually attractive

Hydrogen bonding

partially electrostatic force of attraction between a H bound to a more electronegative atom & another adjacent atom bearing a lone pair of e^-

attractive

Aromatic interactions

also called π-stacking interactions

attractive

ENTROPIC

Steric interactions

interactions between objects that touch each other

repulsive

The hydrophobic effect

directly related to the H-bonding of water (not purely entropic)

attractive or *repulsive*

Depletion attraction

arises in fluid suspensions when an additive, smaller than the particles, is introduced due to excluded volume

attractive

Energy scales of various interactions

Thermal energy

internal energy present in a system in a state of thermodynamic equilibrium by virtue of its temperature

$\mathbf{E_{th} = k_B T}$; $k_B = 1.38 \times 10^{-23}$ m^2 kg s^{-2} K^{-1}

@ room T (=20 ^{o}C): $\boldsymbol{E_{th} = k_B T_{room} \approx 4 \times 10^{-21}\ J}$

if an association energy is less or of the order of E_{th}, then thermal motion destabilizes the associated state

Covalent C-C bond

$\boldsymbol{E_{cov} \sim 100\ k_B T_{room}}$

Hydrogen bond

$\boldsymbol{E_{H\text{-}bond} \sim 10\ k_B T_{room}}$

van der Waals interaction between two CH_4 molecules

$\boldsymbol{E_{vdW} \sim 1\ k_B T_{room}}$