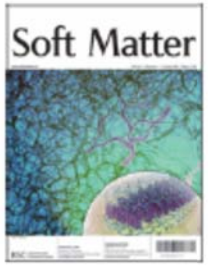
What is soft matter?

Pierre-Gilles de Gennes (Nobel prize in physics 1991):

> ”All physicochemical systems that have *large response functions.*”
> (That is, a mild external influence has a big effect)



Helmut Möhwald (Editorial board member, *Soft Matter*):

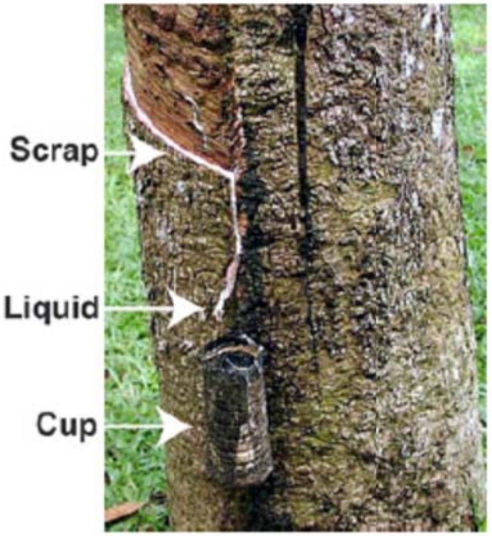
> ”Materials that are held together by non-covalent interactions. These interactions are typically weak, often on the order of kT and thus comparable to entropic forces.”

Richard A. L. Jones, in *Soft Condensed Matter*:

> ”Materials in states of matter that are neither simple liquids nor crystalline solids of the type studied in other branches of solid state physics.”

Before tackling actual complex soft matter systems, we need to understand (amongst other things) these *response functions*, *non-covalent interactions* and *entropic forces*.

Example: Rubber boots of the Amazon indians

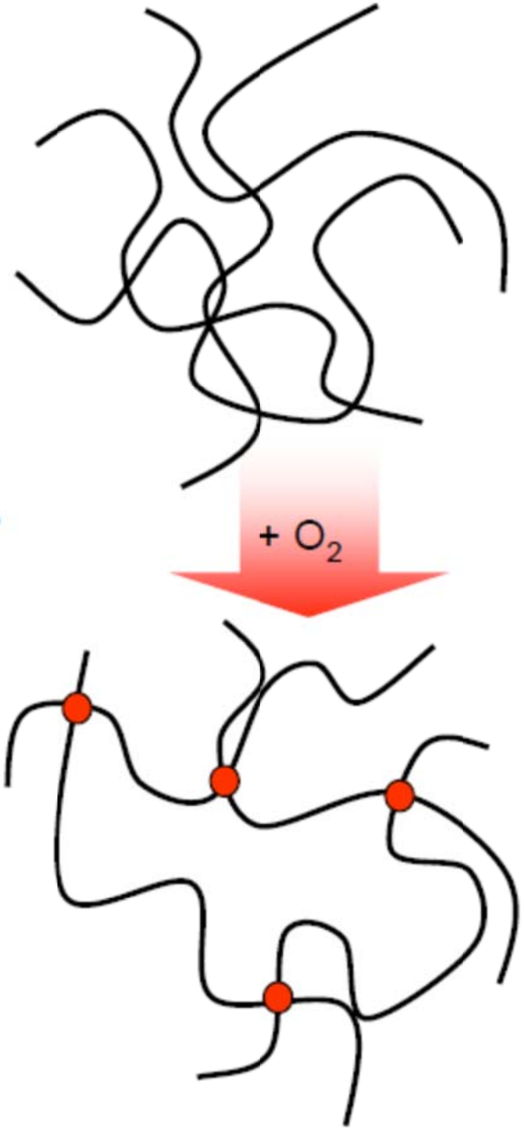


Sap from a rubber tree is collected and spread on the feet.

At this stage the long molecules comprising the latex liquid can easily slide over one another.

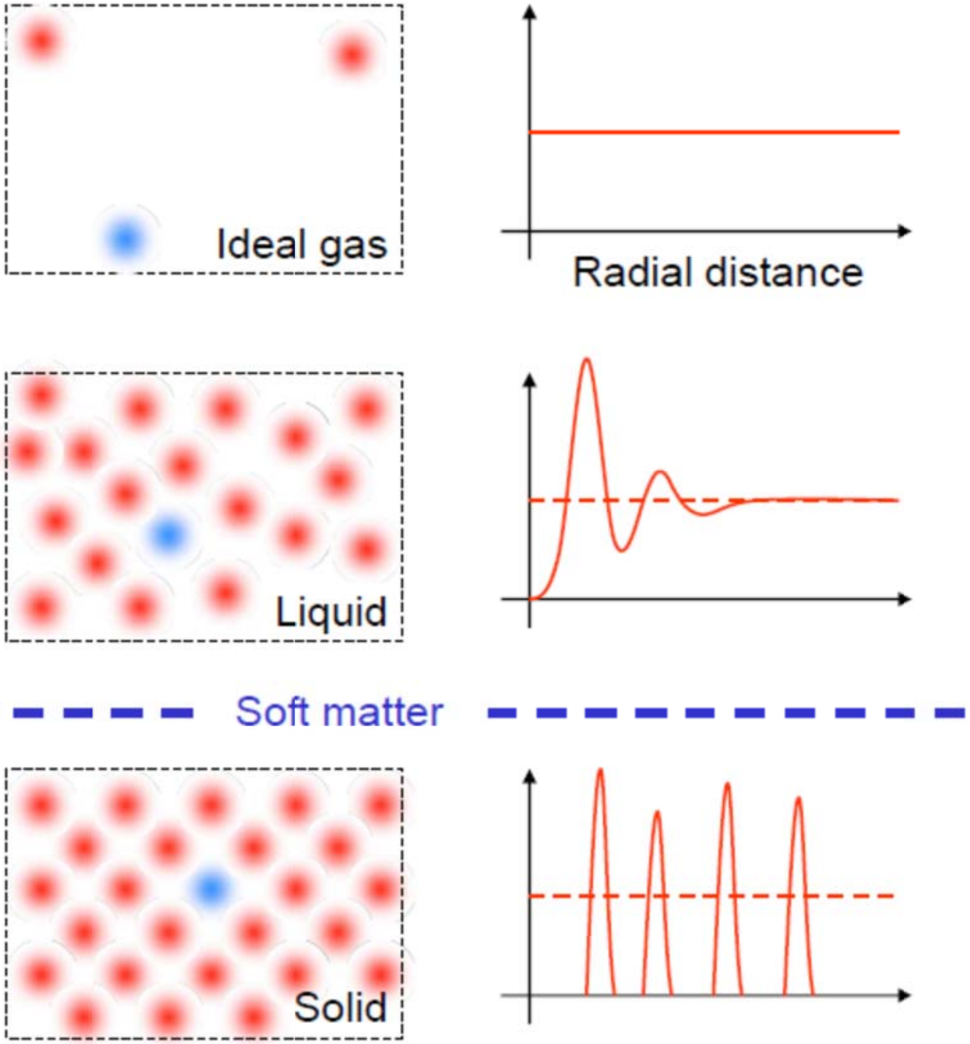
Oxygen from the air (●) reacts with the molecules and binds them together.

The latex on the feet hardens, resulting in rubbery ”boots”.

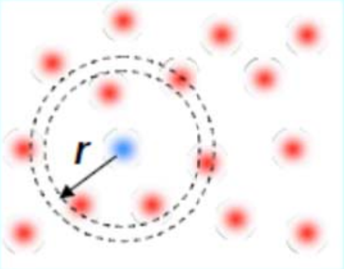


Significant change in mechanical properties due to mild chemical action.

"Structured fluids"



Radial distribution function



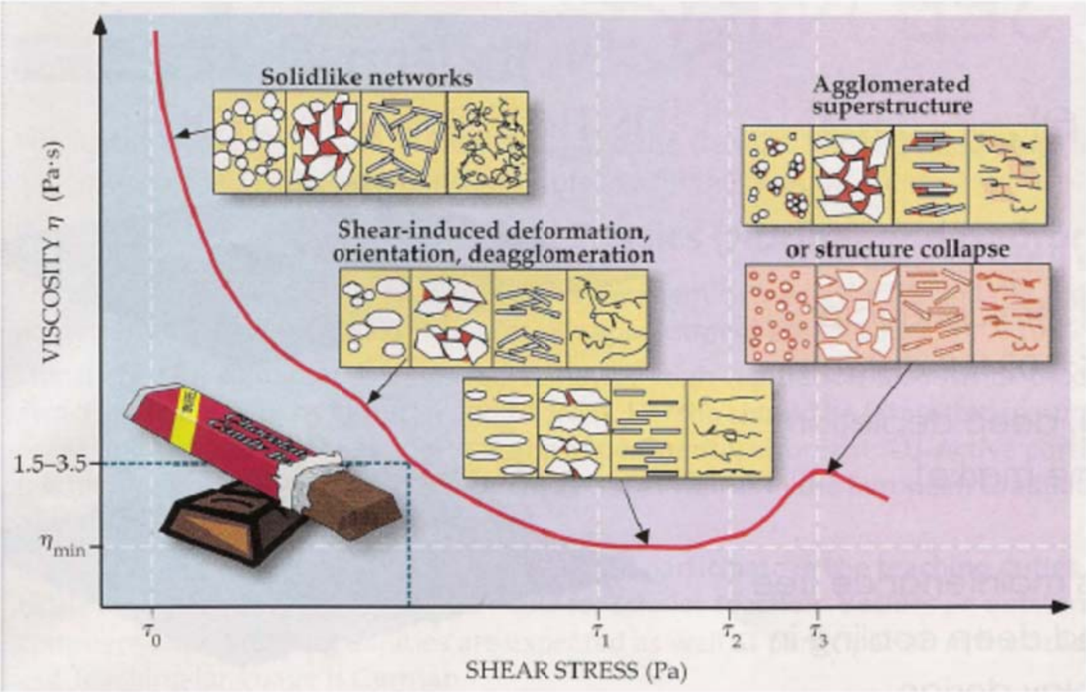
Calculate the number of particles ● inside a radial segement **$(r, r+\Delta r)$** from one specific particle ● in the system.

Average the distribution over all particles in the system.

Divide the (average) number of particles in a segment by the segment volume.

Finally, normalize thus obtained radial density profile with the bulk density **N/V** of the system.

Complexity – chocolate as an example



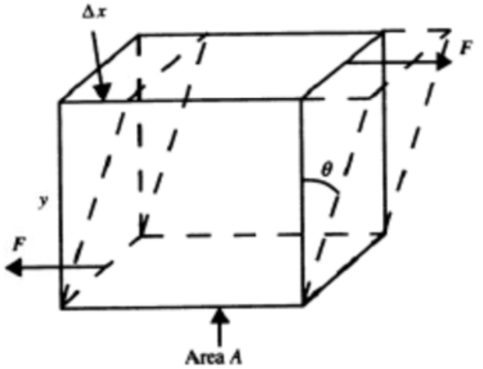
Even such simple and every-day substance as chocolate has a quite complex structure and mechanical properties

A delicious piece of chocolate – solid at room temperature, liquid-like in your mouth

The term for soft matter widely used in, e.g., North America is 'complex fluid'. However, note that there are soft matter systems that are not really fluid: rubber, gels, ...

Mechanical properties

Viscoelasticity: substance exhibits both viscous and elastic properties, depending on the time scale over which an external stress is applied (dough, silly putty)

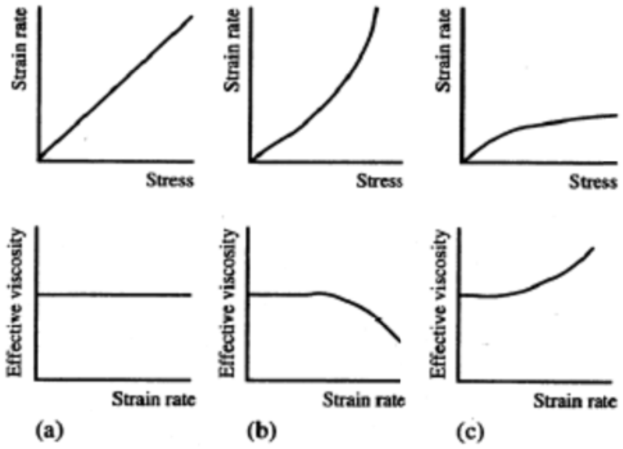


Dilatant materials: Apparent viscosity increases with the rate of shear, "shear-thickening" (**c**) (concentrated solution of sugar in water, suspension of corn starch)

Pseudo-plastics: Apparent viscosity decreases with the rate of shear, "shear-thinning" (**b**) (clay, milk, blood)

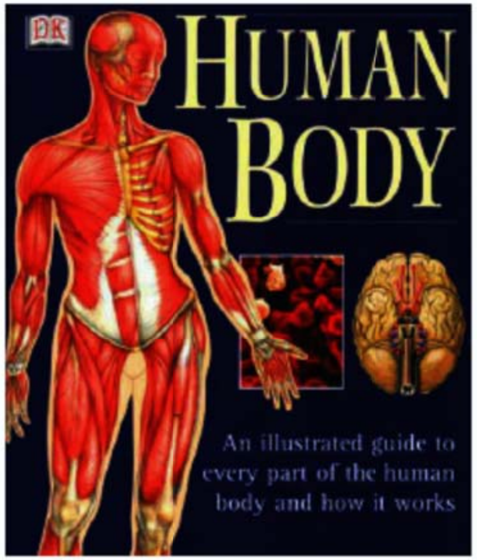
Thixotropic: Apparent viscosity decreases with duration of stress (ketchup, honey, paints)

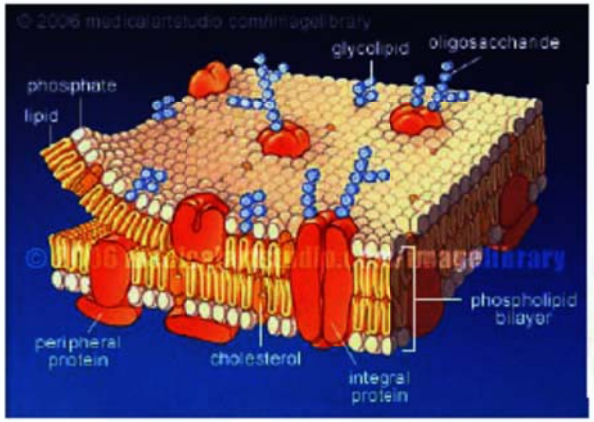
Rheopectic: Apparent viscosity increases with duration of stress (some lubricants)



Importance of the conformations, relaxation times, and aggregation processes of the microscopic particles dispersed in the substance (cf. chocolate)

Some Examples of Soft Matter



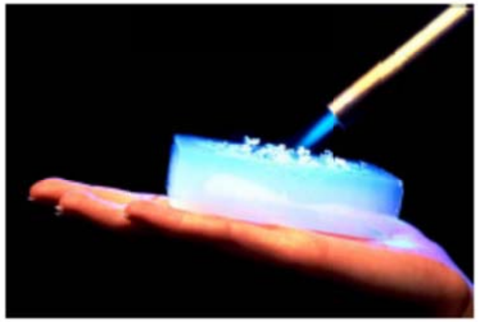


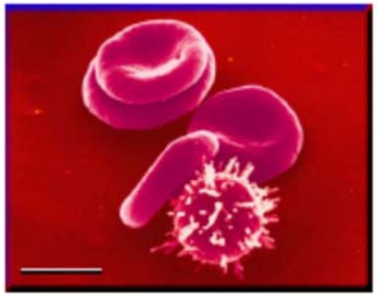
Colloids


Foams


Milk


Fog, mist, smoke


Aerogel ("frozen smoke")


Blood


Paints

Classification of colloids

Colloids consist of one or more phases, with some characteristic dimensions between ~ 10 nm – 1 µm, dispersed in an external phase.

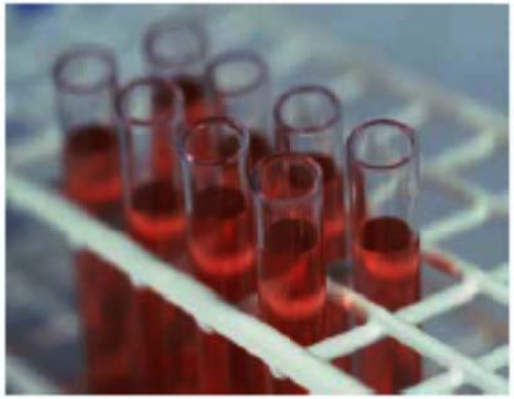
Dispersed phase	*External phase* **Gas**	**Liquid**	**Solid**
Gas	-	Foam	Solid foam
Liquid	(Liquid) Aerosol	Emulsion	(Solid) Emulsion
Solid	(Solid) Aerosol	Sol, colloidal dispersion	Solid suspension

Colloids with a liquid external phase can also be classified on the tendency of the dispersed particles to aggregate:

Lyophilic: dispersed particles tend to stay dispersed throughout the external phase
Lyophobic: dispersed particles tend to spontaneously aggregate

Michael Faraday and gold colloids

In 1857, Michael Faraday observed the properties of a dilute solution of colloidal gold. Under normal conditions, the such a colloidal dispersion has a clear red color. However, adding some NaCl into the solution made it turn blue.



Faraday realized that the change in color had to do with the sizes of the dispersed particles:

In a dispersion, gold colloid particles (< 100 nm) absorb on the green and blue parts of the spectrum, but *transmit* on the red part. Furthermore, the gold particles are all negatively charged, thus electrostatically repelling each other.

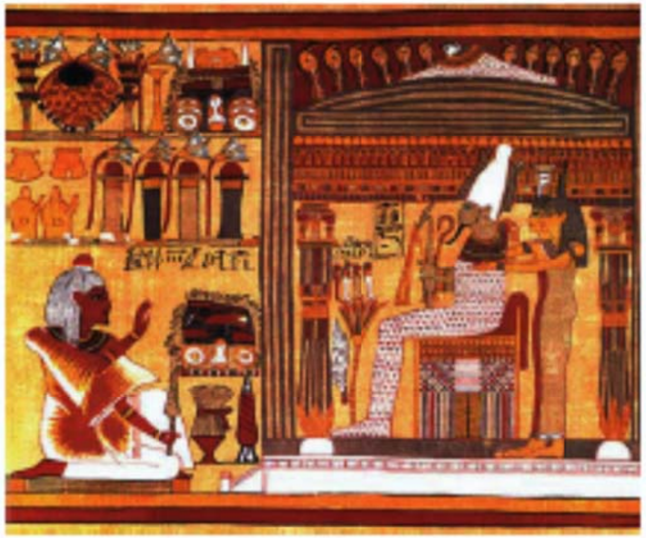
Adding salt screened these repulsive interactions, and the gold particles started to coagulate. The formation of larger aggregates then resulted in the *scattering* of blue light from the dispersion.

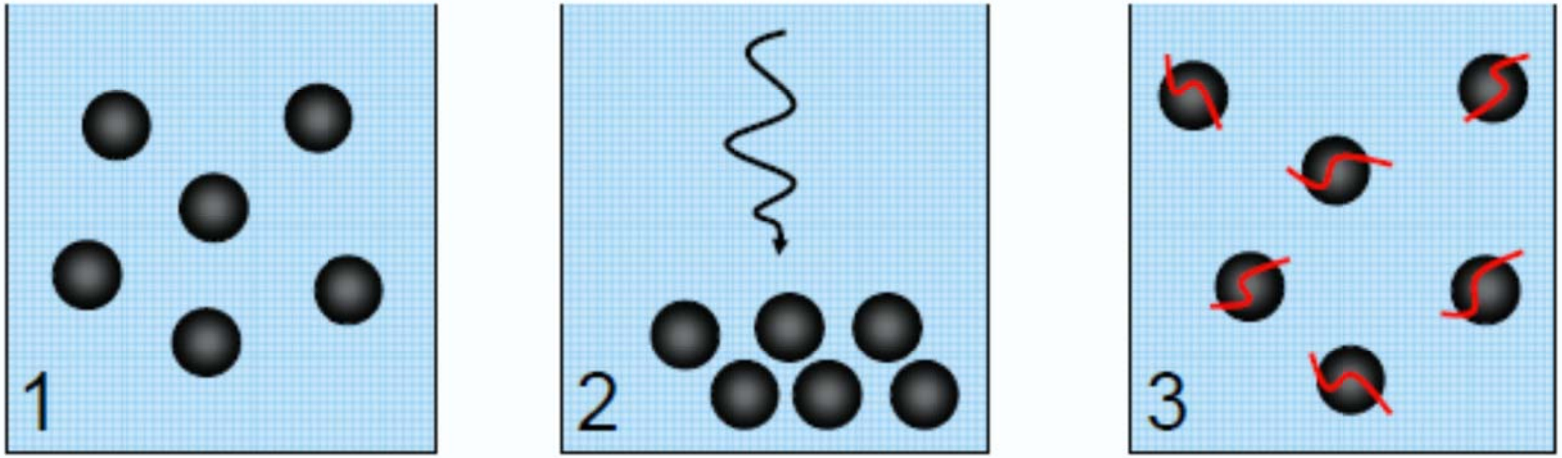
Scribes of the ancient Egypt

1) Traditionally, ink was made by dissolving particles of carbon black in water.

2) However, within a day or so, the particles started to flocculate and sedimented at the bottom of the container.

3) Adding some gum arabic (~) into the solution sterically stabilized the colloidal particles, making the solution more stable.





Einstein relation

In 1905, Albert Einstein published his PhD thesis on osmotic pressure. Developing the ideas therein further, later that year he published one of his ground-breaking papers of that year: the theory of Brownian motion.

Deriving a result, which nowadays is called a fluctuation-dissipation theorem, Einstein showed that the diffusion coefficient of a particle undergoing Brownian motion is

$$D = \frac{k_{\mathrm{B}}T}{\xi} \longleftarrow$$

Friction factor of the particle;
the frictional force is given by $F_{\mathrm{drag}} = -\xi v$

Specifically,

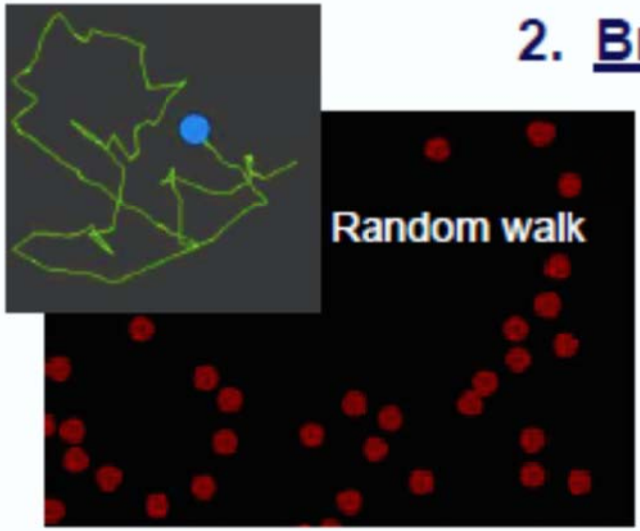
$$D = \frac{k_{\mathrm{B}}T}{6\pi\eta R}$$

For a spherical particle much larger than the sovent molecules (Stokes-Einstein equation)

The relation between the diffusion coefficient D and the displacement of a particle undergoing Brownian motion is

$$D = \lim_{t\to\infty} \frac{1}{2dt}\langle r^2(t)\rangle$$ whence, for long enough times t $$\langle r^2(t)\rangle = 2dtD$$

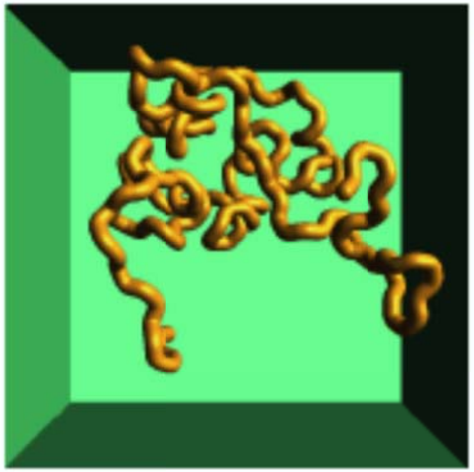
2. Brownian Motion



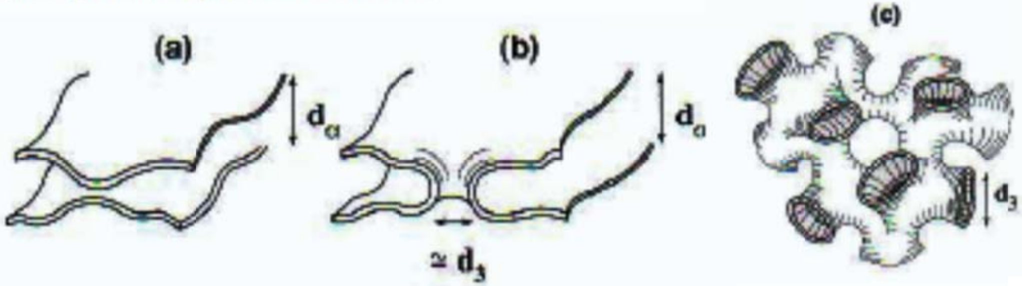
Continuous bombardment of solvent molecules.

Constant fluctuating net force: Particle moves.

--- *Colloidal particles undergo Brownian motion*
--- *Energy associated with bonds are comparable to thermal energies.*

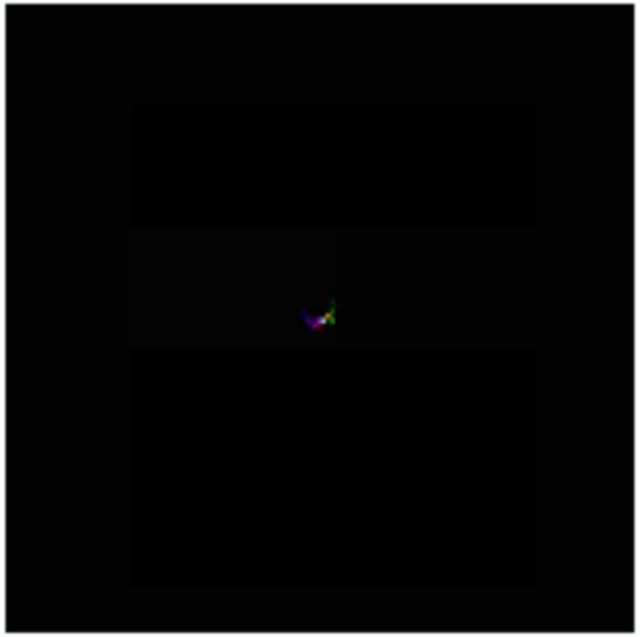


Wriggling of polymer chains



Amphiphilic systems

Drunken sailor = random walk in 2D

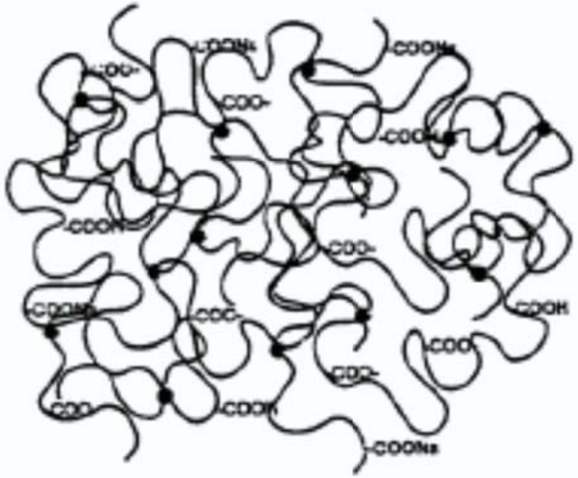


2. Brownian Motion

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

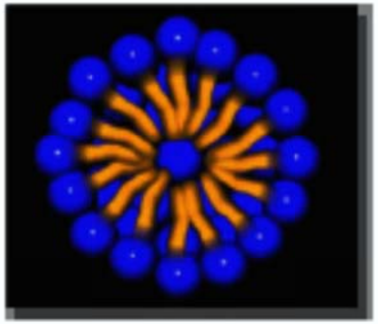
Stoke-Einstein equation

Typical D of molecules in liquid: $\approx 10^{-9}$ m^2 s^{-1}.



Large polymers move slowly

$D \approx 10^{-18}$ m^2 s^{-1}.



Micelles in water

$D \approx 2 \times 10^{-11}$ m^2 s^{-1}.

Chapter 9

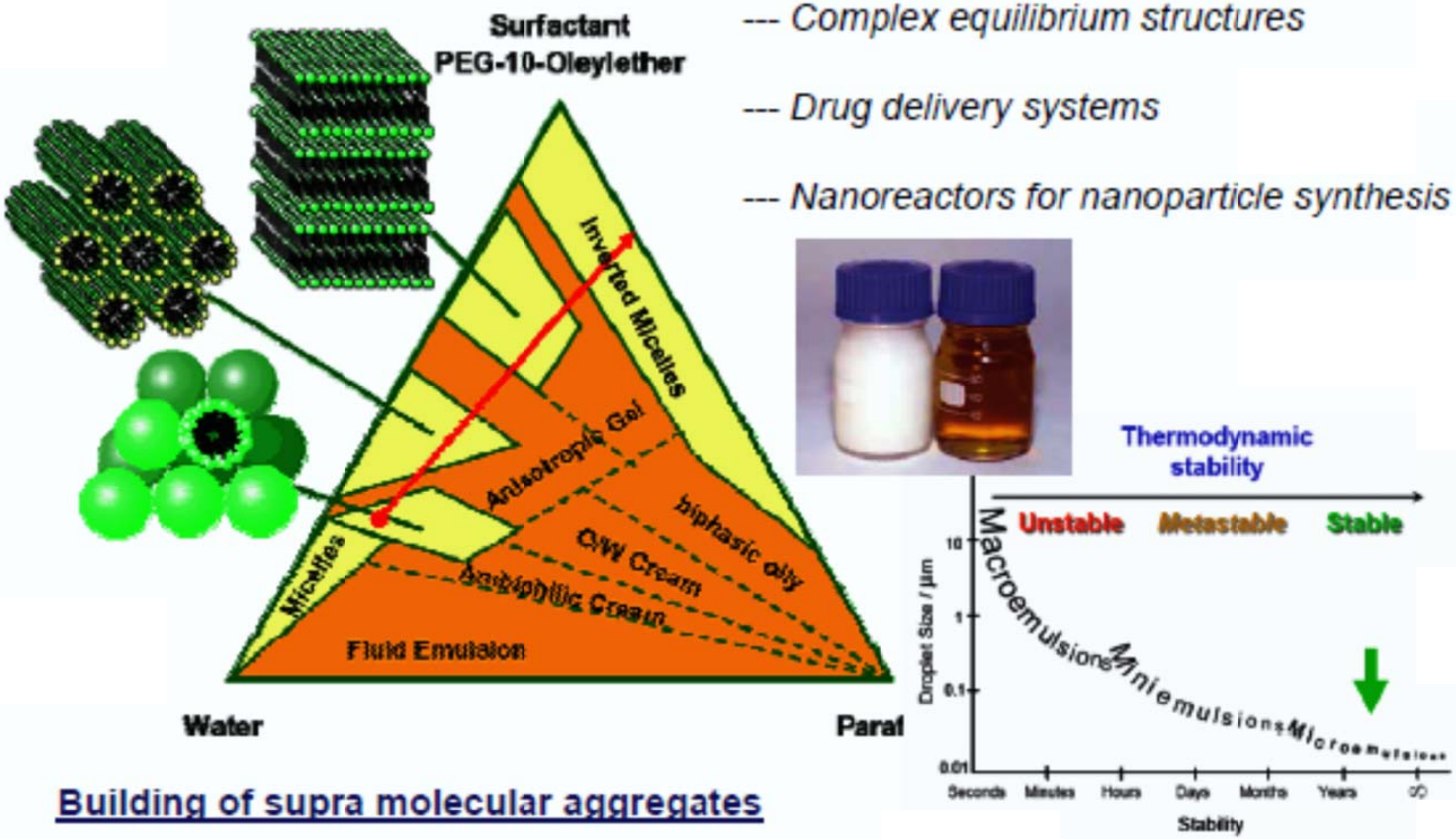
3. Self-Assembly

--- *Remarkable property of soft-matter*

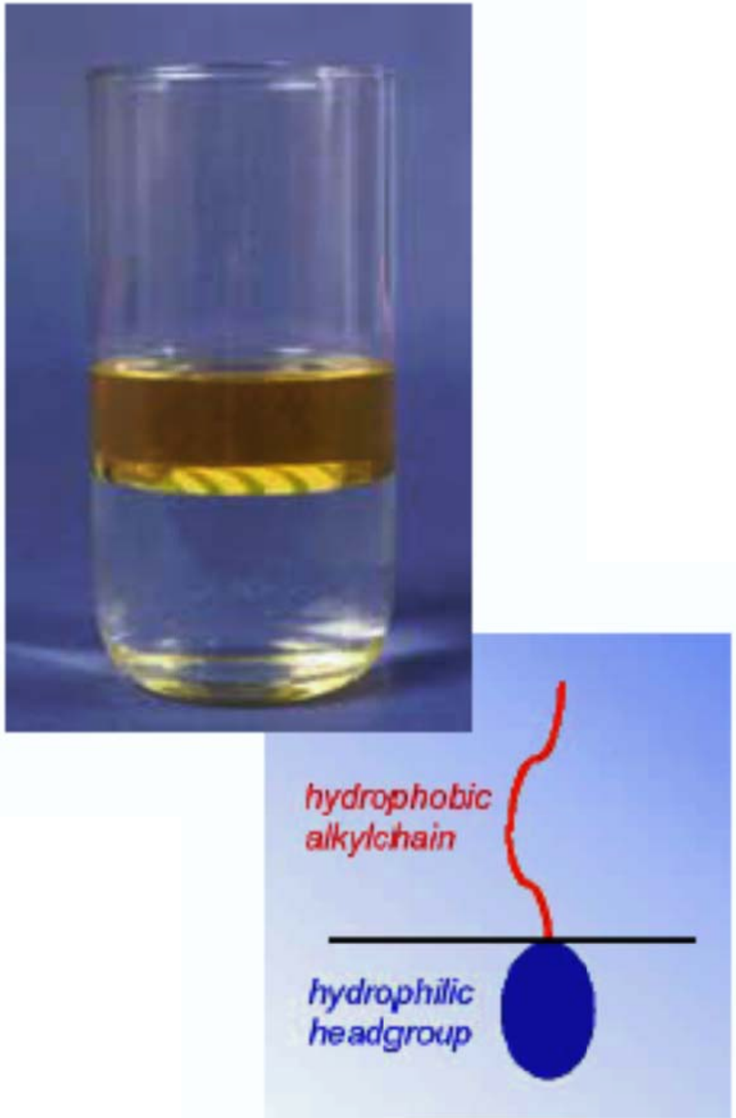
--- *Complex equilibrium structures*

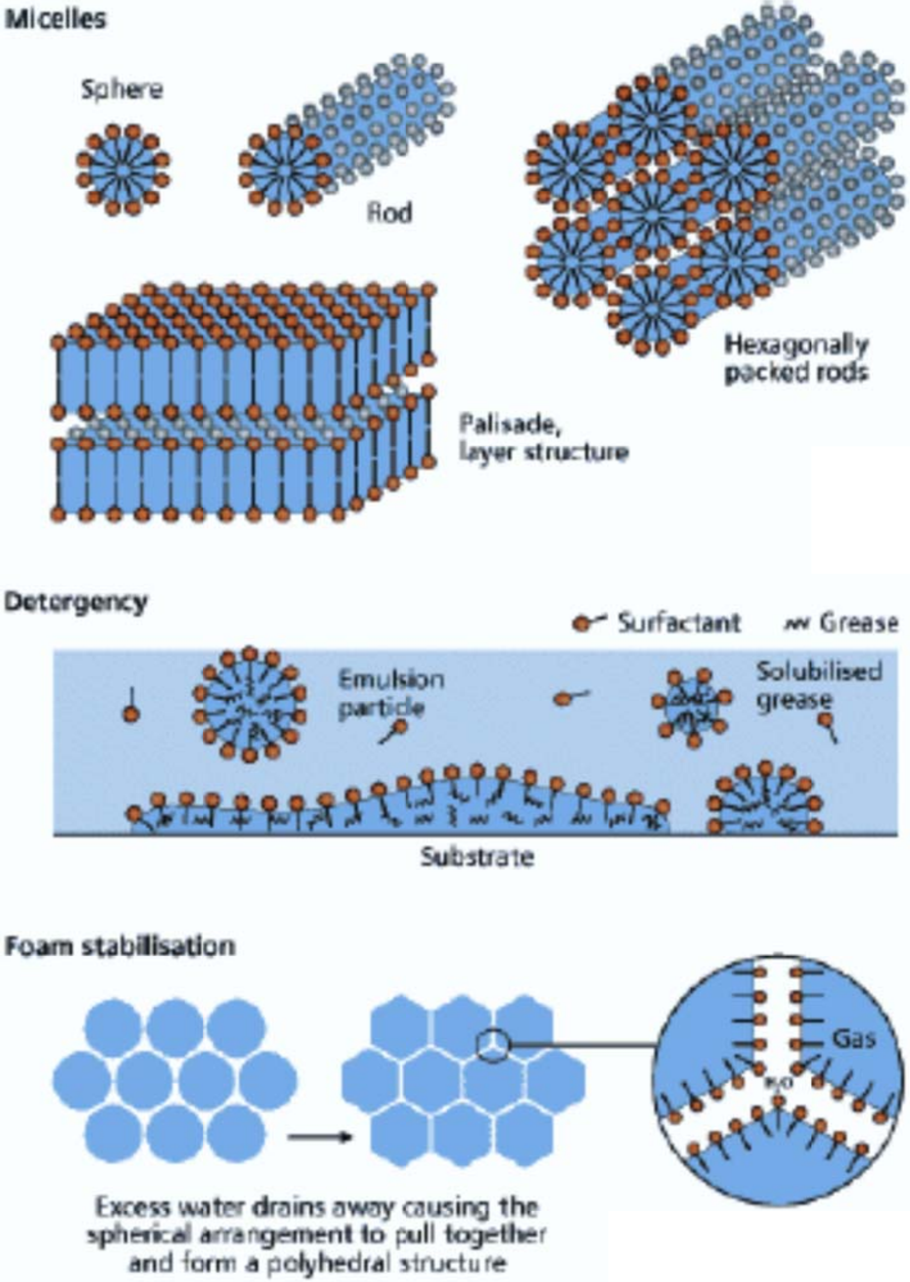
--- *Drug delivery systems*

--- *Nanoreactors for nanoparticle synthesis*



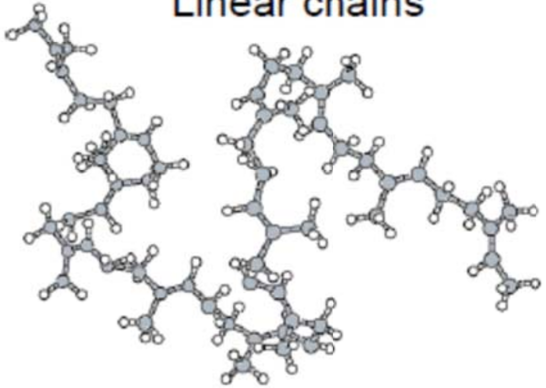
Building of supra molecular aggregates

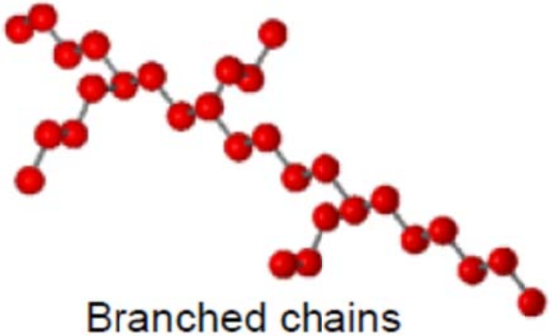

hydrophobic alkylchain
hydrophilic headgroup


Micelles
Sphere
Rod
Hexagonally packed rods
Palisade, layer structure
Detergency
Surfactant
Grease
Emulsion particle
Solubilised grease
Substrate
Foam stabilisation
Gas
H_2O
Excess water drains away causing the spherical arrangement to pull together and form a polyhedral structure

Polymers

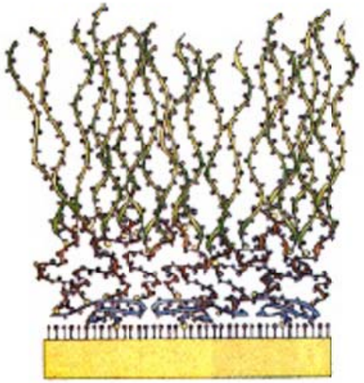
Linear chains





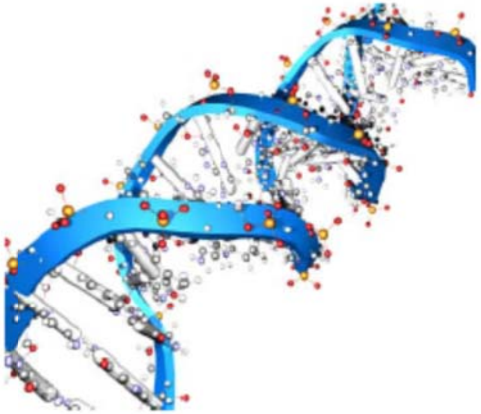
Branched chains

Dendrimers

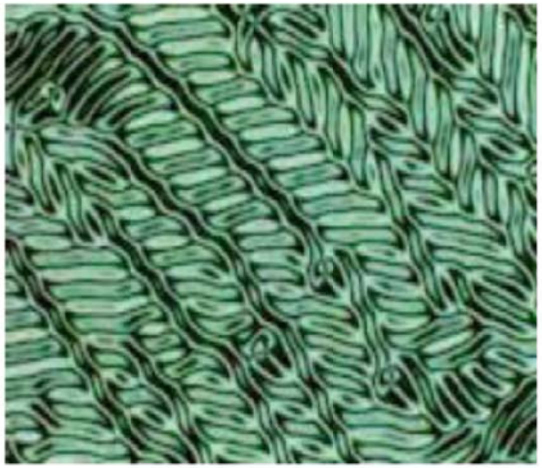


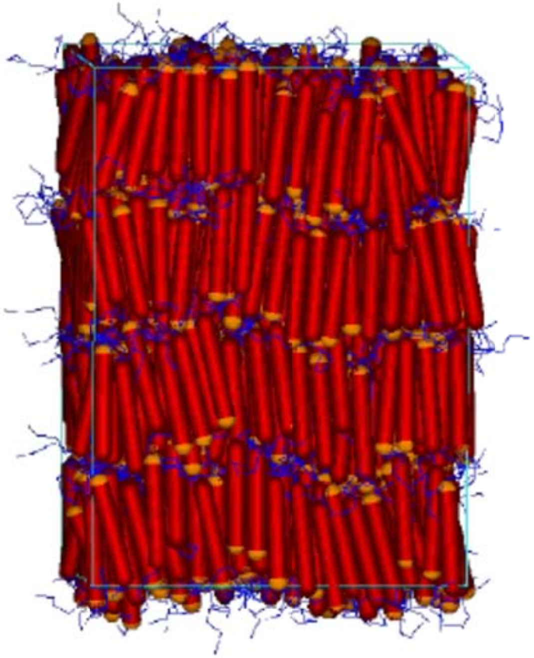
Grafted polymers

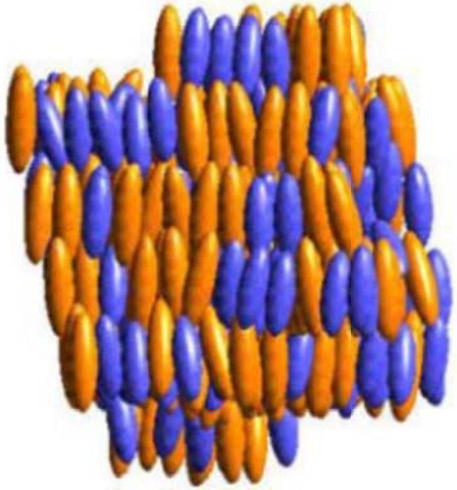
Polyelectrolytes

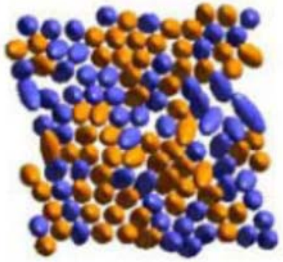


Liquid crystals



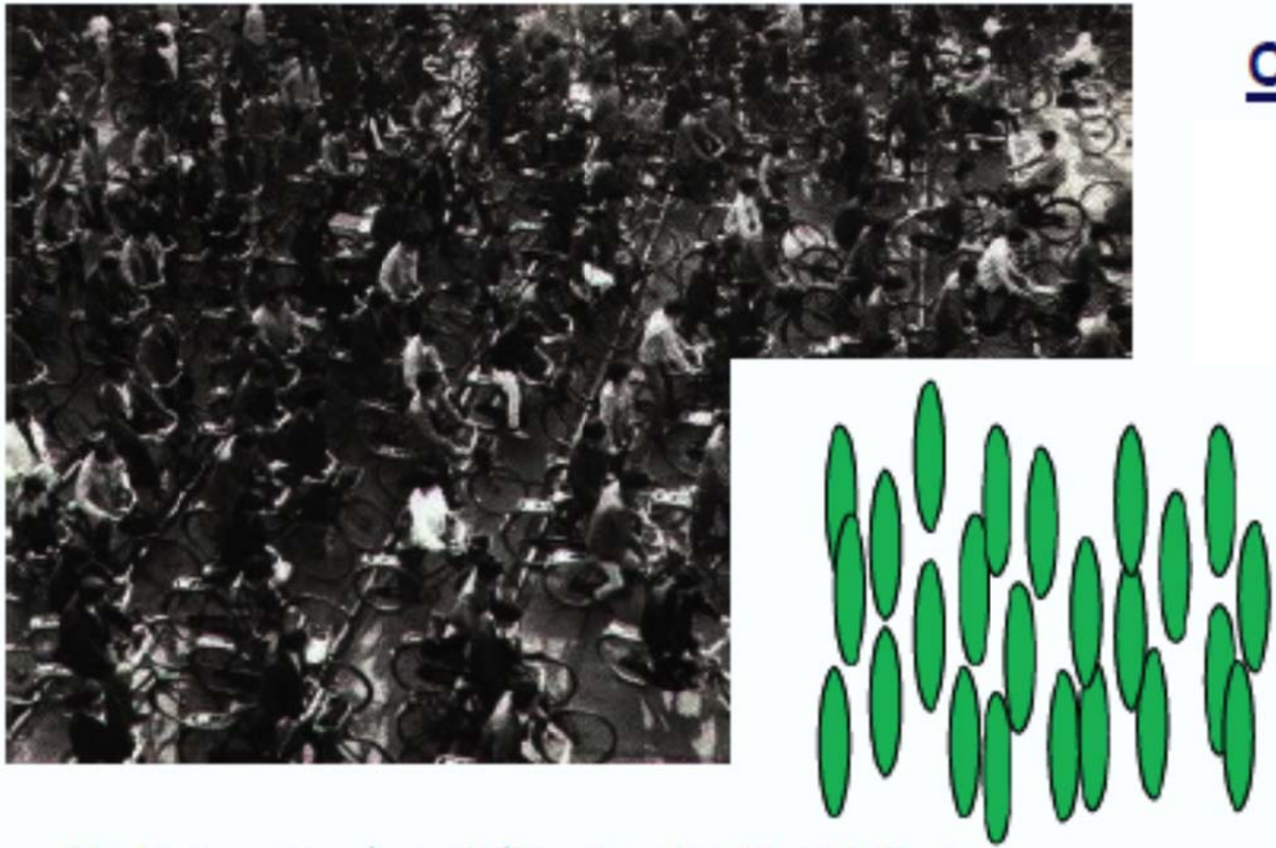






Nanoscale or Mesoscopic Ordering in Soft Materials

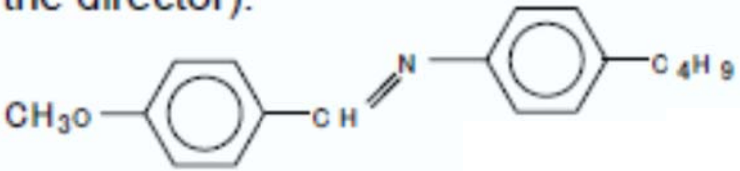
Chapter 7



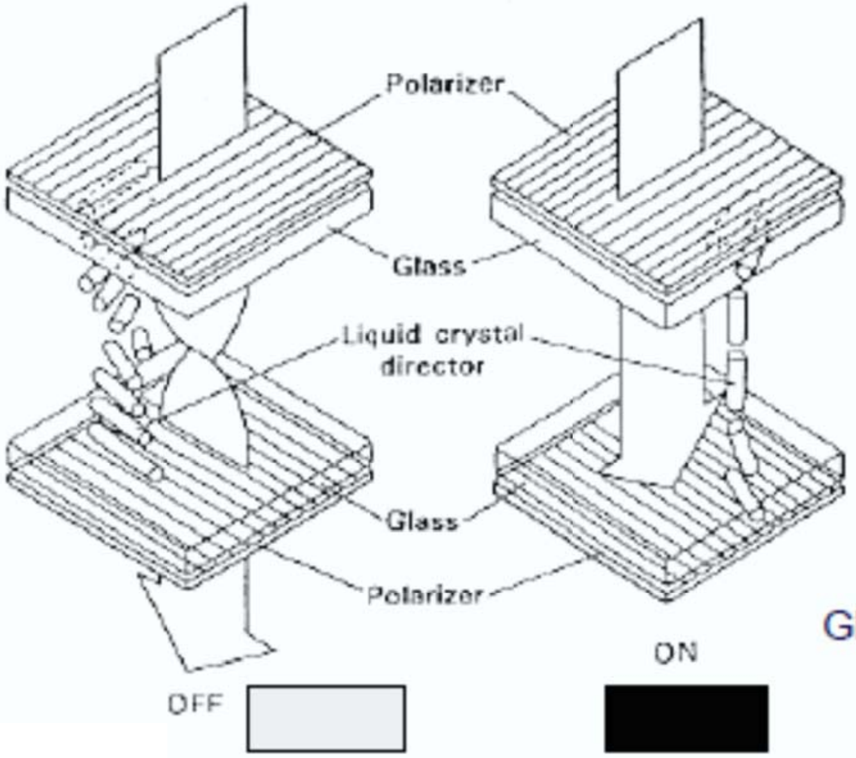
No long range translational order (liquid-like)

Orientationally ordered (tend to point along the director).

N-(4-methoxybenzylidene)-4'-butylaniline (MBBA)

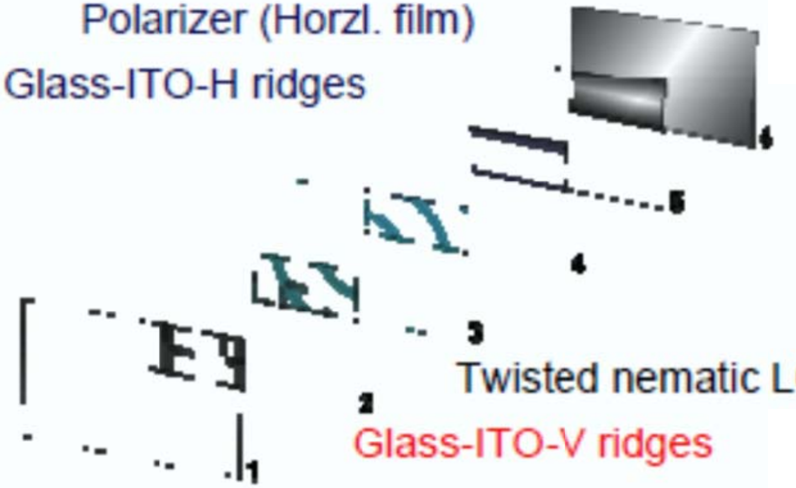


Liquid Crystal display



Fréedericksz transition

Long range orientational order



Polarizer (Horzl. film)

Glass-ITO-H ridges

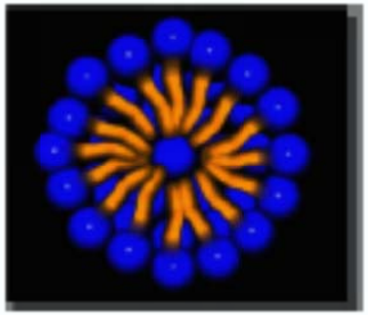
Twisted nematic LC

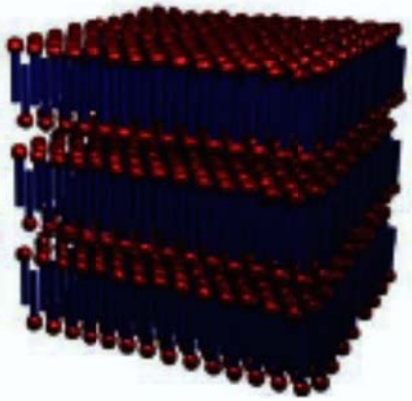
Glass-ITO-V ridges

Polarizer (vertical film)

Lyotropic Phases

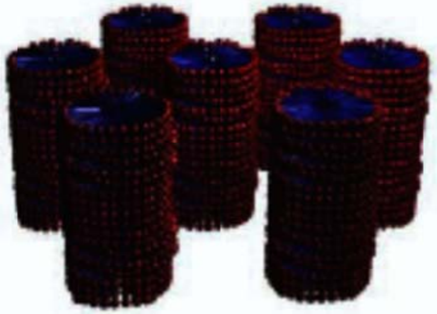
Micelle





Lamellar

1D translational order



Hexagonal phase

2D translational order

Much softer than graphite.

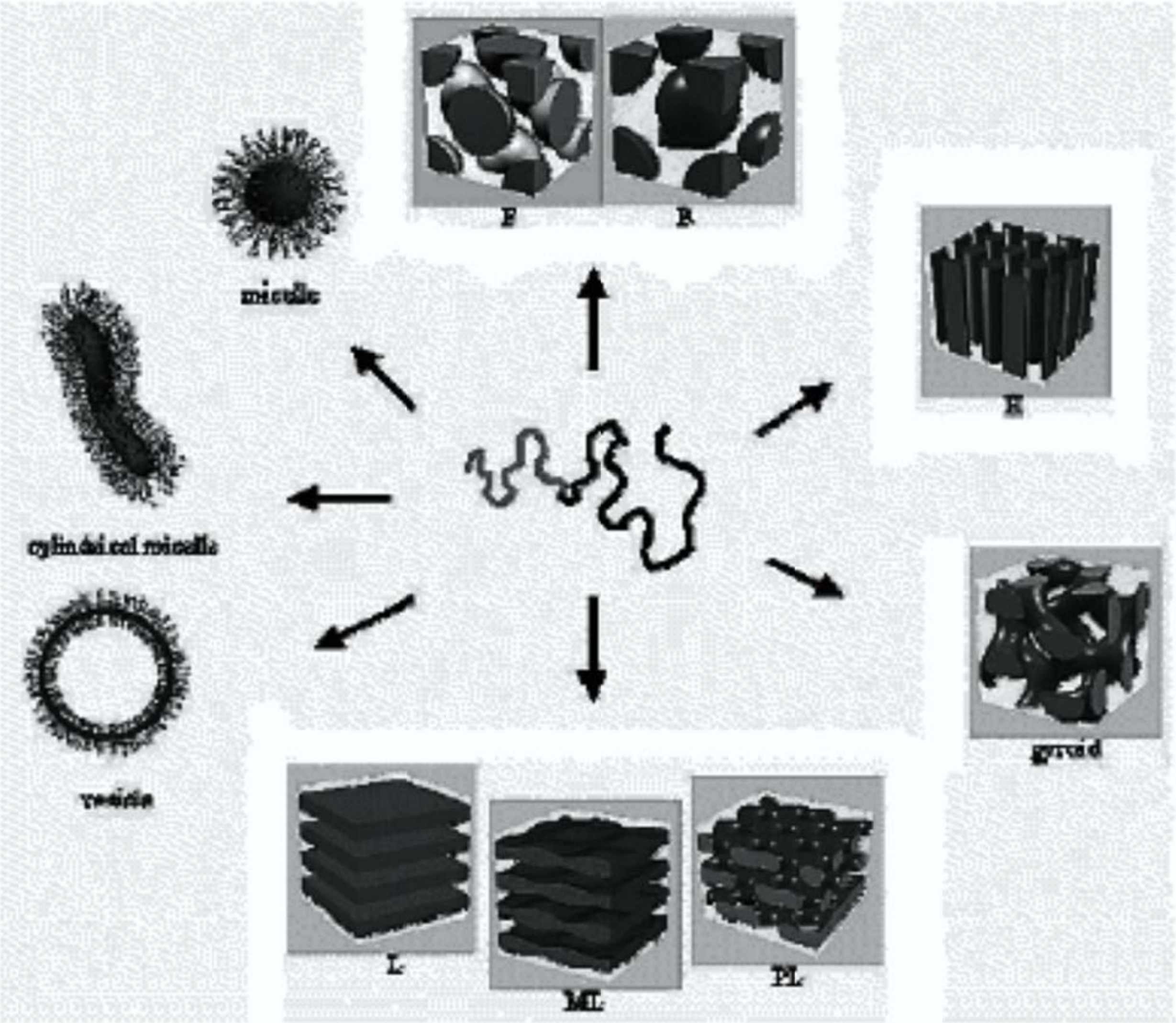
Cubic phase

3D translational order

All built from supramolecular aggregates.

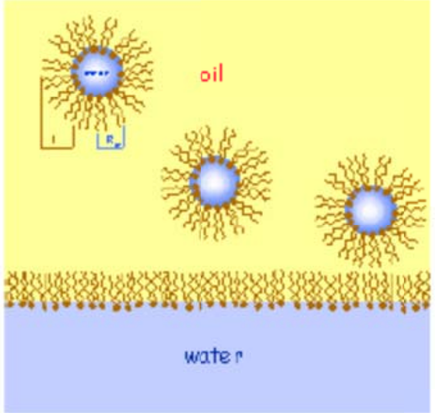
Nanoscale or Mesoscopic Ordering of Soft Matter

Block Copolymer Morphology

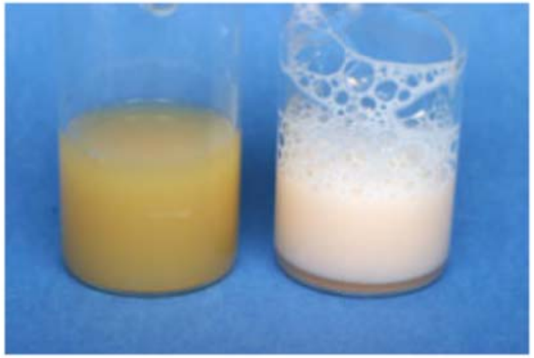


Surfactants

= **Surf**ace **act**ive **agents**; substances that reduce the surface tension between two phases (e.g., water and oil)



Emulsifier in action

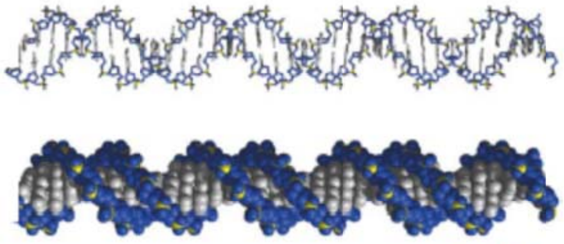


Important role in detergents, inks, ski waxes etc.

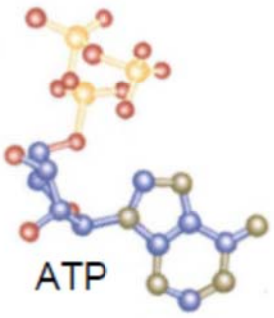
Surfactants are also often featured in self-assembly processes, where energetic and entropic effects determine the structure and dynamics of complex aggregates.

Water has a special place in soft matter physics. In addition to its biological importance, water has many unusual properties and is often regarded as the universal solvent.

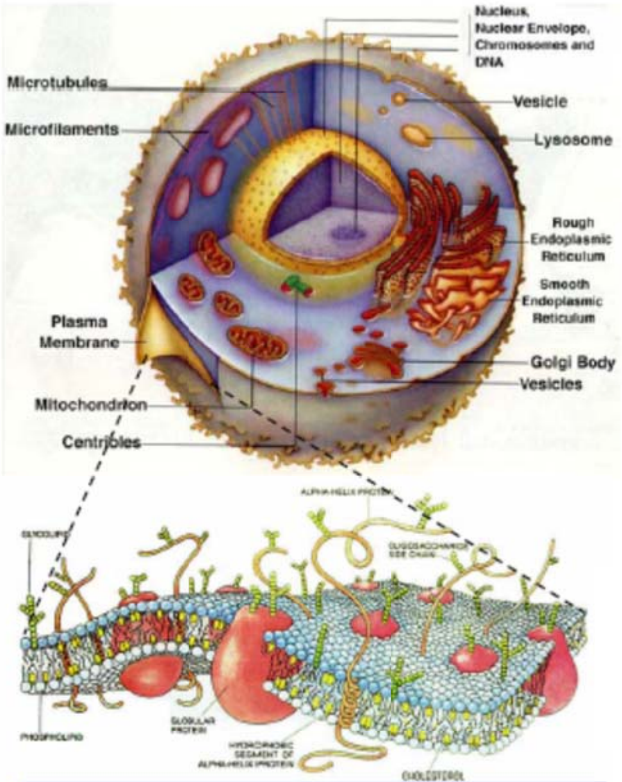
Biological systems



DNA



ATP



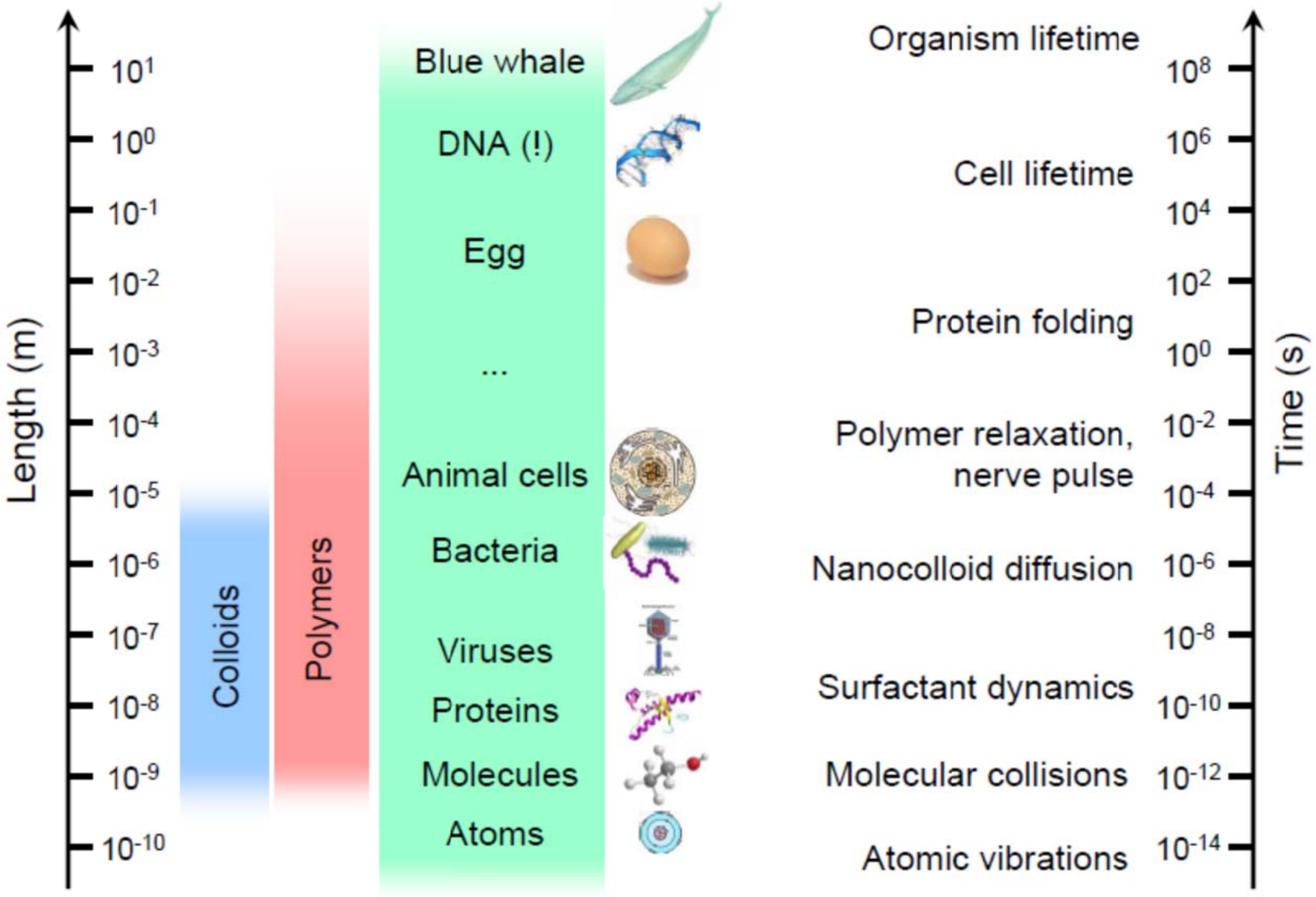
Cell: cannot get much more complex than that.

Common features of living systems

1. Organization – cells as basic building blocks
2. Metabolism – energy in, garbage out
3. Growth – increase in size
4. Adaptation – can change its environment
5. Response to stimuli – often via motion
6. Reproduction

Soft matter is ubiquitous. We are all soft matter.

Examples of length and time scales



Blue whale

DNA (!)

Egg

...

Animal cells

Bacteria

Viruses

Proteins

Molecules

Atoms

Organism lifetime

Cell lifetime

Protein folding

Polymer relaxation,
nerve pulse

Nanocolloid diffusion

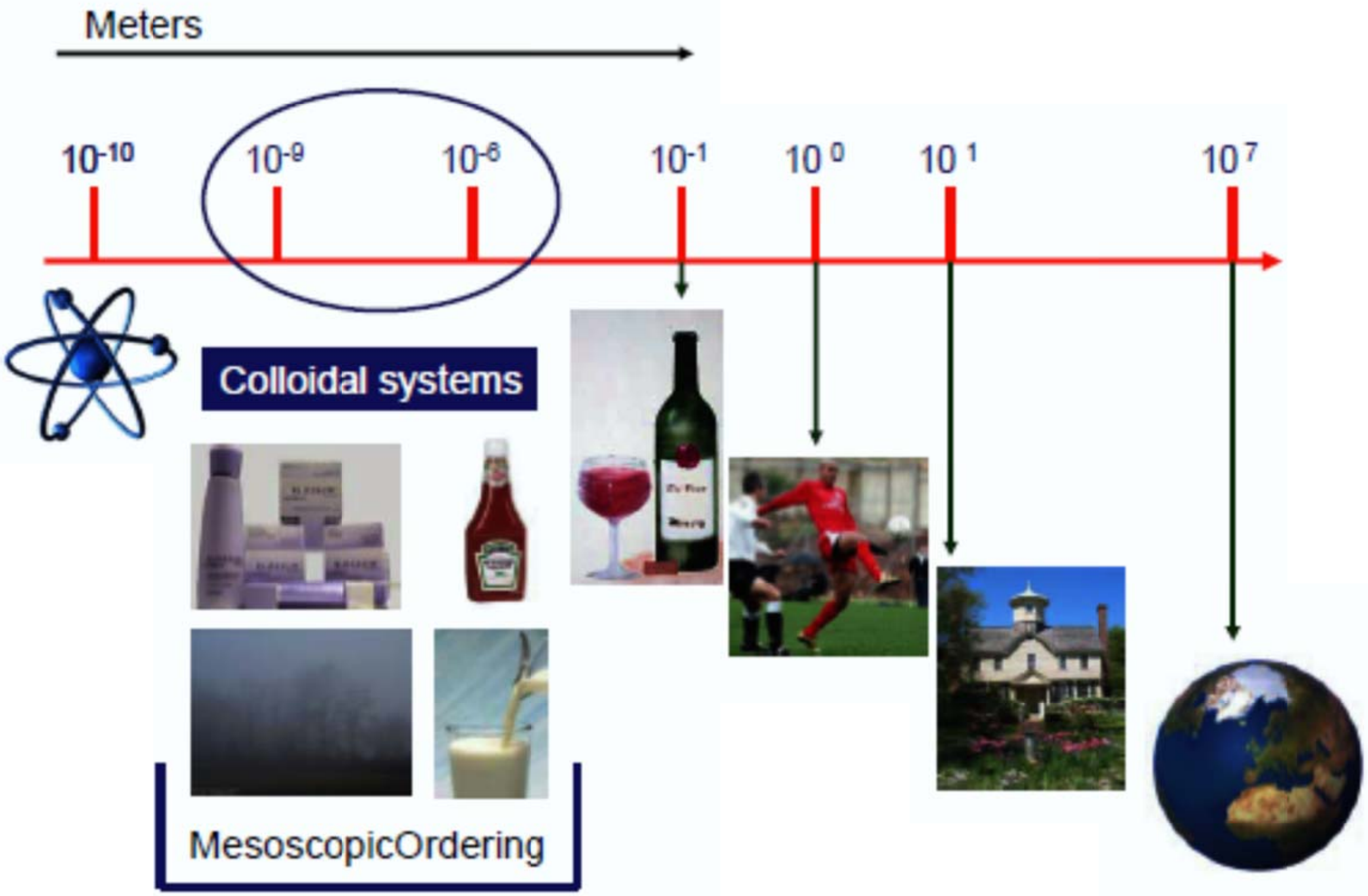
Surfactant dynamics

Molecular collisions

Atomic vibrations

Features of Soft Matter

1. Intermediate length scales: between atomic and macroscopic:



Meters

10^{-10} 10^{-9} 10^{-6} 10^{-1} 10^{0} 10^{1} 10^{7}

Colloidal systems

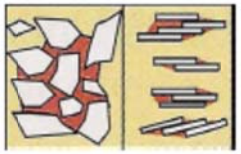
MesoscopicOrdering

Summary

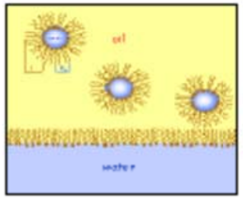
Soft matter

- Is susceptible to small external influences ("large response functions")

- Has a complex microscopic structure, composition and internal dynamics

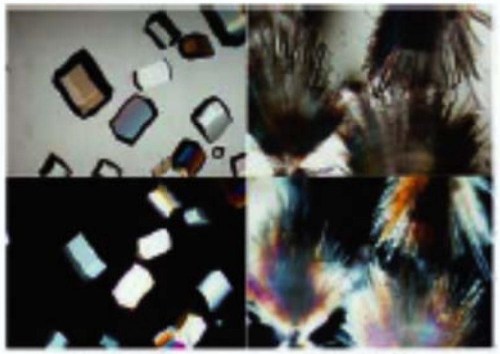


- Means such systems as colloids, polymers, liquid crystals, surfactants, and biological matter



- Exhibits a huge range of different time and length scales

Characterization Techniques for Soft Matter



1. Microscopy

--- *Polarized microscope*
--- *Confocal microscope*
--- *Scanning Electron Microscope (SEM)*
--- *Transmission Electron Microscope (TEM)*
--- *Atomic Force Microscope (AFM)*

2. Scattering methods

--- *Light scattering (LS)*
--- *Small angle X-ray scattering (SAXS)*
--- *Small angle Neutron scattering (SANS)*

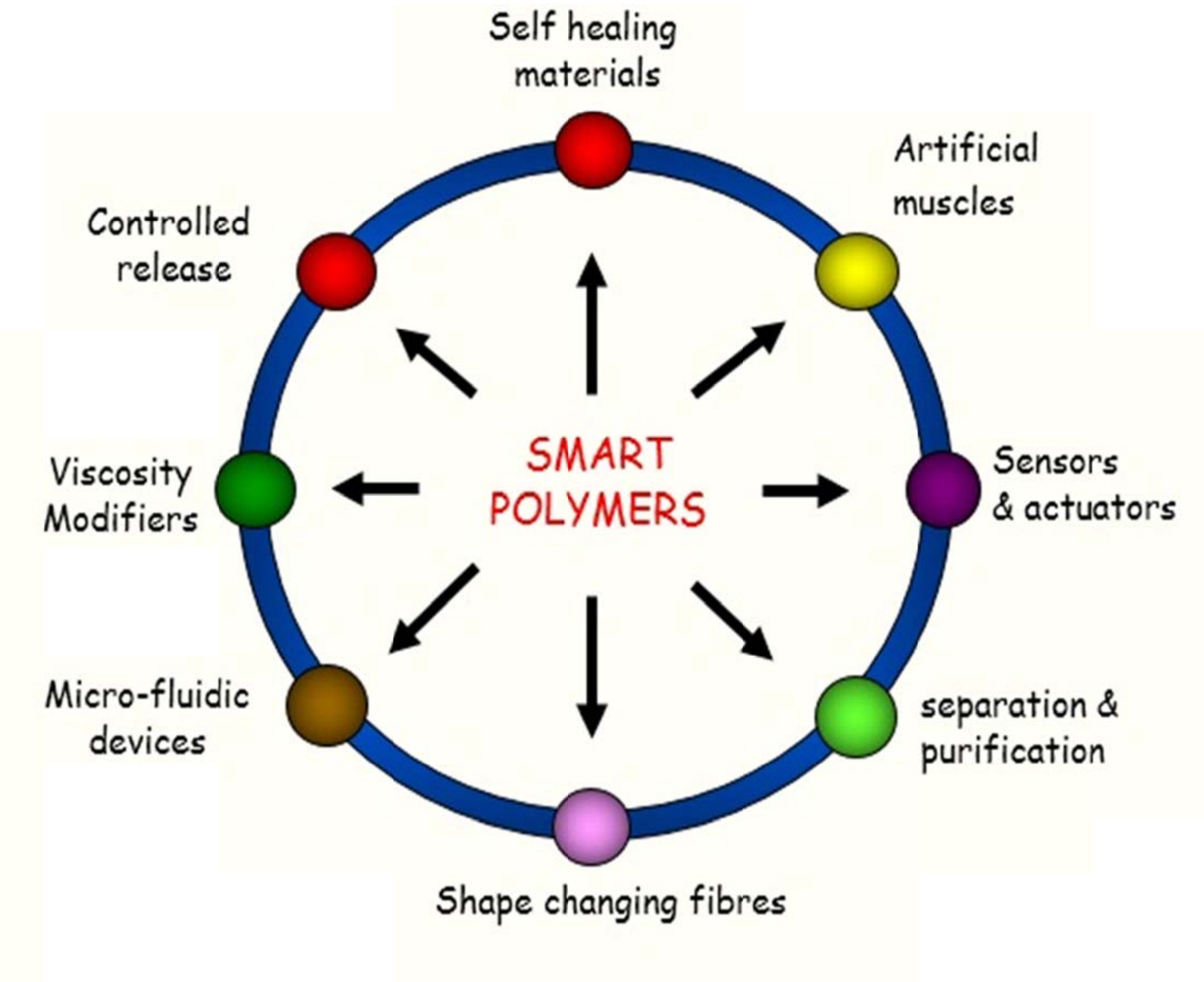
3. Rheology

4. Electrokinetics

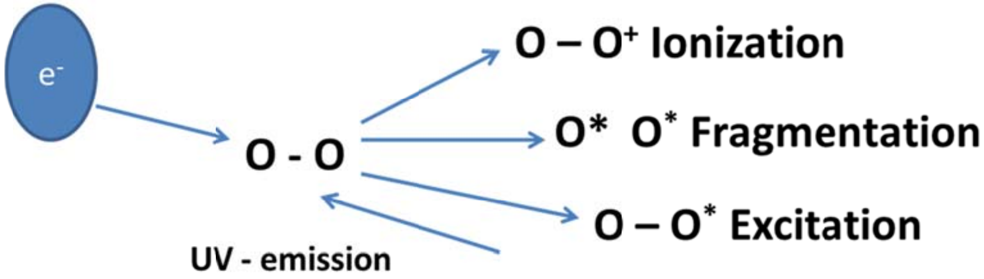
5. Calorimetry & Spectroscopy

--- *DSC, NMR, IR, Raman*

6. Computer Simulations



Polymers and their applications in multi-fields



Elemental process in a plasma

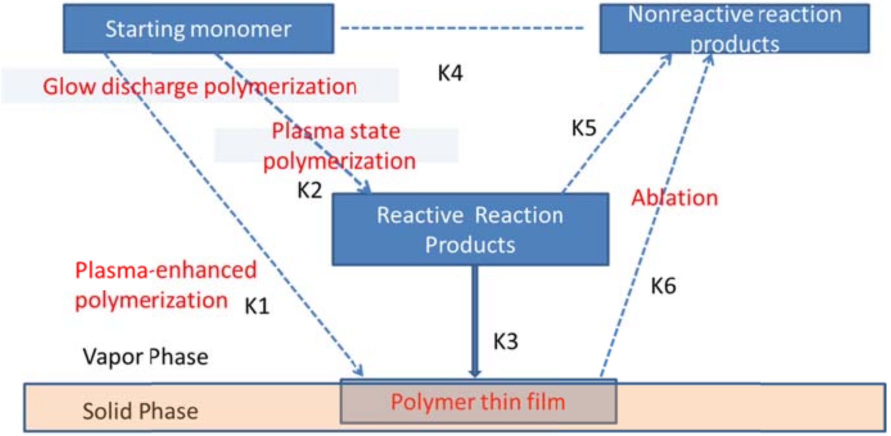


Diagram of plasma polymerization

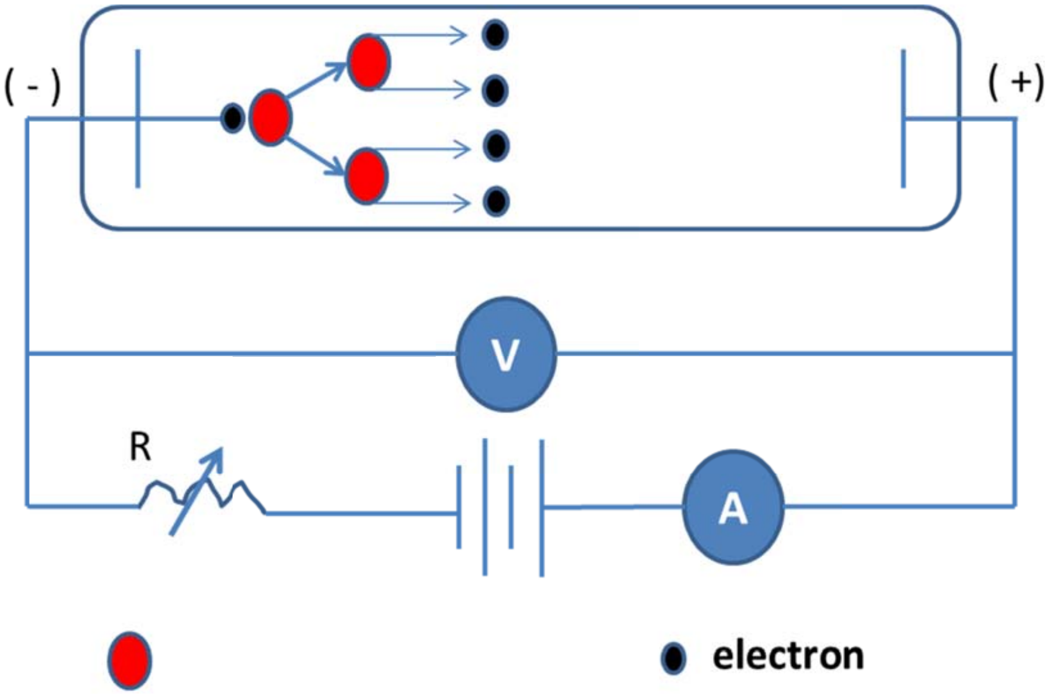
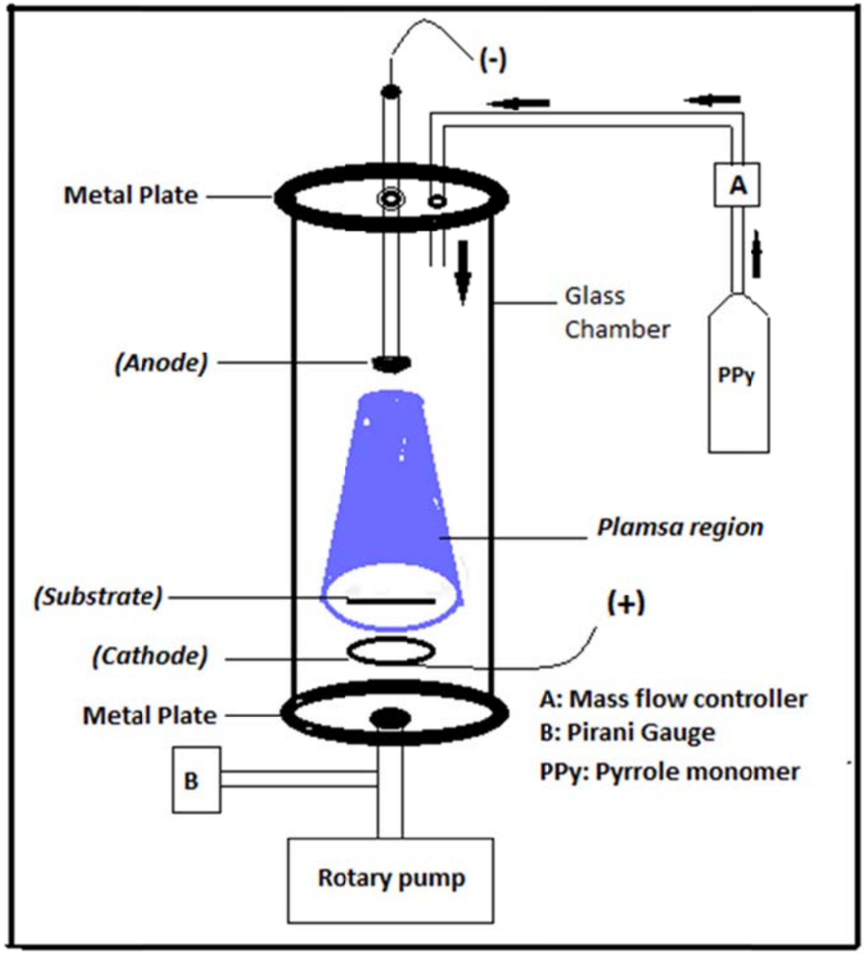
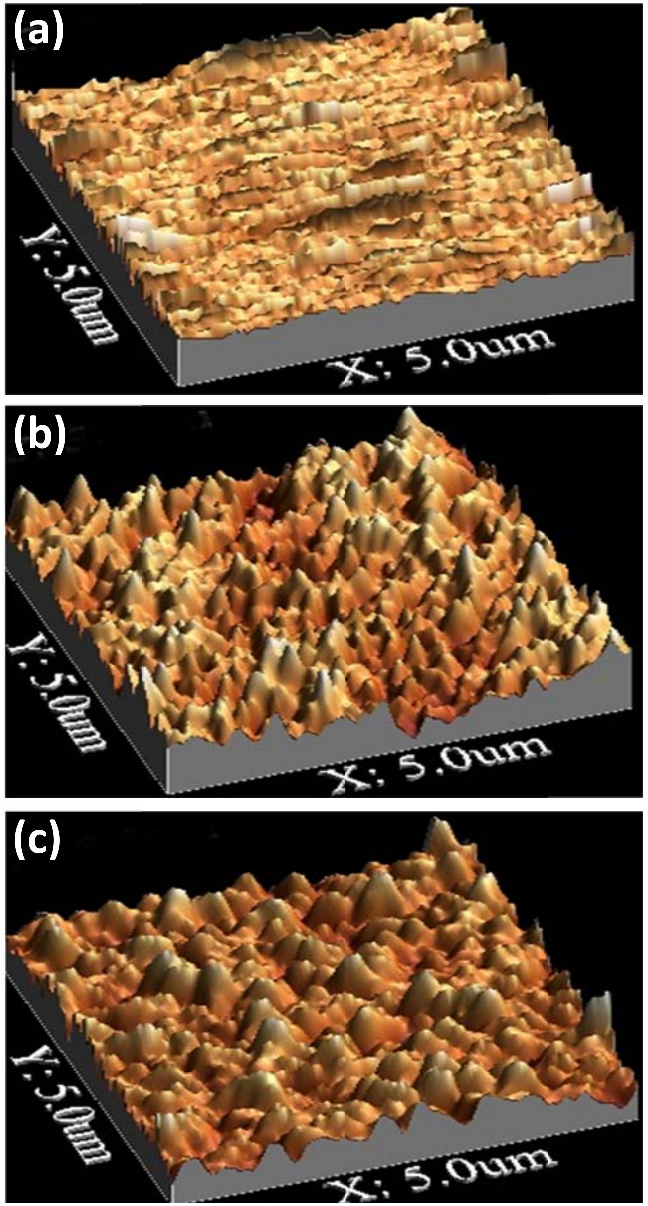


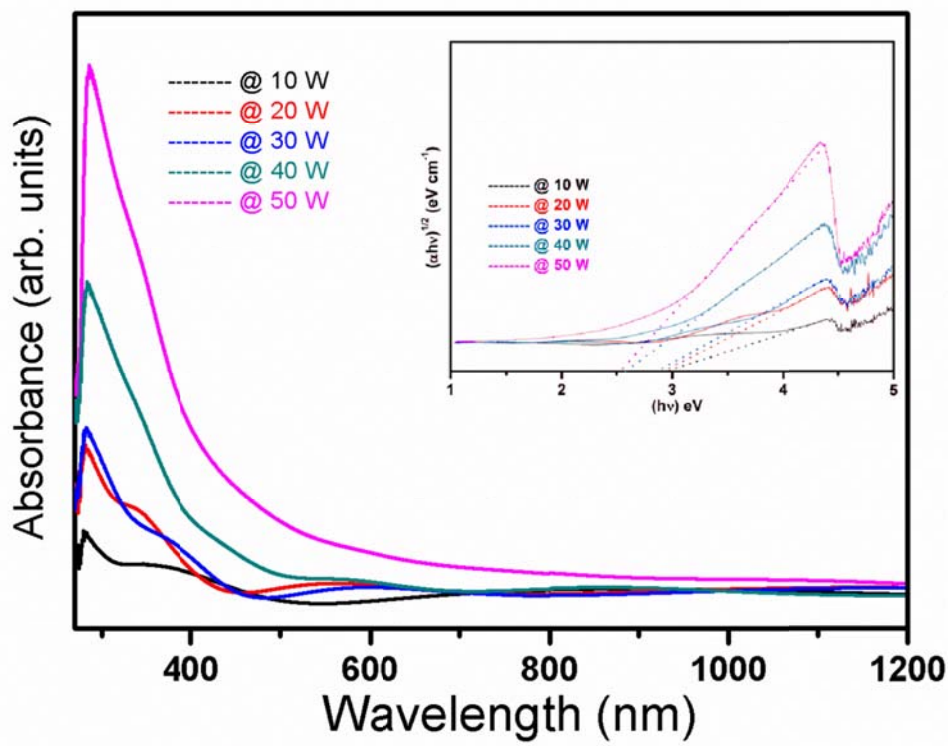
Diagram of a DC Plasma Reactor



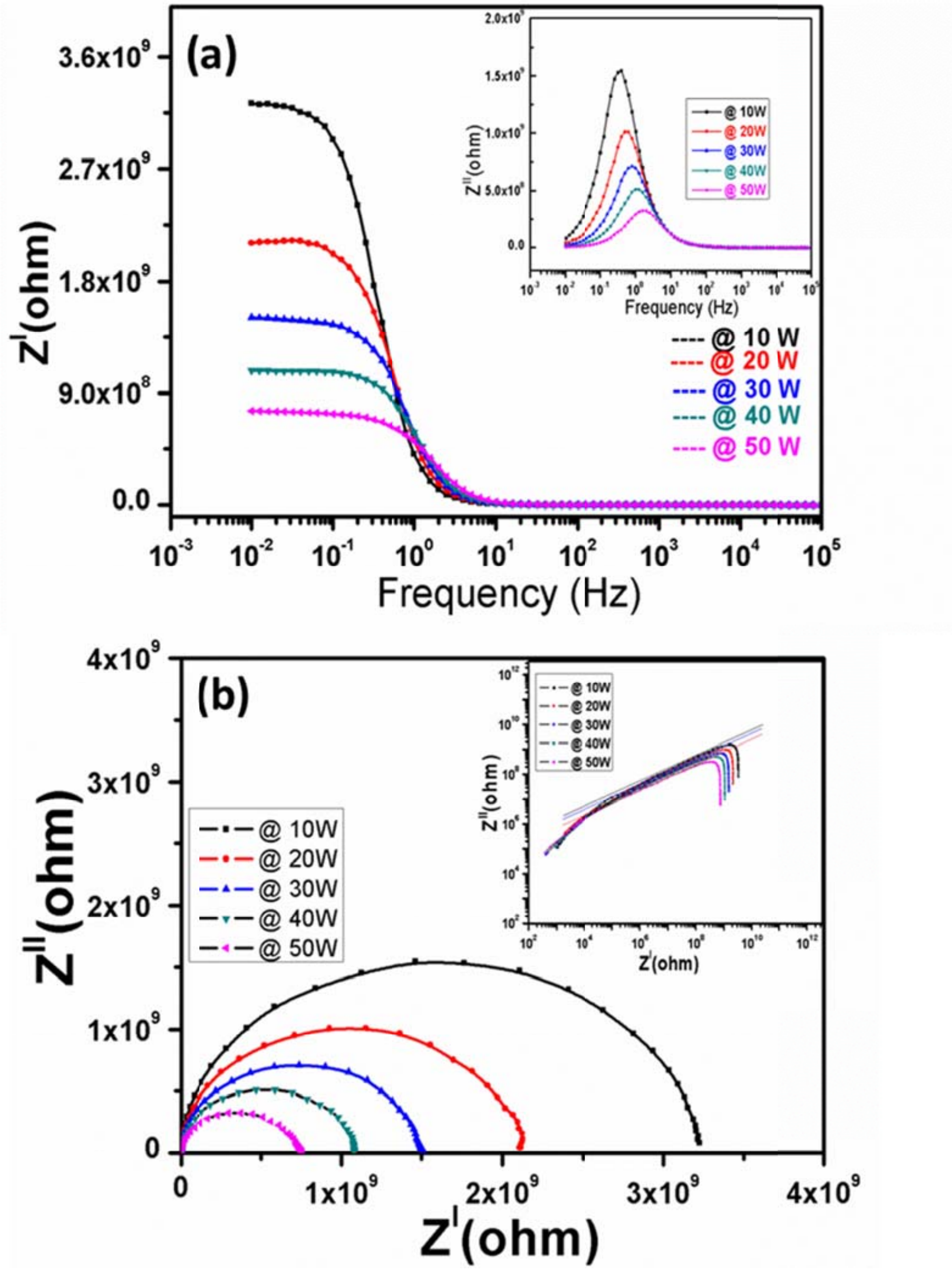
Schematic representation for cold plasma polymerization thin film deposition setup



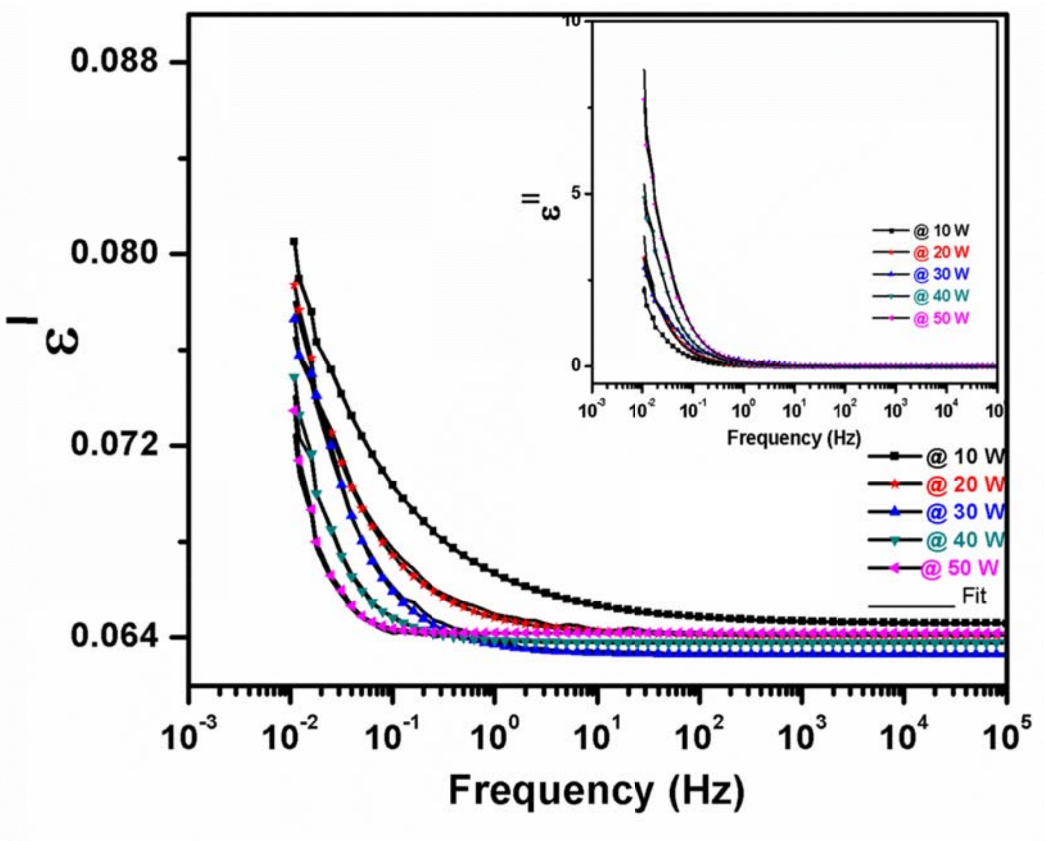
AFM images corresponding to PPy thin films prepared at plasma powers (a) 10 W (b) 30 W and (c) 50 W



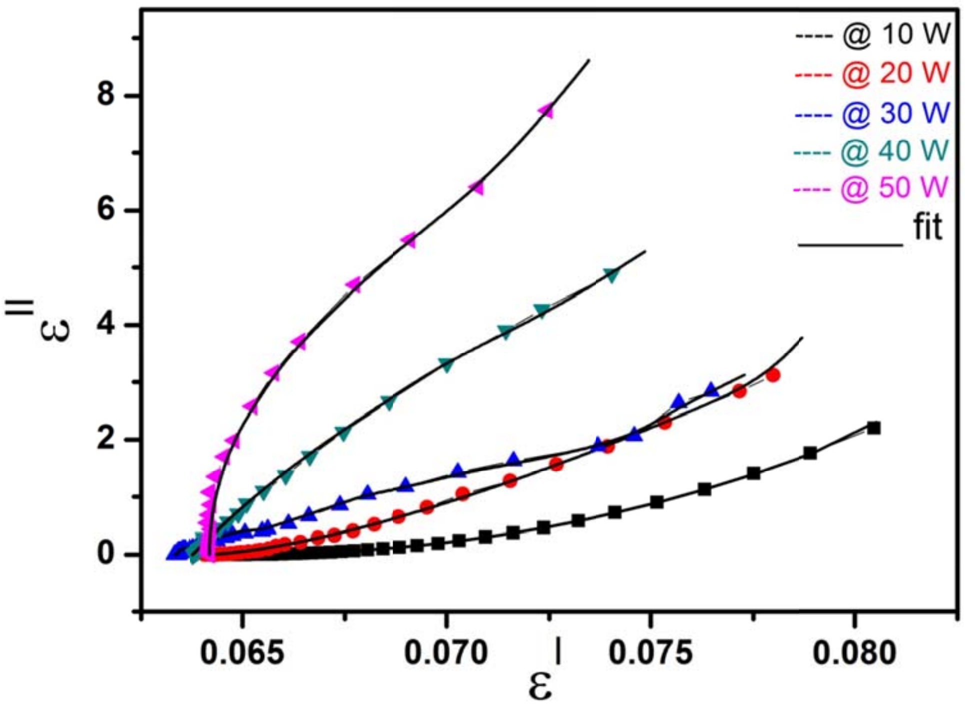
UV – visible absorption spectra for plasma polymerized PPy films at various plasma powers


(a)
3.6x10^9
2.7x10^9
1.8x10^9
9.0x10^8
0.0
Z^I(ohm)
10^-3
10^-2
10^-1
10^0
10^1
10^2
10^3
10^4
10^5
Frequency (Hz)
@ 10 W
@ 20 W
@ 30 W
@ 40 W
@ 50 W
2.0x10^9
1.5x10^9
1.0x10^9
5.0x10^8
0.0
Z^II(ohm)
Frequency (Hz)
@ 10W
@ 20W
@ 30W
@ 40W
@ 50W
(b)
4x10^9
3x10^9
2x10^9
1x10^9
0
Z^II(ohm)
1x10^9
2x10^9
3x10^9
4x10^9
Z^I(ohm)
@ 10W
@ 20W
@ 30W
@ 40W
@ 50W
10^12
10^10
10^8
10^6
10^4
10^2
Z^II(ohm)
10^2
10^4
10^6
10^8
10^10
10^12
Z^I(ohm)
@ 10W
@ 20W
@ 30W
@ 40W
@ 50W

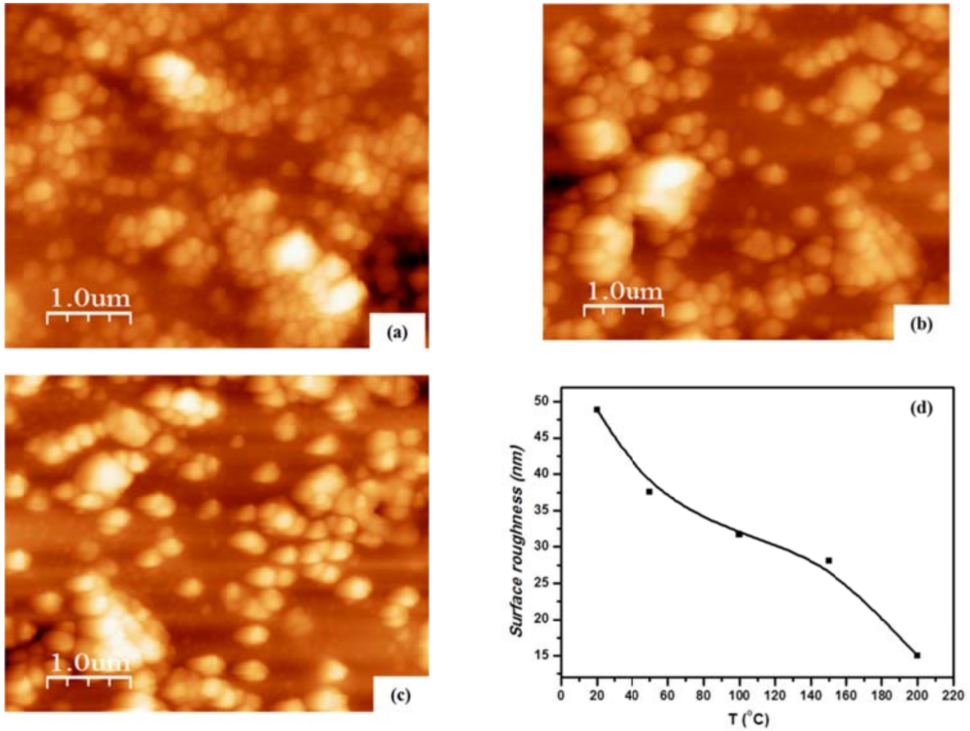
Impedance measurements for PPy thin films as a function of plasma powers (a). The variation real impedances as a function of applied frequency in the range 10 mHz – 100 KHz. (b). Nyquist plots (Z^{II} versus Z^{I}) for grown films at various growth conditions.



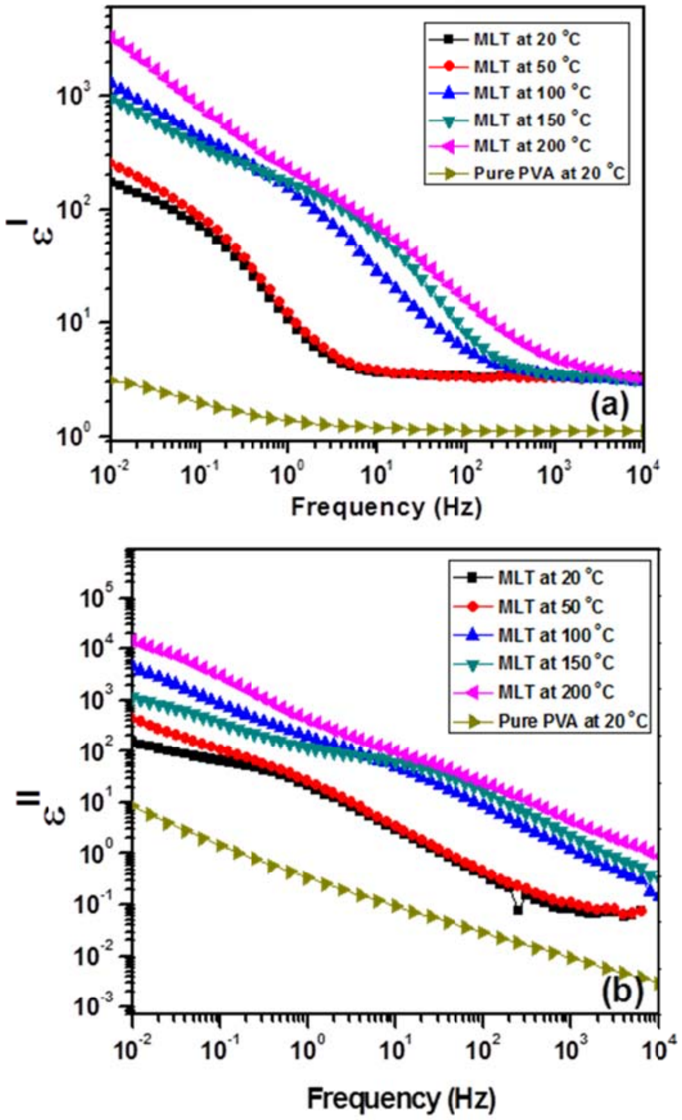
Behavior of estimated dielectric constants of grown films as a function of frequency (solid black line represents the fit).



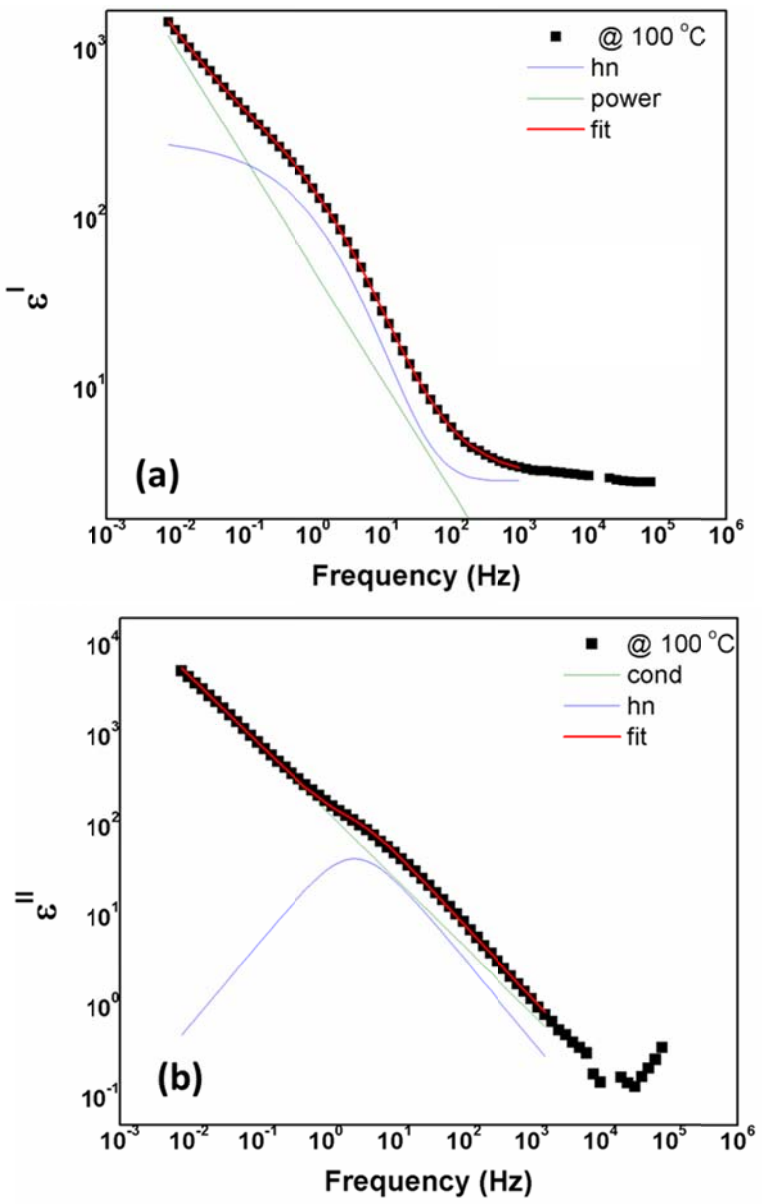
Cole – Cole plots for plasma polymerized PPy films



Atomic force micrographs for 'PVA/AgNPs' thin films various temperatures (a) T = 20 ^{o}C (b) T = 100 ^{o}C (c) T = 200 ^{o}C (d) variation of rms roughness



Plots of the dielectric permittivity vs. log of frequency (log f) as a function of temperatures for 'PVA/AgNPs/PVA' thin films (MLTs).



Fitting results for dielectric spectrum of 'PVA/AgNPs/PVA' thin films (MLTs) at T = 100 °C: (a) real part, (b) imaginary part.