

## Biobased and functional materials

The term ‘functional materials’ covers different material classes ranging from semiconductors over polymers and molecular crystals to nanoparticles with peculiar electrical, magnetic and optical properties.

Bioinspired materials are synthetic materials whose structure, properties or function mimic those of natural materials or living matter.

### Bioinspiration:

nature provides examples of the systems whose exceptional properties and performance might be replicated for all sorts of applications.

our understanding of biological systems is limited, and for this the attempts to create synthetic analogs have been largely unsuccessful.

### Bioderivation:

using an existing biomaterial in concert with an artificial material to create a hybrid (eg. Biologically derived proteins into polymeric assemblies for drug delivery).

### Biomimetics:

seeking sustainable solutions to human challenges by emulating nature’s patterns and strategies. Biological material usually are multifunctional.

It could be argued that all materials are hierarchically structured, since the changes in dimensional scale bring about different mechanisms of deformation and damage.

In biological materials, this hierarchical organization is inherent to the design.

The design of the structure and of the materials are intimately connected in biological systems, whereas in synthetic materials there often is a disciplinary separation.

## Bones

- first level (1.5 nm) sees tropocollagen combining with hydroxyapatite.
- second level, tropocollagen fibrils combine with HA, dispersed between and around the collagen, forming mineralized fibrils.
- third level, the fibrils are oriented into structures depending on the location in the bone.
- fourth level, cortical bone is lamellar-cylindrical and parallel-plate lamellae can be found.
- fifth level, Bouligand structure of lamellae around osteons and struts in trabeculae.
- sixth level, osteon with a central vascular channel and cancellous bone with porosity.

Stiffness, strength and toughness of a structure depend on the level in the hierarchy and on the total number of levels in the hierarchy.

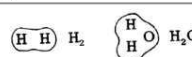
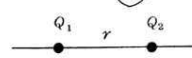
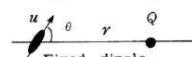
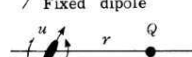
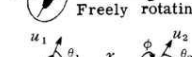
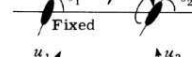
## Fundamental forces

Strong interactions are nuclear interactions that hold protons and neutrons in the nucleus

Weak interactions are nuclear interactions responsible for nuclear decay, electron emission etc.

Electromagnetic interactions bind electrons to nucleus, binds atoms to molecules etc.

Gravitation is negligible in molecular dimensions, important for mesoscopic to macroscopic scale.

type of interaction		interaction energy $w(r)$
Covalent, metallic		Complicated, short range
Charge-charge		$Q_1 Q_2 / 4\pi\epsilon_0 r$ (Coulomb energy)
Charge-dipole		$-Qu \cos \theta / 4\pi\epsilon_0 r^2$
		$-Q^2 u^2 / 6(4\pi\epsilon_0)^2 k T r^4$
Dipole-dipole		$-u_1 u_2 [2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos \phi] / 4\pi\epsilon_0 r^3$
		$-u_1^2 u_2^2 / 3(4\pi\epsilon_0)^2 k T r^6$ (Keesom energy)

The strength of the interaction can be calculated as  $W = X/r^n$

The interaction parameter X determines the strength of the interaction.

The exponent in the distance variable r determines the range of interaction (short-long range).

The larger the exponent n the shorter the range of interaction.

Interactions: covalent, metallic, ionic.

Charge-charge, charge-dipole, dipole-dipole

Charge-nonpolar, nonpolar-nonpolar, hydrogen bond.

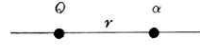
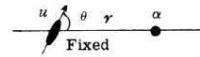
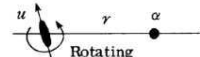
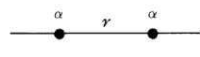
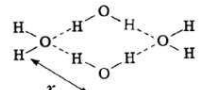
The 'pair potential' describes complex intermolecular interactions:  $V(r) = -\frac{A}{r^m} + \frac{B}{r^n}$  (Mie)

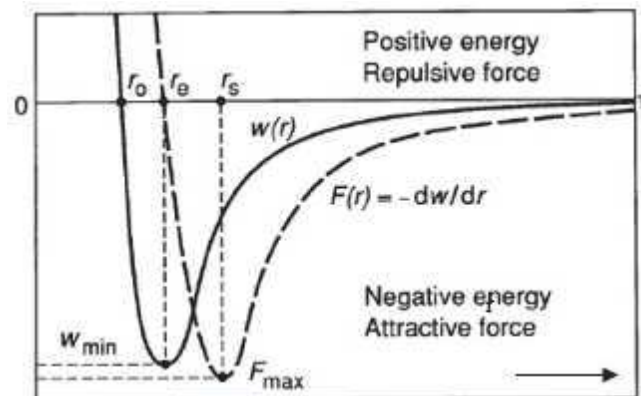
Van der Waals describes the behavior of real gases:

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

Leonard Jones equation for computational simplification:  $V(r) = \frac{A}{r^{12}} - \frac{B}{r^6}$

Thee bond energy per atom increases linearly with the number of bonds per atom.

type of interaction		interaction energy $w(r)$
Charge-non-polar		$-Q^2\alpha / 2(4\pi\epsilon_0)^2 r^4$
Dipole-non-dipolar		$-u^2\alpha(1 + 3\cos^2\theta) / 2(4\pi\epsilon_0)^2 r^6$
		$-u^2\alpha / (4\pi\epsilon_0)^2 r^6$ (Debye energy)
Two non-polar molecules		$\frac{3}{4} \frac{h\nu^2}{(4\pi\epsilon_0)^2 r^6}$ (London dispersion energy)
Hydrogen bond		Complicated, short range, energy roughly proportional to $-1/r^2$



The liquid interface changes its shape to reduce the total free energy of the system.

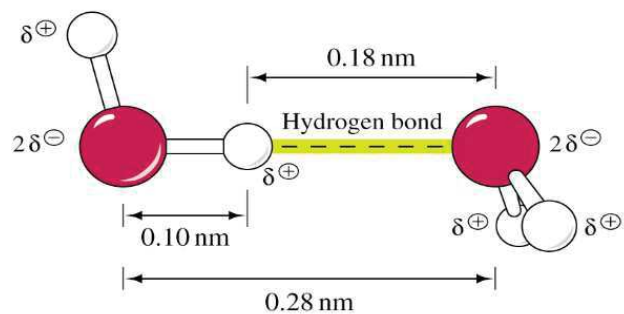
Water plays a crucial role in materials interaction with the environment and in biochemistry.

Protein, polysaccharides, nucleic acids, membranes assume their characteristic shapes in response to water.

Water shows polar bonds at 104.5°, creating a permanent dipole. Water molecules attract each other due to their polarity.

A hydrogen bond is formed when a H+ attracts an O- from a second water molecule.

A water molecule can form up to 4 hydrogen bonds, 2 for O, 1 for each H.



Molecules can be divided into polar and nonpolar. Materials can be divided into hydrophilic and hydrophobic.

Hydrophilic substances readily dissolve in H2O. water molecules align around other polar molecules.

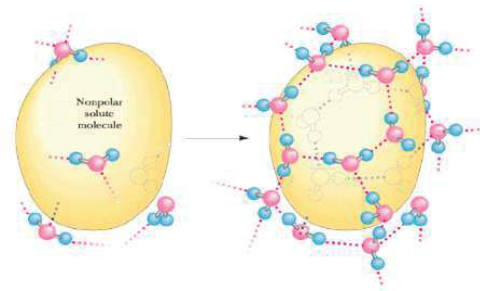
A molecule surrounded by solvent is said to be solvated. When the solvent is water, it is hydrated. The larger the portion of nonpolar groups, the less soluble the molecule is in water.

Glucose has five hydroxyl groups and a ring oxygen which can form hydrogen bonds: it is therefore very soluble in water.

Nonpolar solutes do not form hydrogen bonds with water and are difficult to solubilize.

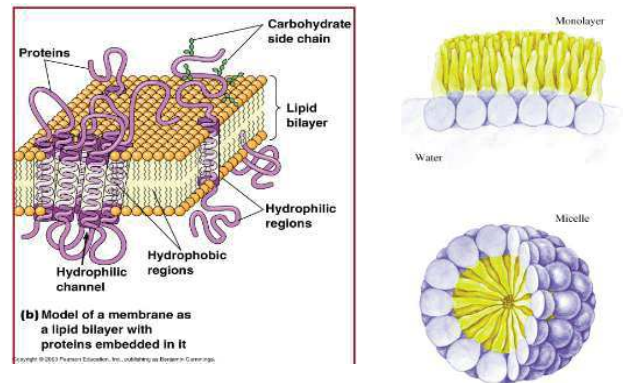
Dissolving such compounds requires reorganization of water molecules which surround them. This results in cage-like structures called CLATHRATES.

Hydrophobic interaction rises when two nonpolar molecules come in contact. By associating together, part of the hydration shell is liberated and the attraction results in an increase of entropy.



Amphiphilic molecules have hydrophobic chains and ionic or polar ends.

- At low concentrations, monolayers can form on the surface.
- at higher concentrations, surfactants can form micelles.



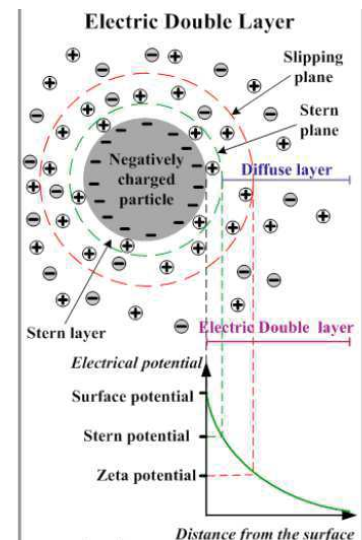
Cell membranes are barriers controlling material exchange between internal and extracellular environments. They are hydrophobic permeability barriers consisting of phospholipids, glycolipids and proteins. They form a lipid bilayer with proteins embedded in it.

Membranes are selectively permeable: molecules with MW < 100 D are free to diffuse.

Lyophobic (lyo=solvent) colloids are formed by encounters between particles as a result of Brownian motion. The stability of a suspension is determined by the interaction between particles during these encounters.

Attraction occurs from Van der Waals forces, repulsion occurs between similar charges in double electrical layers. Electrostatic repulsion results from the interpenetration of the diffuse part of the DEL around each particle.

DLVO model: at the secondary minimum the system flocculates, but the aggregates are weak: this may imply reversible flocculation. The height of the energy barrier indicates how stable the system is.



Electrostatic stabilization is highly sensitive to surface charge and salt concentration.

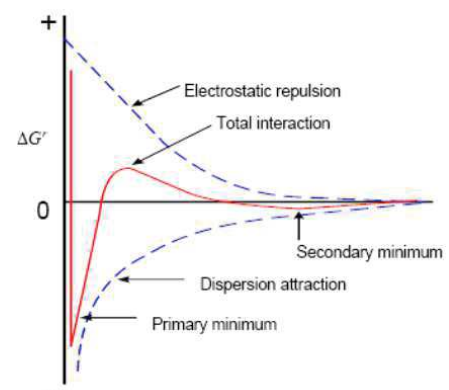
Primary minimum: irreversible flocculation.

Secondary minimum: reversible flocculation, sol-gel formation.

If the potential energy maximum is large compared to the thermal energy  $kT$  of the particles, the system should be stable, otherwise it will coagulate.

MILK: colloidal system with H<sub>2</sub>O, fat globules, casein micelles, whey proteins, lactose.

Coagulation is done to encourage casein micelles to stick together. Rennet, acid and heat drive this process.



## Self assembly

Spontaneous organization of individual components into an ordered structure.

It involves elements from molecular scale to galaxies.

There are two main kinds of self assembly:

- static self-assembly: involves systems that are at equilibrium and do not dissipate energy. Formation of an ordered structure may require energy, but once it is formed, it is stable.
- dynamic self-assembly: dissipation of energy is involved in the formation of structures between components. Biological cells and patterns formed by competition between chemical reactions and diffusion are examples.

Templated self-assembly: interaction between components and regular features in their environment determine the structure that forms.

Biological self-assembly regards biological tissues.

Self-assembly reflects information coded in individual components; these characteristics determine the interaction among them.

The components must be able to move with respect to one another.

Molecular self-assembly involves non-covalent weak interactions. Covalent bonds involve much higher energies which would break the order of the molecules.

Self-assembly usually takes place in fluid phases or smooth surfaces.

The use of boundaries or templates can reduce defects and control structures.

Self-assembly requires that the components either equilibrate between aggregate and non-aggregate state, or bound/unbound state.

Living cells self-assemble, so understanding life requires understanding of self-assembly.

Nanostructured materials and nanoparticles are often based on self-assembly.

Self-assembly allows to create complex 3D structures at nanometric scale. This would be impossible by direct assembly ie. moving atoms one by one.

One can incorporate biological systems (eg. Lipid bilayer + toxin)

It is very accurate because the structure obtained has the lowest free energy.

Self-assembly is more efficient than direct assembly.

Biological molecules, especially proteins, cannot be produced by direct assembly because they feature four structures, not only the configuration of the atoms.

Crystallization at any scale can be tailored by self assembly.

Nanoparticles and nanocrystals are preferably produced by self-assembly rather than direct assembly.

Mesoscopic metal-polymer amphiphiles show hydrophilic Au + hydrophobic polypyrrol (PPy)

Surfactants are defined by the ratio between hydrophobic and hydrophilic parts. The ratio is a technological number used by industries that produce surfactants: it influences the shape of the micelles.

Drug delivery of hydrophobic drugs can be achieved by encapsulating the molecules in micelles that are hydrophilic in the outermost part. Endocytosis delivers the micelle inside cells, and pH change inside the cell can induce changes in the micelle and lead to drug release. The leakiness of tumor blood vessels (EPR, enhanced permeation and retention) allows the colloidal particles to preferentially accumulate in the tumor, reducing exposure to organs.

Self-assembled monolayers are particularly important because they are predictable, durable and the surface concentration is well-assessed. Entanglement in normal systems makes materials unpredictable.

Alkanethiols assemble monolayers on the surface of metal parts, forming strong chemical bonds with the substrate.

Different functional groups can be bond to the head of the molecule.

The distance between thiols is about 4.6 Å, maximizing Van der Waals attraction when inclined (30°).

The longer the chain, the better the packing, as Van del Waals forces interact between the chains.

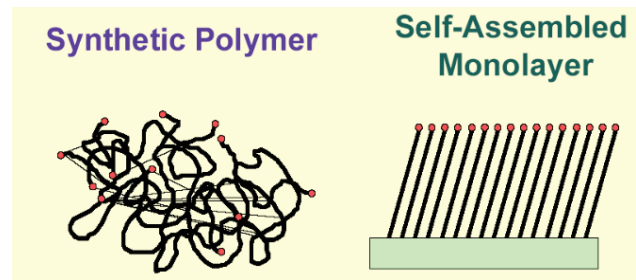
Different alkanethiols can be mixed to form a monolayer with different properties or functional groups.

The substrate should be very flat: this is obtained by plasma sputtering.

The substrate should also be very clean, and the environment should be controlled.

The wettability of a surface can be modulated by adding more or less CH<sub>3</sub> groups.

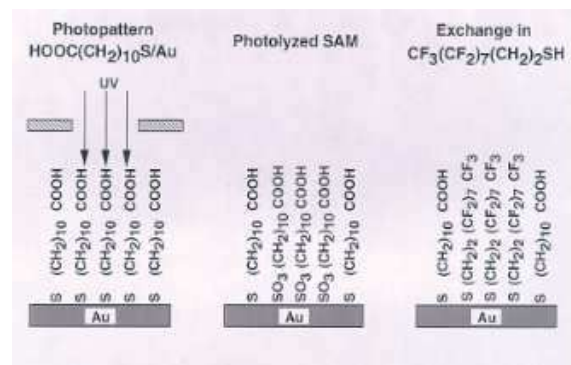
By using molecules with different end groups, one can change the contact angle of the surface making it more or less wettable. This is a possible solution to make hydrophobic metals.



UV photooxidation can be carried out to substitute some regions of the SAM with different molecules.

By adding a mask and impinging the surface with UV radiation, thiols are oxidized and detach from the surface, so the molecules can be substituted.

SAM are employed in microcontact printing and micromachines.



## Gecko effect

Geckos are able to climb walls, attaching and detaching from the surface. This means that their feet have a very strong and reversible adhesive.

Foot hair have setae with micrometric and nanometric structure.

Each foot has five toes, each toe has about 20 rows of setal arrays with 200000 setae per toe.

Each seta terminates with about 100 spatulae.

Adhesion is probably due to capillary forces and Van der Waals forces.

Features of gecko's feet:

- anisotropic: gecko's toes can switch their direction for easy attachment and detachment
- low normal detaching force
- high compatibility to wet/dry conditions, smooth/rough surfaces
- self-cleaning and anti-collapse systems

On nanometric scale, both capillary forces and Van der Waals forces play an important role.

Single hair produce a very low force, but the whole system permits a very strong adhesion (10 N/100 mm<sup>2</sup>).

Forces can be calculated with a dual-axis piezoresistive AFM cantilever.

Atomic Force Microscopy works with a tip (10 nm) which touches the ample and the cantilever bends. From the bending of the cantilever, one can calculate the force.

While some insects attach because they have some reversible glue in their feet, geckos use pure physical adhesion.

Gecko-foot mimicking adhesives must meet specific structural requirements:

- small fibril radius: adhesion force is inversely proportional to the fibril radius (contact splitting theory)
- high aspect ratio
- slanted structures: directional angle on nanostructured fibers yields anisotropic, reversible dry adhesive
- fibrils with hierarchical structure.

The production involves polymer molding: heating the polymer, pressing the mold and remove the mold. Cold removal yields a perfect replica, whereas hot mold can be used to stretch the pillars. With thermal annealing, the leaning angle can be tailored by heating up at different temperatures and times. Dual scale can be achieved by double curing with two different molds (micro- and nanoscale).

Self-assembled monolayers do not work because the molecules are very compact, so even if they have a leaning angle, they behave as a single structure at molecular level. Micrometric scale interaction is required.

### Breath figures

It is a self-assembly phenomenon observed when casting a polymer solution and letting the solvent evaporate.

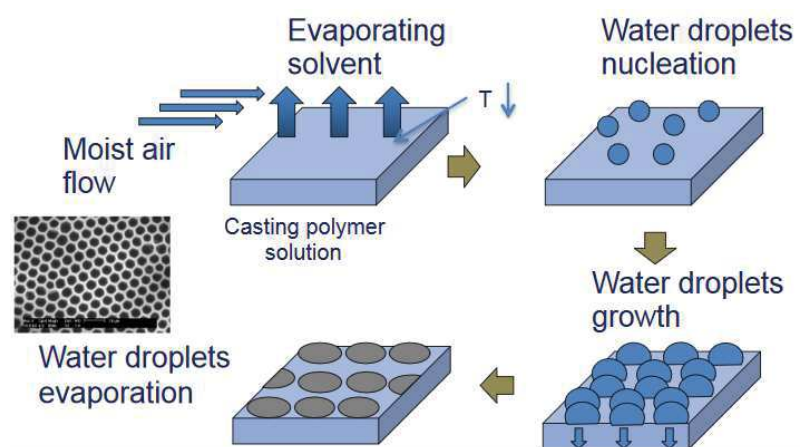
The solvent should be hydrophobic, non-mixable and fast evaporating.

Evaporation leads to a temperature drop. Water droplets are able to nucleate, grow and then evaporate, producing pores in the solidified structure.

Pore size can range from a few hundred nanometers to micrometers

depending on experimental conditions: relative humidity, flow rate of moist air, temperature, polymer concentration, surface tension solvent-water.

Eg. PDLLA + DCM (low surface tension), CHL (low wettability), EA (H<sub>2</sub>O spreads on surface).



High surface energy materials interact with dirt to decrease surface energy.

Glass cleaning involves detergents which are not rinsed because they form a layer decreasing surface energy.

-A monolayer maintains the escape angle, so it does not distort light.

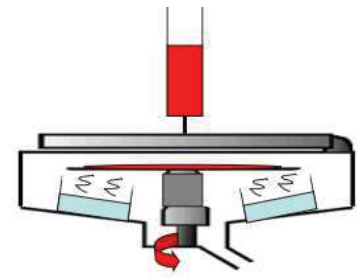
-Detergent gets stuck on the glass and prevents dirt to get stuck.

-Wax layer on the surface of the car to protect and decrease surface tension.

Two production methods:

- humid air flow chamber
- spin casting, to obtain lower thickness and pore diameter.

Spin casting



Breath figures can be used as protein traps: fibrinogen (hemostasis) + fibronectin (cell adhesion) are stuck inside the pores to enhance the biological response to the material.

Fluorescent agents can be used for quality control, detecting the depth at which the agents arrived.

Ter-butyl acrylate + EGDMA + photoinitiator systems can be crosslinked by UV radiation.

Mesoporous surfaces can be produced for biomedical devices: bones.

Chemical and morphological interactions can be tailored, allowing the release of molecules and ions, and mimicking the bone structure.

Cells are approximately 10 micrometers: nanometer-thick pores allow the adhesion of cells, but micrometer-thick pores permit also orientation and mobility of the cells, replicating the structure of the bone.

### Superhydrophobic surface

Surface tension of liquids involve attractive interaction between molecules in the condensed phases.

For liquids, surface tension is the same as the surface free energy: it keeps molecules together.

Two definitions, from the force and energy point of view.

- the force necessary to increase the surface area:  $\gamma = \frac{1}{2L} \left[ \frac{N}{m} \right]$
- energy required to let the fluid spread:  $W = F\delta x \rightarrow \gamma = \frac{F}{2L} = \frac{W}{\Delta A} \left[ \frac{J}{m^2} \right]$

Liquids with low surface tension tend to spread on a surface.

Increasing surface tension, the liquid tends to aggregate.



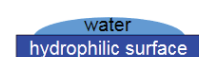
Solid surfaces have well defined free energy; the surface tension is experimentally impossible to calculate.

-hydrophobic materials: polyolefins, PTFE, oily surfaces

-hydrophilic materials: glass, rust

-superhydrophobic surfaces: hydrophobic material with nanoscale roughness.

The classification depends on the contact angle.

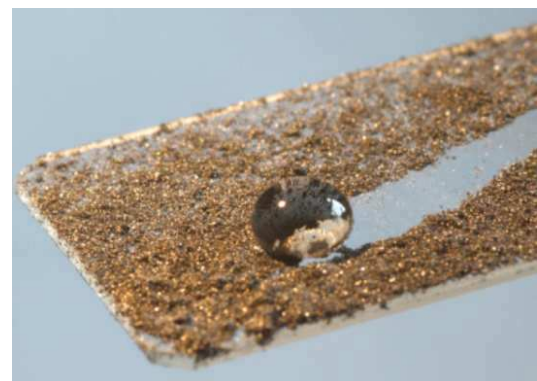


Lotus effect: water drops do not slide on the surface; they roll and clean the surface as they trap the dirt particles.

Lotus leaves show a double roughening on micro- and nanoscale on a hydrophobic surface, yielding superhydrophobicity.

With micropores in a hydrophobic material, water cannot wet the pore as the contact angles of two adjacent pillars intercept. The system becomes much more efficient as it has a double structure with nanorods on the micropillars.

Lotus leaves have micropillars decorated with wax nanorods.



## Polymer brush

Polymers can be grafted onto a silicon wafer with -OH groups on the surface to add functionalities. PS-PVP mixtures are pH-responsive: in acidic medium, PVP is swollen (hydrophilic) and PS is collapsed (hydrophobic). The wettability of the structure changes with PVP content.

PS-PVP mixtures are also solvent-responsive:

- in toluene (non polar), PS is swollen, PVP collapses: the contact angle of the surface is that of PS;
- in methanol, PS collapses and PVP is swollen: the contact angle of the surface is that of PVP.

PNIPAM is the most common temperature-responsive polymer. It shows a lower critical switch temperature, above which it is hydrophobic and below which it is hydrophilic.

Growing cells on PNIPAM-grafted Petri dish above LCST makes cells adhere to the surface. Cells can be detached by decreasing temperature below LCST.

Layered structures hardly allow gas permeation, so cell survival is difficult over 3-4 cell layers.

If no vascularization occurs, there is no transfer of nutrients or oxygen.

Cardiomyocyte patches can be used to bypass ischemic regions in heart diseases.

Prevascularized tissues have problems of attaching the grown vessels to the ones already present in the biological tissue.

Fog occurs as water vapor condenses onto the surface due to temporary changes in temperature, humidity, convection.

Water droplets size and contact angle influence fog deposition.

Fog yields light scattering, so that transmittance decreases up to 50%.

Very highly hydrophilic surfaces will let all the light to be transmitted, but the surface gets dirty.

Human eyes have a tear film to protect the eye but it never gets foggy.

The tear film is less than 10  $\mu\text{m}$  thick, with an outer layer of lipids (surfactants) to keep it together and an inner layer of proteins to let it adhere on the substrate.

Technological solutions for foggy surfaces are ventilation and surface modification.

Surface modification can be achieved by different solutions:

- plasma treatment to decrease surface energy, but molecular mobility lets the oxidized parts inside and the surface energy increases again after a while;
- metal oxide film sputtered on the surface, as nanostructured  $\text{TiO}_2$ ,  $\text{SiO}_2$  etc.
- double grafting with hydrophilic PEG and hydrophobic PTFE on top so to have low contact angle for water, high contact angle for oils.

## Liquid crystals

Liquid crystals are mesomorphic phases, with long range order with respect to the position of the molecules. Anisotropic like crystals but show fluid properties like liquids.

-Lyotropics (lyo=solvent) are amphiphilic molecules, which form LC when mixed with a solvent.

-Thermotropics have a hydrophobic tail and a rigid core, so their shape is anisotropic.

There are two possible morphologies: disk-like or rod-like.

Both disk-like and rod-like liquid crystals can assemble in a head-tail or side-side configuration.

Discotic liquid crystals can be columnar or nematic.

The nematic director  $n$  is the spatial, temporal average of the long molecular axis.

Chirality influences the nematic director, producing spirals.

The thickness for a  $360^\circ$  turn of the nematic director is called 'pitch'. The pitch changes with the temperature.



The degree of order of a system with liquid crystals is quantified by means of the Legendre order parameter:  $S = \langle 3 \cos^2 \theta - 1 \rangle$

-1 for a perfect crystal,

-0 for an isotropic liquid,

-0.3-0.8 for liquid crystals.

## **Biorelated photonic materials**

Iridescence is a color change depending on the angle from which the surface is viewed.

Different thicknesses or nanofeatures create iridescence, as noticed in several biological tissues (butterfly wings, peacock wings, jewel beetles)

Butterfly wings are lined with many wing scales.

Structural colors are bright and metallic. Iridescent colors depend on the viewing angle.

The complex microstructure giving structural colors is of interest for microelectronic industry, but there are limitations related to the difficulty of making defect-free components.

Different optical phenomena:

- scattering: random process due to surface roughness, incident light is reflected in all directions.
- diffraction: regularly repeating pattern, the color changes depending on the angle.
- thin-film interference: incident light is partially reflected and transmitted.
- non-planar specular reflection: thin film interference + scattering.

The curvature of the surface influences the interaction with light.

Nanoscale ribs in butterfly wings reflect light to create iridescent colors. As the density and the number of layers change, the color changes too.

Spectroscopy must be performed considering a specific incident angle: absorbed and transmitted light patterns are different. The absorption part is transformed into heat.

Numerical models predict spectral reflectivity due to thin-film interference.

Polyester fibers have been produced with a multilayer structure showing wavelength-selective reflection, changing with the viewing angle.

-Jewel beetles show very bright colors thanks to the transmission over a layered structure. Each layer can polarize light and absorb reflected light from lower layers, creating very complex reflected colors.

-peacock feathers display patterns with nanoscale holes, reflecting light to create iridescent colors.

-buttercup petals have unusually shaped starch cells that form a diffuse but strong reflection.

Curved petals become very bright but also warmer, producing strong scents.

Biomimicry of iridescence is used for security issues in banknotes, credit cards etc.

New Qualcomm e-screen increases its brightness with sunlight. This uses much less power than a normal display, but it is much more complex.

Camouflage is a feature of octopuses and cephalopods that can change color.

30% of the brain of these animals is a central core, but the movement is controlled by peripheral distributed brain regions.

The color change is driven by peripheral control of epidermis cells as chromatophores, iridophores, leukophores. These cells are able to spread onto the surface to make a color change appear.

Chromatophores are complemented by reflecting cells. When chromatophores are spread, no light can pass and the surface becomes dark.

Applications range from military camouflage to disease detection by means of color change. Sylgard elastomers show fluorescent patterns by means of the application of a voltage or a stress. Spiropyran groups undergo reversible ring opening reactions yielding fluorescence. Azobenzene compounds can switch from trans- to cis- configuration with light and heat. The two configurations have different absorption so they could be used as detectors. The system can also bend or deform when a light is applied, so it could be used for drug delivery. PNIPAM is both thermo-responsive and pH-responsive. Making composites with SiO<sub>2</sub> beads, the reflectivity changes as the matrix swells and the distance between the beads changes. PDMS + PS beads composites can swell or shrink as a solvent is added to the system, and this leads to a change in the distance between the beads. This can also be achieved by mechanical stress, electrical or magnetic fields applied.

Electronic paper displays require low energy, high contrast and reflectivity. There are three main technologies: polymer dispersed liquid crystals, rotating balls, microencapsulated electrophoretic beads. Electrophoresis occurs in a liquid, so it is much slower, and can be used only for prints. Electronic ink has millions of tiny microcapsules with white (+) and black (-) regions, so that greyscale images can be obtained by applying a voltage. Zeta potential makes particles move when a potential is applied.

## **Bioluminescence**

More than 80% of the organic world is bioluminescent. Bioluminescence occurs thanks to two molecules: luciferin and luciferase. Luciferase catalyzes luciferin oxidation, leading to the emission of a photon. Luciferin is a reduced riboflavin (Vitamin B2) phosphate, which is oxidized. It requires ATP as a cofactor, so it can be used as an indicator of the presence of energy for life. It can be derived from chlorophyll. Coelenterazine is the most famous marine protein as it is the light emitter of the photoprotein acuatorin, related to the discovery of Green Fluorescent Protein (GFP).

Bioluminescence Resonance Energy Transfer consists in the movement of energy between two conjugated molecules, yielding a shift in the wavelength at which the molecule would emit.

There are three main illumination systems:

- incandescence: heat is transformed to light with low efficiency (most energy is in the IR range)
- fluorescence: fluorescent lamps have low pressure gas excited by electrodes and release photons when unloaded. The energy provided makes electrons move and produce ions ie. stable plasma. A fluorescent coating is applied to inlet UV rays and shift them output in Vis range.
- bioluminescence: chemical energy is transformed into light with the highest efficiency

The problem with bioluminescence is that the output light is very weak: it takes 25000 fireflies to match the output of a 60W bulb.

Medical scanning systems let patients undergo harmful radiations. In vivo imaging is used to provide non-invasive insight on the state of the patient.

Bioluminescence imaging (BLI) is used to label and monitor bacterial cells, viral agents or genes. The patient is placed in a highly sensitive Charged-Coupled Device (CCD) camera to have 3D images.

Food contamination detection can be performed as ATP is present when bacteria are present in food. ATP reacts with luciferin, so bacteria glow as they proliferate in food. This is an easy, non-expensive, fast reaction to detect food contamination.

## **Stimuli responsive polymers**

Polymers responding to external stimuli undergoing physical change under controlled conditions: pH, temperature, light, electric and magnetic field, etc.

Proteins are polyelectrolytes that can expose different functional groups and change the charge groups by folding or unfolding.

pH-responsive polymers work due to the presence of certain functional groups in the polymer chain: acidic groups (-COOH), alkaline groups (-NH<sub>2</sub>). After the ionization of these groups, the hydrodynamic volume increases due to electrostatic repulsion. Drug delivery systems can swell in certain pH conditions and release the drug. Eg. Controlled release of insulin by PMAA-EG hydrogel reservoirs grafted with glucose oxidase.

Temperature-responsive polymers exhibit a critical phase temperature, above/below which the system switches from monophase to separated phase. Eg. PNIPAAm sheet used for cell sheet engineering.

There are two main types: UCST, LCST (separate phase above/below  $T_{crit}$ , respectively)

PNIPAAm is used for drug delivery, with the polymer swelling as the temperature increases.

Ploxamers are thermoreversible gels which switch from liquid to gel phase as the temperature increases.

Pluronic F-127 is the most common ploxamer (PPO-PEO-PPO blocks).

In porous bulk materials, pore sized increase by swelling; in thin films the opposite phenomenon occurs. This can be exploited to regulate transport and diffusion of substances.

Shape memory materials can 'remember' the original shape under specific conditions. They are produced by cheap conventional manufacturing methods. The recovery temperature can be tailored by working on the chemistry of the material.

The original shape is maintained by crosslinking, entanglement and hard domains.

The temporary shape is given by the formation of crystallites on glassy phase; by re-heating the material, the shape is reverted to the original one.

The presence of crosslinks makes the system much more efficient than thermoplastics.

The number of cycles for shape memory processes is limited: after a certain number of repetitions, the strain decreases and the material is no longer able to completely recover the original shape.

Eg.1 Biodegradable shape memory polymer for suturing wounds that tightens as the polymer is heated.

Eg.2 SMP anchor for fixing tendons, ligaments, bones are attached to the most resistant phase by expanding in the specific location.

Eg.3 stents or intravenous devices that expand in loco to improve adhesion to blood vessels.

Some particular SMP can remember four different shapes and switch depending on different factors such as pH, temperature, relative humidity, etc.

## **Artificial muscles**

Electro-active polymers change shape and size when a current or a voltage is applied. They behave similarly to biological muscle and mimic their mechanism. EAP are lightweight, low-power, inexpensive, noiseless.

Muscles are multifunctional: they act as energy absorbers, variable stiffness suspensions, position sensors.

Sarcomeres are the functional units of muscle contraction. Myofibrils are the strings of sarcomeres. The mechanism of contraction works at macro as well as nanoscale: it is size invariant.

EAP movements are smoother than mechanical ones, so they are closer to the behavior of muscles. EAP can be electronic or ionic.

Electronic EAP can be electrostrictive, piezoelectric or dielectric. Motion is caused by electrostatic forces applied to the elastic dielectric between two compliant electrodes.

Ionic EAP move as the ions inside the polymer are displaced. Few volts are needed for actuation, but higher power is required, and energy is needed to keep a given position.

Ionomers are polymers with neutral repeating units and ionized units covalently bonded to the structure. Typically, up to 15% of the polymer is ionized with groups such as COOH, SO<sub>3</sub> etc.

Ionic composites are produced with ionomers and noble metal sheets.

Eg. Nafion has a backbone of PTFE and SO<sub>3</sub> groups. It is used for closing fuel cells.

Electrorheological fluids have ions moving inside the system and change the viscosity.

Stimuli-responsive gels change reversibly their volume, optical, mechanical and other properties by small alterations of certain physical and chemical stimuli.