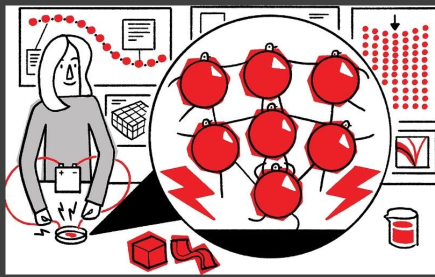
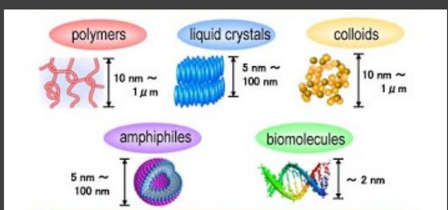


Introduction to Soft Matter

1

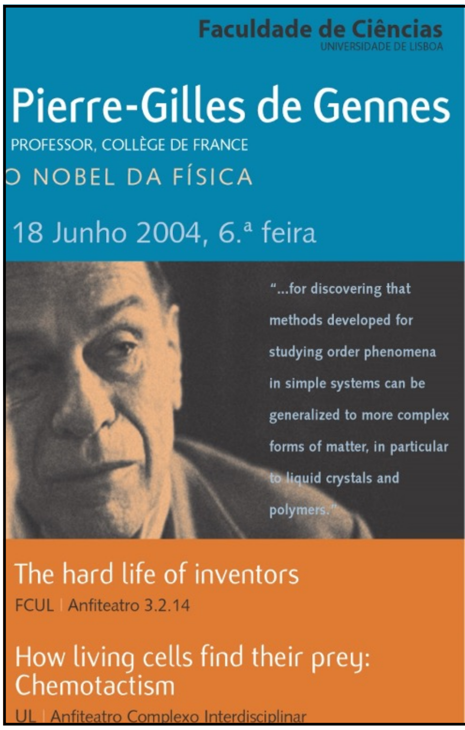
Soft Matter



As its name implies, soft matter deals with materials that are easily deformed. These materials, which include polymers, gels, colloids, emulsions, foams, surfactant assemblies, liquid crystals, granular materials, and many biological materials, have in **common that they are organized on mesoscopic length scales, with structural features that are much larger than an atom, but much smaller than the overall size of the material.**

The large size of the basic structural units and the relatively weak interactions that hold them together are responsible for the characteristic softness of these materials, but they also lead to many distinct features of soft materials, **such as sensitivity toward thermal fluctuations and external stimuli and a slow response with long relaxation times, often resulting in complex flow and arrest in non-equilibrium states.** These features make soft matter problems challenging.

2



Soft Matter

In hard condensed matter physics, it is possible to predict material properties based on the interactions between the individual atoms, which are organized on a regular crystalline lattice. For soft matter systems, with their intrinsically heterogeneous structure, complex interactions across different length scales, and slow dynamics, this is much more difficult.

The subtle interplay between interactions and thermal fluctuations can lead to complex emergent behavior, such as spontaneous pattern formation, self-assembly, and a large response to small external forces.

The realization that liquid crystals and polymers exhibit symmetry breaking and many fluctuating degrees of freedom has revived classical fields of physics such as elasticity and fluids, including non-Newtonian, and helped to establish the field of soft condensed matter Physics (de Gennes, Nobel Prize 1991).

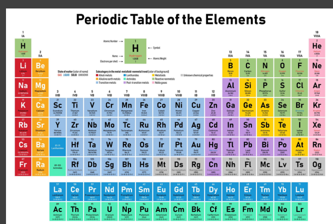
3

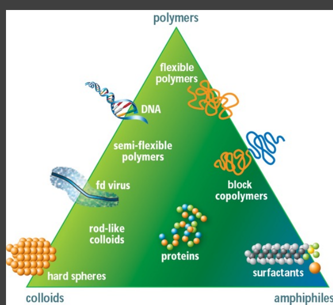
Building blocks and interactions

Atoms and small molecules, in Nature or synthesized in the laboratory, on the (sub)nanometer scale are the building blocks of solid state Physics.

Colloids, polymers and other macromolecules, the size of which lies between 5 nanometers and 5 micrometers, may be considered the building blocks of soft matter.

The interactions between nanometer and micrometer sized particles are radically different, both in nature and strength. While at the nanoscale the interactions are mostly electronic (order of eV) and quantum mechanics rules, on larger length scales the interactions between the particles are much weaker. They are effective interactions obtained from the free energy of the (two) particle system. They are often entropy driven and are of the order of the room temperature thermal energy (order of kT, where k is the Boltzmann constant or 1/40 eV at room temperature).





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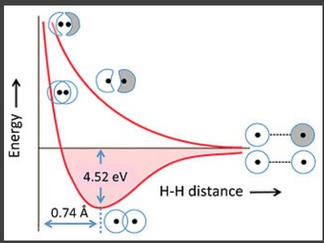
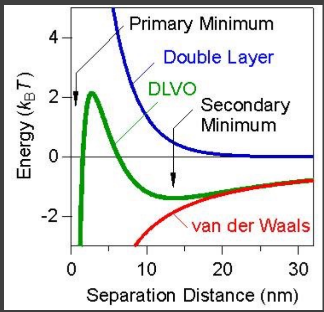
Building blocks and interactions

Colloidal particles are particles typically between 1 and a 1000 nm that can be dispersed (suspended) in fluids and for which Brownian forces are usually stronger than gravitation – the particles do not (usually) precipitate. Model colloidal particles are made of monodisperse spheres (polystyrene, silica ...)

In suspension, the particles are attracted by London dispersion or van der Waals forces. In water, the colloidal particles can have like charges, for example, through attaching ionisable acid groups on the surface. These like charges repel, but the repulsion is usually screened. DLVO theory (Deryaguin-Landau-Verwey- Overbeek) puts together the attractive London part and the screened Coulomb repulsion, and the potential takes the form depicted by the green curve in Figure on the bottom.





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Defining characteristics

The weak interactions between particles may be used as the defining characteristic of soft matter.

Soft matter comprises a variety of states, best distinguished as being dominated by energies of the order of room temperature thermal energy.

At these temperatures, quantum aspects are generally unimportant.

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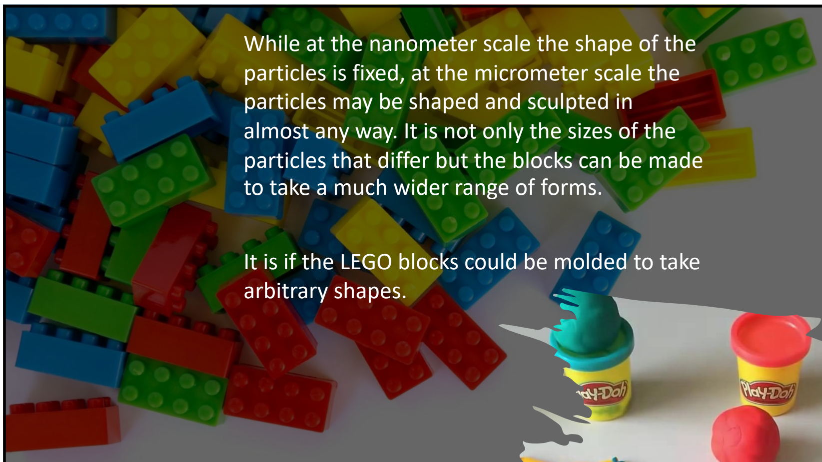

While at the nanometer scale the shape of the particles is fixed, at the micrometer scale the particles may be shaped and sculpted in almost any way. It is not only the sizes of the particles that differ but the blocks can be made to take a much wider range of forms.

It is if the LEGO blocks could be molded to take arbitrary shapes.

More on the building blocks

7

Soft materials

Soft materials are important in a wide range of technological applications. They appear as packaging materials, foams and adhesives, detergents and cosmetics, paints, food additives, lubricants, rubber, etc.

In addition, a number of biological materials (blood, muscle, milk, yogurt, jello) are classifiable as soft matter.

Liquid crystals, another category of soft matter, exhibit a responsivity to electric fields that makes them very important as materials in display devices (LCDs).

8

Soft materials

In spite of the various forms of these materials, many of their properties have common origins:

- a large number of degrees of freedom,
- weak interactions between the structural elements,
- a balance between entropic and enthalpic contributions to the free energy.

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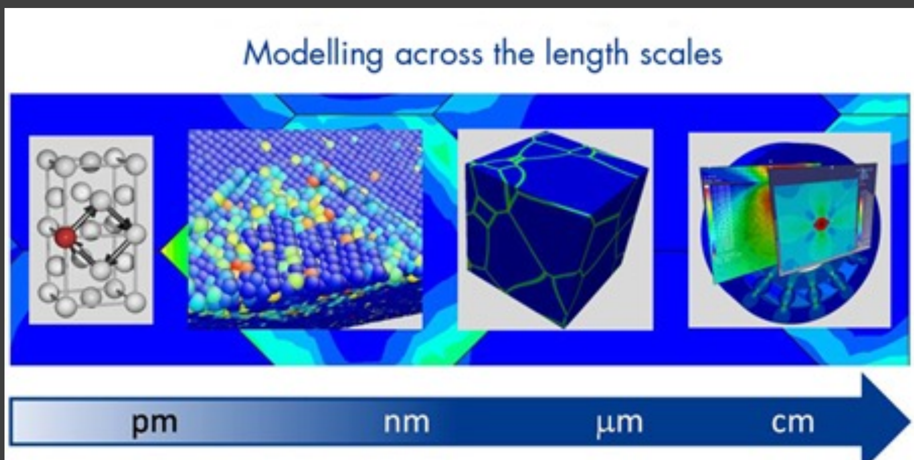

Challenge

The macroscopic properties of soft matter depend on its structure at the mesoscale and the challenge is to understand this mesoscale structure and how it determines the material properties.

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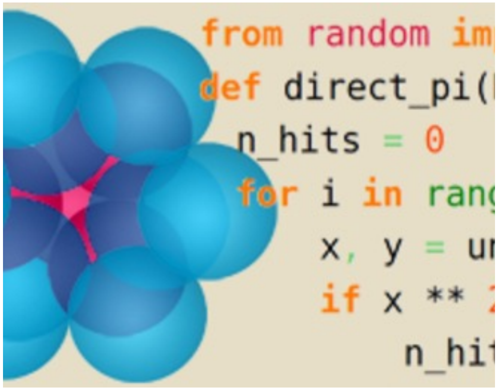
Bridging the scales



- Computer simulations & theoretical concepts and a range of experimental tools are required to investigate these systems and to bridge the length and time scales.
- Clearly, the interaction between colloidal particles with billions of atoms cannot be calculated from first principles, i.e., by solving Schrodinger's equation.
- Effective interaction potentials, coarse-grained dynamics and collective Monte Carlo moves are needed.

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Examples

Most soft materials are made of linear or branched polymers, amphiphilic (macro)molecules, colloids, granular matter and liquid crystals.

In some cases the building blocks are not very large but they self-assemble into units or phases that respond to external forces and move collectively (amphiphiles and liquid crystals).

In others, the building blocks contain millions or billions of atoms (polymers, colloids and granular matter).

In all cases the response of the system is large and the dynamics slow, leading to non-equilibrium and non-linear response, which make the properties of soft materials challenging and unique.

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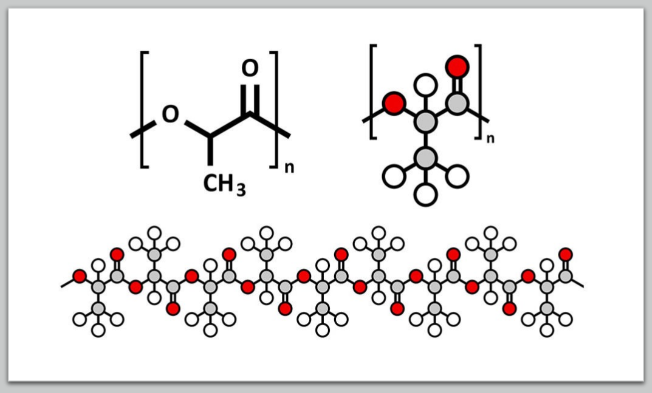

Polymers

A polymer is a substance consisting of very large molecules, or macromolecules, also called polymers. The defining feature of polymer macromolecules is their chain-like structure, made up of repeating monomers. The number of monomers in a polymer is typically thousands but can be as large as tens of millions.

The structure of a polymeric material can be described at different length scales, from the sub-nm length scale up to the macroscopic one. At the sub-nm scale the structure of a polymer is that of its constituent monomers.

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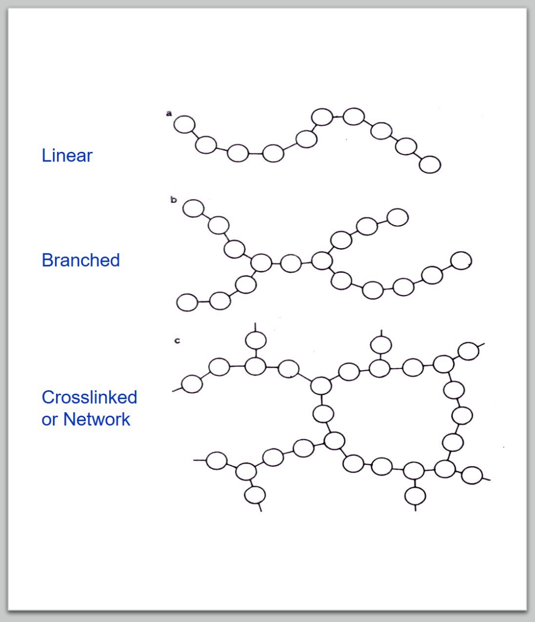
Polymers

Next, the structure essentially describes the arrangement of these monomers within the polymer at the scale of a single chain, which may be linear or branched.

Crosslinked or networked structures are also possible.



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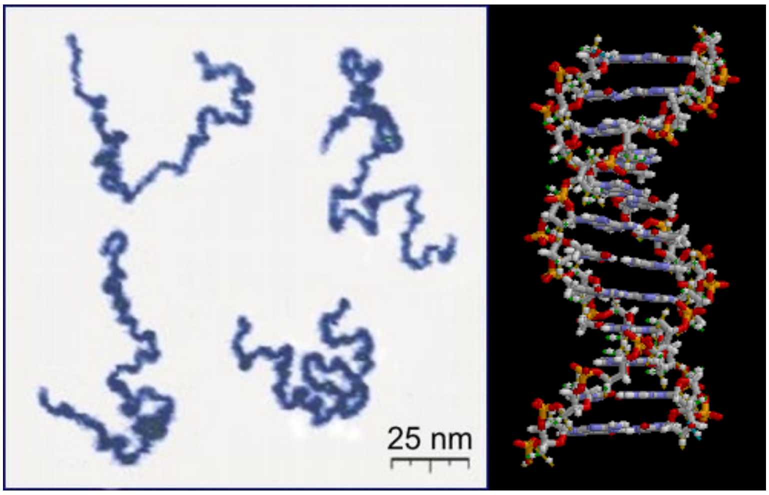

Left: Appearance of real linear polymer chains as recorded using an atomic force microscope on a surface, under liquid medium. Chain contour length is approximately 204 nm; thickness is approximately 0.4 nm. Right: Microstructure of part of a DNA double helix biopolymer

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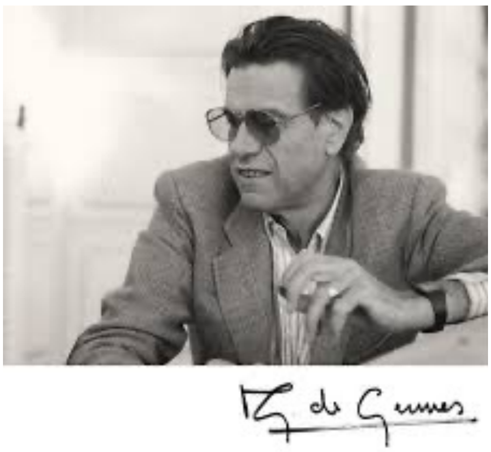

In his book Scaling Concepts in Polymer Physics, Pierre-Gilles de Gennes describes three developments that have been essential for advances in the study of large-scale conformations and motions of flexible polymers in solutions and melts.

They are neutron-scattering experiments on selectively deuterated molecules; inelastic scattering of laser light, which allows the study of cooperative motions of the chains; and the discovery of an important relationship between polymer statistics and critical phenomena, leading to many simple scaling laws, for which de Gennes was awarded the Nobel prize.

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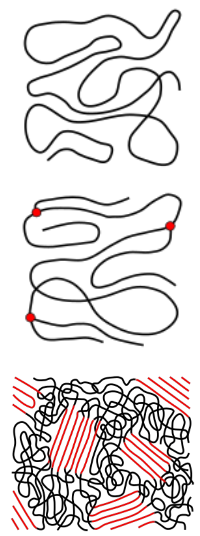

Polymer structure

The microstructure determines the possibility for the polymer to form phases with different arrangements, through crystallization, the glass transition or microphase separation. Polymer crystallization is a hard problem both theoretically and experimentally.

These phases play a major role in determining the physical properties of a polymer.

Polymers are indispensable materials in modern technology; they are used as plastics, rubbers, films, and textiles.

Polymers are also the basic molecules of life as proteins (machinery of biological functions) or DNA (genetic information).

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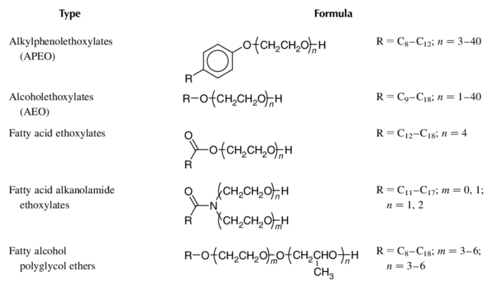
Amphiphiles

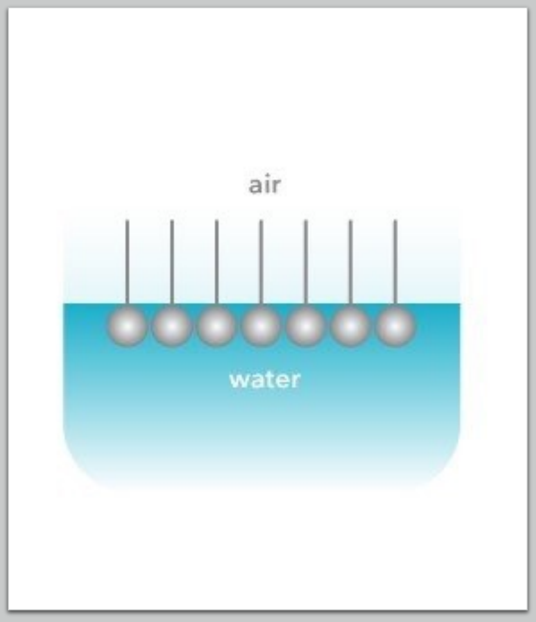
Amphiphile is a molecule possessing both hydrophilic (water-loving) and hydrophobic (water-hating) properties.

Typical amphiphiles are: sodium dodecyl sulfate (anionic), benzalkonium chloride (cationic) and 1-octanol (long-chain alcohol, non-ionic).



Type	Formula	
Alkylphenolethoxylates (APEO)	$R-C_6H_4-O(CH_2CH_2O)_nH$	$R = C_8-C_{12}$; $n = 3-40$
Alcoholethoxylates (AEO)	$R-O(CH_2CH_2O)_nH$	$R = C_9-C_{18}$; $n = 1-40$
Fatty acid ethoxylates	$R-C(=O)-O(CH_2CH_2O)_nH$	$R = C_{12}-C_{18}$; $n = 4$
Fatty acid alkanolamide ethoxylates	$R-C(=O)-N[(CH_2CH_2O)_nH][(CH_2CH_2O)_mH]$	$R = C_{11}-C_{17}$; $m = 0, 1$; $n = 1, 2$
Fatty alcohol polyglycol ethers	$R-O(CH_2CH_2O)_m O(CH_2CH(CH_3)O)_nH$	$R = C_8-C_{18}$; $m = 3-6$; $n = 3-6$

18



Surfactants

An important class of amphiphiles are surfactants, or surface active agents, responsible for the reduction of the interfacial tension between two immiscible phases.

The relation that links the surface tension and the surface excess is the Gibbs isotherm.

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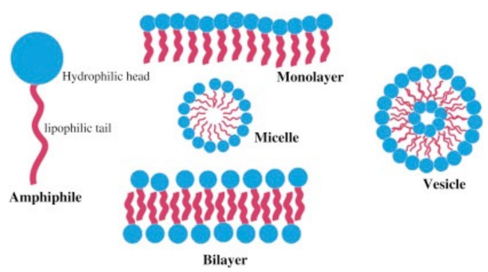
Surfactant self-assemby

Surfactants exhibit spontaneous formation of mesoscopic structures from smaller building blocks, by self-assembly.

The simplest example of self-assembly is into micelles or vesicles in water.

Much more intricate examples can be found in biology, where self-assembly leads to complex structures, such as viruses and hierarchically organized collagen fibers.



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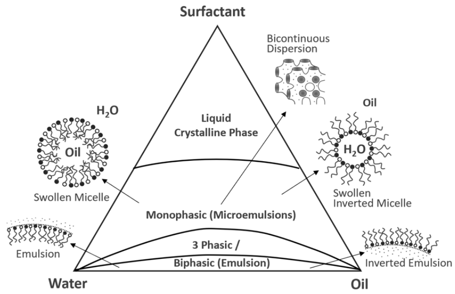
When in a two-phase system the surfactant self-assembles to partition the two immiscible phases. The extent of the hydrophobic and hydrophilic portions and the concentrations determine the partitioning and the structure of the resulting phases.

Phase diagram of water-oil-surfactant mixtures, exhibiting emulsion, microemulsion and liquid crystalline phases. On the left the system is water-rich, on the right oil-rich and in the middle water-oil balanced. The surfactant composition increases from bottom to top.



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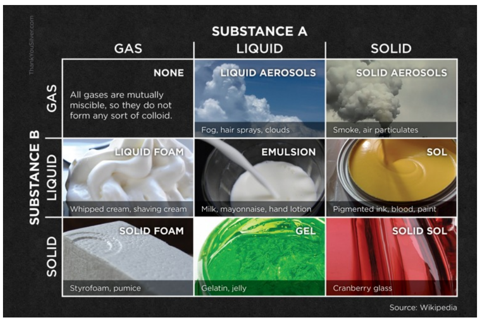
Colloids

A colloid is a phase separated mixture in which one substance of microscopically dispersed particles (A) is suspended throughout another substance (B).

Sometimes the dispersed substance alone is called the colloid; the term colloidal suspension refers unambiguously to the overall mixture.

Unlike a solution, whose solute and solvent constitute only one phase, a colloid has a dispersed phase (the suspended particles, A) and a continuous phase (the medium of suspension, B).



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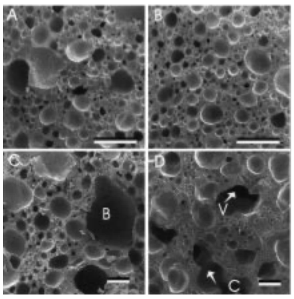
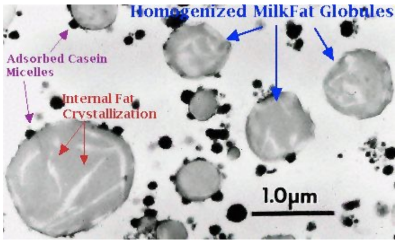
Microstructure

Left: Freshly whipped (A, B) and aged (C, D) cream. A and C are unstabilized, while B and D are stabilized. Bar 150 μm.

Right: milk (oil droplets in water)





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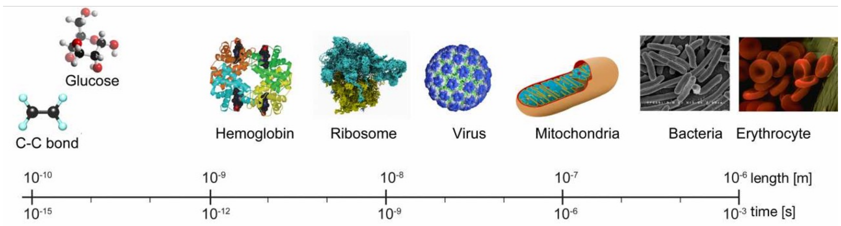
Colloidal sizes

Typically, colloids do not completely settle or take a long time to settle. The dispersed-phase particles have a size between 5 nanometers and 5 micrometers.



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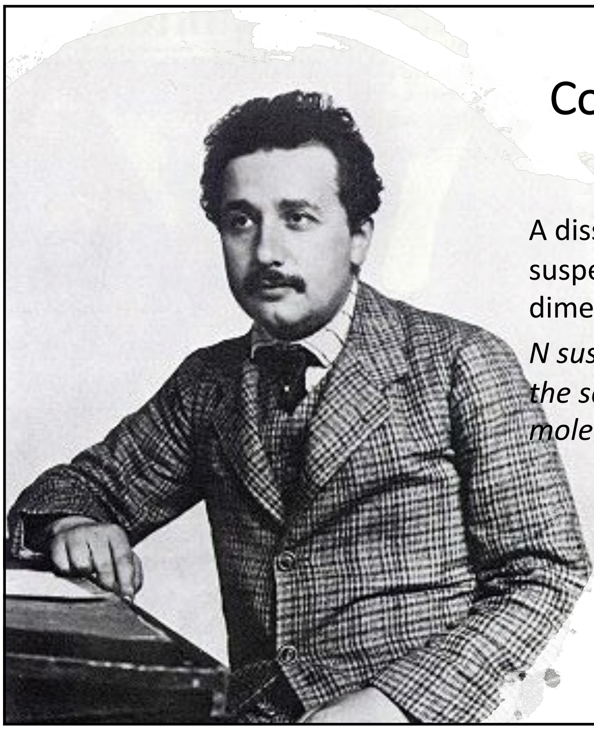

Colloids as atoms

A dissolved body differs from a suspended one *solely* by its dimensions and

N suspended particles produce the same osmotic pressure as N molecules.

Ann. d. Physik, <u>17</u>, 549 (1905)

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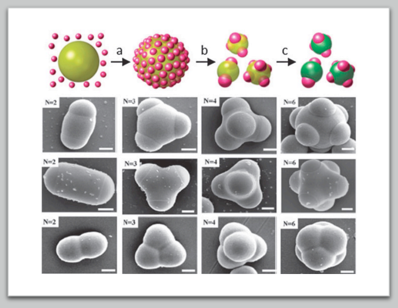
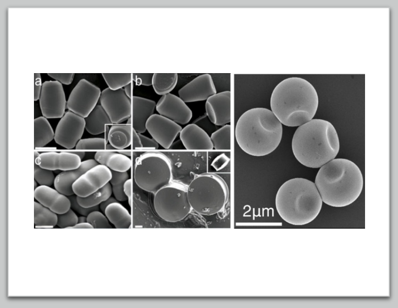
Colloidal shapes

Many of the forces that govern the structure and behavior of matter, such as excluded volume interactions or electrostatic forces, govern the structure and behavior of colloidal suspensions. For example, the same techniques used to model ideal gases can be applied to model the behavior of a hard sphere colloidal suspension.

Colloidal particles can be synthesized in many sizes and shapes, and the interactions between them can be finely tuned, by varying the surface charge, by changing the pH, by adding polymeric depletants, or by decorating the particles surfaces with complementary DNA strands.

This can lead to self-organization into a large variety of structures and phases, such as colloidal liquids, crystals, liquid crystals, and glasses, mimicking and going beyond the assembly of atoms.





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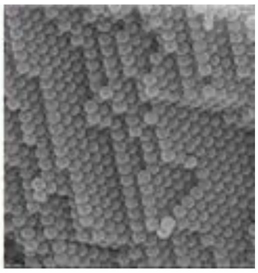

Bottom-up strategy

A strategy to control material properties from the bottom up, is by starting with colloidal building blocks.

Carefully designed colloidal building blocks may become the "atoms" and "molecules" of future materials, with potentially very interesting optical and mechanical properties.

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Confocal microscopy

Since colloids are big and slow enough to be followed individually using an optical microscope, they can be used to study fundamental physics problems at the single particle level, such as nucleation, melting, and crystal defects.

Non-equilibrium states are more prominent for colloids than for molecules. For example, gelation of particles can arrest the particles in a non-equilibrium aggregated state, completely suppressing crystallization.

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Granular matter

Granular matter is defined as a collection of particles that are large enough that thermal motion ceases to be important, and dissipation upon collisions of particles dominates the dynamics.

The grains may be solid particles (as in sand), liquid droplets (as in emulsions), or gas bubbles (as in foams). The lower size limit for grains in granular matter is a few µm. On the upper size limit, the physics of granular matter may be applied to asteroid belts of the Solar System with individual grains being asteroids, with sizes of several metres.

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Characterization

The most important parameter characterizing the behaviour of a granular system is its density.

Loose granular matter can flow like a fluid, while dense granular packings behave like a solid. Both cases have their own physics. At intermediate densities the granular material can switch from fluid to solid, as in avalanches.

Granular gases, granular fluids, and granular packings are discussed within the framework of statistical physics of disordered media, carried from equilibrium into out-of-equilibrium.

There is at present no microscopic model that explains the rich flow behavior of granular suspensions and emulsions.

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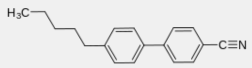
Liquid crystals



Liquid crystals (LCs) are a state of matter which has properties between those of conventional liquids and those of solid crystals. For instance, a liquid crystal may flow like a liquid, but its molecules may be oriented in a crystal-like way.

If a material is made of rod-like molecules, in the crystalline state the molecules are regularly placed on lattice sites and are also aligned. There is order in position and in orientation. In the liquid state, the position and orientation of the molecules are both random. In the liquid crystalline state, molecules have orientational order and lack full positional order.

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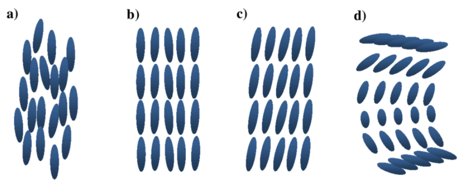
LC phases

In nematics the molecules retain the orientational order, while there is no positional order, a).

In smectics, in addition to the orientational order, there is partial positional order: the molecules are regularly placed along one direction, but are random on the plane perpendicular to it. If the direction of the positional and the orientational order is the same the phase is called semectic A, b), while if these directions do not coincide the phase is a smectic C, c).

In the cholesteric the direction of the orientational order twists with a characteristic period, d).



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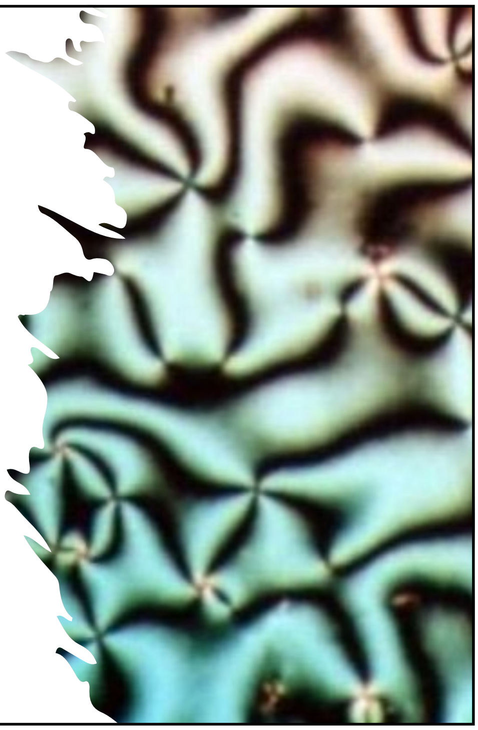
Textures & Applications

LC phases, are distinguished by their different optical properties (such as textures). The contrasting areas in the textures correspond to domains where the LC molecules are oriented in different directions. Within a domain the molecules are ordered.

Examples of liquid crystals can be found both in the natural world and in technological applications. Widespread LC displays (LCD) use liquid crystals, since their optical properties are easily controlled by electric fields.

Lyotropic LC phases are abundant in living systems. For example, many proteins and cell membranes are LCs.



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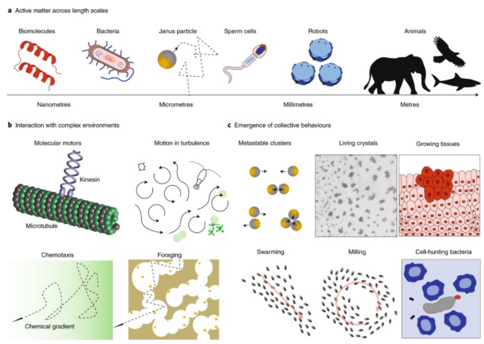
Active matter

Systems intrinsically out of equilibrium, as the particles continuously consume energy to propel active motion or to exert mechanical forces.

The interplay between a large number of these active particles can lead to very complex patterns of collective motion and self-organized structures.



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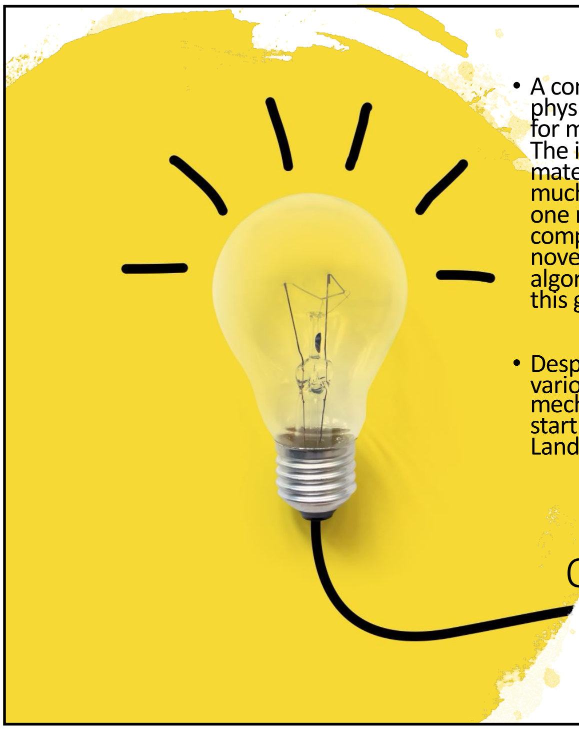

- A common thread in soft matter physics is to find microscopic models for macroscopically observed behavior. The inverse problem—designing a material with a specific property—is much more difficult. Yet, it is certainly one major goal. With the increase in computer power, the development of novel experimental tools, and new algorithms for analyzing large data sets, this goal may be within reach.
- Despite the differences among the various soft matter systems mechanistic insight and modelling may start by using standard tools such as Landau theory.

OUTLOOK

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Objetivos

Compreensão das propriedades de agregados macroscópicos de micropartículas. Estes componentes, à escala do mícron, agregam-se em materiais com um comportamento por vezes inesperado.

Muitos são utilizados na vida quotidiana e têm um número crescente de aplicações tecnológicas. Exemplos destes materiais incluem cristais líquidos, polímeros, colóides e matéria granular.

As descrições teóricas atuais da matéria mole são baseadas nas ferramentas da mecânica estatística clássica de equilíbrio e de nãoequilíbrio, na quebra espontânea de simetria e na física de muitos corpos.

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Programa
Margarida Telo da Gama

1. Introdução

1.1 O que é matéria mole ?

1.2. Polímeros, Colóides, Surfactantes e Cristais Líquidos.

1.3. O que é comum em matéria mole ?

2. Soluções de matéria mole

2.1. Termodinâmica de soluções

2.2. Separação de fases

2.3. Modelo de rede

2.4. Soluções de polímeros

2.5. Soluções coloidais

2.6. Soluções multi-componentes

3. Superfícies e surfactantes

3.1. Tensão superficial

3.2. Wetting

3.3. Surfactantes

3.4. Potenciais interfaciais

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Programa
Margarida Telo da Gama

4. Cristais Líquidos

4.1. Cristais líquidos nemáticos

4.2. Teoria de campo médio para a transição isótropo-nemático

4.3. Teoria de Landau-de Gennes

4.4. Efeitos de um gradiente espacial na ordem nemática

4.5. Teoria de Onsager para a transição isótropo-nemático de soluções coloidais

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Programa

Nuno Araújo

5. Movimento Browniano, flutuações térmicas e partículas ativas

5.1. Movimento Browniano de uma partícula esférica: aproximação de Langevin, funções de correlação e movimento num potencial

5.2. Movimento Browniano de uma partícula com forma generalizada

5.3. Flutuação-dissipação

5.4. Movimento de uma partícula ativa

6. Princípio variacional em matéria mole:

6.1. Princípio variacional para a dinâmica de sistemas partícula-fluído

6.2. Princípio de Onsager

6.3. Difusão em soluções diluídas e concentradas

7. Difusão e permeabilidade

7.1. Correlações espaciais

7.2. Sedimentação de partículas

7.3. Cinética de separação de fases

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Salas 8.2.04 e 8.2.19

Avaliação

Grupos de até 2 alunos

50%: 5 conjuntos de exercícios (Termodinâmica de soluções, Superfícies e surfactantes, Cristais Líquidos, Princípio variacional, Difusão e permeabilidade).

Submissão até 2 semanas depois da data em que os exercícios forem propostos.

Para cada conjunto de exercícios a avaliação tem em conta a resolução escrita (50%) e a oral (50%).

50%: projeto de Soft Matter (50% relatório escrito e 50% apresentação e discussão oral)

Submissão em data a anunciar

Horário

Segundas 8h30-10h30

Quartas 15h00-1600

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Salas 8.2.04 e 8.2.19

Bibliografia

Principal

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Secundária

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