Soft Condensed Matter Physics

Amphiphilic materials;
Poly-electrolytes; Liquid Crystals;
Foams and gels;
Soft matter?

- Hard matter: iron; steel
- Soft matter: e.g. polymers, bio-molecules

Interdisciplinary subject: physics, chemistry, materials science,

Outline of lectures: 1) liquid crystals and amphiphiles; 2) colloids and foams and gels; 3) biopolymers
Liquid crystals: Introduction I

Liquid crystal: a substance having liquid-like imperfect long range order in at least one direction of space, but positional or orientational order in at least one other direction.
Liquid crystals: Introduction II

Example of a compound that shows no liquid crystal phase:

- Ice cube
- Liquid water
- Steam

Example of a compound that shows liquid crystal phases:

- Crystals of organic compound
- Nematic phase
- Liquid crystal
- Isotropic liquid

Phases of liquid crystals:

- Nematic (thread)
- Smectic (soap)
Types of molecules that form liquid crystals

Generally the constituent molecules of liquid crystals are anisotropic; they have rod- or disk-like shapes and in the liquid crystal state the rods or discs have, on average, a preferential direction of alignment.
Some definitions: liquid crystals

**Thermotropic liquid crystals:** the alignment arises solely from packing effects—the molecules all tend to point in the same direction because they can pack more efficiently that way. The randomizing effect of thermal fluctuations opposes this orientational organization, so that when heated sufficiently, the thermotropic liquid crystals lose their order, and instead form a isotropic fluid. This means that liquid crystal phases occur between the fully ordered crystalline phase at low temperatures, and the disordered liquid phase at high temperatures.

**Lyotropic liquid crystals:** The lyotropic liquid crystals generally are two-component systems where an amphiphilic compound is dissolved in a solvent. The building blocks forming lyotropic liquid crystals are characterized by two distinct parts, a hydrophilic polar head and a hydrophobic non-polar tail. We will discuss these in the amphiphilic molecule section.

**Mesogen:** molecules that are capable of forming liquid crystals

**Mesophase:** the liquid crystal phase
**Director and Order parameters**

**Director:** The average direction of the molecular long axes in the liquid crystalline phase defines the director $\mathbf{n}$, which gives the direction of the preferred orientation of the liquid crystal molecules. In most liquid crystals both directions of the vector $\mathbf{n}$, $+\mathbf{n}$ and $-\mathbf{n}$ are equivalent. However, for molecules with permanent dipole moments this may not be the case, and the sign of $\mathbf{n}$ becomes important.

**Order parameter:** To specify quantitatively the amount of the orientational order in the liquid crystal phase, the scalar order parameter $S$ is commonly used ($0 < S < 1$) where $\theta$ is an angle between the individual molecular long axis and the director $\mathbf{n}$ and the brackets indicate the average value. In a perfectly oriented system $S = 1$, and in an isotropic liquid state, with no orientational order, $S = 0$.

$S = \frac{1}{2} < 3 \cos^2 \theta - 1 >$

$T_c =$ Clearing temperature; the temperature where the liquid crystal is transformed into an isotropic liquid.
Characteristic molecules that form liquid crystal phases

Main type of mesogens: rod-like (calamitic) and disk-like (discotic) mesogens

Rod-like mesogens

Disc-like mesogens
Classification of liquid crystal phases

**Nematic phase**: the molecules have no long-range translational order; However, they do possess long range orientational order.

**Smectic phase**: the molecules have a weak layering; in a *smectic A* phase the molecules are on an average, normal to the layers. In contrast, in a *smectic C* phase the director is tilted with respect to the layers.
The nematic phase formed by chiral molecules is itself chiral, and is called the chiral nematic phase (old name: cholestoric phase). The director twists round in a helix.
Columnar Phases

Columnar phases are formed by discotic mesogens. Discotic molecules can form a nematic phase just like rod-like mesogens. In addition, several types of columnar phases have been observed.
Anisotropy of properties

**Alignment by electric and magnetic fields**: the anisometry of mesogenic molecules leads to anisotropic polarization in electric fields. If an electric fields is applied to a molecule, a dipole moment is induced. The dipole tends to orient in the direction of the field. The response of liquid crystals to magnetic fields is analogous to that in electric fields.

**Optical anisotropy**: liquid crystal phases are optically anisotropic. The refractive index $\eta$ has a different value parallel to the director than when perpendicular to it. The difference leads to the definition of optical anisotropy (*birefringence*) $\Delta \eta = \eta(\text{par}) - \eta(\text{per})$ The optical anisotropy of liquid crystals is put to use in liquid crystal displays.

**Mechanical alignment**: when a liquid crystal is oriented adjacent to a flat substrate the orientation of the director with respect to the surface is said to be planar, or homogenous, if the director is parallel to the surface, or homeotropic if it is perpendicular.

**Alignment by flow**: the flow behavior of nematics is anisotropic. This is evident from experiments on nematic liquid crystals confined between parallel plates when the director orientation varies with respect to the flow direction.
Phase transitions in liquid crystals

The phases can interconvert when the temperature is changed
Identification of liquid crystal phases

Polarized microscope

X-ray crystallography

Differential scanning calorimetry (DSC)

DSC plot with phase diagram
Example of application of liquid crystals

1. Polarization filter
2. Glass substrate with ITO electrodes
3. Nematic liquid crystal
4. Glass substrate with common electrode film (ITO)
5. Polarizing filter film
6. Reflective surface to send light back to viewer
Amphiphiles

Hydrophilic "water loving"

Hydrophobic "water hating"

Amphiphiles are molecules that contain hydrophilic and hydrophobic parts

Amphiphilic molecules are also known as detergents, tensides or surfactants

Surfactant = surface active agent

\[ \text{CH}_3(\text{CH}_2)_{11}\text{SO}_4^-\text{Na}^+ \]

equation: sodium dodecylsulfate
Types of amphiphiles: ionic surfactants

Typical anionic surfactants

Typical cationic surfactants
Types of amphiphiles: nonionic surfactants

Typical nonionic surfactants

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\text{Typical nonionic surfactants}
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Types of amphiphiles: lipids

- Fatty acid salt
- Triglyceride
- Phospholipids
- Sphingolipid

amphoteric
What happens when an amphiphile is put in contact with water?

- Charge repulsion (for ionic structures)
- Stabilization by Van der Waals forces

Arrangement of large organic ions into micelles. The polar head group form the outer hydrophilic surface that protects the hydrophobic aliphatic chains from having to interact with water.
Micellization and the critical micelle concentration

Micelles form only above the Critical Micelle Concentration (CMC) and above the Krafft temperature. The critical micelle concentration is not a thermodynamic phase transition. It is defined phenomenologically from a sharp increase in the number of molecules associated into micelles. The precise location of the CMC thus depends on the technique used to measure it,
Examples of different types of aggregates formed by amphiphiles

The hydrophobic-hydrophobic nature of amphiphilic molecules leads to their self-assembly into a variety of structures in aqueous solution.

a) Spherical micelle; b) disc-like micelle; c) rod-like micelle; d) inverted micelle
Prediction of different types of aggregates formed by amphiphiles

As seen above in the Figure, for $p < \frac{1}{3}$, the surfactant forms a cone shape. Therefore, the corresponding micelle is spherical. The truncated cone surfactant shape is valid for $\frac{1}{3} < p < \frac{1}{2}$, forming a rod-like micelle. If $\frac{1}{2} < p < 1$, the surfactant is cylindrical in shape and a bilayer is formed.

Micellar size and shape can vary, depending on surfactant type, temperature, and the presence of salts. The packing properties of surfactants are dependent upon cross-sectional surface area of the head-groups ($a_0$), the volume (V) of the hydrocarbon chains, and the maximum length, ($L_c$), of the chains. The packing parameter is dimensionless where $p = \frac{V}{a_0 L_c}$. The packing parameter determines the geometry of the surfactants.
Variations of the critical micelle concentration

Temperature: For most surfactants the CMC is essentially independent of Temperature

Surfactant type: the CMC is usually lower for nonionic surfactants than for Ionic ones, when the comparison is made for equal hydrophobic chain lengths.

Hydrophobe chain length: Increasing the length of the hydrophobic part of an amphiphile favors micellization: Thus, an increase in the chain length leads to a reduction in the CMC.

Salts and co-solutes: For ionic surfactants, addition of salt decreases the CMC. Addition of co-solute can either increase or decrease the CMC, depending on the polarity of the co-solute.
Krafft temperature

The solubility of ionic surfactants is strongly dependent on temperature. The solubility is often very low at low temperatures, but increases rapidly in a narrow range as the temperature increases. The point at which the solubility curve meets the Critical Micelle Concentration (CMC) is termed the Krafft point, which defines the Krafft temperature.

Fig. 2.—Phase diagram close to the Krafft point of sodium decyl sulfonate.
Solubilization in micelles

Micelles can dissolve organic molecules into the hydrophobic interior thereby enabling otherwise insoluble molecules to be dissolved in water.
Detergency

Micelles are important in industry and biology on account of their solubilizing function: matter can be transported by water after it has been dissolved in their hydrocarbon interior.

For this reason, micellar systems are used as detergents and drug carriers.
Lyotropic liquid crystals

At high concentrations, amphiphiles tend to self-assemble into ordered structures called lyotropic liquid crystal phases.
Lyotropic liquid crystals: cell membranes