Chapter 1

Review of Soft Matter Systems

Contents

1.1 Introduction

Soft matter comprises a variety of mater in different physical states that are easily deformed by thermal stresses or thermal fluctuations, Figure 1.1. All soft matter materials share an important common feature, this is that the predominant physical behaviors occur at an energy scale comparable with room temperature thermal energy. Soft matter systems include liquids, colloids, polymers, foams, gels, granular materials, and a number of biological materials.

Soft matter systems often have interesting behaviours that are difficult to predict as they arise directly from its atomic or molecular constituents. This is because soft matter often self-organises into mesoscopic physical structures; these are much larger than the microscopic scale (the arrangement of atoms and molecules), and much smaller than the macroscopic (overall) scale of the material. The properties and interactions of these mesoscopic structures determine the macroscopic behaviour of the material. For example, the bubbles that comprise a foam are mesoscopic because they individually consist of a vast number of molecules, and yet the foam itself consists of a great number of these bubbles, and the overall mechanical stiffness of the foam emerges from the combined interactions of the bubbles, Figure 1.2. By way of contrast, in hard condensed matter physics it is often possible to predict the overall behaviour of a material because the molecules are organised into a crystalline lattice with no changes in the pattern at any mesoscopic scale.
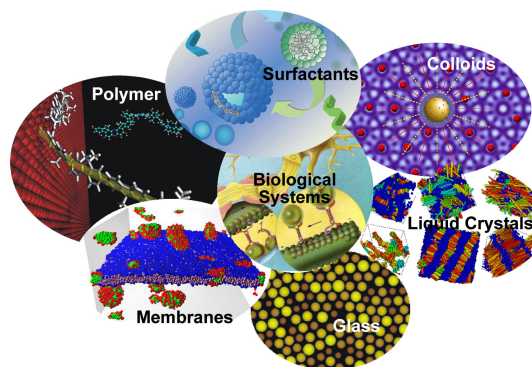

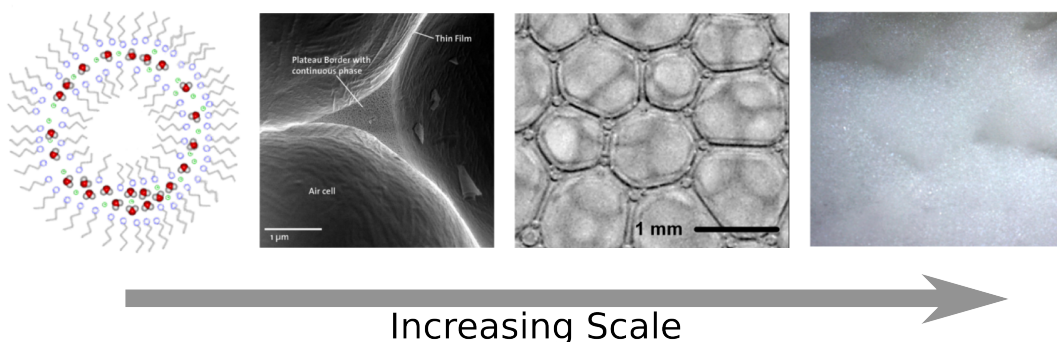Figure 1.1: Examples of soft matter systems.

Figure 1.2: Range of scales in foam, from the molecular arrangement (left) to the macroscale structure (right).

Soft materials are important in a wide range of technological applications. They may appear as structural and packaging materials, foams and adhesives, detergents and cosmetics, paints, food additives, lubricants and fuel additives, rubber in tires, etc. In addition, a number of biological materials (blood, muscle, milk, yogurt) are classifiable as soft matter. Liquid crystals, another category of soft matter, exhibit a responsivity to electric fields that make them very important as materials in display devices (LCDs). In spite of the various forms of these materials, many of their properties have common physicochemical origins, such as a large number of internal degrees of freedom, weak interactions between structural elements, and a delicate balance between entropic and enthalpic contributions to the free energy. These properties lead to large thermal fluctuations, a wide variety of

forms, sensitivity of equilibrium structures to external conditions, macroscopic softness, and metastable states.

1.2   Colloids

A colloid is a substance microscopically dispersed evenly throughout another substance. A colloidal system consists of two separate phases: a dispersed phase and a continuous phase in which the colloid is dispersed. A colloidal system may be solid, liquid, or gas[1]. The dispersed-phase particles typically have a diameter of between approximately 1 and 1000 nanometers; however, liquid-liquid systems can have larger dispersed-phase droplets (especially if stabilised). The dispersed-phase particles or droplets are affected largely by the surface chemistry present in the colloid.

1.2.1   Classification

Because the size of the dispersed phase may be difficult to measure, and because colloids have the appearance of solutions, colloids are sometimes identified and characterized by their physico-chemical and transport properties. Colloids can be classified as in Figure 1.1.

Table 1.1: Classification of colloid systems.

Medium		Dispersed Medium		
		Gas	Liquid	Solid
Continuous Medium	Gas	**None** (all gases are mutually miscible)	**Liquid aerosol** fog, mist, hair spray	**Solid aerosol** smoke, cloud, inhalers
	Liquid	**Foam** shaving cream, head on beer	**Emulsion** milk, mayonnaise, shampoo	**Sol** paint, ink, blood
	Solid	**Solid foam** aerogel, pumice, styrofoam	**Gel** jelly, agar	**Solid sol** pearl

1.2.2   Interactions Between Colloid Particles

There are several forces that play an important role in the interaction of colloid particles:

van der Waals forces There is an attractive force between any pair of atoms or molecules, even when the atoms are uncharged or have no dipole moment. The origin of this force is quantum mechanical arising from the interaction between fluctuating dipoles in each of the atoms. The van der Waals potential actually depends on the

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[1]Emulsion is often used interchangeably with colloid, but an emulsion specifically refers a liquid-liquid system

shape of the colloid particles, equation 1.2.1, where A is the Hamaker constant.

$$V\left(x\right) = - \begin{cases} \dfrac{Ar}{12x} & \text{Spherical particles of size } r \\ \dfrac{A}{12\pi x^2} & \text{Plate-like particles} \end{cases} \qquad (1.2.1)$$

Electrostatic interaction Colloidal particles often carry an electrical charge and therefore attract or repel each other. The charge of both the continuous and the dispersed phase, as well as the mobility of the phases are factors affecting this interaction. Dissolved ions interact with the colloids and modify the nature of the electrostatic interactions. In particular, the electrostatic interactions are screened by dissolved ions.

Entropic forces According to the second law of thermodynamics, a system progresses to a state in which entropy is maximized. This can result in effective forces even between hard spheres.

Excluded volume repulsion It is impossible for two hard particles to overlap each other. This means that there is a finite size of the system.

Steric forces Polymer-covered surfaces or solutions containing non-adsorbing polymer can modulate interparticle forces, producing an additional steric repulsive force (which is predominantly entropic in origin) or an attractive depletion force between them.

1.3 Polymers

A polymer is a large molecule (macromolecule) composed of repeating structural units. These sub-units are typically connected by covalent chemical bonds. Although the term polymer is sometimes taken to refer to plastics, it actually encompasses a large class of compounds comprising both natural and synthetic materials with a wide variety of properties. Because of the extraordinary range of properties of polymeric materials they are widely used. Their roles range from synthetic plastics and elastomers to natural biopolymers such as nucleic acids and proteins that are essential for life. Natural polymeric materials such as shellac, amber, wool, silk and natural rubber have been used for centuries. A variety of other natural polymers exist, such as cellulose, which is the main constituent of wood and paper.

Most commonly, the continuously linked backbone of a polymer used for the preparation of plastics consists mainly of carbon atoms. A simple example is polyethene, whose repeating unit is based on ethene monomer. However, other structures do exist; for example, elements such as silicon form familiar materials such as silicones, examples being Silly Putty and waterproof plumbing sealant. Oxygen is also commonly present in polymer backbones, such as those of polyethylene glycol, polysaccharides (in glycosidic bonds), and DNA (in phosphodiester bonds).

1.3.1 Polymer Properties

Polymer properties are broadly divided into several classes based on the scale at which the property is defined as well as upon its physical basis. The most basic property of a polymer is the identity of its constituent monomers. A second set of properties, known as

microstructure, essentially describe the arrangement of these monomers within the polymer at the scale of a single chain. These basic structural properties play a major role in determining bulk physical properties of the polymer, which describe how the polymer behaves as a continuous macroscopic material. Chemical properties, at the nano-scale, describe how the chains interact through various physical forces. At the macro-scale, they describe how the bulk polymer interacts with other chemicals and solvents. The physical properties of a polymer are strongly dependent on the size or length of the polymer chain. For example, as chain length is increased, melting and boiling temperatures increase quickly. This is a result of the increase in chain interactions such as Van der Waals attractions and entanglements that come with increased chain length. Some of the main parameters used are:

Degree of Polymerisation is given by equation 1.3.1.

$$DP = \frac{\text{Molar Mass of Polymer}}{\text{Molar Mass of Repeat Unit}} \tag{1.3.1}$$

Number Average Molar Mass is given by equation 1.3.2.

$$\bar{M}_n = \frac{\sum\limits_i N_i M_i}{\sum\limits_i N_i} \tag{1.3.2}$$

Weight Average Molar Mass is given by equation 1.3.3.

$$\bar{M}_w = \frac{\sum\limits_i N_i M_i^2}{\sum\limits_i N_i M_i} \tag{1.3.3}$$

Polydispersity Index is given by equation 1.3.4 and for polydispersed polymers $n < w < z$ while as uniform polymers have $n = w = z$.

$$PDI = \bar{M}_z = \frac{\bar{M}_w}{\bar{M}_n} \tag{1.3.4}$$

Radius of Gyration describes the dimensions of a polymer chain as in equation 1.3.5, and is the average distance from the center of mass of the chain to the chain itself.

$$R_g^2 = \frac{1}{N} \sum\limits_{k=1}^{N} (\mathbf{r}_k - \mathbf{r}_{\text{mean}})^2 \tag{1.3.5}$$

1.3.2 Phase behaviour

Crystallinity

When applied to polymers, the term crystalline has a somewhat ambiguous usage. A synthetic polymer may be loosely described as crystalline if it contains regions of three-dimensional ordering on atomic (rather than macromolecular) length scales, usually arising from intramolecular folding and/or stacking of adjacent chains. Synthetic polymers may consist of both crystalline and amorphous regions; the degree of crystallinity may be expressed in terms of a weight fraction or volume fraction of crystalline material. Few synthetic polymers are entirely crystalline. Polymers with a degree of crystallinity approaching zero or one will tend to be transparent, while polymers with intermediate degrees of crystallinity will tend to be opaque due to light scattering by crystalline or glassy regions.

Melting point

The term melting point, when applied to polymers, is not a solid-liquid phase transition but a transition from a crystalline or semi-crystalline phase to a solid amorphous phase, abbreviated as T_m. Some polymers will actually decompose at high temperatures rather than melt.

Glass transition temperature

A parameter of particular interest in synthetic polymer manufacturing is the glass transition temperature (T_g), which describes the temperature at which amorphous polymers undergo a transition from a rubbery, viscous amorphous liquid, to a brittle, glassy amorphous solid. The glass transition temperature may be engineered by altering the degree of branching or crosslinking in the polymer or by the addition of plasticizer.

1.3.3 Polymer Mixtures

In general, polymeric mixtures are far less miscible than mixtures of small molecule materials. This effect results from the fact that the driving force for mixing is usually entropy, not interaction energy (enthalpic). In other words, miscible materials usually form a solution not because their interaction with each other is more favorable than their self-interaction, but because of an increase in entropy and hence free energy associated with increasing the amount of volume available to each component. This increase in entropy scales with the number of particles (or moles) being mixed. Since polymeric molecules are much larger and hence generally have much higher specific volumes than small molecules, the number of molecules involved in a polymeric mixture is far smaller than the number in a small molecule mixture of equal volume.

The energetics of mixing, on the other hand, is comparable on a per volume basis for polymeric and small molecule mixtures. This tends to increase the free energy of mixing for polymer solutions and thus make solvation less favorable. Thus, concentrated solutions of polymers are far rarer than those of small molecules. Furthermore, the phase behaviour of polymer solutions and mixtures is more complex than that of small molecule mixtures. Whereas most small molecule solutions exhibit only an upper critical solution temperature phase transition, at which phase separation occurs with cooling, polymer mixtures commonly exhibit a lower critical solution temperature phase transition, at which phase separation occurs with heating.

Block co-polymers (e.g. AAAAABBBBBBAAAAA-) can also self-assemble into separated phase structures such that the different types of monomer units are separated from each other similar to surfactant liquid crystals, Figure 1.3.
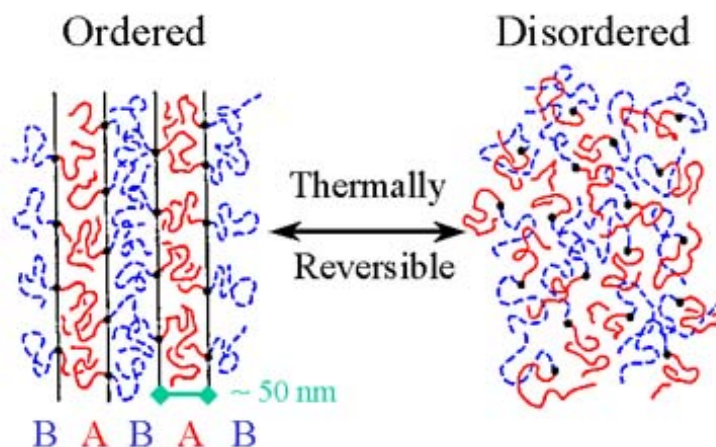

Figure 1.3: Block co-polymer ordering into lamellar phase on cooling.

1.4   Surfactants

The term surfactant comes from a catenation of surface active agent first coined by Antara Products in 1950 [1]. Surfactants have been used for many years in a wide range of everyday applications such as cleaning products, food, pharmaceuticals and paints to name but a few [2]. Surfactants even occur in nature forming biological structural systems [3]. Their functionality is due to their molecular structure in that they have parts soluble in a specific fluid (lyophilic) and parts insoluble in that same fluid (lyophobic).

In the case of water, as a solvent, they have a hydrophilic head group, which is water soluble, attached to a hydrophobic tail group, which is insoluble in water. This structure drives the formation of self-assembled aggregates by trying to keep the lyophobic parts away from the fluid they "dislike".   A simplified surfactant molecule is shown by Figure 1.4. Most surfactants are chain-like molecules, although many colloidal particles can display amphiphilic behaviour.
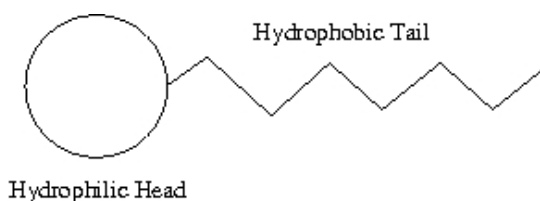

Figure 1.4: Schematic of simplified surfactant molecule.

1.4.1   Surfactant Classification

The hydrophobic tails of surfactants are generally limited to hydrocarbon, perfluorocarbon, and polydimethylsiloxane chains [3]. The hydrophilic head group is usually shorter and bulkier than the tail and its polarity is used to classify the surfactant. Surfactants are classified into four groups:

Anionic surfactants have a head group that is negatively charged with a positively charged counter-ion.

Cationic surfactants have a head group that is positively charged with a negatively charged counter-ion.

Zwitterionic surfactants have a head group that contain both a positively and negatively charged ion; these often comprise of a base connected to an acid.

Non-ionic surfactants have no overall charge and no ions, the hydrophilic part of the molecule is produced from polar species, commonly poly(ethylene oxide) groups are used.

These classifications accommodate the main types of surfactants, but are not exclusive: a surfactant can have a hydrocarbon tail, a poly(ethylene oxide) section, and a charged head group.

1.4.2 Surfactant Self-Assembly

As previously mentioned, when in solution surfactant molecules have a tendency to self assemble into different structures depending on the concentration, temperature, and surfactant structure [4]. At very low concentrations, surfactant molecules are solubilized as unimers. In a dilute solution the surfactants will self-assemble into aggregates such as micelles and cylinders. The form that gives the minimum free energy for the given set of conditions will be the optimum aggregate. The free energy can be said to be mainly made up of three terms:

Hydrophobic contribution which is favourable due to the hydrocarbon chains sequestering themselves within the interior of the aggregates. This reduces the enthalpy as it reduces the hydrocarbon-solvent repulsive interaction energy. This is the main driving force for surfactant self-assembly.

Surface term reflecting the resistance of the head groups packing together and their attraction the fluid. This increases the enthalpy as it increases the head-head repulsive interaction energy. This is the main force that limits micellar size.

Packing term reflecting the exclusion of fluid from the aggregate interior and the limited geometric structures available. This decreases the entropy as the free chains with many degree of freedom are packed together.
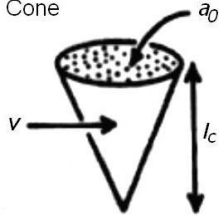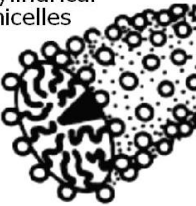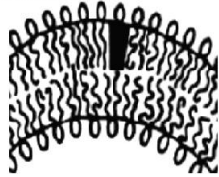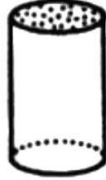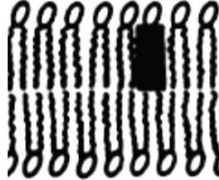
For these dilute systems the shape of the aggregates can be predicted using a packing parameter [5], surface curvature [6], or molecular simulations. The packing parameter, N_s, can be given by equation 1.4.1, where v is the volume of the hydrophobic chain, l_c is the length of the hydrophobic chains and, a_0 is the effective area per head group.

$$N_s = \frac{v}{l_c a_0} \qquad (1.4.1)$$

The value of the packing parameter relates to the structure of the aggregate as shown in Table 1.2. This is only an approximation; each surfactant will behave differently depending on the conditions it is subjected to, and concentration of the surfactant itself, therefore a full phase diagram should be used to determine the aggregate structures if possible. Mixtures of the aggregates can exist, as well as intermediate structures between those shown in Table 1.2 [5].

Tanford (1972) [8] used the data of Reiss-Husson and Luzzati (1964) [9], generated by X-ray scattering, to produce relations for the values of the hydrocarbon core volume

Table 1.2: Shapes of aggregates formed from surfactants with different packing parameters [7]

Surfactant Type	Packing Parameter	Packing Shape	Aggregate
Single-chained surfactants with large head-group areas	$\leq \dfrac{1}{3}$	Cone a_0 v l_c	Spherical micelles
Single-chained surfactants with small head-group areas	$\sim \dfrac{1}{2}$	Truncated cone	Cylindrical micelles
Double-chained surfactants with large head-group areas, fluid chains	$\dfrac{1}{2} - 1$	Truncated cone	Flexible bilayers, vesicles
Double-chained surfactants with small head-group areas, frozen chains	~ 1	Cylinder	Planer bilayers
Double-chained surfactants with small head-group areas, poly unsaturated chains	> 1	Inverted truncated cone	Inverted micelles

and the length of the hydrocarbon chains, equation 1.4.2, where n_c is the total number of carbons per hydrocarbon chain.

$$v = (0.0274 + 0.0269 n_c) \, \text{nm}^3 \text{ per hydrocarbon chain}$$
$$l_c = (0.15 + 0.1265 n_c) \, \text{nm per hydrocarbon chain} \tag{1.4.2}$$

The numbers in these relationships can be explained in terms of the molecular properties of the groups with in the hydrocarbon chains. The volume of a $-\text{CH}_2-$ group is $0.0294 \, \text{nm}^3$, i.e. approximately the second number in the relationship for v, and the volume of a $-\text{CH}_3$ group is about twice this value [10]: the difference in the two volumes thus gives rise to the first number in the relationship for v. The van der Waals radius of

a terminal methyl group is $0.21\,\mathrm{nm}$ and a carbon-carbon bond length is $0.154\,\mathrm{nm}$ [11]: this explains the numbers in the relationship for l_c. The bond length taken in the *trans* configuration gives an atom spacing of $0.133\,\mathrm{nm}$, which is approximately the 0.1265, and the van der Waals radius minus half this length is equal to 0.143, which is approximately 0.15. [1]

These relationships can be substituted into equation 1.4.1 to allow calculation of the packing parameter. The value to be calculated is the effective area per head group, a_0. This value is affected by the type of surfactant used, the material the surfactant is dissolved in, and the temperature [4].

The number of monomers required to form a spherical type micelle is termed an aggregation number, N_0, and it varies from typically 50 to 100, depending on the surfactant type, aggregate shape, temperature, and concentration. However, for a given surfactant under given conditions this number is fixed, therefore these micelles can be treated as mono-dispersed structures. Cylindrical micelles do not have such well defined aggregation numbers as the cylinders can grow to varying lengths, producing a poly-dispersed system [4].

1.4.3 Critical Micelle Concentration

Self-assemblies only form when it is thermodynamically favourable for them to do so; as low concentrations of surfactant then they can exist as unimers. As the concentration increases the aggregates will form; the concentration at which the micelles first form is called the critical micelle concentration, CMC. The chemical structure of the surfactant, the temperature, and any co-solutes are all known to influence the CMC [2].

Many physical properties of surfactant solutions undergo a sudden change at the CMC. These changes allow the value of the CMC to be determined for surfactant solutions. Figure 1.5 shows the general trends for some physical properties around the CMC.

Several methods have been used in the literature to measure the CMC of different surfactants in an aqueous solution, including surface tension ([13]), conductivity measurements ([14]), and fluorescence intensity ([15]).

1.4.4 Krafft Point

As stated, micelles will only form above the CMC, but they will also only form above a certain temperature. At low temperatures, the surfactant has low solubility and the concentration dissolved may be below the CMC. The point at which the dissolved concentration at the given temperature is equal to the CMC is called the Krafft point (or Krafft temperature); every surfactant has a characteristic Krafft point. The temperature dependence of the surfactant solubility in the region of the Krafft point is shown in Figure 1.6. Below the Krafft point, the solubility of the surfactants is less than the CMC and hydrated surfactant crystals will formed.

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[1]Fennell Evans and Wennerström (1999) [4] give slightly modified versions of these relationships, where n_{Me} is the number of methyl groups. These contain values that appear to have been rounded from equation 1.4.2,

$$v = 0.027\left(n_c + n_{Me}\right)\mathrm{nm}^3 \text{ per hydrocarbon chain}$$
$$l_c = \left(0.15 + 0.127 n_c\right)\mathrm{nm} \text{ per hydrocarbon chain.}$$
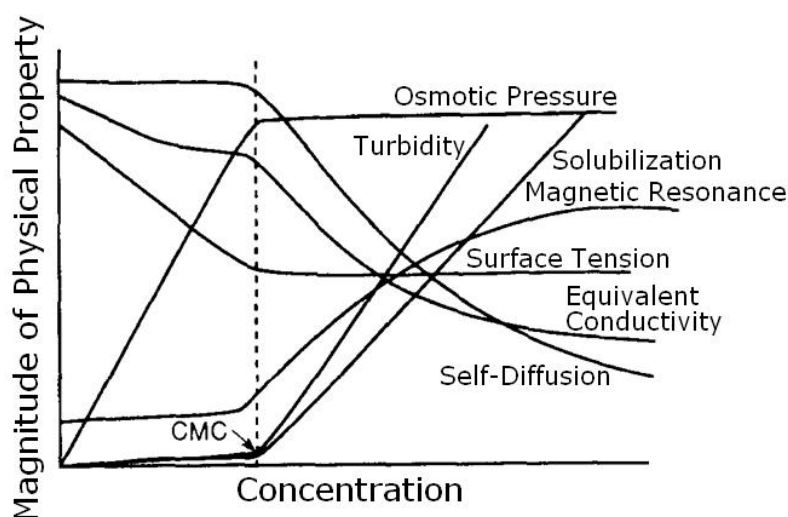
Figure 1.5:   Effect of surfactant concentration on physical properties around the CMC [12].
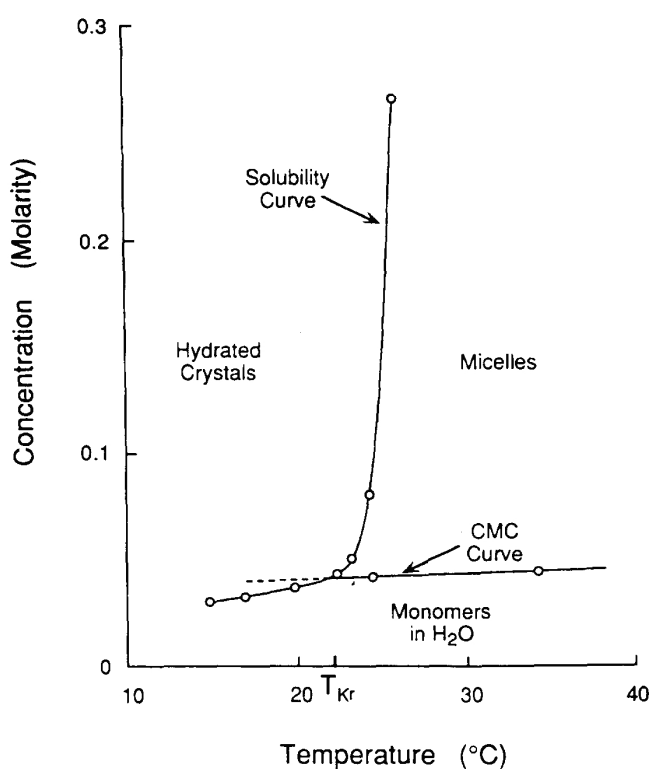

Figure 1.6: Representation of Krafft temperature.

1.5   Micellization

Micelles are the simplest and most thoroughly characterised self-organising structures. When surfactants associate into micelles, they form a liquid-like aggregate. No obvious mechanism leads to a specific aggregation number, as seem with micelles, therefore it is natural to describe the association in terms of a stepwise addition of a monomer, S to the aggregate, S_{n-1}, as in,

$$S + S_{n-1} \rightleftharpoons S_n.$$
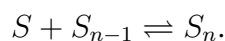
If we assume that interactions between aggregates are negligible, then the equilibrium of the stepwise addition can be given by equation 1.5.1.

$$K_n = \frac{[S_n]}{[S][S_{n-1}]} \tag{1.5.1}$$

In situations that involve aggregation numbers of order 100, technically we need a very large number of equilibrium constants. Therefore, we obtain more useful values and understanding with some simplified models. The three main models used are:

The **isodesmic model** assumes that the K_n is independent of n. This model does well to describe some dyes, but does not capture the cooperative nature associated with amphiphilic aggregation.

The **phase separation model** approximates aggregation as a phase separation process in which the activity of the monomer remains constant above the CMC. It is useful to capture the start mechanism of aggregation, but not the stop.

The **closed-association model** assumes that one aggregation number, N, dominates and relates the free energy of micellization to the measured CMC. This model captures both the start and the stop cooperative features associated with aggregation processes.

1.5.1 Isodesmic Model

The isodesmic model assumes that K_n is independent of n. In this case it can be shown that regardless of either the total concentration or of K that $[S]K < 1$. The aggregate distribution function can be given by equation 1.5.2, which decays exponentially with $[S_1] > [S_2] > [S_3]$.

$$f(n) = \frac{[S_n]}{\sum\limits_{n=1}^{\infty} [S_n]} \tag{1.5.2}$$

The concentration of each aggregate size can be determined from knowledge of the monomer concentration and the equilibrium constant, equation 1.5.3, with the free energy of each monomer addition given by equation 1.5.4.

$$[S_n] = K^{n-1}[S] \tag{1.5.3}$$

$$\Delta G = -RT \ln K \tag{1.5.4}$$

The isodesmic model describes the association of some dyes in aqueous solution quite well [, dyemodel] but is less successful as a description of the formation of micelles as it does not show an abrupt onset in a narrow concentration range that typifies micelle formation. This means that this model cannot predict a CMC.

1.5.2 Phase Separation Model

Micelle formation has several features in common with the formation of a separate liquid phase. In terms of the equilibrium described by equation 1.5.1 the phase separation model assumes that aggregates with large n dominate all others except monomers. This assumption implies strong cooperativity because, once aggregation begins it becomes more and

more favourable to add another monomer until a large aggregation number is reached. The surfactant possesses a chemical potential, $\mu\left(\text{agg}\right)$, in the aggregate and a different chemical potential, $\mu\left(\text{sol}\right)$, in the solvent. When equation 1.5.5 is true, the monomers and aggregates coexist in equilibrium and $[S]$ is the CMC (neglecting other oligomers).

$$\mu\left(\text{agg}\right) = \mu\left(\text{sol}\right) + RT \ln\left[S\right] \tag{1.5.5}$$

The standard free energy of micelle formation, ΔG_{mic}, represents the standard free energy difference between a monomer in the micelle and the standard chemical potential in dilute solution, equation 1.5.6.

$$\Delta G_{mic} = \mu\left(\text{agg}\right) - \mu\left(\text{sol}\right) = RT \ln\left[\text{CMC}\right] \tag{1.5.6}$$

This method gives a very useful approximation for obtaining the free energy of micelle formation, but does not capture all the essential features of micelle formation. Although it describes the start mechanism it does not describe the stop mechanism.

1.5.3   Closed-Association Model

If it is assumed that one aggregation number, N, dominates for the aggregate sizes, and there only exists these aggregates and monomers, then the association can be simplified to,

$$N\,S \rightleftharpoons S_N,$$
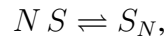
producing the equilibrium constant as equation 1.5.7.

$$K_N = \frac{[S_N]}{[S]^N} \tag{1.5.7}$$

The total surfactant concentration can be expressed as equation 1.5.8.

$$[S]_T = N\left[S_N\right] + [S] = NK_N\left[S\right]^N + [S] \tag{1.5.8}$$

Experiments identify the CMC as the concentration at which surfactant preferentially starts to enter the aggregate. A good measure of this concentration point is where an added monomer is as likely to enter the aggregate as to remain in solution, i.e. equation 1.5.9.

$$\left.\frac{\partial\,N\left[S_N\right]}{\partial\left[S\right]_T}\right|_{CMC} = \left.\frac{\partial\left[S\right]}{\partial\left[S\right]_T}\right|_{CMC} = 0.5 \tag{1.5.9}$$

This means that the concentration of the surfactant in solution at the CMC in terms of the aggregate size and the association constant, equation 1.5.10, can be solved.

$$\left.\frac{\partial\left[S\right]_T}{\partial\left[S\right]}\right|_{CMC} = 2$$
$$[S]_{CMC}^{N-1} = \left(N^2 K_N\right)^{-1} \tag{1.5.10}$$

As the CMC refers to the total surfactant concentration equation 1.5.10 can be combined with equation 1.5.8 to give the CMC value, equation 1.5.11.

$$CMC = [S]_{CMC}\left(1 + N^{-1}\right) = \left(N^2 K_N\right)^{-1/(N-1)}\left(1 + N^{-1}\right) \tag{1.5.11}$$

From equation 1.5.11 it can be seen that the amount of micellized surfactant at the CMC is $[S]/N$, which becomes more and more negligible as the value of N increases.

From equation 1.5.8 a solution for the fraction of surfactant entering the aggregates on addition of surfactant can be calculated, equation 1.5.12.

$$\frac{\partial N\,[S_N]}{\partial\,[S]_T} = \frac{N^2\,[S_N]}{\left(\dfrac{[S_N]}{K_N}\right)^{1/N} + N^2\,[S_N]} \tag{1.5.12}$$

Figure 1.7 shows the change in the fraction of surfactant entering the aggregates for different values of the aggregation number, N. The larger the values of N the more abruptly the derivative $\partial N\,[S_N]\,/\partial\,[S]_T$ changes from low concentration to higher concentration. This means that for high values of N the CMC is a more easily defined point, with a discontinuity in the derivative at the CMC when $N \to \infty$.
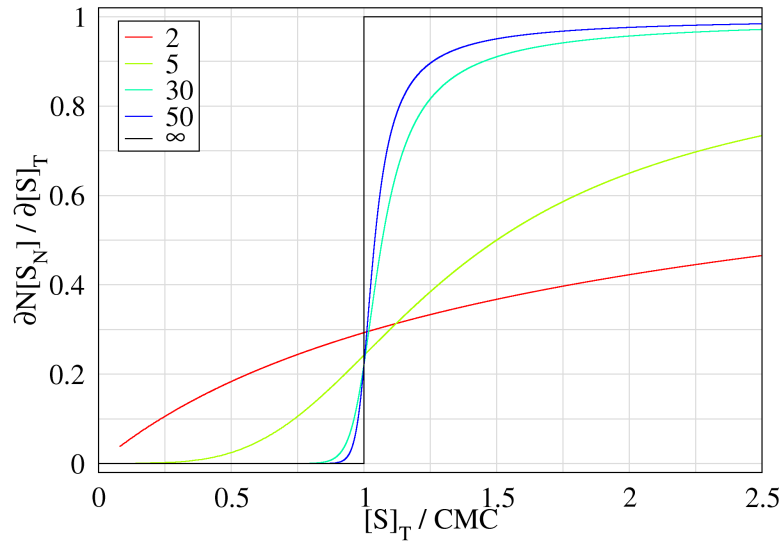
Figure 1.7: Variation of the fraction of added surfactant entering micelles for different aggregation numbers, N.

As in the isodesmic model the free energy for the aggregate formation per mole of aggregates can be given by equation 1.5.13.

$$\Delta G = -RT \ln K_n = -RT \ln [S_N] + NRT \ln [S] \tag{1.5.13}$$

1.6 Liquid Crystals

Many soft matter systems have liquid crystal phases. These phases, as suggested by the name, are phases that are part way between a crystalline and a liquid state, exhibiting properties of both. Crystals are characterised by having long range positional and directional order in all three spacial dimensions; in a liquid this is not the case and molecules can simply diffuse freely and have no internal order, except for some loose correlation between neighbours. Crystals can support stress without significant deformation, while liquids deform and flow. Liquid crystals exhibit some of the positional and directional order of the crystals, but have molecular motion, usually anisotropic, and their properties under shear can vary between very little deformation to free flowing.

Liquid crystals can be thermotropic or lyotropic:

Thermotropic liquid crystals are liquid crystals that do not require a solvent (although a solvent can be present); the order-disorder phase transition is purely due to a

temperature change. These are usually organic compounds with a rigid polyaromatic section connected to a flexible alkyl chain. The liquid crystal order is often determined by anisotropic nature of the molecule and anisotropic intermolecular attraction that thus arises. It is the rigid polyaromatic section that will determine the liquid crystal structure: these can be classed into two broad groups: calamitic (long, narrow molecules) and discotic (disc-shaped molecules). These tend to form nematic, smectic and, columnar liquid crystals.

Lyotropic liquid crystals are formed on the dissolution of amphiphilic molecules in a solvent with much smaller molecules. This means that lyotropic liquid crystal phase transitions are driven not just by temperature but also by solute concentration. These are often produced from polymers that align together and are repulsed by the solvent or from surfactant micellar structures (as individual surfactant molecules are generally not large or rigid enough to form liquid crystals in the absence of solvent). Surfactant micelles can form lyotropic liquid crystal phases, which tend to form at higher surfactant concentrations. There are six classes of surfactant liquid crystal phases: lamellar, hexagonal, cubic, nematic, gel (all of which are well documented), and intermediates (which are not) [3].

1.6.1 Thermotropic Liquid Crystal Phases

Nematic Phase

One of the most common liquid crystal phases is the nematic, this is also the simplest liquid crystal phase. In a nematic phase, the calamitic or rod-shaped molecules have no positional order, but they self-align to have long-range directional order with their long axes roughly parallel [16], Figure 1.8. Thus, the molecules are free to flow and their center of mass positions are randomly distributed as in a liquid, but still maintain their long-range directional order. Most nematics are uniaxial: they have one axis that is longer and preferred, with the other two being equivalent (can be approximated as cylinders or rods). However, some liquid crystals are biaxial nematics, meaning that in addition to orienting their long axis, they also orient along a secondary axis [17]. Nematics have fluidity similar to that of ordinary (isotropic) liquids but they can be easily aligned by an external magnetic or electric field. Aligned nematics have the optical properties of uniaxial crystals and this makes them extremely useful in liquid crystal displays (LCD) [18].
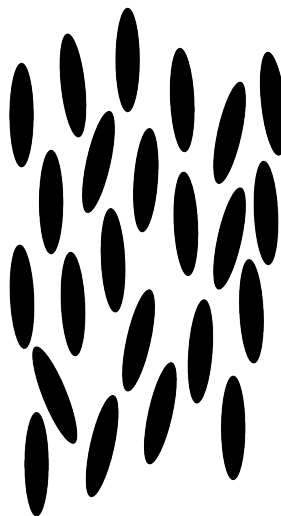

Figure 1.8: Schematic representation of a nematic phase liquid crystal.

As nematic liquid crystals are composed of rod-like molecules with the long axes of neighboring molecules aligned approximately to one another a dimensionless unit vector n called the director, is introduced to represent the direction of preferred orientation of molecules in the neighborhood of any point. Because there is no physical polarity along the director axis, n and $-n$ are fully equivalent [19]. The local nematic director, which is also the local optical axis, is given by the spatial and temporal average of the long molecular axes. A second rank symmetric traceless tensor order parameter is used to describe the orientational order of a nematic liquid crystal, although a scalar order parameter is

usually sufficient to describe uniaxial nematic liquid crystals. To make this quantitative, an orientational order parameter is usually defined based on the average of the second Legendre polynomial, equation 1.6.1.

$$S = \langle P_2 \left(\cos\theta \right) \rangle = \left\langle \frac{3\cos^2\theta - 1}{2} \right\rangle \tag{1.6.1}$$

θ is the angle between the liquid crystal molecular axis and the local director (which is the 'preferred direction' in a volume element of a liquid crystal sample, also representing its local optical axis). The brackets denote both a temporal and spatial average. This definition is convenient, since for a completely random and isotropic sample, $S = 0$, whereas for a perfectly aligned sample $S = 1$. For a typical liquid crystal sample, S is on the order of 0.3 to 0.8, and generally decreases as the temperature is raised. A sharp drop of the order parameter to 0 is observed when the system undergoes a phase transition from an liquid crystal phase into the isotropic phase [20]. The order parameter can be measured experimentally in a number of ways, e.g. diamagnetism, birefringence, Raman scattering, or NMR [21].

Smectic Phase

The smectic phase differs from the nematic phase in the fact that as well as the molecules being aligned they are also organized into layers. As the smectic phases, which are found at lower temperatures than the nematic, form well-defined layers, these can slide over one another. There are many different smectic phases, all characterized by different types and degrees of positional and orientational order [19], Table 1.3.

Chiral phases

The chiral nematic phase, N*, (also called the cholesteric phase) and the smectic C* phase exhibit chirality (handedness). This phase is often called the cholesteric phase because it was first observed for cholesterol derivatives. Only chiral molecules (i.e., those that have no internal planes of symmetry) can give rise to such a phase. This phase exhibits a twisting of the molecules perpendicular to the director, with the molecular axis parallel to the director. The finite twist angle between adjacent molecules is due to their asymmetric packing, which results in longer-range chiral order, Figure 1.9(a). In the smectic C* phase, the molecules have positional ordering in a layered structure (as in the other smectic phases), with the molecules tilted by a finite angle with respect to the layer normal, Figure 1.9(b).

The chiral pitch, p, refers to the distance over which the liquid crystal molecules undergo a full $360°$ twist (but note that the structure of the chiral nematic phase repeats itself every half-pitch, since in this phase directors at $0°$ and $\pm 180°$ are equivalent). The pitch typically changes when the temperature is altered or when other molecules are added to the liquid crystal host (an achiral liquid crystal host material will form a chiral phase if doped with a chiral material), allowing the pitch of a given material to be tuned accordingly. In some liquid crystal systems, the pitch is of the same order as the wavelength of visible light. This causes these systems to exhibit unique optical properties, such as Bragg reflection and low-threshold laser emission [22], and these properties are exploited in a number of optical applications [23].
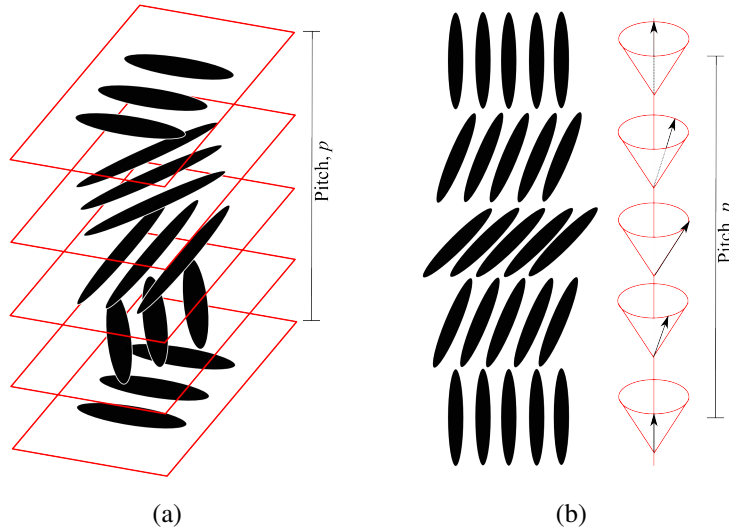
(a)   (b)

Figure 1.9:   Schematic representation of the (a) chiral nematic and the (b) smectic C* phases.

Blue phases

Blue phases are liquid crystal phases that appear in the temperature range between a chiral nematic phase and an isotropic liquid phase. Blue phases have a regular three-dimensional cubic structure of defects with lattice periods of several hundred nanometers, and thus they exhibit selective Bragg reflections in the wavelength range of visible light corresponding to the cubic lattice, Figure 1.10.

(a)   (b)
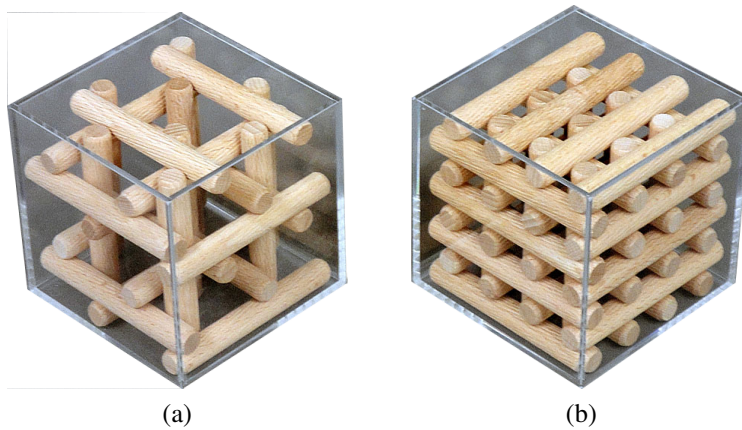
Figure 1.10: Schematic representation of the blue phase (a) type I and (b) type II.

Although blue phases are of interest for fast light modulators or tunable photonic crystals, they exist in a very narrow temperature range, usually less than a few kelvin. Recently the stabilization of blue phases over a temperature range of more than 60 K including room temperature (260-326 K) has been demonstrated [24].

Discotic phases

Disk-shaped liquid crystal molecules can orient themselves in a layer-like fashion known as the discotic nematic phase, which can be chiral id the disks are chiral. The disks can also pack into ordered columns (or stacks), called a discotic columnar [25]. The columns

themselves may be organized into rectangular or hexagonal arrays, Figure 1.11. In the simplest case the short axes of the molecules lie parallel to the axis of the column and the columns are randomly distributed in space. More complicated discotic phases exist, where the short molecular axes lie at an angle to the column and translational order exists between the columns, analogous to the more complicated smectic phases.
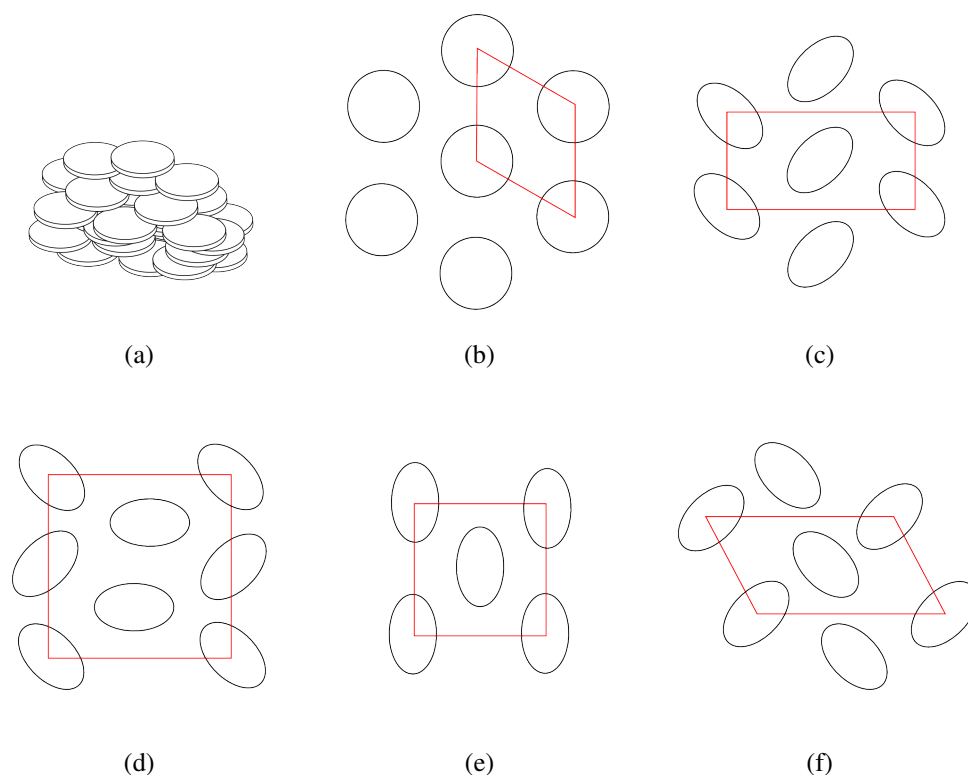

Figure 1.11: Schematic representation of the discotic phases (a) nematic N_D, (b) hexagonal D_{ho}, (c) rectangular $D_{rd(P2_{1/a})}$, (d) rectangular $D_{rd(P2/a)}$, (e) rectangular $D_{rd(2C/m)}$, and (f) oblique D_{ob}.

Other Thermotropic Phases

Bent-core molecules can form 'banana' phase liquid crystals [26]. Some of these phases are chiral although the molecules forming them are achiral. The chirallity is caused by the bend in the molecules being a fixed angle and direction.

Some high molecular mass polymers, liquid crystalline polymers, can also form liquid crystal phases [25]. These fall into two categories depending on where the mesogenic part of the molecule is located. If the mesogenic unit is contained within the main polymer chain then it is termed a main chain liquid crystal polymer. If it is attached to a side chain of the polymer then it is termed a side chain liquid crystal polymer. As well as depending on the nature of the mesogenic core, the mesophases formed by these materials are dependent on the flexibility of the polymer backbone and the side chains.

Closely related to liquid crystalline polymers are dendritic liquid crystals [27, 28]. These molecules consist of a central core with the mesogenic units attached to flexible spacers that radiate out from the core.

1.6.2   Lyotropic Liquid Crystal Phases

Lamellar Phase

The most common surfactant liquid crystal structure is the lamellar phase. The lamellar phase is built up of bilayers of surfactant separated by solvent, Figure 1.12. The thickness of the bilayer generally varies from about 1 to 1.9 times the all-*trans* alkyl chain length, while the thickness of the water layers varies over a much larger range of around 8 to 200 Å [3]. Depending on the surfactant, the bilayer can range from being stiff and planar to being very flexible. The lamellar phase does not normally flow under gravity but can have a relatively low apparent viscosity. The lamellar phase is also birefringent and can be easily identified from its optical properties, i.e. oily streaks and Maltese crosses [29]. X-ray diffraction studies show sharp reflections in the ratio $1 : 1/2 : 1/3 \ldots$ due to the repeating nature of the structure with the repeat spacings being the sum of the water and the alkyl chain layers.
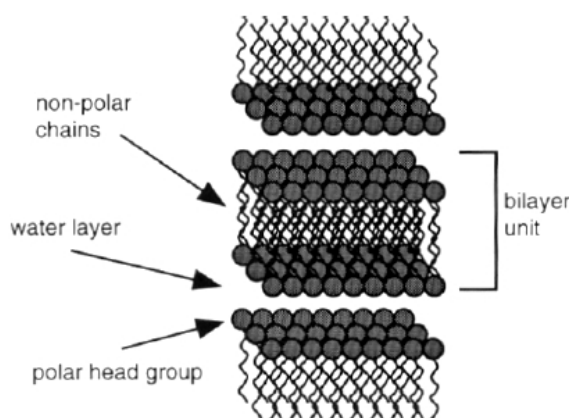
Figure 1.12: Schematic representation of a lamellar phase liquid crystal.

The lamellar phase is generally considered to play a central role in the evolution of the other liquid crystal phases, as their geometric features are relatively small changes to the lamellar structure [30].

Hexagonal Phases

The next most common liquid crystal type is the hexagonal phase, which itself consists of two types: "normal hexagonal" and "reversed hexagonal". The normal phase is water continuous, while the reversed phase is alkyl chain continuous. Both these phases consist of structures similar to cylindrical-type micelles but closely packed together, Figure 1.13. Both hexagonal phases usually have a relatively high apparent viscosity and do not flow easily. X-ray diffraction studies of both types show sharp reflections in the ratio $1 : 1/\sqrt{3} : 1/\sqrt{4} : 1/\sqrt{7} : 1/\sqrt{12} \ldots$ due to the nature of the cylinders.

Cubic Phases

Cubic phase liquid crystals encompass the broadest range of liquid crystals as they can be based around one of several cubic lattices (primitive, face-centered, or body-centered) and can be either made up of small micelles or three-dimensional bicontinuous aggregates, both in the normal and reversed arrangements. It is still partially unclear which types of cubic structures can occur for the different aggregates [31]. The two different classes of the cubic phase (micellar and bicontinuous) can be distinguished from each other by
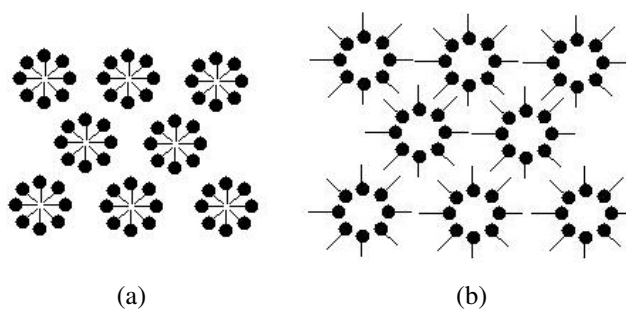
(a)   (b)

Figure 1.13: Schematic representation of the (a) normal and the (b) reverse hexagonal phases.

their locations in the phase diagram. Micellar cubic phases are found between micellar solutions and hexagonal phases, while the bicontinuous cubic phases are found between hexagonal and lamellar phases. The factors determining which cubic structure occurs are not understood [3].

Nematic phases

Surfactant nematic phase liquid crystals are less common than the other types of surfactant liquid crystal. If they do form for a particular system, they tend to form in the region between the micellar and hexagonal phases or the micellar and lamellar phases. There are two types of nematic liquid crystal for surfactants: one type is thought to be composed of small cylindrical micelles related to the hexagonal phase and the other is composed of planar disc type micelles related to the lamellar phase [32]. These phases are often found for short-chain surfactants and tend to have a low viscosity [3].

Gel Phases

The gel phase is similar to the lamellar phase in that it is also made up of surfactant layers. In this phase the surfactant layers are fixed in a rigid mostly all-*trans* configuration and the water phase is in a "liquid-like" state. There are three common types of gel phase; the first is the normal type where the surfactant layer is approximately twice the alkyl chain length [33], the second is the tilted type where the larger head groups force the alkyl chains to angle to pack efficiently [34], and the third is the inter-digitated type where the surfactant layer is closer to the alkyl chain length [35] (Figure 1.14).

    The gel phase is normally formed upon cooling of a lamellar phase through the transition temperature. The rigid alkyl chains give rise to a high apparent viscosity.

Intermediate Phases

Intermediate phases cover any other type of structure that has been reported for any surfactant system. These phases, as the name suggests, seem to be structures that appear on the boundaries between two of the other phases and contain properties of both structures. The observed structures can be broadly divided into three types: rectangular ribbon structures, layered mesh structures, and bicontinuous structures that do not have cubic symmetry [36]. Ribbon structures can be considered as a distorted hexagonal phase, mesh phases are distorted lamellar phases where the surfactant layers have water filled defects, and the bicontinuous phases are distorted cubic structures.
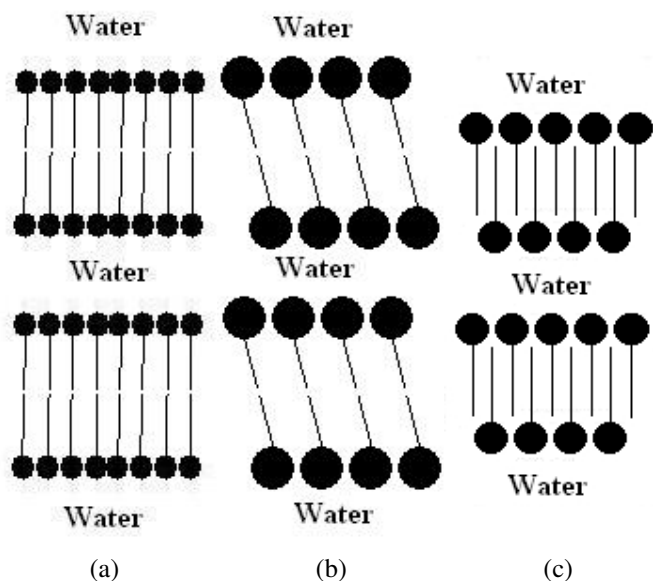
Figure 1.14:   Schematic representation of the (a) normal, the (b) tilted and (c) inter-digitated gel phases.

1.6.3   Phase Behaviour

Throughout the literature there is not a consistent system used to refer to the different liquid crystal phases. However some notations are more common than others, Table 1.4.

As mentioned in Section 1.4.2 the micelle shape is determined by the molecular structure of the surfactants. However, there is a critical volume fraction (i.e. concentration) of surfactant above which these individual micelles cannot be supported. This leads to the disordered solutions (micellar solutions) becoming ordered (liquid crystals). In addition, there is a maximum volume fraction of ordered micelles before they cannot fit together; e.g. spheres and cylinders cannot be packed together, no matter how tight, to totally fill a volume. (The existence of the micellar cubic phase also depends on the size and stability of the micelles. Micelles with a large energy barrier to size change will tend to increase in number rather than in size, which encourages packing of the micelles. However, if the stable micelle size is small there will be a large entropic barrier to overcome to form an ordered micellar structure, which will encourage the disordered solution to prevail until a higher concentration favours a larger aggregate phase, e.g. hexagonal or lamellar.) When all the available volume is occupied for a given shape, then the only way more surfactant can be accommodated is with a change of structure towards less curvature [37]. For the normal surfactant structure types these phase changes can be summarised by Figure 1.15 (modified from Mitchell *et al.* (1983) [37]).

In the phase diagram not all the phases may take part: e.g. the nematic and bicontinuous cubic phases may not occur, and there also may be added intermediate phases that are in a similar region to the bicontinuous cubic phase. The gel phase may exist in the lamellar region at lower temperatures.

The sequence for the reversed phase surfactant structures is much more complicated than for the normal phases due to less radius limitations on micellar shapes; water on the inside could swell almost indefinitely until packing limits are reached. This means that these phase changes are not yet understood in terms of the surfactant structure [3].
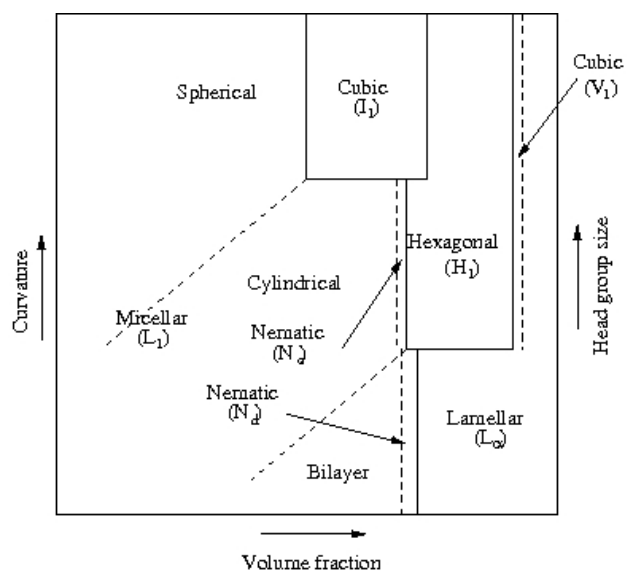
Figure 1.15: Schematic representation of the phase changes for the normal surfactant structure types.

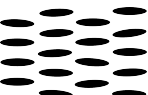| Group	Side	Plan
A		
B		
C		
D		Molecules arrange in a micellar type shape and then pack into a body centred cubic phase
E		
F		
G		
H		
I		
J		
K		
L		

Table 1.3: Smectic phases.

Table 1.4: Notations used for the common phases.

Phase structure	Notation
Lamellar	L_α
Hexagonal	H_1
Reversed hexagonal	H_2
Micellar cubic	I_1
Reversed micellar cubic	I_2
Bicontinuous cubic	V_1
Reversed bicontinuous cubic	V_2
Nematic	N
Cylindrical Nematic	N_c
Discotic Nematic	N_D
Chiral Nematic	N*
Smectic	S
Chiral smectic C	C*
Gel	L_β
Micellar	L_1
Reversed micellar	L_2
Sponge phase	L_3
Reversed sponge phase	L_4
Vesicular	V
Microemulsion	L
Water	W

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