

Chapter 1

INTRODUCTION

It has been known for a long time that amphiphilic molecules like soaps, oils and phospholipids spread spontaneously at the air water interface to form monomolecular films. The effect of calming of rough seas by the addition of small quantities of oil was known to the ancients. In 1774 Benjamin Franklin [1] carried out a semi-quantitative experiment by spreading a teaspoonful (~ 2.5 ml) of olive oil on water. He estimated the area covered by the oil to be half an acre. The first surface manometric studies were carried out by Agnes Pockels [2] who studied the effects of soap and mastic on the surface tension of water. In 1899, Lord Rayleigh [3] proposed that such a film consisted of a single layer of molecules which were assumed to be spherical in shape. The monomolecular nature of the films was established independently by Langmuir and Harkins [4]. They also recognised the importance of the amphiphilic nature of the molecules in monolayer formation. In the literature these monomolecular films at the air-water interface are called *Langmuir Monolayers*. In collaboration with Katherine Burr Blodgett, Langmuir [5] proposed a method of transferring the monolayer from the water surface to a solid substrate. These transferred films are called Langmuir Blodgett (LB) films. In recent years there has been an explosive growth [6, 7, 8, 9, 10, 11] in the studies of Langmuir monolayers and LB films, mainly due to a rapid increase in their technological applications. LB films are useful in the construction of molecular devices for electronics, opto-electronics etc. Langmuir monolayers are useful in the study of biological systems like cell membranes, respiratory systems, bone

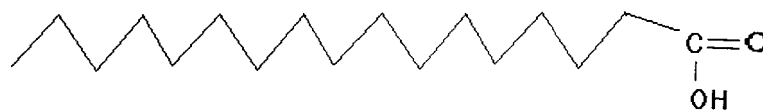


Figure 1.1 Molecular structure of Stearic Acid (SA).

formation etc.

1.1 Amphiphilic Molecules

To understand the properties of amphiphilic molecules, one has to begin by comparing the solubility of organic compounds in water and hydrocarbons. Water is a strongly polar solvent (dielectric constant $\epsilon \sim 80$) and readily dissolves substances that dissociate into ions *e.g.* alcohols, short chain organic acids and their salts. The resulting ions interact with the H^+ and OH^- groups already present in water. This is the reason for their high solubility. These compounds are called hydrophilic *i.e.* water loving.

There is another class of organic compounds like hydrocarbons that dissolve in nonpolar solvents like carbon tetrachloride, hexane or other hydrocarbons. The Coulomb interaction is not of much importance in this dissolution and the dispersive forces are not very sensitive to details of molecular structure. Hence the dissolved molecules replace the solvent molecules. These molecules do not dissolve in water as their incorporation breaks the hydrogen bonds between the water molecules without any energy compensation. These molecules are called hydrophobic *i.e.* water fearing.

Apart from these two classes, there is also another class of interesting molecules

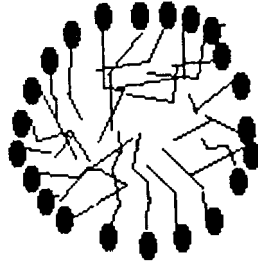


Figure 1.2. Schematic diagram of a micelle. The hydrophilic headgroups are represented by black circles, and the hydrophobic chains by the lines.

that have both these parts incorporated in them. For example, a molecule of stearic acid has a hydrophilic polar head, the COOH group, and a hydrophobic hydrocarbon tail $C_{17}H_{35}$ (Fig 1.1). These molecules are called amphiphilic i.e. dual loving. On placing such a molecule on water, the polar head gets attracted to water, while the tail tries to be out of water. This way the headgroup is in water while the tail is in air, forming a monomolecular film at the surface. Thus, a compromise is reached where the molecule is forced to stay at the air water interface.

A different kind of monolayer, called a Gibb's monolayer is formed by molecules in which the hydrophilic group is stronger than the hydrophobic chain. In such cases, some of the molecules remain at the interface, while the remaining go into the substrate forming closed structures called micelles, shown in Fig 1.2. These monolayers are also called unstable monolayers as they are inherently unstable with the molecules having a tendency to go into the subphase. The Gibb's monolayers do show some properties similar to the Langmuir monolayers [12].

Monolayer forming substances can be classified into two broad classes [6], namely the monomeric and the polymeric. The monomeric amphiphiles include

substances like long chain fatty acids, alcohols, amines etc, which have the requisite hydrophobic and hydrophilic parts. If we choose a short chain fatty acid or alcohol, like acetic acid or ethyl alcohol, the molecules dissolve in water, as the hydrophilic $-\text{COOH}$ or $-\text{OH}$ group is very strong compared to the hydrophobic chain, which is very short, and hence weak. For a chain length of 4 or 5 carbon atoms, (valeric acid or amyl alcohol) the solubility comes down to around 3g per 100ml of water. Compounds of the homologous series with 10 to 12 carbon atoms in the chain are practically insoluble in water. These materials, with strong hydrophilic groups and hydrophobic chains form stable monomolecular films or Langmuir monolayers. It may be remembered in this context that groups like $-\text{CH}_2\text{OCH}_3$ and $-\text{COOCH}_3$ have a weak affinity for water. A strong attraction is provided by groups like $-\text{CH}_2\text{OH}$, $-\text{COOH}$, $-\text{CN}$ etc. Groups like $-\text{SO}_3^-$ or $-\text{OSO}_3^-$ provide a very strong attraction to water.

The criteria for monolayer formation with polymeric materials are somewhat different. Here again, the presence of hydrophilic groups is needed, but a strong hydrophobic group is not required. It is sufficient if the monomer units making up the polymer have a finite free energy of adsorption from the bulk solution to the surface so that a stable monolayer is formed. Many liquid crystal forming polymers form monolayers [13] under suitable conditions. Many proteins also form monolayers [14].

1.2 Properties of Monolayers

Langmuir monolayers resemble two dimensional (2D) systems and show very intricate phase behaviour. The phase behaviour of monolayer systems is described in details later. This phase behaviour, with many liquid like phases is interesting in view of the Kosterlitz – Thouless [15, 16] theory of dislocation mediated melting in 2D. These monolayers are one of the easiest to form 2D systems. Also, many liquid crystal forming molecules are amphiphilic in nature. The monolayers of some of these molecules transform into three dimensional (3D) structures at

the air – water interface [17, 18, 19]. This smooth reversible transition from a 2D to a 3D system is of importance.

Langmuir monolayers are of considerable industrial importance. A monolayer spread on the water surface reduces the evaporation rate dramatically. This property can be used to conserve water in reservoirs in arid conditions. Monolayers are also of biological importance as they resemble biological membranes and can be used to simulate them. The human lung uses amphiphiles to reduce surface tension of alveolar fluid [14], which is necessary for breathing. In case of a deficiency of these amphiphiles, the patient has to be given a substitute. In order to prepare a substitute, it is important to understand the workings of all the components present in this amphiphile. This makes monolayer studies of such compounds important. The study of monolayers of polypeptides like salmon calcitonin is useful in understanding its use in bone formation and have implications in the treatment of osteopathies. Langmuir monolayers can also be transferred onto solid substrates. This property is made use of in molecular electronics, as one can have a layer by layer controlled formation of films of desired molecules.

1.3 Phase Rule for Monolayers

The phase rule for a 2D film embedded in 3D systems was proposed by D. J. Crisp in 1949 [20]. According to this rule the number of degrees of freedom f for a 2D film is given by

$$f = C^B + C^S - P^B - q + 3; \quad (1.1)$$

where C^B = number of components in bulk;

C^S = no of components confined to the interface;

P^B = number of bulk phases; and

q = number of different phases of the monolayer in equilibrium.

For a single component monolayer at the air-water interface, $C^B = 2$, (air and

water) $C^S = 1$, $P^B = 2$ (gas and liquid). Hence we get,

$$f = 4 - q. \quad (1.2)$$

If $q = 1$, $f = 3$. Thus if temperature and **3D** pressure be kept constant, there is a monovariant relation between surface pressure (τ) and area per molecule. If $q = 2$, *i.e.* there are two phases in equilibrium in the monolayer, then $f = 2$. In such a case, on fixing the temperature and **3D** pressure, we obtain an invariant τ . In other words, π is constant during the two phase co-existence.

In case of a two component monolayer, $C^S = 2$, hence we have

$$f = 5 - q. \quad (1.3)$$

In such a case, even on fixing the temperature and pressure, we get two degrees of freedom for a single phase monolayer and one degree of freedom for a two phase monolayer. Hence a three phase co-existence in a monolayer can also be supported at any temperature and bulk pressure.

1.4 Techniques used to study Monolayers

Langmuir monolayers are studied on a Langmuir trough. A typical trough contains a movable barrier to adjust the area over which the monolayer is spread and arrangements to measure the parameters of interest. A schematic diagram is given in Fig 1.3. The main techniques used in the studies are described here.

1.4.1 Surface Manometry

Surface pressure, the 2D equivalent of pressure, was first measured by Pockels [2] in her experiments on soap and mastic and the technique was later developed by Langmuir [4].

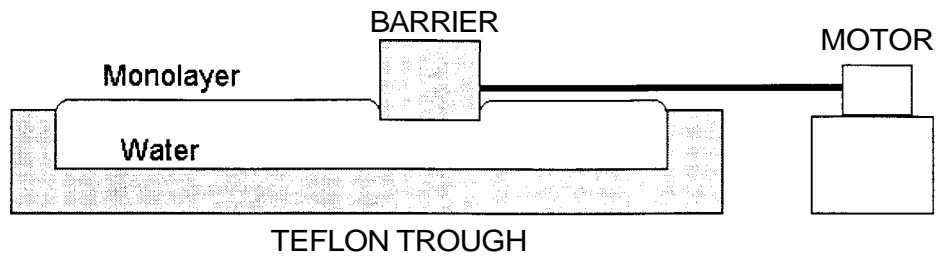


Figure 1.3. A schematic diagram of a Langmuir Trough.

The surface pressure π is defined by

$$\pi = \gamma_o - \gamma \quad (1.4)$$

where γ_o = surface tension of pure water

and γ = surface tension of water with the monolayer.

The measurement of π as a function of area per molecule (A), the inverse of surface molecular density, gives rich information about the phases and phase transitions in the monolayer. Measuring π as a function of A at constant temperature leads to $\pi - A$ isotherms. These isotherms provide information about the configurations of the molecules at the interface and are analogous to the $P - V$ diagrams for 3D systems. These isotherms were first studied by Pockels [2] and later by Langmuir [4]. A typical isotherm is shown in Fig 1.4.

According to the Crisp's phase rule (Equation 1.1), for a single component monolayer, we expect the isotherm to be flat during a two phase co-existence. A single phase monolayer should exhibit a region of steadily increasing π . These

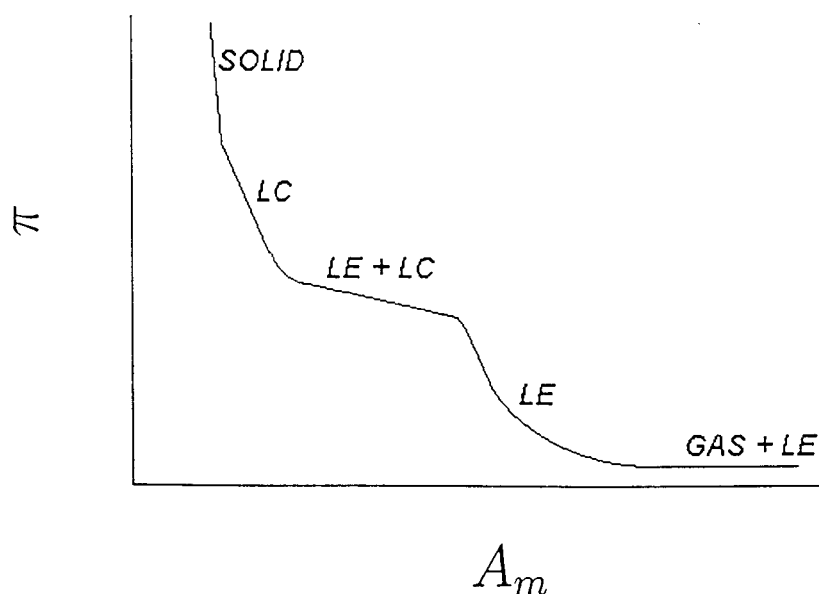


Figure 1.4. A typical isotherm of a monolayer showing different phases.

properties of the isotherm can be used to understand whether the monolayer is in a single phase or is exhibiting a two phase co-existence for a particular concentration. They also help us in understanding the order of phase transitions.

1.4.2 Epifluorescence Microscopy

Epifluorescence microscopy [7] is a relatively new and simple technique to visually observe the phases being formed as the monolayer is compressed or expanded. This technique was developed by Tschärner and McConnell [21] for the study of biological membranes. In this technique, a small amount ($\sim 1\%$ or less molar concentration) of a fluorescent dye, which is also amphiphilic, is added to the monolayer. The monolayer is directly observed under a fluorescence microscope. The different phases show different intensities under the microscope, depending on various factors. We will describe these in detail later. This technique allows a direct observation of the phases of the monolayer, pattern formation, domain shape, domain size, phase co-existence etc. This information can be used to estimate line tension of the domain boundaries and to determine the order of the

phase transitions. This method requires the doping of the monolayer with a dye. So it is not useful to study a pure monolayer, unless one studies the monolayer of a dye molecule [16].

1.4.3 Surface Potential Measurement

This technique [17] can be used to detect film homogeneity or the presence of more than one phase. The surface potential of the monolayer is the Volta potential change occurring on spreading the monolayer at the surface. In terms of the surface potential ΔV , the surface dipole moment can be written as

$$P_{\perp} = \frac{A_m \Delta V}{12\pi} \quad (1.5)$$

1.4.4 Brewster Angle Microscopy

This technique depends on the fact that the intensity of light reflected at the Brewster angle is strongly dependent on interfacial properties [22]. The intensity depends on (i) the thickness of the interface over which the refractive index changes, that is, the thickness of the monolayer, (ii) the roughness of the interface and (iii) the anisotropy of the monolayer. This method is another technique for a direct visualisation of different monolayer phases. This method can also be used to study pure monolayer systems.

1.4.5 Second Harmonic Generation

When an intense laser beam strikes a medium with a structure that is non-centrosymmetric, a radiation in the second harmonic of the laser frequency is generated [7]. This technique can be used to determine the presence or absence of a centre of symmetry in the monolayer. Since the subphase is isotropic, it has a centre of symmetry. So it does not produce any second harmonic signal. Hence the signal comes only from the monolayer.

1.4.6 X-ray Studies

This technique is used [7] to actually probe the molecular ordering at the surface, both within the plane of the monolayer and in the normal direction. This requires a very high intensity x - ray source since scattering from a monolayer is weak. Normally, a synchrotron x - radiation is used. This technique has been used to unravel a rich variety of phases which could not have been possible by other techniques.

1.4.7 Ellipsometry

In this technique [7], one measures the intensity and polarisation of a beam of light (laser) reflected from the monolayer. This can give information on molecular alignment and film thickness.

1.4.8 Viscosity Measurement

Surface viscosity can be demonstrated qualitatively by blowing on a liquid surface with a few dust particles floating about [11]. If the surface is clean, the particles are blown to the edge easily. If there is a monolayer present, the particles cannot be moved so easily, indicating a high surface viscosity. Surface viscosity of a monolayer has been measured by a variety of methods – Poiseuille flow, damping, rotation etc.

1.4.9 Miscibility Studies

This technique makes use of the fact that two compatible molecules which are in the same phase are miscible. So, an immiscibility of two domains indicates that they are in different phases [23]. This has been successfully used to distinguish 2D phases with different molecular ordering. This technique does not provide any information about the actual ordering of molecules in the phases.

1.5 Phase Transitions in Monolayers

The beauty of Langmuir monolayers is the exhibition of a wide variety of 2D phases. These phases have some similarities with the phases seen in bulk, yet there are peculiarities. The study of phase transitions in 2D is important in view of many interesting theories regarding 2D systems. For example, the Kosterlitz – Thouless [15, 16] theory of dislocation mediated melting. Some of the phases seen in Langmuir monolayers are shown schematically in Fig 1.5 [8]. We shall describe the relevant ones here.

1.5.1 Gas Phase

At a very low π *i.e.* at high A_m , there are no interactions between the molecules as they are very far apart at the interface. The monolayer behaves like an ideal 2D gas obeying the perfect gas equation

$$\pi A_m = kT \quad (1.6)$$

As in real gases, a decrease of A_m by compression of the monolayer causes the molecules to come close enough to interact with each other. Here one can use the 2D equivalent of van der Waal's equation

$$\left(\pi + \frac{a}{A_m^2}\right)(A_m - b) = kT \quad (1.7)$$

where a allows for molecular interactions and b accounts for excluded area.

1.5.2 Liquid Expanded Phase

A decrease in A_m results in a first order phase transition from the gas phase to a 2D isotropic liquid phase, called the liquid expanded (LE) phase. The co-existence region exhibits a constant π , indicating that the transition is first order. Here the molecules interact with each other strongly, but there is no orientational or positional order. The compressibility of the monolayer is given by

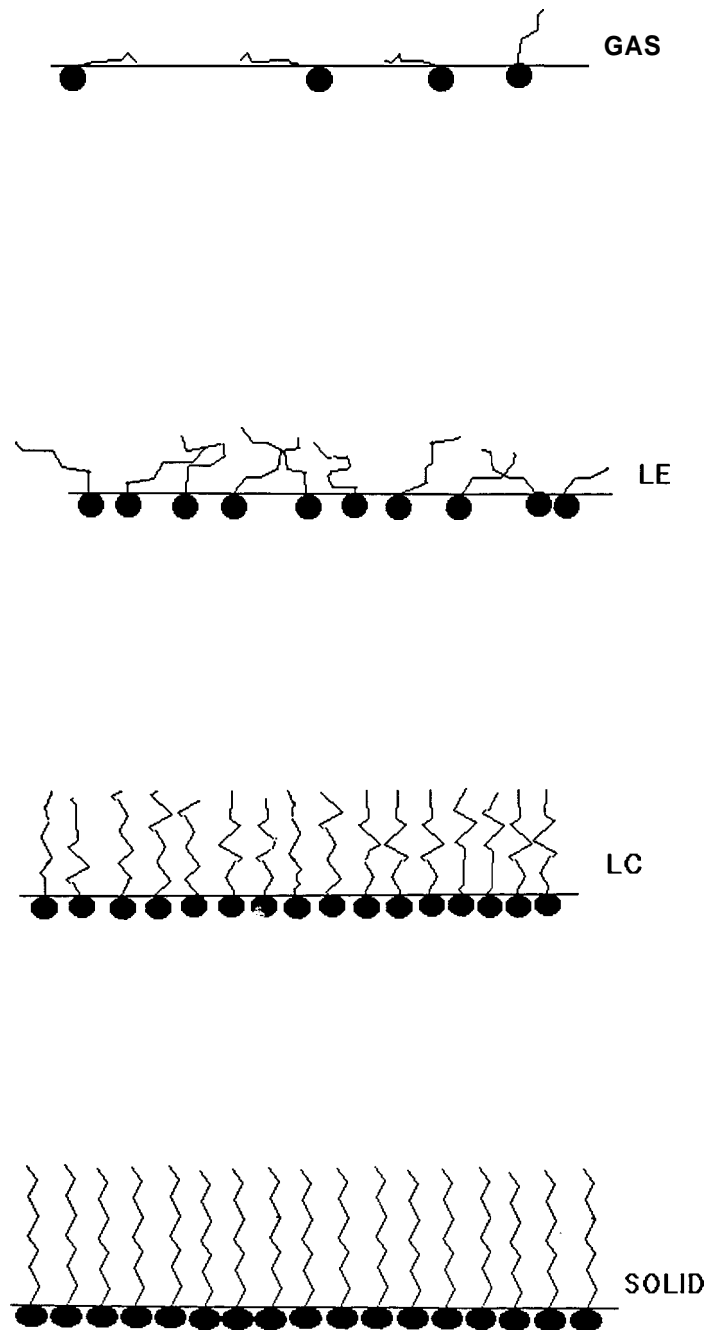


Figure 1.5. A schematic diagram of the molecular arrangement in the different phases of a Langmuir monolayer.

$$\delta = \frac{-1}{A_m} \left(\frac{\partial A_m}{\partial \pi} \right)_T \quad (1.8)$$

The compressibility in the LE phase is much lower than in the gas phase or in the gas – LE co-existence region.

1.5.3 Liquid Condensed Phase

When some monolayers are compressed even further, there is a transition from the LE phase into a high density liquid like phase, called the Liquid Condensed (LC) phase. Here the molecules still do not have any positional order, but the hydrocarbon tails are oriented on the average along the normal to the surface, which prompts some authors to call it a liquid crystalline phase [8]. The nature of the LE – LC phase transition is an object of curiosity and controversy [24]. The $\pi - A$, isotherm in the co-existence region is not horizontal. For sometime there was a speculation that the transition may be second order. It was also argued that the transition is first order but the coexistence curve is not horizontal due to impurities. Recently, epifluorescence, Brewster angle microscopy etc. have shown a clear two phase co-existence region, indicating that the transition is first order. The non-horizontal nature of the isotherm has been attributed to the formation of small surface micelles or *hemimicelles* in the monolayer at the nano length scale with aggregation numbers in the range 10 to 1000 [24, 25].

1.5.4 Solid Phase

A further compression of the monolayer transforms the LC phase into a 2D crystalline phase. The hydrocarbon tails lose their flexibility and there is positional order between neighbouring molecules. This positional order is only quasi long range, as a true long range positional order is not permitted in a 2D system. The occurrence of the solid phase is generally accompanied by a slope change in the isotherm, indicating a second order phase transition. The solid phase has an extremely low compressibility (about 1/10th of the LC phase) and hence a small

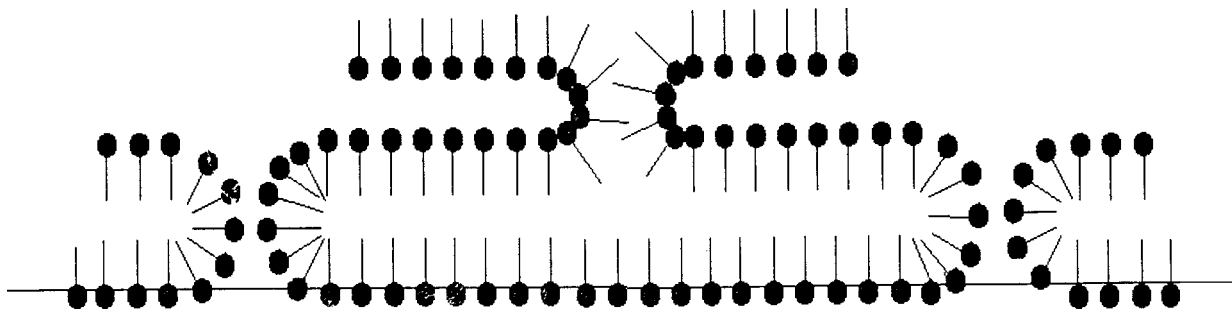


Figure 1.6. Schematic representation of monolayer collapse.

decrease in A_m leads to a large increase in π .

1.5.5 Collapsed State

If the monolayer in the solid state be compressed further, there is a sudden anomaly in the $\pi - A$ isotherm where π starts falling rapidly. This corresponds to the collapse of the monolayer where the molecules leave the interface and transform into a 3D phase. The collapse procedure is shown schematically in Fig 1.6 [9].

The collapse pressure π_{col} is the highest surface pressure to which a monolayer can be compressed without the molecules leaving the interface. It depends on the strength of the hydrophilic headgroup.

1.5.6 Phases of Fatty Acid Monolayers

The phase diagrams of monolayers of fatty acids, fatty alcohols and some esters have been studied in great detail using x - ray diffraction and miscibility studies [23, 26, 27, 28, 29]. Based on these studies, many new phases have been identified. At least 12 different phases have been detected and identified and there is a possibility of having as many as 17. The complete phase diagram is shown schematically in Fig 1.7.

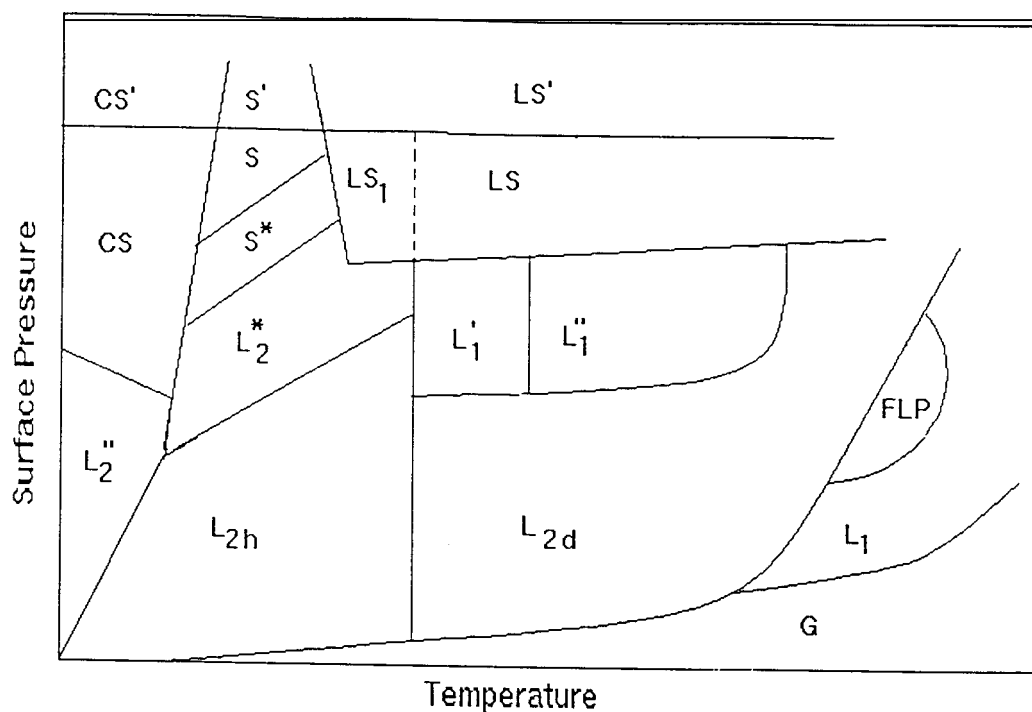


Figure 1.7. A schematic phase diagram of the monolayer of a fatty acid or alcohol. Here 17 different phases are indicated.

Varying the chain length of the molecules is equivalent to a shift in the temperature scale. Going from the acid to an ester, only the pressure scale is shifted by the change in the head group, the qualitative features of the phase diagram remain the same.

An elaborate nomenclature has been developed to describe these phases. According to this nomenclature, the LE phase is called the L_1 phase. The molecules have a 2D liquid like order. The hydrophobic chains point upwards, like in a smectic A liquid crystal layer.

The LC phase is further classified into phases called L_{2d} , L_{2h} , L'_2 and L''_2 , depending on the structure. In the L_{2d} and L_{2h} phases, there is a certain order in which every molecule is surrounded by six nearest neighbours (NN) which form a distorted hexagon. The unit cell is either primitive or centered. The molecules are tilted in the direction of a NN along the short axis. The L_{2d} and L_{2h} phases are different only in the sense of their distortions. The L'_2 phase again has a similar structure, except that the molecules are tilted towards the next NN. In

the L_2'' phase, the molecules are tilted in a direction intermediate between the NN and the next NN.

The solid phase is subdivided into LS, S, S', S*, CS and CS' phases, depending on the molecular order and the degree of crystalline order. In all these phases, the chain orientation is vertical. In the LS phase, the molecules are hexagonally close packed. There is a distortion in the case of the S and CS phase, and the unit cell represents a distorted rectangle. The S and CS phases are different in the range over which the positional correlation decays. The S', S* and CS' phases are modified forms of the S and CS phases. FLP is the fluid lamellar phase [30].

In this thesis, the traditional nomenclature of LE, LC and solid, which is sufficient to understand the work, has been used. Also, since the work is based on surface manometry and microscopy studies, it is not possible to detect the subtle structural differences of the various phases which is required to correctly identify all the phases in detail.

1.6 Monolayers of Liquid Crystal Forming Molecules

Many liquid crystalline compounds are amphiphilic and they form Langmuir monolayers [18, 19, 31]. The study of such monolayers is interesting as one can investigate whether there is a correlation between the phases seen in bulk and the phases seen in the monolayer. On compression, many of these monolayers do not collapse, instead they smoothly transform into 3D ordered structures [17, 18, 19, 32, 33].

1.6.1 Liquid Crystals

In order to appreciate the study of monolayers of liquid crystals, it is necessary to have a background of the properties of liquid crystals. We briefly describe liquid crystals here. Some organic compounds exhibit a variety of phases between the positionally and orientationally ordered crystalline phase and the isotropic liquid

phase. These intermediate phases are called *plastic crystals* when the positional order is retained and the orientational order is lost and *liquid crystals* when the orientational order is retained but the positional order is partly or totally lost. Liquid crystals possess both liquid like and crystalline properties and are formed of molecules that are geometrically anisotropic, either rod-like or disk-like in shape. Phase transitions in these materials occur either with changes in temperature or concentration in an appropriate solvent, giving rise to *thermotropic* or *lyotropic* liquid crystals respectively. Here we will be dealing with thermotropic liquid crystals only.

Many different liquid crystalline phases [34] are recognised depending on positional and orientational order in the medium. Here we take a look at the phases that are relevant to this thesis.

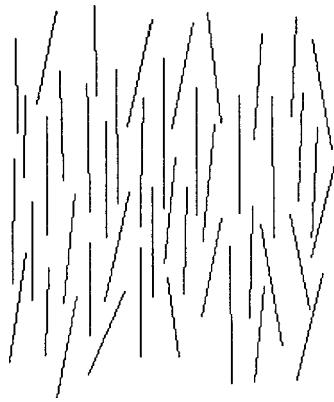
a) Nematic: This is the simplest liquid crystal phase. It is a fluid in which the molecules have orientational order and totally lack positional order. Here we describe molecular order by means of an apolar unit vector called the director. In case of rod-like molecules, the director points along the average orientation of the long axis of the molecules. For disk-like molecules, it points along the average orientation of the normal to the molecular plane. A schematic diagram of the nematic phase with rod-like molecules is shown in Fig 1.8 (a). This phase exhibits a characteristic schlieren texture under a polarising microscope.

b) Smectic A: In this phase there is a layering arrangement of the molecules, but no positional order within the layers. The director is parallel to the layer normal, as shown in Fig 1.8(b).

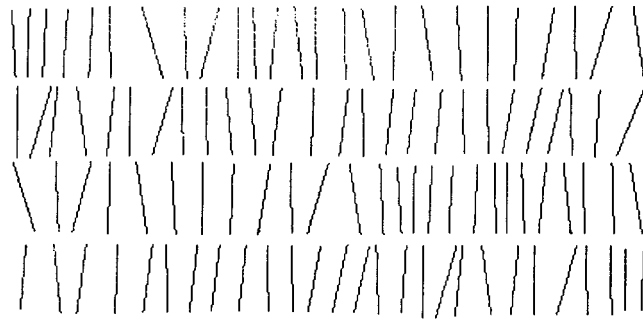
c) Smectic C: This phase is similar to the Smectic A, except that here the molecules are tilted at a uniform angle to the layer normal (Fig 1.8(c)), *i.e.* the director is inclined to the layer normal.

Apart from the phases mentioned above, there are many more liquid crystalline phases, known as cholesteric, smectic C*, discotic etc.

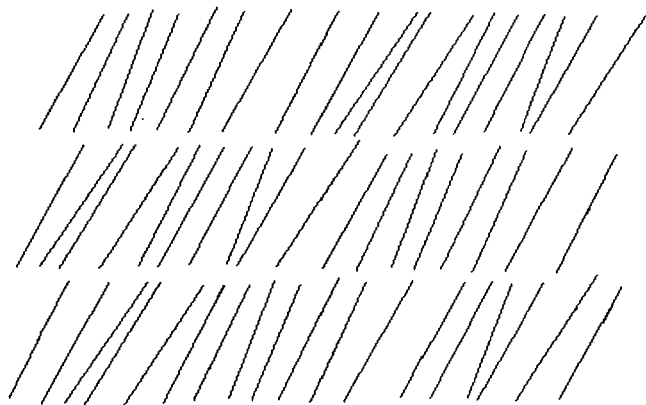
The Langmuir monolayers of liquid crystal forming molecules are interest-



(a)



(b)



(c)

Figure 1.8. Schematic representation of different liquid crystal phases. (a) Nematic, (b) Smectic A and (c) Smectic C.

ing systems as one can look for correlations between the different phases in the monolayer and those seen in bulk [18].

In usual cases, the molecules at the edges of the sample are influenced by the container, and it is only the molecules in the bulk of the sample that show the macroscopic order characteristic of the phase. If such a material is spread at the air water interface, we get a liquid crystal sample with very weak anchoring. Many such monolayers, on compression undergo a transition into ordered multilayers, while others go into ordered 3D structures. Such behaviour has been reported in octylcyanobiphenyl (8CB) where the monolayer at room temperature in the LE phase goes to a three layer structure on compression.

1.7 Polymer Monolayers

The study of monolayers of polymers especially polypeptides is useful as the molecular orientation of these compounds at interfaces is of significance for biological and technological processes. Liquid crystal polymers have the advantage of greater mechanical and thermal stability over their monomeric counterparts [13]. Also of interest are the LB films of such substances both industrially and academically [35]. The isotherms of some liquid crystal polymers show a marked compression expansion hysteresis as shown in Fig 1.9. These monolayers are very stiff and require a long time to stabilise.

1.8 Mixed Monolayers

The monolayers of mixtures are important in view of their relevance in the functioning of many natural systems like lung surfactant [14] and biological membranes. Cell membranes have a structure very similar to these monolayers [13, 36]. Mixed monolayers show a number of new phases and sequences due to additional degrees of freedom allowed by the Crisp's phase rule (Equation 1.1).

In case of a two component monolayer, $C^S = 2$, $C^B = 2$ and $P^B = 2$, hence

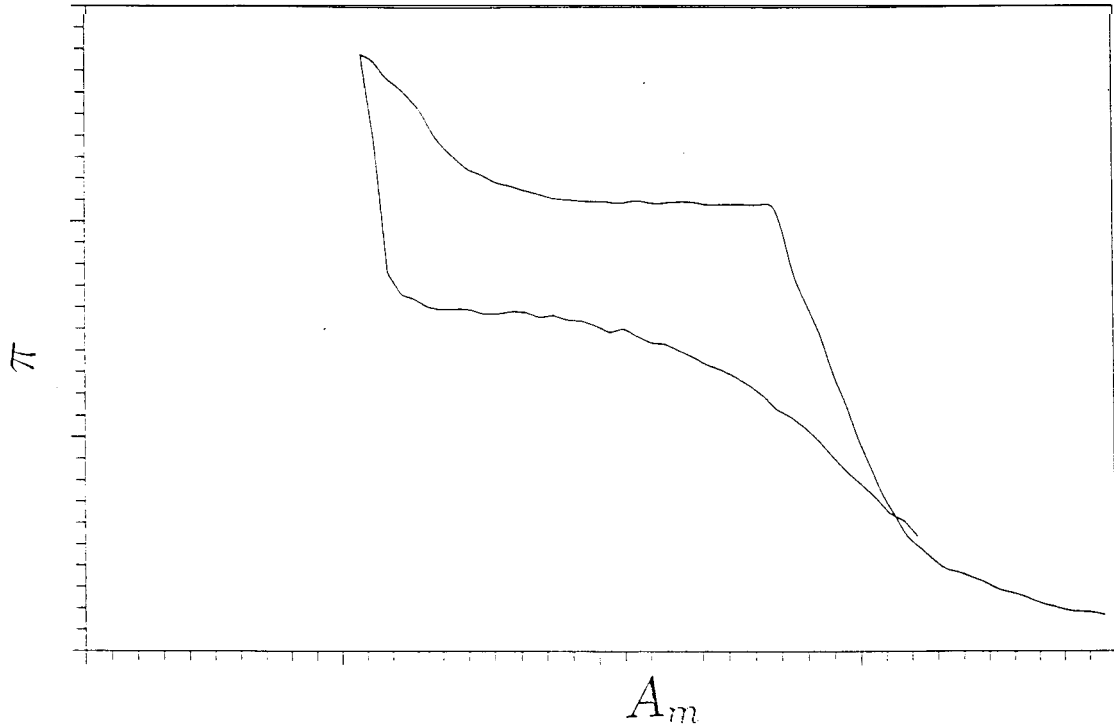


Figure 1.9. Schematic diagram of the isotherm of a polymer monolayer showing compression - expansion hysteresis.

from Equation 1.1, we have

$$f = 5 - q. \quad (1.9)$$

In such a case, at any given temperature and 3D pressure, we get two additional degrees of freedom for a single phase monolayer and one degree of freedom for a two phase monolayer. Hence, it is possible to stabilise a three phase monolayer at any temperature and 3D pressure.

A lot of work has gone into monolayers of binary mixtures where one of the components is a liquid crystal [36, 37, 38]. These studies show that at very low A_m , the two components of the homogeneous monolayer get segregated. In some cases [36, 37], at very high surface densities, the component with weaker anchoring on water is forced out of the monolayer. In other cases, [38] one component is pulled into the water and the other component stays at the interface.

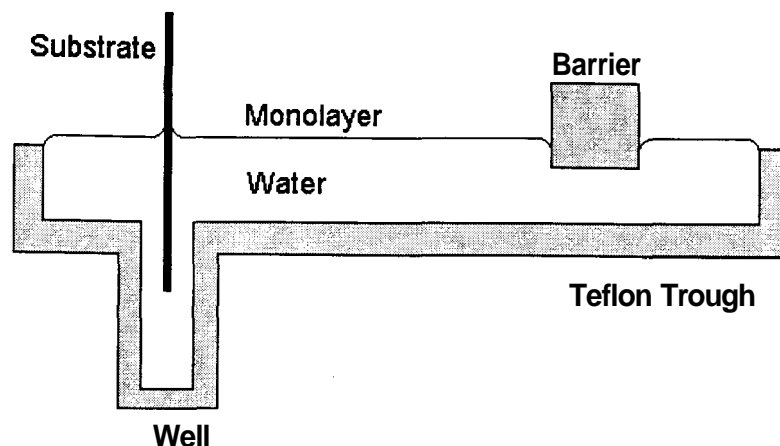


Figure 1.10. Experimental setup for Langmuir Blodgett transfer. The monolayer is transferred to the substrate by moving it sequentially up and down.

1.9 Langmuir Blodgett Films

Langmuir Blodgett films [5] are formed by transferring a monolayer onto a solid substrate. This technique was developed by K. B. Blodgett [5]. In this technique the solid substrate is kept vertically. The monolayer is transferred by dipping the substrate into the water and pulling it out slowly. In this process, the barrier is moved to maintain a constant π . The monolayer gets transferred and sticks to the solid substrate. This requires specialised troughs which allow for synchronised movement of the substrate and the barrier. The monolayer can be transferred repeatedly to form multilayers of appropriate thickness. The monolayer can be transferred while moving the substrate upwards or downwards, depending on the way in which the molecules are to be attached to the substrate. The experimental setup is shown in Fig 1.10.

The transfer can also be achieved by another technique. In this technique, the substrate is placed horizontally under the substrate. After the monolayer is spread at the air water interface and stabilised, the water is slowly removed by

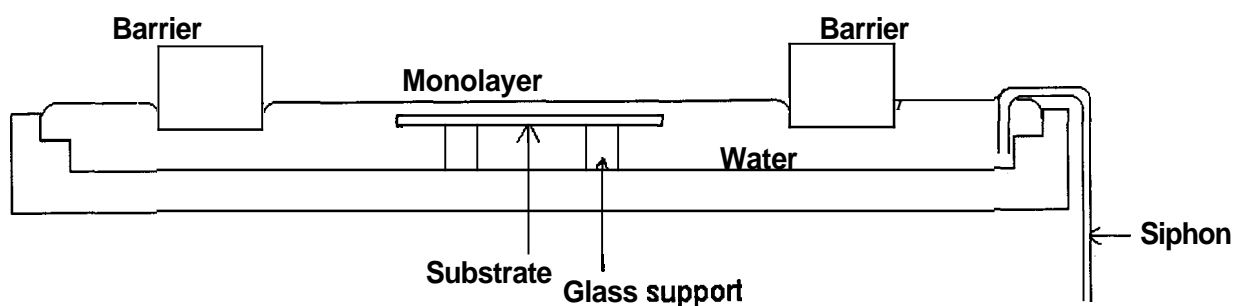


Figure 1.11. Schematic diagram of the experimental setup used for transfer of monolayers onto a horizontal substrate.

a siphon. The monolayer slowly settles on the substrate, as shown in Fig 1.11. This technique is simple and efficient, but only one layer can be transferred onto the substrate.

In another technique [39] where the substrate is kept horizontally, the monolayer is spread on water contained in a conical trough. The substrate is placed under water and the water is drained out through a tap at the bottom of the trough.

Measurements on LB monolayers can provide information about the structures of the Langmuir monolayers from which they were prepared [7]. Several powerful probing techniques can be employed only when the monolayer is on a solid substrate, *e.g.* electron diffraction, scanning tunneling microscopy [40], atomic force microscopy, surface plasmon microscopy [41] etc. These films are of immense technological importance as they provide a means of controlled layer by layer growth of material with desired properties. They can be used in electronics and opto-electronics.

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