

Langmuir and Langmuir-Blodgett Films

WHAT and HOW ?

1. Introduction

Thin organic films of a thickness of a few nanometers (a monolayer) are the source of high expectations as being useful components in many practical and commercial applications such as sensors, detectors, displays and electronic circuit components.^(1,2,3) The possibility to synthesize organic molecules, almost without limitations, with desired structure and functionality in conjunction with a sophisticated thin film deposition technology enables the production of electrically, optically and biologically active components on a nanometer scale. An organic thin film can be deposited on a solid substrate by various techniques such as thermal evaporation, sputtering, electrodeposition, molecular beam epitaxy, adsorption from solution, Langmuir-Blodgett (LB) technique, self-assembly, etc..⁽⁴⁾ The LB-technique is one of the most promising techniques for preparing such thin films as it enables (i) the precise control of the monolayer thickness, (ii) homogeneous deposition of the monolayer over large areas and (iii) the possibility to make multilayer structures with varying layer composition. An additional advantage of the LB technique is that monolayers can be deposited on almost any kind of solid substrate.

2. Short history of L- and LB- films

When describing the history of Langmuir or Langmuir-Blodgett films one is bound to start with an American statesman, Benjamin Franklin, who in 1774 reported the following to the British Royal Society⁽¹⁾:

"At length at Clapman where there is, on the common, a large pond, which I observed to be one day very rough with the wind, I fetched out a cruet of oil, and dropped a little of it on the water. I saw it spread itself with surprising swiftness upon the surface.. the oil, though not more than a teaspoonful, produced an instant calm over a space several yards square, which spread amazingly and extended itself gradually until it reached the leaside, making all that quarter of the pond, perhaps half an acre, as smooth as a looking glass."

Had Franklin made some simple quantitative calculations he would have found out that if a teaspoonful (2 ml) of oil is spread over an area of half an acre, the thickness of the film on the surface of water must be less than 2 nm.

It was not until over a hundred years later when Lord Rayleigh suspected that the maximum extension of an oil film on water represents a layer one molecule thick. At the same time the foundation for our ability to characterize monolayers on an air-water interface was set by a German woman called Agnes Pockles. She developed a rudimentary surface balance in her kitchen sink, which she used to determine (water) surface contamination as a function of area of the surface for different oils. Publication of Pockels's work in 1891 in *Nature*^(5,6) set the stage for Langmuir's quantitative work on fatty acid, ester and alcohol monolayers⁽⁷⁾.

Irving Langmuir was the first to perform systematic studies on floating monolayers on water in the late 1910's and early 1920's. These studies led to him being awarded the Nobel prize. As early as 1920 he reported the transfer of fatty acid molecules from water surfaces onto solid supports. However, the first detailed description of sequential monolayer transfer was given several years later by Katherine Blodgett⁽⁸⁾. These built-up monolayer assemblies are therefore referred to as Langmuir-Blodgett (LB-) films. The term "Langmuir film" is normally reserved for a floating monolayer.

After the pioneering work done by Langmuir and Blodgett it took almost half a century before scientists all around the world started to realize the opportunities of this unique technique. The first international conference on LB-films was held in 1979 and since then the use of this technique has been increasing widely among scientists working on various different fields of research. Today, we are in a situation where the production of ultrathin organic films with the LB-technique has slowly started to find possible practical

applications in many fields. However, even though the ideas for practical applications are growing the L and LB films are still mostly used as model systems for example for biomembrane research and multilayer coatings.

3. Short background info

In order to understand what we are measuring and how we are measuring the properties of floating monolayers (L films) it is useful to introduce some common knowledge of surface chemistry.

3.1. Surface tension^(9,10)

The molecules in a liquid have a certain degree of attraction to each other. The degree of this attraction, also called cohesion, is dependent on the properties of the substance. The interactions of a molecule in the bulk of a liquid are balanced by an equally attractive force in all directions. The molecules on the surface of a liquid experience an imbalance of forces i.e. a molecule at the air/water interface has a larger attraction towards the liquid phase than towards the air or gas phase. Therefore, there will be a net attractive force towards the bulk and the air/water interface will spontaneously minimize its area and contract.

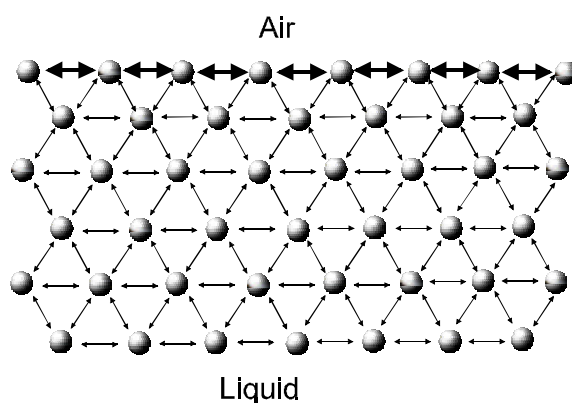


Figure 1. Schematic illustration of the interaction of molecules at an interface and in bulk.

The net effect of this situation is the presence of free energy at the surface. The excess energy is called surface free energy and can be quantified as a measurement of energy/area. It is also possible to describe this situation as having a line tension or surface tension which is quantified as a force/length measurement. Surface tension can also be said to be a measurement of the cohesive energy present at an interface. The common units for surface tension are dynes/cm or mN/m. These units are equivalent. Solids may also have a surface free energy at their interfaces but direct measurement of its value is not possible through techniques used for liquids.

Polar liquids, such as water, have strong intermolecular interactions and thus high surface tensions. Any factor which decreases the strength of this interaction will lower surface tension. Thus an increase in the temperature of this system will lower surface tension. Any contamination, especially by surfactants, will lower surface tension. Therefore researchers should be very cautious about the issue of contamination.

Cleanliness is the keyword in surface chemistry.

3.2. Surfactants⁽¹¹⁾

Surface active agents (surfactants) is a larger class of molecules which have a significant technological and biological importance. Generally these molecules consist of a hydrophilic (water soluble) and a hydrophobic (water insoluble) part. This amphiphilic nature of surfactants is responsible for their association behaviour in solution (micelles, bilayers, vesicles, etc.) and their accumulation at interfaces (air/water or oil/water). The hydrophobic part usually consists of hydrocarbon or fluorocarbon chains, while the hydrophilic part consists of a polar group (-OH, -COOH, -NH₃⁺, -PO₄⁻(CH₂)₂NH₃⁺ etc.).

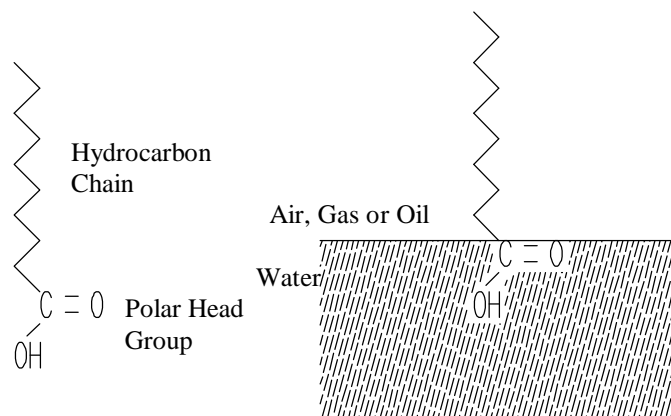


Figure 2. A schematic illustration showing the components of an amphiphile (left), and the orientation of an amphiphile adopted at an interface (right).

The association behaviour of surfactants in solution and their affinity for interfaces is determined by the physical and chemical properties of the hydrophobic and hydrophilic groups, respectively. The size and shape of the hydrocarbon moiety and the size, charge and hydration of the hydrophilic head group are of utmost importance in this respect. Depending on the balance between these properties a wide variety of self-assembled structures, both at interfaces and in bulk, have been observed. The driving force behind the association is the reduction of the free energy of the system. Therefore, when a surfactant comes in contact with water it accumulates at the air/water interface causing a decrease in the surface tension of water.

4. Insoluble monolayers^(1, 12, 13)

There exists a wide range of surfactants with an amphiphilic nature which drastically lower the surface tension of water. Many of these amphiphilic substances insoluble in water can with the help of a volatile and water insoluble solvent easily be spread on a water surface to form an insoluble monolayer at the air/water interface. These monolayers, also called Langmuir (L) films, represent the extreme case when considering adsorption to interfaces because all molecules are concentrated in a one molecule thick layer at the interface. The amphiphilic nature of the surfactants dictates the orientation of the molecules at the interface (air/water or oil/water) in such a way that the polar head group is immersed in the water and that the long hydrocarbon chain is pointing towards air, gas or oil.

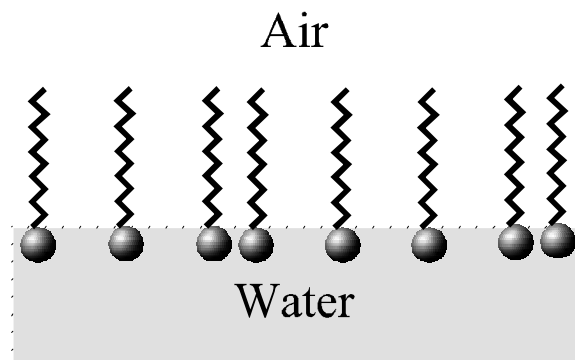


Figure 3. A schematic illustration showing a spread monolayer at the air/water interface.

The hydrocarbon chain of the substance used for monolayer studies has to be long enough in order to be able to form an insoluble monolayer. A rule of thumb is that there should be more than 12 hydrocarbons or groups in the chain ($(\text{CH}_2)_n$, $n > 12$). If the chain is shorter, though still insoluble in water, the amphiphile on the water surface tends to form micelles. These micelles are water soluble, which prevents the build-up of a monolayer at the interface. On the other hand if the length of the chain is too long the amphiphile tends to crystallize on the water surface and consequently does not form a monolayer. It is difficult to determine the optimal length for the hydrocarbon chain because its film forming ability also depends on the polar part of the amphiphile. Furthermore, the amphiphile has to be soluble in some organic solvent which is highly volatile and water insoluble (chloroform or hexane is commonly used).

5. Surface pressure^(1, 13)

As earlier was mentioned the air/water interface possesses an excess free energy originating from the difference in environment between the surface molecules and those in the bulk. This interfacial free energy is accessible by measurements of the surface tension, γ . The surface tension of water is around 73 mN/m at 20°C, which is an exceptionally high value compared to other liquids and consequently makes water a very good subphase for monolayer studies.

When a solution of an amphiphile in a water insoluble solvent is placed on a water surface with a microsyringe, the solution spreads rapidly to cover the available area. As the solvent evaporates, a monolayer is formed (see Figure 3). When the available area for the monolayer is large the distance between adjacent molecules is large and their interactions are weak. The monolayer can then be regarded as a two-dimensional gas. Under these conditions the monolayer has little effect on the surface tension of water. If the available surface area of the monolayer is reduced by a barrier system (see Figure 4) the molecules start to exert a repulsive effect on each other. This two-dimensional analogue of a pressure is called surface pressure, Π , and is given by the following relationship

$$\Pi = \gamma - \gamma_0$$

where γ is the surface tension in absence of a monolayer and γ_0 the surface tension with the monolayer present.

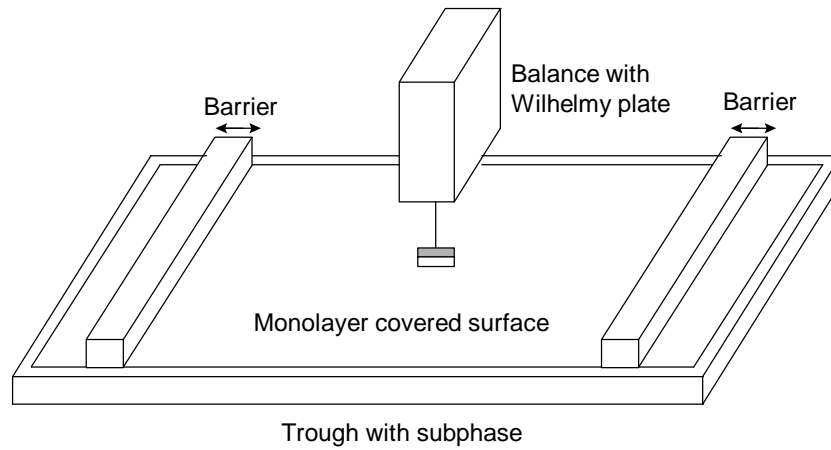


Figure 4. Schematic illustration of a Langmuir film balance with a Wilhelmy plate electrobalance measuring the surface pressure, and barriers for reducing the available surface area.

6. The Langmuir film balance^(1, 13)

Figure 4 shows a schematic picture of a Langmuir balance. The trough holding the subphase is usually made of Teflon[®] to prevent any leakage of the subphase over the edges. The trough is thermostated by circulating water in channels placed underneath the teflon trough. The surface area of the trough can be varied by sweeping movable barriers over the surface of the trough. The barrier is made of Delrin[®], a hydrophilic material, and heavy enough to prevent any leakage of the monolayer beneath the barrier. The surface pressure and the mean molecular area are continuously monitored during the compression.

The surface pressure is measured by the Wilhelmy plate-method. In this method a measurement is made by determining the force due to surface tension on a plate suspended so that it is partially immersed in the subphase (see Figure 5). This force is then converted into surface tension (mN/m or dynes/cm) with the help of the dimensions of the plate.

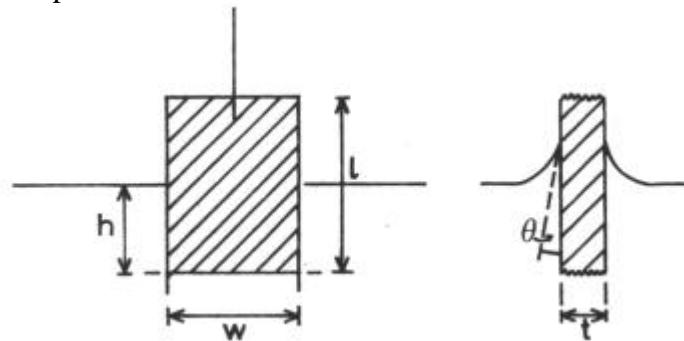


Figure 5. A Wilhelmy plate partially immersed in a water surface⁽¹⁾.

The plate is often very thin and made of platinum, but even plates made of glass, quartz, mica and filter paper can be used. The forces acting on the plate consist of the gravity and surface tension downward, and buoyancy due to displaced water upward. For a rectangular plate of dimensions l_p , w_p and t_p , of material ρ_p , immersed to a depth h_l in a liquid of density ρ_l , the net downward force is given by the following equation:

$$F = \rho_p g l_p w_p t_p + 2\gamma (t_p w_p) (\cos \theta) - \rho_l g t_p w_p h_l,$$

where γ is the liquid surface tension, θ is the contact angle of the liquid on the solid plate and g is the gravitational constant. The surface pressure is then determined by measuring the change in F for a stationary plate between a clean surface and the same surface with a monolayer present. If the plate is

completely wetted by the liquid (i.e. $\cos\theta = 1$) the surface pressure is then obtained from the following equation:

$$\Pi = -\Delta\gamma = -[\Delta F / 2(t_p + w_p)] = -\Delta F / 2w_p, \text{ if } w_p \gg t_p.$$

The sensitivity can thus be increased by using a very thin plate. The force is in this way determined by measuring the changes in the mass of the plate, which is directly coupled to a sensitive electrobalance. The monolayer can also be held at a constant surface pressure, which is enabled by a computer controlled feedback system between the electrobalance and the motor responsible for the movements of the compressing barrier. This is useful when producing LB films i.e. when the monolayer is deposited on a solid substrate.

There are even other ways to control the area of the monolayer and to measure the surface pressure but the constructions above are the most commonly used.

7. Surface pressure - Area isotherms^(1, 12, 13, 14)

The most important indicator of the monolayer properties of an amphiphilic material is given by measuring the surface pressure as a function of the area of water surface available to each molecule. This is carried out at constant temperature and is known as a surface pressure - area isotherm or simply "isotherm". Usually an isotherm is recorded by compressing the film (reducing the area with the barriers) at a constant rate while continuously monitoring the surface pressure. Depending on the material being studied, repeated compressions and expansions may be necessary to achieve a reproducible trace. A schematic Π -A-isotherm is shown in Figure 6.

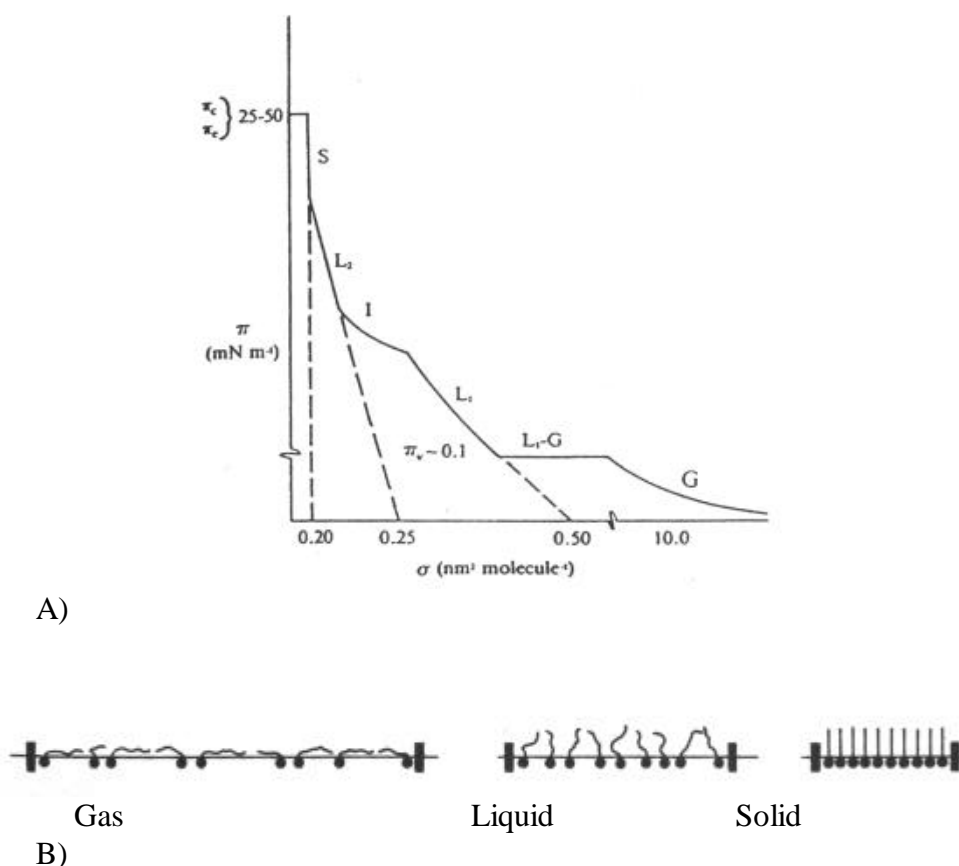


Figure 6. A) Schematic Π -A-isotherm⁽¹³⁾ and B) Orientation of the molecules in different phases⁽¹⁾.

A number of distinct regions is immediately apparent on examining the isotherm. These regions are called phases. As one can see when the monolayer is compressed it can pass through several different phases which are identified as discontinuities in the isotherm. The phase behaviour of the monolayer is mainly determined by the physical and chemical properties of the amphiphile, the subphase temperature and the subphase composition. For example, various monolayer states exist depending on the length of the hydrocarbon chain length and the magnitude of other cohesive and repulsive forces existing between head groups. An increase in the chain length increases the attraction between molecules, condensing the Π -A-isotherm. On the other hand, if an ionisable amphiphile is used the ionisation of the head groups induces repulsive forces tending to oppose phase transitions.

A simple terminology used to classify different monolayer phases of fatty acids has been proposed by W.D. Harkins as early as 1952.⁽¹⁵⁾ At large the monolayers exist in the gaseous state (G) and can on compression undergo a phase transition to the liquid-expanded state (L_1). Upon further compression, the L_1 phase undergoes a transition to the liquid-condensed state (L_2), and at even higher densities the monolayer finally reaches the solid state (S). If the monolayer is further compressed after reaching the S state the monolayer will collapse into three-dimensional structures. The collapse is generally seen as a rapid decrease in the surface pressure or as a horizontal break in the isotherm if the monolayer is in a liquid state.

There are also many other critical points in a Π -A-isotherm such as the molecular area at which an initial, pronounced increase in the surface pressure is observed, A_i , and the surface pressures at which phase transitions occur between the L_1 and L_2 state and the L_2 and S state.

Typical isotherms of a fatty acid with a single hydrocarbon chain (left) and a phospholipid with two hydrocarbon chains (right) are illustrated in Figure 6. Following the definitions above one can see that the fatty acid has three distinct regions gas (G), liquid (L_1) and solid (S), while the phospholipid has an additional almost horizontal transition phase (L_2 - L_1) between the two different liquid phases. This is very common for phospholipids and the position of this horizontal transition phase is very temperature dependent. As the temperature is increased the surface pressure value at which the horizontal transition phase occurs will increase and vice versa.

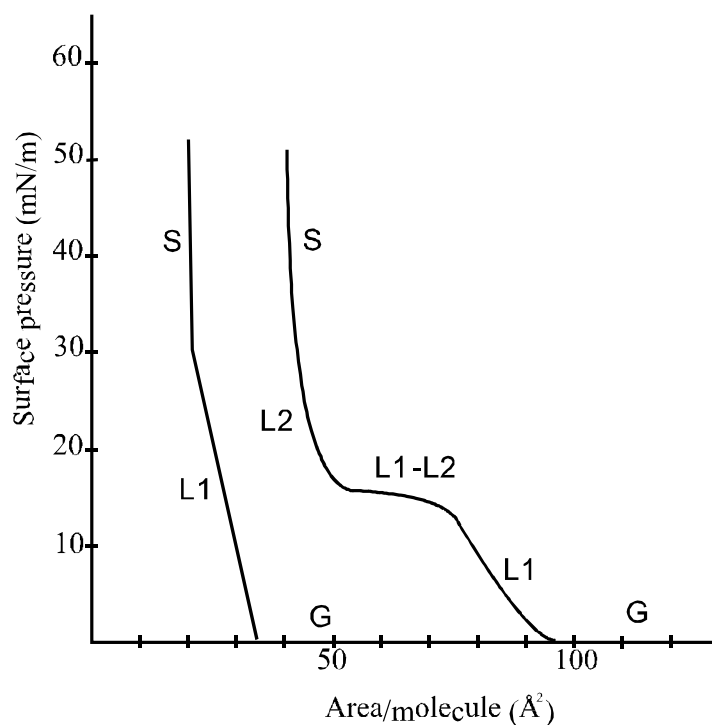


Figure 7. Typical isotherm of a fatty acid and a phospholipid.

8. Deposition - LB films^(1, 14)

Apart from being used as a tool for monolayer studies the Langmuir film balance can also be used for building up highly organised multilayers of the used amphiphile. This is accomplished by successively dipping a solid substrate up and down through the monolayer while simultaneously keeping the surface pressure constant by a computer controlled feedback system between the electrobalance measuring the surface pressure and the barrier moving mechanism. Consequently the floating monolayer is adsorbed to the solid substrate. In this way multilayer structures of hundreds of layers can be produced. These multilayer structures are commonly called Langmuir-Blodgett or simply LB films. The deposition process is schematically shown in Figure 8.

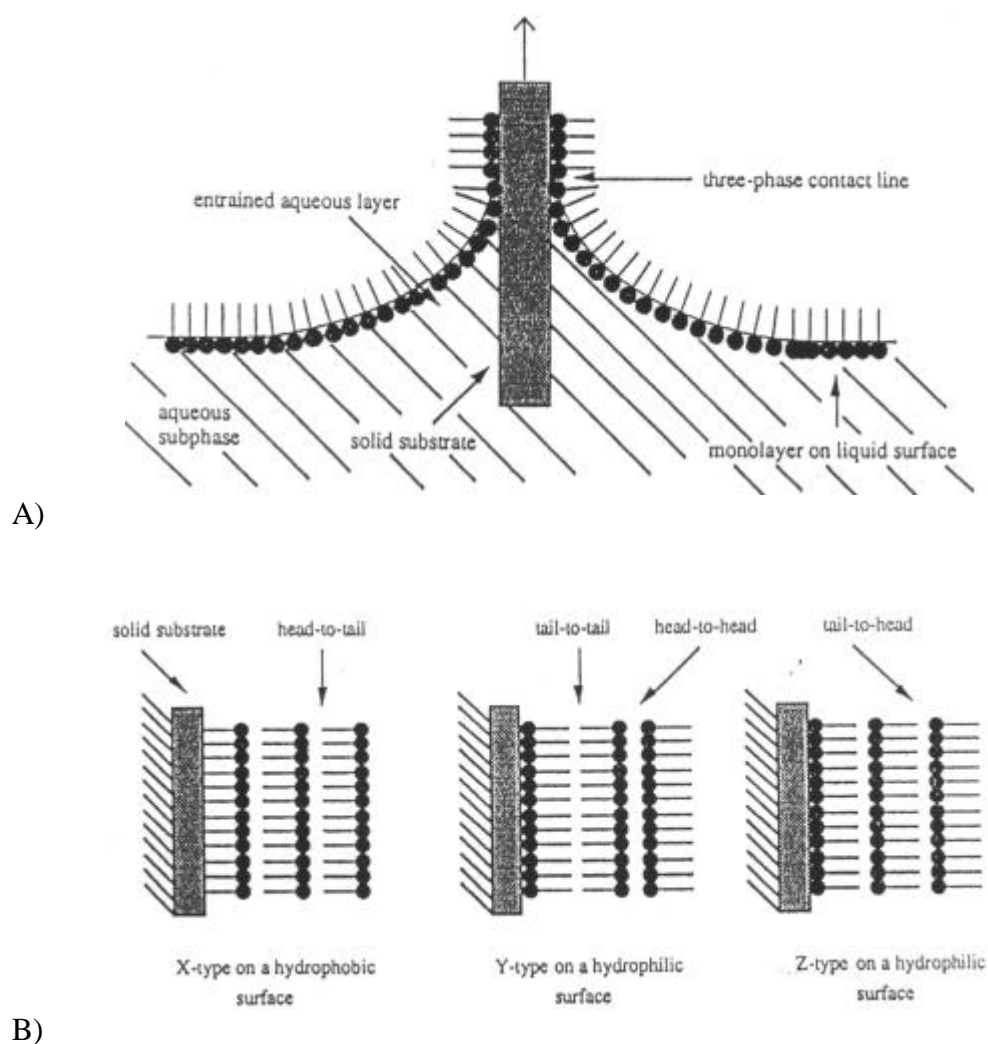


Figure 8. A) Deposition of a floating monolayer on a solid substrate and B) Different types of deposited LB films.⁽¹⁴⁾

The LB deposition is traditionally carried out in the “solid” phase. The surface pressure is then high enough to ensure sufficient cohesion in the monolayer, e.g. the attraction between the molecules in the monolayer is high enough so that the monolayer does not fall apart during transfer to the solid substrate. This also ensures the build up of homogeneous multilayers. The surface pressure value that gives the best results depends on the nature of the monolayer and is usually established empirically. However, amphiphiles can seldom be successfully deposited at surface pressures lower than 10 mN/m, and at surface pressures above 40 mN/m collapse and film rigidity often pose problems. When the solid substrate is hydrophilic (glass, SiO₂ etc.) the first layer is deposited by raising the solid substrate from the subphase through the monolayer, whereas if the solid substrate is hydrophobic (HOPG, silanized SiO₂ etc.) the first layer is deposited by lowering the substrate into the subphase through the monolayer.

There are several parameters that affect on what type of LB film is produced. These are the nature of the spread film, the subphase composition and temperature, the surface pressure during the deposition and the deposition speed, the type and nature of the solid substrate and the time the solid substrate is stored in air or in the subphase between the deposition cycles.

The quantity and the quality of the deposited monolayer on a solid support is measured by a so called transfer ratio, t.r. This is defined as the ration between the decrease in monolayer area during a deposition stroke, A_1 , and the area of the substrate, A_s . For ideal transfer the t.r. is equal to 1. Depending on the behaviour of the molecule the solid substrate can be dipped through the film until the desired thickness of the film is achieved. Different kind of LB multilayers can be produced and/or obtained by successive deposition of monolayers on the same substrate (see Figure 8). The most common one is the Y-type multilayer, which is produced when the monolayer deposits to the solid substrate in both up and down directions. When the monolayer deposits only in the up or down direction the multilayer structure is called either Z-type or X-type. Intermediate structures are sometimes observed for some LB multilayers and they are often referred to be XY-type multilayers.

The production of so called alternating layers which consist of two different kind of amphiphiles is also possible by using highly sophisticated instruments. In such an instrument there is a trough with two separate compartments both possessing a floating monolayer of a different amphiphile. These monolayers can then be alternatingly deposited on one solid substrate.

An alternative way to deposit the monolayer is the Langmuir-Schaeffer (LS) technique. This technique differs from the vertical technique described above only in the sense that the solid substrate is horizontally lowered in contact with the monolayer.

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