A modified Langmuir Schaefer method for the creation of functional thin films
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Chapter 1

An introduction to the hybrid Langmuir-Schaefer approach

1.1 Motivation

This thesis reports on research that was part of a joint effort to generate new knowledge on what we believe to be an emerging field, the hybrid Langmuir-Blodgett (LB)/Langmuir-Schaefer (LS) approach (HLS), aiming at the study and fabrication of complex material for fundamental and applied purposes. Although LB deposition has already been studied for about a century and has brought forth outstanding advances (leading to a Nobel Prize), the hybrid LB/LS is facing a great future as well because it is not only a tool for producing monomolecular thin layers with outstanding control but also apt for realizing a plethora of complex three-dimensional (3D) systems and will for sure contribute to some of tomorrow’s great discoveries of new functional materials.

The various chapters of this thesis demonstrate this potentially great future and are intended to give the reader a taste of today’s advances in the field. For that reason, each chapter has as a common foundation the use of the HLS method and can be read independently, all are focused on the use of this technique for assembling various materials, interesting from a purely fundamental point of view or suitable for more applied purposes.

This thesis is like very few oil drops in the hybrid Langmuir-Blodgett-Schaefer sea, but, as you will see, oil can influence its surroundings and spread in a more extended way than what you may think.

1.2 The history of the discovery – the timeline

As described by G.G. Robert\(^1\), the history of the technique now called Langmuir-Blodgett deposition, namely the creation and transfer of a monolayer thick film formed at an air-water interface, started centuries ago. Indeed the beauty of the pattern created by spreading oil on water inspired the Babylonians who used it to practice divinity by observing such an event. The earliest technical application of floating organic films and their transfer to a substrate, dates from the 12\(^{th}\) century
and is believed to come from the Japanese art of Sumi Nagashi, were colour dyes composed of submicron particles (basically ink) mixed with proteins were spread on a water surface followed by the spreading of a gelatin, to create patterns as the one depicted in Figure 1. One could transfer the naturally formed drawings by lowering a sheet of paper onto the air-water interface (horizontal dipping).

![Figure 1 Example of a Sumi Nagashi](image)

Although his purpose was not the study of a molecular layer, but rather curiosity about wave damping phenomena, Benjamin Franklin became the author of the first scientific report on surface chemistry\(^2\) (1774). As recalled by P. Behroozi \textit{et al.}\(^3\) in a recent manuscript, during one of Franklin’s numerous trips across the seas, some intriguing wave damping effect (that he thought to be due to leaking oil around some ships) inspired him to perform a series of experiments on the calming effect of oil on water. When depositing a minute amount of oil on the surface of a very large pond, and allowing the wind to spread the substance over the water surface, Franklin noticed that the extended oil film had indeed a damping effect on the water it covered while the uncovered area remained turbulent under the action of the wind. Franklin was definitely more focused on the understanding of this damping phenomenon and did not realize that experiment after experiment; he was describing the creation of an oil monolayer. Nevertheless his precise descriptions\(^2\) of the experiments where he relates how an oil drop “when put on water it spreads instantly many feet around, becoming so thin as to produce prismatic colours, for a considerable space, and beyond them so much thinner as to be invisible, except in its effect of smoothing the waves at a much greater distance” might definitely have inspired his successors. If Franklin had been less distracted by geopolitics and inspired to calculate the thickness of the oil volume of \(~2\,\text{cm}^3\) that he observed spreading over \(~2000\,\text{m}^2\) (as describe in his first paper), he would have found that the coating produced on water was \(~1\,\text{nm}\) thick. Franklin’s paper could have been one of history’s great classics - the first measurement of molecular size! In fact, although the existence of "ultimate particles" was fairly generally accepted, nobody had the slightest idea what size they would turn out to be. Roughly a century later
(1890), Lord Rayleigh\(^4\) did this calculation in an attempt to measure accurately the quantity of olive oil (triolein, see structure in appendix 1) that was needed to cover a given surface of clean water. He found that 0.81 mg of olive oil was necessary to cover an area of 555 cm\(^2\) and calculated the film thickness to be 16 Å. Lord Rayleigh did not realize that this value was the length of the trioilen molecule (C\(_{57}\)H\(_{104}\)O\(_6\)) forming a monomolecular layer. At about the same time, Agnes Pockels (described as one of the most remarkable woman scientists of all time) invented a prototype of what today is known as the LB trough, namely a shallow container equipped with movable strips that can be used to sweep the surface clean from any impurities prior to an experiment and to compress or relax any oil film while maintaining the amount of material constant. She introduced a proper way to measure surface tension (while Langmuir, unaware of her work, did all his pioneering work measuring lateral pressure—which is an equivalent quantity). Amazingly, Pockels originating from Braunshweig, Germany and without a formal education, did all her work in her kitchen, apparently inspired by the behaviour of oil floating on the top of soup and stew. She had no idea of the value of her work until her brother, a professor of physics at the University of Göttingen, discovered the work of Lord Rayleigh on oil behaviour on water\(^4\). He showed her that paper, and confident about her findings she wrote to Lord Rayleigh who immediately recognized the value of her results, published them in Nature\(^5,6\) and replicated her apparatus for his own research. In spite of his stated great interest in the "determination of molecular magnitudes", Lord Rayleigh appears not to have speculated at all about molecular shape, it was Langmuir who introduced the modern concept of molecular "conformation" in his brilliant work\(^7\) on this topic. By not considering molecules as spheres but as asymmetric objects, he reached the conclusion that molecules pack with identical orientation at the air-interface. This concept of orientation arises from the hydrophilic or hydrophobic nature of the employed molecules. His measurement of hydrocarbon chain length and flexibility on hydrophobic films had a truly revolutionary impact at a time when the understanding of molecular structure was virtually non-existent. While the study of the formation and stability of monolayer films was the main purpose of Langmuir’s research and the motivation for being awarded the Nobel Prize in 1932, he reported as well that the film formed at the air-water interface could be transferred to a substrate. However, the study of sequential and controlled transfer of a monolayer to a substrate is attributed to Katharine Blodgett who devoted her research to that problem. Her first results\(^8,9\) appeared in the Journal of the American Chemical Society in 1934 and 1935; this period can be defined as the birth of what is now termed the Langmuir-Blodgett (LB) method, Langmuir film being the name usually attributed to the monomolecular layer at the air-water interface. The
collaboration of Langmuir and Schaefer came later and was focussed mainly on the
deposition of proteins in the LB fashion. Still later, in 1938, Langmuir and
Schaefer reported on a new approach where the sample plate was not lowered into
the trough vertically but in an almost perfectly horizontal fashion. This method,
now called the Langmuir Schaefer (LS) deposition, led to equally good results for
the type of films they were trying to form.
After a long phase of inactivity in the field during the Second World War and the
post war period (since LB was not considered useful in any way to produce
weapons), the research interest re-emerged in the 1980’s thanks to some
publication promoting the use of LB deposited organic films for electronic
applications. From then on, an active collaboration between physicists, chemists
and biologists perfected the use and application of LB films to a higher level of
controllability and over a broader range of molecules.

1.3 Langmuir-Blodgett-Schaefer – the principle

1.3.1 Monolayer formation
As we have just discussed, the investigation of the formation of a monolayer at an
air-water interface was mainly performed by Langmuir starting in 1917, while the
deposition of such a film was extensively studied by Blodgett (vertical dipping)
and Schaefer (inventor of the horizontal dipping), who both collaborated with
Langmuir. Let us here introduce the basic principles behind that method.
In an oversimplified vision of the world, all compounds may roughly be divided
into two categories, substances that are water soluble or water insoluble. The
former are generally polar, i.e. characterized by a non-uniform distribution of
charge which can be quantified as the dipole moment, $\mu$, defined as $q$ times $r$, $q$
being the charge carried by the partners forming the dipole and $r$ representing the
distance between them. Molecular polarity is dependent on the difference in
electron negativity between atoms in the compound and the asymmetry of the
compound's structure. As a perfect example to illustrate this concept we will use
the case of water; each of the two hydrogen atoms shares an
Figure 2 Origin of the dipole moment in the example of a water molecule.

electron pair with the oxygen atom (as depicted in figure 2), the geometry of the shared electron pairs in the outer shell of the oxygen causes the molecule’s V-shape. The strong electron-withdrawing tendency of the oxygen atom results in a local negative charge located on the vertex of the V-shaped molecule while the two hydrogen atoms bare a local positive charge. Though water molecules are neutral overall, this charge separation induces the creation of a permanent dipole. The solvent properties of water are associated with the attraction between its electrical dipole and the charge of the solute. Symmetrical molecules, where electrons are shared equally between two bonding atoms as in benzene ring, C=C or C-C long chains, do not possess a dipole moment and are therefore called non-polar. The majority of non-polar molecules are water insoluble (hydrophobic) at room temperature.

Most of the monolayer forming substances used by the pioneers of the method, and still mostly used today, are composed of two parts: one that is water loving and if alone, dissolves in water; the second part has the opposite property. Such molecules composed of a hydrophilic and a hydrophobic part are called amphiphiles or surface active agents (in short surfactants) The most common prototypes of surfactant are the long chain fatty acids. An example of such a molecule is arachidic acid C_{20}H_{40}O_2, depicted in figure 3. The long carbon-carbon chain CH_{3}(CH_{2})_{18} constitutes the non-polar (hydrophobic) part and the carboxylic acid group (COOH) the asymmetric polar (hydrophilic) head of the surfactant. As revealed by Langmuir, these molecules are far from being spheres but highly asymmetric in aspect ratio (long length compared to the cross section). The balance between the chain length and/or the force of the polar group is what enable those
molecules to float and conveys to them the ability to form a monolayer. If the hydrocarbonated chain is too long or the polar group too strong, then the molecule just dissolves.

Most monolayer forming surfactants are brought onto a subphase surface by first dissolving them in a proper solvent (often chloroform). The subphase is defined as the substance on which the monolayer is going to be formed. In most of the classic LB experiments the subphase is demineralized-deionized water with a 18.5 MΩ resistivity. This low ion-content ensures that the surfactant polar head will not be hybridized with minerals contained in natural water and therefore leave the properties of the monolayer undisturbed. Minute amounts of the solvated surfactant are then sprayed onto the subphase. As we have seen in the introduction, in Benjamin Franklin’s experiment, 2 ml of olive oil were sufficient to cover 2000 m² of water; here a surfactant solvated in 200 µl chloroform at an usual concentration of ~0.1 mg ml⁻¹, means that 20 µg of a surfactant are sufficient to cover ~300 cm² of the water trough. In practice the operation is achieved by spraying the surfactant in mic droplets onto the surface and allowing the solvent to evaporate. Only then the organic molecules may be compressed to form a floating two-dimensional (2D) solid.

1.3.2 Surface tension

In the following we shall describe the physics of the air water interface, the forces involved as well as the simple way to measure them. Water molecules while in the liquid state are attracted to each other by electrostatic forces. Even though the water molecule as a whole is electrically neutral, the distribution of charge in the molecule is not symmetrical (as explained above) and results in a dipole moment. This leads to a net attraction between such polar molecules which finds expression in the cohesion of water molecules and contributes to viscosity and surface tension. That said, one understands easily that the bulk water liquid state is held through the isotropic cohesion between water molecules (see figure 4a) where every single molecule of the bulk liquid state is equally and uniformly pulled or pushed in all directions of space by its neighbouring H₂O molecules. Therefore the net applied force acting on each molecule (neglecting gravity for a moment) is zero. But what about the interface, i.e. the boundary between the water liquid bulk state and the air gas bulk state? This question is what makes surface science in general so interesting: surface states by nature are at the boundary of two worlds, representing a kind of ‘transition’ between pure bulk and the outside world, and are therefore different from the pure bulk (this applies equally to solid-solid or liquid-liquid interface of different materials). These ‘transition’ or interface states are very often
simply structurally different, but this structural difference frequently leads to dramatically altered properties as compared to the pure bulk material. In that respect water is no exception, the surface water molecules behave quite differently from the bulk. Figure 4 represents drawings that one should imagine embodying air-water interfaces where the water molecules are the black dots, the arrows the forces acting on them, the grey zone designates the bulk and the lighter zone the interface. In a first case (a), the water molecules located at the top, at the boundary between air and water, are under the action of lateral and downward cohesion forces. This concept holds in a zero gravity environment.

Because of the net force pulling them inwards, the molecules “do not like” to be on the surface, they “want” to be in the bulk where no net force acts, and therefore migrate until forming a shape where the number of surface versus bulk atoms is minimized, a flat levelled surface in a container (in the presence of gravity) or a sphere (in zero gravity). This initial diffusion of molecules from surface to bulk to reach the equilibrium state will decrease the mean atomic separation and therefore increase the intermolecular forces at the surface. The force acting on any surface is called surface tension $\gamma$ and is measured in N/m (with an equivalent definition; the surface tension is regarded as an excess free energy/unit area and measured in J/m$^2$). The surface tension is analogous to the vapour pressure, constant at equilibrium at a solid-gas interface but changing with temperature. But, unlike the vapour pressure which increases with increasing temperature, the surface tension decreases when the temperature increases.

As we just defined, the interaction or cohesion between the water molecules is a key aspect to understanding the liquid-gas interface. One can therefore comprehend that contamination of the water will alter its surface tension but, more interestingly

**Figure 4** Intuitive representation of the origin of surface tension (a) for a liquid inside a container (b) for a liquid in a zero gravity environment. (Representation in both case are just before equilibrium).
for us, the presence of a molecular film on a liquid surface will influence its surface tension as well.

As a convention, surface pressure $\Pi$ is defined as the difference between the surface tension of pure subphase (for example water) and the same subphase covered with molecules ($\Pi = \gamma_0 - \gamma$).

One usually measures surface pressure using the Wilhelmy plate. The principle is rather simple: a plate, most often made of paper, is partially immersed in water (as depicted in figure 5), the force acting on the plate is the sum of three forces: the gravity and the surface tension both acting downwards

\[ F = F_{\text{Gravitation}} + \gamma \cos \theta \cdot P - F_{\text{Buoyancy}} \]
\[ F = m_p g + \gamma \cos \theta \cdot P - m_i g \]

where the size of the plate is defined by $l_p$, $w_p$ and $t_p$, $\rho_p$ is the plate density, and $P$ the perimeter of the plate. When the plate is immersed to a depth $h$ in a liquid of density $\rho_l$, the net downward force is given by the following equation:

\[ F = \rho_p g l_p w_p t_p + 2\gamma (t_p + w_p) \cos \theta - \rho_l g t_i w_i h \]

where $\gamma$ is the liquid surface tension, $\theta$ the contact angle of the liquid on the solid plate and $g$ the gravitational constant. We can therefore deduce the surface pressure simply by measuring the change of force $F$ acting on a plate with and without a molecular film present at the surface. If the plate is completely wetted by the liquid $\theta$ becomes zero (i.e. $\cos \theta = 1$) and the surface pressure is then obtained from the following equations:

[Figure 5 Wilhelmy plate – Copyright free - Wikipedia commons.]
An introduction to the hybrid Langmuir-Schaefer approach

\[ F_0 = F_G + 2\gamma_0 (t_p + w_p) - F_B \]

\[ F = F_G + 2\gamma (t_p + w_p) - F_B \]

\[ \Pi = \gamma_0 - \gamma = \frac{F_0 - F}{2(t + w)} \]

The sensitivity can be increased by using a very thin plate. The force is determined by measuring the changes in the mass of the plate, which is directly coupled to a sensitive electrobalance.

1.3.3 Controlled packing and deposition

Now that we know what surfactants are and understand surface tension, it is time to put these two notions in use to discover the interface. As briefly mentioned at the end of paragraph 1.3.1, the injection of few microgram of surfactant at the air-water interface will at first get the molecules to spread all over the available surface area. Applying an external force to those floating surfactant molecules will affect their positions within the trough (trough being the term commonly use to describe the water tank in which LB or LS experiment are performed) and ultimately, if compression is sufficient, create a solid film. This compression of the monolayer goes through several phase transitions which are two-dimensional analogues to the gas, liquid and solid state of matter as sketched in figure 6. The phase diagram of a peculiar surfactant can therefore be identified simply by measuring (\(\Pi\)-a) an isotherm, in other words by determining the pressure versus area per molecule curve at constant temperature.

In a typical experiment, right after the dispersion of the molecules on the surface and the evaporation of the carrier solvent, a so-called 2D gas state (zone A, figure 6) is formed with relatively large distances between the molecules. After the evaporation stage, the barrier can be moved to compress the molecules (while pressure and area per molecule are recorded). The pressure area isotherm, rich of information, was extensively used by Langmuir and enabled

\* Since we know the total number of molecules and the total area that the monolayer occupies, one can calculate the area per molecule (Å^2), and as stated earlier the surface pressure is the difference between the surface tension of pure water and water with the molecule present.
Figure 6 Surface pressure versus area isotherm for a long chain organic molecule (schematic curve).

him to postulate the existence of different phase conformations and/or phase transitions for various types of systems. It is still today the first step in the investigation of a new material floating at the air water interface. Books like “The Introduction To Ultrathin Organic Films From Langmuir-Blodgett to Self assembly” by Abraham Ulman\textsuperscript{12} (pp 48-237) give a complete description of those stages for a variety of systems; here we just give a simple overview.

The area per molecule in the gas state is large and therefore the floating surfactant molecules are strictly speaking barely interacting, indeed, each molecule possessing an energy kT (kT/2 per degree of freedom) will just move about and collide with other molecules and with the wall of the container like in a perfect 2D gas. The pressure of this 2D gas is deduced from the ideal gas law (PV=NkT) which becomes PA=NkT, where P is the pressure of the 2D gas, A the total area of the container, N the number of molecules and kT the Boltzmann constant times the temperature. When doing the math\textsuperscript{*}, one finds that the 2D pressure of the surfactant is \( \sim 1 \text{ mN m}^{-1} \) for an area per molecule of 4 nm\(^2\), which explains the slope of the isotherms on going from the fully extended state to the 2D solid state. As the barriers keep moving one can observe a first transition from gas to liquid, for values of surface area roughly determined by the size of the long axis of the

\textsuperscript{*} PA=NkT can be transformed in Pa=kT where “a” became the area per molecule, if kT= 1.38 \( 10^{-23} \text{ J K}^{-1} \times 300 \text{ K}= 4 \times 10^{-21} \text{ J} \) and taking a=4 nm\(^2\) one finds P.(4 \( 10^{-18} \text{m}^2\)) = 4.\( 10^{-21} \text{ J} \), therefore P\( \sim 1 \text{ mN.m}^{-1} \)
Figure 7 schematic representation of the so-called collapse, increasing the applied pressure on the monolayer beyond its solid state create a rupture that lead to and overlap and the formation of double or triple-layer or sometimes crystallite.

molecules (note that not all surfactants show such a transition). In this phase (zone B, figure 6), the molecules are arranged coherently but still loosely packed. Further compression leads to the next phase transition, liquid to solid; at this stage the molecules are densely packed (zone C, figure 6) and any further compression leads to a rapid increase in surface pressure (just like a 3D solid). Applying more pressure to the monolayer induces a so-called collapse, which can be visualized as a sharp breaking of the solid state. When such a collapse occurs a decrease in pressure is observed (dotted line in the scheme of figure 6) and the monolayer becomes locally a bi- or trilayer and eventually forms a micocrystallite. This collapse process is depicted in figure 7, where the compression of a well-ordered compact layer (top left panel) lead to the formation of cracks (left middle and bottom panels), and a further increase in the pressure results in a kind of turn over of the molecules as schematically depicted in the right part of figure 7.

The state chosen for the film transfer (deposition) is therefore going to be mostly the solid state. This leads us to the last part of this section, namely the discussion of the actual deposition process and the result of monolayers transferred from the water-air interface onto a solid substrate. Two methods can be used, the first and most common is the vertical deposition as demonstrated and developed by Blodgett and Langmuir (depicted schematically in figure 8 left). Key aspects of the LB type deposition are the formation of the meniscus and the transfer speed. For very low transfer speed, dipping up- and/or down-stroke, the crystalline packing and orientation of the monolayer film is preserved and transferred to the substrate - if the range of surface pressure and substrate are well chosen. As soon as the transfer speed is too high, the crystalline structure is either altered or lost and no transfer
occurs. This issue was studied by the French Nobel prize winner De Gennes. The most common vertical deposition involves a repeated immersion (downstroke movement) and emersion (upstroke movement) of the substrate, and results in the multilayer depicted in figure 9 called Y-type; it consists of a sequence of surfactant layers with alternating hydrophobic-hydrophobic and hydrophilic-hydrophilic interactions (this structure gives the most stable films). However, it is also possible to create X and Z type films, also shown in figure 9, when depositing respectively by downstroke or
upstroke movement only. Such films can be formed with surfactants having a weakly hydrophilic head group or a slightly polar terminated alkyl chain.

A second transfer method, the one exclusively used in this thesis, is the horizontal lifting method, introduced in 1938 and commonly referred to as Langmuir-Schaefer (LS) method, which is depicted schematically in the right panel of figure 8. This process, generally used for very rigid films, consists of approaching the rigid substrate at very low speed of typically \( \approx 2-4 \text{ mm min}^{-1} \) until contact with the monolayer is made (kissing the water) and then lifting it up at even slower speed, \( \approx 1-2 \text{ mm min}^{-1} \) until the substrate and water are separated. The crystalline order is preserved also in this transfer and X-type films can be produced (see figure 8).

1.3.4 First achievements

In her first paper, entitled “Monomolecular Films of Fatty Acids On Glass” and published in 1934 in the Journal of the American Chemical Society, Katharine Blodgett describes with enthusiasm the beauty and the simplicity of fatty acid multilayer films with various properties depending on whether the number of layers is even or odd. “The nicest experimental procedure is that in which water peels completely off the glass as the glass is withdrawn from the water-bath. This occurs when molecules of the fatty acid, which are spread on the water surface, leave the water and attach themselves to the edges of the glass slide as soon as one end of the slide emerges from the bath” \(^8\).

Five years later, Vincent Schaefer, while studying films of proteins and their conformation in films of type X or Z, depositing in the classical LB fashion, realized that another dipping mode was possible and suitable for deposition. Here are selected sections of his paper describing his discovery. “We find, however, that even at \( F = 0.4 \) good A films can be deposited by holding the plate face down in a nearly horizontal position and lowering it onto the surface of the water in a tray covered with a monolayer of urease… The film produced by this technique is an A-type of film, for it presumably has the same orientation as that deposited on a vertical plate during the down-trip into water. We shall describe a film of this kind as a lifted film, and denote it by \( A_l \).” Here \( F = 0.4 \) refers to the surface pressure in dynes/cm and A refers to what was later called X-type films. \(^10\)

1.4 The rebirth

Although the application of the Langmuir-Blodgett technique never really stopped after its discovery, a clear rise in the research interest for this method appeared in the 1980s. However, we shall focus in this section only on the short history of the so-called hybrid Langmuir-Blodgett (HLB) method.
1.4 The rebirth

1.4.1 Past and present

The history of what we denote as hybrid Langmuir Blodgett method (HLB) started in 1994 with a report from Kotov et al.\textsuperscript{14}. In this experiment, pure surfactant was replaced by hexadecylammonium- and dioctadecylammonium-ion-exchanged hectorites (commonly called organoclay). The butanol benzene (1:1) organoclay dispersions as represented in figure 10 (left), were injected and studied on various aqueous solutions by means of $\Pi$-a isotherm, Brewster Angle Microscopy (BAM) and in situ optical reflectivity measurements.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure10.png}
\caption{First hybrid Langmuir-Blodgett experiment\textsuperscript{14} involving organoclay as surface active agent. Surfactant-functionalized clay platelets were injected over ultrapure water or electrolyte aqueous solutions. (Right) Evolution of the hybrid method, clay solution in the trough hybridized by the surfactant at the surface only.\textsuperscript{15,16}}
\end{figure}

This first pioneering attempt led to quite poor results in terms of “monolayer” properties: the film formed by the injection of the already assembled organoclay on the pure water subphase was found to create “whitish patches on the water surface” while the injection on electrolyte solution “was not observable by the naked eye”\textsuperscript{14} testifying to the creation of a film with a thickness in the nanometer range. This first attempt was shortly followed by, among others, Yamagashi et al.\textsuperscript{15,16}. In their later experiment\textsuperscript{16} using a hexa-amineruthenium(III)chloride([Ru(NH$_3$)$_6$]Cl$_3$) intercalated clay template formed by LB for electrochemistry, the authors deduce from injected volume vs trough area calculations that the floating material would be made of a double layer at most.

Improvement of the true monolayer aspect of those hybrid films arrived later with a slightly different approach still in use today. This type of approach was used for most of the experiments described in the later chapters (2, 3, 5-7) of this thesis. To the best of our knowledge, Yamagashi et al.\textsuperscript{17,18,19,20} in “Application of the Langmuir-Blodgett Technique to Prepare a Clay-Metal Complex Hybrid Film”
were the first to introduce the “in trough” hybridization of clay with the metal complex [Ru(phen)$_2$(dC18bpy)]$^{2+}$ as surfactant. This method is depicted in figure 10 (right), where one can see clay in solution and surfactant hybridizing the negatively charged clay at the surface only. Non-functionalized surfactant might remain present depending on the clay loading as will be discussed later. For the first time Atomic Force Microscopy (AFM) was used to prove the true single layer character of the deposited films.

A year later, in 2001, Umemura and co-workers$^{21}$ published a thorough investigation of the HLB system and identified the hybridization of clays at the air-water interface as a function of the clay loading in the subphase as the key process which determines the quality of the transferred films. In this work the authors report an improved and more controlled method (for further reading we refer to this seminal work and a later publication from the same authors$^{22,23}$). It seems to us that this dramatic improvement in the result in terms of control and quality is mainly due to a new deposition procedure, where the hybrid film is deposited by horizontal dipping of the substrate (LS method) and not by vertical dipping (LB method), as for all the previously reported results.

Figure 11 proposed models for the morphology of a hybrid clay – surfactant film produced by HLB. (a) Unlikely structure, (b) structure proposed by Umemura et al.$^{24}$; (c) structure proposed by Gengler et al.$^{25}$ Chapter 2 (d) structure created by an alternative route combining HLB and SA, proposed by Umemura et al.$^{24}$ and confirmed by Gengler et al.$^{25}$

The morphology of the HLB assembled organoclay multilayer transferred to a substrate is still today a matter of controversy. This will be part of the focus of the second chapter where we discuss the hybridization process in detail. Figure 11A depicts a typical X-type HLS film where alternating surfactant and clay layers are arranged in a periodic fashion with the clay platelets grafted to the surfactant head (in the LB trough clay suspended in the subphase hybridizes with the surfactant). Such an X-type structure is possible for surfactants with a weakly hydrophilic head group or a slightly polar terminated alkyl chain as described above. In the clay case
this kind of film is rather improbable mainly because of the clay’s polarity but also because of the weak attachment of the surfactant. Therefore two models of a “more probable” film structure were proposed, one by Umemura et al., the other by us a few years later and are the focus of chapter 2. In short, Umemura and co-workers stated that a structure such as displayed in figure 11B was the most probable. Again one can see surfactant and clay chemically bound and arranged in a periodic fashion, but here part of the surfactants is “flipped over” and this creates a bond between one clay layer and the next. This flip over is supposed to occur during the LS dipping of the substrate at the trough surface. A fraction of the surfactant molecules detaches from the clay, flips over and bonds to the outer surface of the substrate being dipped, which consists of clay. We, however, do not agree with this model and our new claims are supported by a complete investigation of organoclay multilayer films created by LS following two preparation routes detailed in chapter 2. Our model, depicted in figure 11C, has a new type of periodicity, i.e. a repeating unit consisting of surfactant-clay-clay-surfactant. This model is explained by a turn over of every even layer of organoclay through the water-substrate meniscus (one every two dips). Nevertheless, we agree with Umemura et al. that the most stable HLS films of organoclay, as depicted in figure 11D, are formed from 1L (L = Layer) of surfactant-1L Clay -1L surfactant. These films are built in a two step process, the first being the HLS, the second a self-assembly (SA) of surfactant (the same type or not). Through SA of the surfactant on the freshly deposited, exposed clay layer, which is hydrophilic, transforms into a hydrophobic surface. Thereafter LS deposition of organoclay can again be achieved in proper condition (high hydrophobicity of “substrate” needed), no flip over is required to achieve a proper organoclay-substrate interaction.

While most publications before 2002 mostly focused on the properties of organoclay themselves and their fabrication, the exception being some references on their use for electrochemistry, the HL-HLS field has received more and more attention (see discussion in appendix) as a means to produce materials with potential for application mainly in the field of optics and magnetism. As such applications will be discussed further on in this thesis, here we limit the discussion to a review a few milestones in the HLS history regarding functional films. Most likely one of the first functional HLS films were those for the modification of electrodes for electrochemistry. Later, Umemura et al. probably at the same moment as Kawamata, Yamagashi and co-workers promoted HLS clay films as host surface for Second Harmonic Generation (SHG) structure. Many publications

* The flip over does not occur during the first dip, the substrate surface being perfectly hydrophobic.
aiming at the same objective followed\textsuperscript{28,29,30,31,32,33}. While Umemura\textsuperscript{34} focused on the SHG properties, we believe that the iron (II) containing clay stack he prepared through HLS and SA is the first example of a new era where the hybridization happens not only in the LB trough but also by functionalizing the outer surface of clay during a second dip. This key publication definitely inspired a part of the work reported in this thesis (chapters 3, 5, and 6).

Among many functional hybrids prepared using the HLS-SA method, we will just mention two beautiful examples of Yasushi Umemura who is one of the main contributors to this field. Both studies involve switching of magnetic materials. The first case,\textsuperscript{35,36} concerns a photomagnetic material, that is material which can go reversibly from high-spin (HS) to low-spin (LS) state when triggered by the proper stimulus, e.g. light, but also temperature, pressure, pH. Prussian blue analogues (PBA) \( \text{A}_x\text{M(II)}_y[\text{M(III)(CN)}_6]\cdot z\text{H}_2\text{O} \), where A is an alkali ion, M(II) a bivalent metal ion and M(III) a trivalent metal ion are members of this new family of materials but very difficult to prepare as large size crystals or thin films by conventional chemical methods. In the publications in question Fe-Co PBA was synthesized “in-situ” on a substrate: the PBA building blocks self-assembled at the clay surface through cation exchange. The created clay stack then contains PBA inserted in a controlled fashion. The studies show that the photon induced charge transfer process leading to a switching of the magnetic properties is preserved in the HLB systems.\textsuperscript{35,36} We consider this study another milestone since it proved that one could create a functional material inserted between clay platelets without altering dramatically its properties. Even more interesting in terms of new functionality added to an existing material, is the second representative case chosen here, where the HLS-SA using the well known azobenzene (azo) as surfactant is applied to construct a stack alternating clay and a non-photoswitchable Prussian Blue (PB) molecular magnet\textsuperscript{37,38}. In short, the authors showed that this azo-clay-PB stack could be structurally deformed by light exposure\textsuperscript{39}. This deformation derives from the photoinduced trans-sis isomerisation of the azo but seems to induce a deformation of the PBA host compound as well as creating an increased or decreased magnetic interaction.

For more details on the developments and achievements using the LS method to prepare ultrathin hybrid films of clay minerals we refer the reader to the review written by the leaders and the initiator of the field.\textsuperscript{40}

So far we focused on the discoveries related to HLB-HLS films with clay only since clay is used in most applications of the hybrid method presented in this thesis. To finish this introduction chapter, we now review briefly some of the other materials put in use in HLS and discovered in parallel to the clay containing films.
He et al.\textsuperscript{41} reported the deposition of layer double hydroxide (LDH) using the same combination of LS deposition and SA as described above. The full approach is extremely similar to the clay cases (Hectorite, Saponite or Montmorillonite and very recently sepiolite\textsuperscript{42} fibres). The main difference is the opposite charge - LDH is naturally positive while clay platelets are negatively charged, which opens the route for new \textit{in situ} synthesis or SA like in the Umemura case\textsuperscript{24} but now for anion exchange reactions.

Tachibana et al\textsuperscript{43,44} reported on LB films prepared using alkylammonium halide or an alkylamine spread on a dispersion of MoS\textsubscript{2} previously prepared through various steps of exfoliation and sonication.

Last but not least, very recent work by Li et al.\textsuperscript{45} showed relatively poor results (but historically the first) on an attempt to deposit graphene oxide (GO) from an aqueous solution in the HLB-clay fashion (GO in the subphase hybridized by a surfactant). Those results were quickly followed by those of Cote et al.\textsuperscript{46} presenting a much improved control of the layer packing of pure GO, surprisingly without using a surfactant. In both these cases the transfer was done by vertical dipping and little or no process or electrical characterizations were performed to prove the quality of the produced material. Nearly simultaneously, our own results on GO were in press\textsuperscript{47} which presented a controlled deposition complemented with a full electrical characterization of GO and its main sub-product: Graphene.

Looking back at the history of these latest discoveries, its interesting to notice that one of the inventors of the HLB-clay method, Kotov published in 1996 (quite simultaneously with his HLB-clay paper) a paper about the layer-by-layer (LBL) assembly of graphite oxide\textsuperscript{48} therefore one would wonder why he actually never tried to deposit GO using the HLB method as he did for clay. After contacting him, the story got revealed, its seems N. Kotov actually tried (around 1996) to deposit GO using HLB and his work was fruitfull, but due to a succession of events the data could never be completed, neither published. A true question that remain unanswered is why Franklin\textsuperscript{2} did not calculate the thickness of the oil layer he produced on Clapham common’s pond.

\subsection*{1.4.2 Characterization tools}

Here is a short description of the instrumentation used for the investigation of the LB/LS films studied in this thesis.

\subsubsection*{1.4.2.1 Determination of Isotherms (in-situ)}

As we have seen in the section about “controlled packing and deposition” the Π - a isotherm measured in the LB trough yields crucial information for any material under investigation for potential deposition, hybrid or not. This isotherm is
established by recording the surface pressure as a function of the area per molecule obtained by compressing the investigated material floating at the interface between the movable barrier(s) of the LB trough. It bears this name not only because the temperature is kept constant while recording this curve, but more importantly because surface pressure and area are the free parameters of a 2D phase diagram and should be seen as equivalent of pressure and volume in 3D. The isotherm is determined by both the compound and by the subphase the latter is floating on.

1.4.2.2 X-ray diffraction (ex-situ)

Thin film X-ray diffraction is one of the key methods used in the study of Langmuir-Blodgett (LB) or Langmuir-Schaefer (LS) thin films. Its working principle is based on the diffraction of light by the network formed by the material under investigation.

For crystalline/layered materials constructive or destructive interference between the radiation reflected from successive crystalline planes (periodic structure) will occur. The processes leading to diffraction is represented figure 13, one can see a periodic structure formed by a classical LB film and an X-ray radiation beam represented by the continuous parallel black arrows with an incidence and reflected angle \( \theta \). Constructive interference will occur if path difference between the two beams is an integer multiple of \( \lambda \), the X-ray wavelength (commonly 1.54Å). This condition is fulfilled if the length of the optical path \( ABC=n \lambda \). Translated in terms of \( d(001) \) (interplanar distance) and \( \theta \) (beam angle to the surface) \( ABC \) become \( 2dsin\theta \). Those simple considerations lead to the famous Bragg formula.
This formula can then be used to retrieve the spacing \( d(001) \) from the value of the angle where the first peak is observed in a X-ray diffraction experiment.

For LB/LS films, this \( d(001) \) value, which indicates the size of the repeating unit perpendicular to the film surface gives valuable information regarding the conformation and/or tilting angle of the surfactant within the crystalline thin film. In our particular case, XRD was often used to confirm the presence of guest species within an organoclay or pure clay stack as well as for conformational information.

1.4.2.3 Microscopies (ex-situ)

In parallel to the diffraction measurements which probe the multilayer structure of the grown film, we also studied the morphology of the film surface and, when depositing only one layer, measured its height profile to confirm the single layer character. For these studies we used various microscopies, namely atomic force microscopy (AFM), scanning tunneling microscopy (STM) and scanning electron microscopy (SEM).

AFM is based on the following principle: a sharp tip (tip radius 5-20 nm) located at the apex of a flexible cantilever which is 100-150 \( \mu \)m long, is scanned over the sample and its deflection due to interaction with the surface detected. Depending on the nature of the tip and sample, the tip experiences van der Waals, capillary,
electrostatic or magnetic forces (or all of them). The infinitesimal deformation of the cantilever, proportional to the force(s) acting on the tip, are observed and recorded thanks to a laser, mirror (located at the back of the cantilever) and detector assembly as depicted if figure 14 and connected to a feedback system regulating the z-movement of the tip.

If the sample is rough, the cantilever bends under the force exerted when it encounters an obstacle such as a bump on the surface, and the light reflected off the mirror on the backside of the cantilever will be deviated. This deviation, recorded through the detector, will induce a reaction of the system (owing to a feedback loop) moving the tip up or downward to follow the sample roughness. This movement (of the z position) is recorded as a map of the sample topology (z as a function of x and y).

A second scanning probe microscopy used in this thesis is STM. STM was discovered by Binnig and Rohrer (who received the Nobel price in 1986 as a reward for that achievement) half a decade earlier then the AFM. The working

![Figure 15 Working principle of the scanning tunneling microscope (STM).](image)

principle, depicted in figure 15, is based on recording the tunneling current which flows from a metallic tip to a conducting surface or vice versa instead of the force as measured in AFM. As sketched in figure 15, when the supposedly atomically sharp tip scans over the surface, the tunneling current between the tip and sample varies because the electron density of states on the surface changes. Like in AFM, a feedback system reacts to this variation by raising or lowering the tip to keep the tunneling current constant - the STM is then operated in constant current mode. Alternatively, if the STM is operated in the constant z mode, the height of the tip is
kept constant through the feedback system and the tunneling current recorded to draw a map of the electronic density of states. In this thesis we used STM to study guest molecules grafted to the surfactant on a single transferred clay layer.

In SEM, which like STM works only on conducting samples, a finely focused high energy electron beam is scanned over the sample in vacuum. The energy exchange between the electron beam and the sample results in the reflection of high-energy electrons by elastic scattering, emission of secondary electrons by inelastic scattering and the emission of electromagnetic radiation, each of which can be detected by specialized detectors. Since both the reflection and the emission of secondary electrons depend on the surface morphology, SEM can produce very high-resolution images of a sample surface, revealing details on the nanometer scale. Due to the very narrow electron beam, SEM micrographs have a large depth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample. In our studies we employed SEM for the study of the morphology of transferred graphene and graphene oxide platelets and to do statistics on the size of the transferred sheets.

1.4.2.4 Spectroscopies (ex-situ)

In X-ray photoelectron spectroscopy (XPS) monochromatic X-rays are used determine which elements are present at a surface surface and in which chemical environment they are. As stated by its name, the photoelectrical effect, first observed in 1887 by Hertz but explained in 1905 by Einstein (by introducing the concept quanta), is at the centre of XPS’ working principle. A quantum of light or photon striking the surface will give its energy to an electron of a surface and this electron will then have enough energy to leave the material (and named photoelectron). By analyzing the kinetic energy of the photoelectrons one determines which atoms they came from, how strongly they were bound to the nucleus and surrounding. Energy conservation is translated into mathematical terms through the equations

\[ h \nu = E_b + E_k + W_f \quad \text{or} \]
\[ E_b = E_k - h \nu + W_f \]

where is \( h \nu \) the photon energy, \( W_f \) the spectrometer work function in case of a conducting sample, \( E_b \) the binding energy of the photoelectron and \( E_k \) its kinetic energy. One can see that measuring \( E_k \) and knowing the workfunction and the photon energy, allows one to determine the binding energy of the electron. The binding energy is not only element and core level specific, but also influenced by the valence/oxidation and spin states. Though the penetration depth of the
An introduction to the hybrid Langmuir-Schaefer approach

impinging X-ray in a given material is large, the escape depth of the photoelectrons (possessing an energy in the 0-1.5 keV range for a laboratory source) is limited by scattering. The electron mean free path in a solid material for the energy mentioned above is of the order of few nm. This explains the surface sensitivity of the method, only electrons coming out of surface atoms (few first atomic layers) will escape without energy loss (scattering). Photoelectrons emitted from deeper atoms will most likely be scattered several times within the solid matrix before eventually reaching the surface and is then no longer useful for retrieving the information or has simply lost all their energy before doing so. This powerful aspect of the method (its surface sensitivity) will be used in chapter 3 to confirm a structural model of an HLB organoclay film.

1.4.2.5 Infrared spectroscopy

Infrared spectroscopy (IR) was also used to confirm or refute the presence of species within the films grown using our method. This widespread method exploits the fact that molecules absorb specific radiations that are characteristic of their vibrational mode and hence structure. The frequencies depend on the shape of the molecular potential energy surface, the mass of the atoms, and the associated vibronic coupling. For a vibrational mode in a molecule to be "IR active," it must be associated with changes in the permanent dipole.

In practice, IR is performed by recording the transmitted or reflected intensity of a beam of infrared light to determine what wavelengths have been absorbed or attenuated. Each band of absorbed wavelength testifies to the presence of specific bonds assigned to specific molecules within the probed sample.

In this thesis we used IR spectroscopy to confirm the presence of all desired constituents – clay, surfactant and guest molecule – in our HLB organoclay films.

1.5 References

(2) Franklin, B.; Brownrigg, W.; Farish, M. Philosophical Transactions (1683-1775) 1774, 64, 445-460.
(8) Blodgett, K. B. Journal of the American Chemical Society 1934, 56, 495.


Appendix 1
Structural and statistical complementay information

Structure of triolein

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>$\text{C}<em>{57}\text{H}</em>{104}\text{O}_6$</td>
</tr>
<tr>
<td>Molar mass</td>
<td>885.432 g/mol</td>
</tr>
<tr>
<td>Density</td>
<td>0.95 g/cm$^3$</td>
</tr>
<tr>
<td>Melting point</td>
<td>5 °C</td>
</tr>
<tr>
<td>Boiling point</td>
<td>554 °C</td>
</tr>
</tbody>
</table>

Structure:

Molecular structure of triolein

Langmuir-Blodgett-Schaefer in history
In an attempt to understand the position of the Langmuir-Blodgett-Schaefer method and their hybrid version in today’s scientific landscape, a statistical analysis of thousands of articles published in the last century was performed. This statistical
research was based on the publication register in the ISI Web data base only. The starting assumption was that the number of publications containing various topic key words is a reflection of the actual activity of the field. This method obviously does not cover all the activity in a given field but can be considered as an index of the activity of the field.

The key word Langmuir-Blodgett was compared to several other experimental methods like STM, XPS, pump probe and research topics ($C_{60}$, graphene, nanotubes).

![Image of graph showing statistical data for various research topics]

**Figure A1-1 ISI web statistic by topic Langmuir Blodgett versus other techniques.**

At a first glance at the statistics of Langmuir-Blodgett versus other techniques as displayed in figure A1-1, reveals a sharp increase in scientific publications on all subjects around 1990. This feature common to all graphs displayed hereafter will be described later. When compared to other research tools such as XRD or XPS counting several thousand papers a year in the last few years, LB is steady with a few hundred publications/year, an activity roughly equal to that other well know methods like STM or the “pump probe”. The milestone of several methods is the attribution of a Nobel prize for the topic, strangely the later events do not really seem to affect much the activity of a given field. From this first graph the activity in the field of LB emerges as average, but did not explode unlike XPS and XRD which became daily tools. However, the next statistic figure A1-2, LB versus other research topic shows again interesting features.
Fig A1-2 ISI web statistic by topic Langmuir Blodgett versus other fields

Once more, the traces are dissimilar, topics like Graphene or Nanotubes exploded in the last few years and are subject to what appears to be an exponential growth. Interestingly, $C_{60}$ seems to have started exponentially but decays in the same way (but with a longer life time) shortly after its start. A first hypothesis to explain this behaviour, is to assume $C_{60}$ has been totally explored and lost all its interest. A second hypothesis (however related with the first one) is that $C_{60}$ by itself has lost interest but is still used in derivative compounds such as PCBM, used daily in the field of organic electronic. Following that second hypothesis, a material or method could then still be of great use but would (in our statistics) appear to have lost its interest because no longer described with the original keyword. We questioned ourselves whether this is the case for Langmuir-Blo dgett, which as one can see in Fig. A1-2 appears to have a slow decrease in interest lately. Is this loss caused by the rise of SAM? Or is LB still often used but no longer the topic of the research cited in the keywords? Both of these options are viable, it is therefore not clear whether LB looses interest due to lack of application and due to the complexity of the method as compared to SAM. Nevertheless the next graph gives some hope for the field. In figure A1-3, the keyword “Langmuir-Blodgett” is compared to “hybrid Langmuir Blodgett”.

As one can see that the counts of articles bearing LB as keyword is still 10 times higher then those citing the hybrid derivative method. However, while LB is on a slightly decreasing slope since 1995, the hybrid method, born around that time is increasing ever since. One can speculate on the future of the method, and ask oneself whether one day the hybrid is going to surpass classical LB? It is up to us to make that future as bright as possible.

The rise of the internet?

One striking feature appears on every single graph having a record starting prior to 1980, such as LB, STM, XRD, XPS. What happened around 1990? What did create this sudden rise of activity? Why did the overall research landscape get affected at once? Is this rise topic specific? Since all the items we analyzed are somehow related to materials science, maybe the rise of the latter caused the other topics to rise as well? To understand these tendencies we broadened the research topics we examined beyond materials science to actually probe the pure sciences themselves. In figure A1-4 a statistics of the record of articles published in physics and chemistry over the years is displayed. One can clearly see that the 1990’s rise is even more pronounced than in the previous figures. From this behaviour we can deduce that the rise in not affecting material science alone but affects all fields of physics and chemistry.
Figure A1-4 Statistics extracted from the ISI web of science for the record of physics and chemistry items published compared to the rise of computer and internet users. The internet growth data are from (www.internetworldstat.com) computer user data from the International Telecommunications Union data goes up to 2005.

A beginning of answer to clarify the origin of this growth appears when comparing the rise of the number of publications/year to the rise of internet and PC users. Figure A1-4 shows the increasing availability of computer related resources and of the internet* clearly affects the increase in yearly published items. This correlation can be easily understood, since the rise of the computer made all the processes from measurements in the lab to the writing of a manuscript faster. The internet gives a faster access to information, speeds up communication and data exchange and made peer reviewing an easy and “fast” process. Additional factors could

* PC and Internet probably arrived a bit earlier in the academic environment compared to normal households users included in the statistics displayed in figure A1-4
come from an overall population growth, and a growth of the scientific community population.
It is then reasonable to assume that due to the limitations imposed by the capacity of humans to elaborate this information, this rise is going to (hopefully) saturate soon and reach a stable level of few tenth of thousands of publications per year for both the field of physics and chemistry (and most probably other all the academic research).