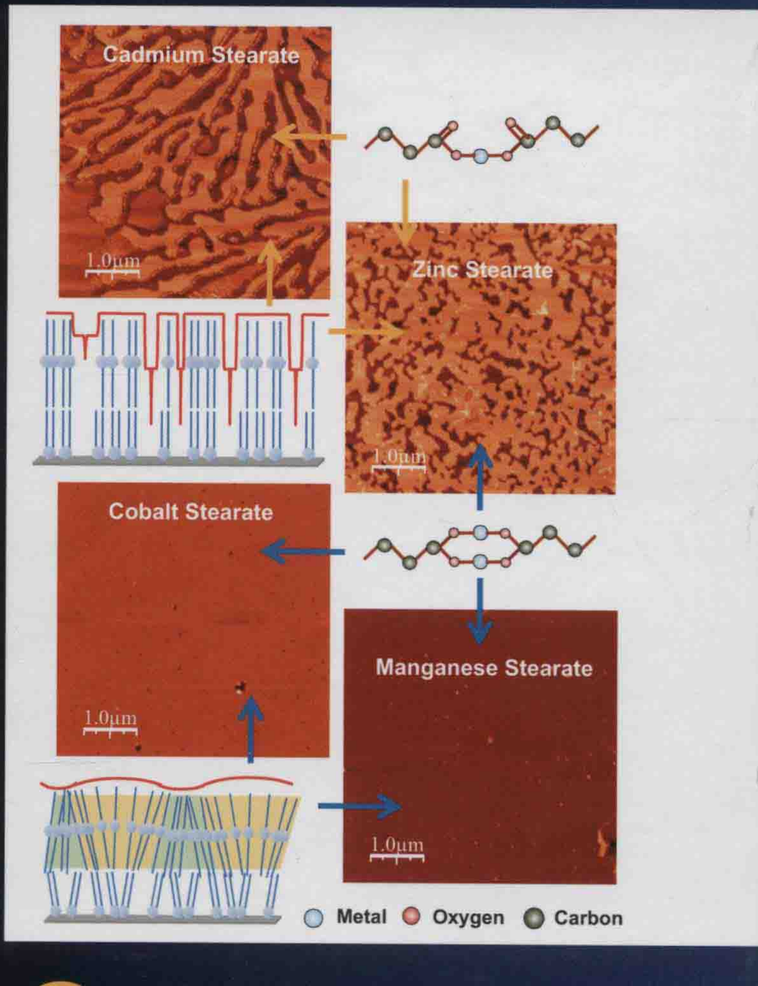
STRUCTURAL AND MORPHOLOGICAL EVOLUTION IN METAL–ORGANIC FILMS AND MULTILAYERS

ALOKMAY DATTA • SMITA MUKHERJEE



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Foreword

Two female scientists tower over the field of organic monolayers and multilayers. In 1891, *Nature* published a remarkable paper titled Surface Tension. The manuscript had been sent to Lord Rayleigh from Germany by Agnes Pockels, who did not have (and at that time could not have obtained) a formal scientific education, but had performed groundbreaking experiments on floating monolayers in her kitchen. Some decades later, in 1918, Katherine Blodgett received a master's degree from the University of Chicago and became the first woman ever hired by the General Electric research laboratory. Working with Irving Langmuir, perhaps the field's most well-known figure, she developed the Langmuir–Blodgett method for building up organic multilayers using layer-by-layer deposition of floating monolayers. It is important to realize that, long before words such as surface science and nanotechnology came into vogue, these scientists were manipulating nanoscale layers of molecules at surfaces, and building artificially structured materials with designed properties and practical applications. (Reportedly, the movie *Gone with the Wind* used Langmuir–Blodgett multilayers as antireflective coatings for their camera lenses.) And they were doing all this not with millions of dollars of shiny stainless steel equipment but with basic, often store-bought tools. Because of the ease and power of these techniques, they have never really gone out of use, and the subject has enjoyed a renaissance in recent years. This revival has been driven by new scientific questions and new molecular materials, but perhaps most of all it has been transformed by new characterization techniques that Pockels, Langmuir, and Blodgett could never have imagined. My own expertise is in the area of x-ray scattering, but methods such as ellipsometry, The other question which intrigued and motivated us was the effect of the lowering of dimensionality on bonding. To put it in a different way: Does a two-dimensional system have different kinds of bonds than a bulk or three-dimensional body? The answer to that, we felt, would tell something about the "weird" chemistry these materials have. As any chemist will tell you, it is impossible to prepare transition element salts of long-chain fatty acids by direct reaction of the fatty acid with the oxide or hydroxide of the transition element. In contrast, as early as the 1930s Irving Langmuir showed that a monolayer of fatty acid on a water surface could "sense" and react to 3×10^{-10} g cm^{-3} of Al ions, or around 7 Al ions per μm^{-3} of water! Hence if you want to prepare, say, cobalt stearate all you need to do is spread a monolayer of amphiphilic stearic acid on water containing cobalt ions as obtained by dissolving cobalt chloride, and the cobalt ions will do the rest themselves. If you now transfer the monolayer onto any substrate and go on repeating the process (as Katherine Blodgett did) you end up with a multilayer of cobalt stearate with some unreacted acid that can be easily washed away. This made us wonder whether the acid molecule at the water surface is the same as that in the bulk body and we found that in fact, it is not.

When, in the course of our work, we got some answers to our queries and published the results in journals, we were lucky to have two sources of inspiration in the form of Professor Gour Prasad Das of the Indian Association for the Cultivation of Science, a premier institute in India and Aastha Sharma of Taylor & Francis. While the first ignited the spark of an idea about writing a book that covers these newfound aspects of these two-dimensional, complex, soft materials, the latter with immense patience has kept the flame burning. This book owes its existence to these two, especially the latter. Then there is Professor Pulak Dutta of Northwestern University, USA, who over and above being the guiding light of one of us (Alokmay) in his research on Langmuir monolayers, agreed to write the foreword for the book, to our great delight and thankfulness. Uttam Basak, our friend (and Alokmay's student), took the trouble of writing the entire section on ellipsometry and Brewster angle microscopy for us.

We should humbly submit that this book is far from an exhaustive survey. We were interested in giving our readers glimpses of the richness hidden in these supposedly well-known systems and, among the amphiphiles, we chose the most well-known, the saturated, aliphatic fatty acids. They have been the "physicists' workhorses," and we also started looking for the mechanisms behind the growth of monolayers and multilayers of these molecules primarily from a physicist's point of view. However, when we brought in the metal ions we saw some interplay between physics and chemistry. We hope that, if nothing else, this book may lead people to take more interest in these issues and ask more questions. In fact, that will be much more than we can expect.

There are a number of people who stood by us in our research. Professor Milan Kumar Sanyal was instrumental in bringing research on surfaces and interfaces to our institute and building up our whole group. Without his active leadership work on monolayers, multilayers and nanomaterials could not have taken the shape we have given them. Professor Stefano Nannarone of the University of Modena e Reggio Emilia and in charge of the BEAR beamline at ELETTRA Synchrotron, Italy, and his dedicated beamline scientists, Dr. Angelo Giglia and Dr. Nicola Mahne, helped us immensely at the beamline and were ready (even at 2 a.m.!) to discuss the nuances of XAFS measurements in the context of our samples. In this connection we gratefully acknowledge the financial support of the Department of Science and Technology, India, and the Programme of Cooperation, Italy, which made these experimental visits possible.

Both of us are extremely fortunate to have immensely supportive families. Our spouses Biswajit and Neepa have been our fountains of strength throughout. Little Bitan (Smita's son), with his happy face and Swapnasopan (Alokmay's son), with his fresh and incisive questions, have provided the ballast to move on with our work. Finally, we can never forget the influences of our parents in shaping our paths, both in and out of the lab.

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Chapter 1

Monolayers and Multilayers

1.1 About This Book

Ultrathin and thin films with carefully designed structures and properties have attracted a great deal of interest in recent years [1–5] due to their potential applications in a number of different fields, such as sensors [6–8], detectors [1–3], surface coating [4, 5], optical signal processing [9–11], digital optical switching devices [12–14], molecular electronic devices [15–21], nonlinear optics and models mimicking biological membranes [22–24]. These applications require, in general, well ordered films consisting of molecules with specific properties, carefully aligned with respect to each other and to the substrates, and possessing high degree of stability to thermal and chemical changes. Langmuir–Blodgett (LB) technique is a simple but powerful tool for creating carefully controlled supramolecular structures of organized molecular assemblies. The structure, morphology, configuration and various other physical properties of the films obtained by LB technique can be easily modified to suit any specific application. The possibility to synthesize organic molecules almost without limitations and with desired structure and functionality, in conjunction with Langmuir–Blodgett film deposition technique, enables the production of electrically, optically, and biologically active components on a nanometer scale. It is thus extremely important to get an idea about the relation between the molecular structure and the domain structure on one hand and the various physical properties of such systems on the other. The basic physics involved in such interrelations, as we shall see in this book, is a topic of fundamental importance.

This book relates some structural, bonding and morphological aspects of ultrathin metal–organic films deposited by the LB technique. Before proceeding on to discuss the outline of our work, in this introductory chapter, we have talked about Langmuir monolayers and Langmuir–Blodgett films, basics of their growth mechanism and some related aspects of metal–organic complexes, along with a brief review of initial scientific observations.

1.2 Langmuir Monolayers

In 1917, Irving Langmuir developed experimental and theoretical concepts which underlie present day understanding of behavior of molecules in insoluble monolayers on water [25]. Organic films can be formed on the water surface very easily by choosing a special type of molecule called an *amphiphilic molecule* [3, 26, 27]. These molecules have two parts, one part (called head) is soluble in water, i.e., hydrophilic and the other part (called tail) is insoluble in water, i.e., hydrophobic (Fig. 1.1). When such molecules are spread on water, the amphiphilic molecules produce a monomolecular layer with the heads touching water and the tails pointing

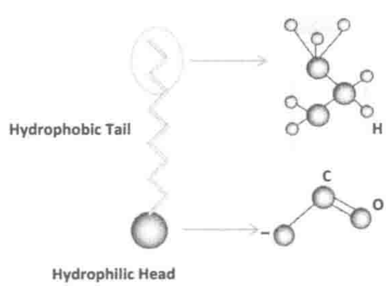

Figure 1.1: *Long chain fatty acid: A typical amphiphile.*