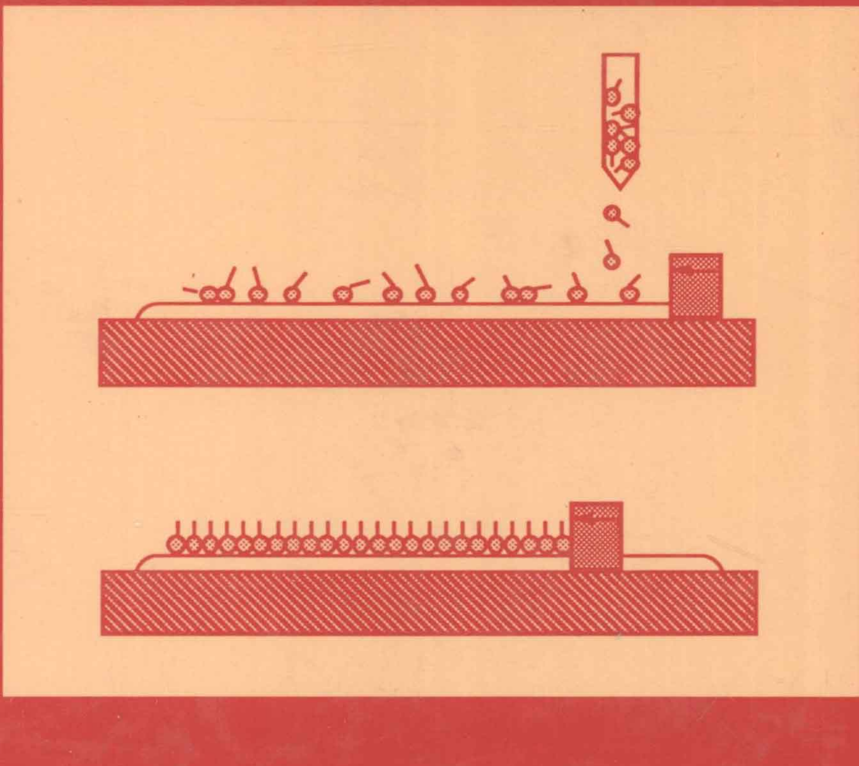
An

Introduction to

ULTRATHIN ORGANIC FILMS

From

Langmuir–Blodgett to Self-Assembly



Abraham Ulman

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To my wife Hanna
and my children Tzipor, Amihai, and Matan.

"Today...I propose to tell you of a real two-dimensional world in which phenomana occur that are analogous to those described in 'Flatland.' I plan to tell you about the behavior of molecules and atoms that are held at the surface of solids and liquids."

— I. Langmuir, *Science* **1936**, *84*, 379.

PREFACE

About 70 years ago, Langmuir published his first work on the study of two-dimensional systems of molecular films at the gas–liquid interface [1]. However, it was only about 10 years ago that interest in this area started to grow at an impressive pace; and in about the same time, a self-assembled (SA) monolayer of octadecyltrichlorosilane ($C_{18}H_{37}SiCl_3$, OTS) was introduced as a possible alternative to the Langmuir–Blodgett (LB) system [2], and, recently, a relatively thick (~0.1 μm) multilayer film was formed by self-assembly of methyl 23-trichlorosilyltricosanoate [3].

That Langmuir–Blodgett and SA films are important is apparent from the exponential growth in the number of publications in these areas. I feel that at least part of this interest results from the fact that optoelectronics [4–10] and molecular electronics [11–19] have become areas at the frontier of materials science. In both cases, there are limitations to what inorganic materials can provide, and therefore ordered organic materials are likely to become increasingly important. In both areas, it is believed that LB and SA monolayers may provide the desired control on the order *at the molecular level* and thus should be considered potential techniques for the construction of future organic materials.

Although nonlinear optics (NLO) and molecular electronics represent distinct areas of investigation, we see that they share a common requirement for the development of thermally stable, ordered organic (or organometallic) molecular systems. It is important that organic materials be developed in which interesting properties can be tailored by incorporating appropriate chromophores or other functional groups. Furthermore, a high degree of control over the orientation of these groups also is desirable.

Thus, it can be seen that the advent of materials science requires research and development in what may be termed *materials engineering*. The goal of such research is to attain the capability of *assembling individual molecules into highly ordered architectures*. Although attainment of such a goal until recently could be considered practically impossible, the development of oriented organic monomolecular layers by the LB and SA techniques opens the way to the realization of this goal. Analogues of nature's lipid bilayers, these two-dimensional structures allow scientists to construct films with a high degree of orientation within layers, and to construct *molecular architectures* by varying the constituents of adjacent monolayers.

One of the exciting aspects of thin organic films, in my view, is that it is an interdisciplinary area, forming bridges between the areas of physics, chemistry, and biology. With all this in mind, this area has not yet been accepted as a legitimate research interest in many chemistry departments in this country.

In 1965, George L. Gaines, Jr., wrote a book entitled *Insoluble Monolayers at Liquid–Gas Interfaces* [20]. This work, which has provided guidance for many of us in the area, still is one of the most used and cited references. However, since that book was published, there has been no other book on this subject. Recent developments in the area of ultrathin organic films have prompted me to write this book, with the idea of starting where Gaines finished, and complementing his work. There are excellent works in related areas, and they are listed as well. I refer the reader to discussions in other books when appropriate.

The continually growing contribution of LB and SA systems to the chemistry and physics of thin organic films, of course, is widely recognized. Equally well-known is the difficulty in keeping up-to-date with the multidisciplinary research in this area that seems to be spawned at an ever-increasing rate. Indeed, when I started the literature search for this book, it became clear very quickly that it would be impossible to cover the entire richness of this area in only one book. The original plan was to have a book of no more than 300 pages, but the book you hold in your hands is considerably longer. This is a result of my desire to cover as many areas—and to provide as many references—as possible. Most of these references are taken from before December 1989; however, in some cases, references from later dates have been included.

The development of surface analytical tools in the last decade makes it possible to address structural issues of monomolecular layers in great detail, and with unprecedented precision. Therefore, I start the book with Part One, "Analytical Tools," with the hope that it will help the reader understand the structure and properties of monolayers and films. Part Two is dedicated to Langmuir–Blodgett films. Part Three describes the preparation and properties of self-assembled monolayers and films. In Part Four, we discuss the modeling of LB and SA monolayers. I decided to write this part because I believe modeling will become an obvious part of any materials science activity in the 1990s and beyond. Finally, in Part Five, we discuss applications of LB and SA films.

One remark has to be made regarding the literature on this subject. This literature contains hundreds of patents and papers in Japanese for which no English version has been available. Therefore, I could not refer to them in a precise way, and, unfortunately, did not even mention most of them in the list of references.

This book is an overview, with a strong emphasis on materials, and has been written for scientists and graduate students; I hope that both will find it useful as an introduction to the field. Let me take this opportunity to invite readers to bring to my attention errors and/or obscurities. I thank everyone in advance for his or her effort.

It is impossible for me to finish this introduction without emphasizing the encouragement, support, and cooperation of my wife, Hanna, throughout my scientific adventures, and during the preparation of this book. To her I dedicate this book with great love.

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Grateful acknowledgment is made to all who extended their permission to reproduce material from their work. These resources are mentioned in the text or in the captions, as appropriate.

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