

Langmuir–Blodgett films

An introduction

MICHAEL C. PETTY

University of Durham, UK



CAMBRIDGE
UNIVERSITY PRESS

Published by the Press Syndicate of the University of Cambridge
The Pitt Building, Trumpington Street, Cambridge CB2 1RP
40 West 20th Street, New York, NY 10011-4211, USA
10 Stamford Road, Oakleigh, Melbourne 3166, Australia

© Cambridge University Press 1996

First published 1996

Printed in Great Britain at the University Press, Cambridge

A catalogue record for this book is available from the British Library

Library of Congress cataloguing in publication data

Petty, M. C.

Langmuir-Blodgett films: an introduction / M. C. Petty.
p. cm.

Includes bibliographical references.

ISBN 0 521 41396 6. – ISBN 0 521 42450 X (pbk)

1. Thin layers, Multilayered. I. Title.

QC176.9.M84P45 1996

530.4'275 – dc20. 95-2781 CIP

ISBN 0 521 41396 6 hardback

ISBN 0 521 42450 x paperback

for Anne

Preface

Langmuir–Blodgett (LB) films have been the subject of scientific curiosity for most of the twentieth century. However, interest has grown significantly since the 1970s – a direct result of the work of Hans Kuhn and colleagues on energy transfer in multilayer systems. This introduced the idea of *molecular engineering*, i.e., using the LB technique to position certain molecular groups at precise distances to others. In this way new thin film materials could be built up at the molecular level and the relationship between these artificial structures and the natural world explored.

There are already several books that cover LB and related thin films. So why another? My own background is in electronics. While I have been involved in LB film research I have spent many hours pondering on chemical formulae, struggling with biological nomenclature and trying to understand the finer points of thermodynamics. The scope of the subject is continuing to grow and anyone now starting work in the area must assimilate an enormous amount of information. My intention therefore has been to provide a gentle introduction to newcomers with an emphasis on the multidisciplinary and interdisciplinary nature of the field.

Each chapter addresses a different issue. Chapter 1 describes the various bulk phases of matter and outlines physical principles that can be used to model these. Monolayer phases are introduced in chapter 2. Much is still to be learnt about the nature of even the simplest monolayers and I have concentrated on experimental aspects rather than theory. The LB process itself is discussed in some detail in chapter 3. Again, my aim has been to provide useful practical information. I have also briefly reviewed related thin film techniques. Materials that can be manipulated at the air/water interface are described in chapter 4. In chapter 5 the main methods of investigation are introduced and some important results outlined. Chapter 6 covers the

electrical behaviour. This is an area that has attracted considerable interest, not least because of the possibilities of exploiting LB layers in electronic device structures; I have included a section outlining such ideas. Finally, chapter 7 provides an overview of the optical properties of mono- and multi-layer films.

At the end of each chapter, I have given the key references. These should be good starting points for the reader wishing to delve deeper. Important subjects such as crystallography, chemical bonding and the interaction of electromagnetic radiation with thin films are dealt with in separate appendices.

I hope that the result is a book readily accessible to both new research students and more experienced workers.

Acknowledgements

I am indebted to colleagues at Durham and elsewhere for the encouragement to write this book. Members of the Durham Centre for Molecular Electronics have helped with many useful suggestions. I am particularly grateful to Jim Feast for the tutorials on organic chemistry and to John Cresswell for advice on nonlinear optics.

Original photographs were provided by Jas Pal Badyal and Simon Evenson, David Batchelder, Harald Fuchs and Mathias Lösche. Dirk Hönig spent many hours working on the cover photograph. Julie Morgan helped with the rest of the photography. Kay Seaton put in a tremendous effort drawing all the diagrams and deserves my very special thanks.

Notes for reference

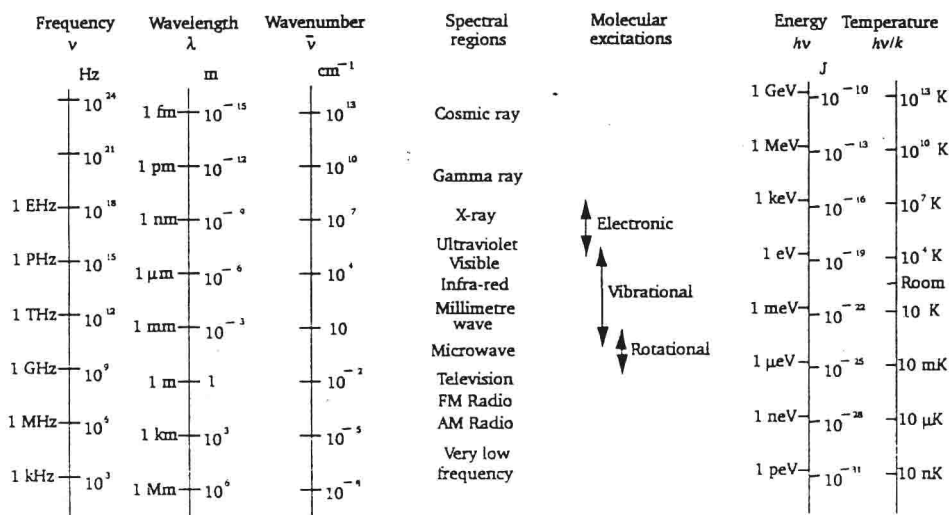
Constants

| | |
|--|--|
| velocity of light in free space c | $2.998 \times 10^8 \text{ m s}^{-1}$ |
| permittivity of free space, ϵ_0 | $8.854 \times 10^{-12} \text{ F m}^{-1}$ |
| electronic charge, q | $1.602 \times 10^{-19} \text{ C}$ |
| Planck's constant, h | $6.626 \times 10^{-34} \text{ J s}$ |
| Boltzmann's constant, k | $1.381 \times 10^{-23} \text{ J K}^{-1}$ |
| Avogadro's number, N_A | $6.022 \times 10^{26} \text{ kilomole}^{-1}$ |
| universal gas constant, R | $8.314 \times 10^3 \text{ J kilomole}^{-1} \text{ K}^{-1}$ |

Useful relationships

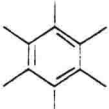
1 electronvolt (eV) = $1.602 \times 10^{-19} \text{ J}$
for vacuum, energy in eV = $1.240/(\text{wavelength in } \mu\text{m})$
1 eV = 8066 cm^{-1}
1 eV per particle = $23\,060 \text{ kcal kilomole}^{-1}$ (= $23.06 \text{ kcal mole}^{-1}$)
1 calorie = 4.186 J
at 300 K, $kT \approx 1/40 \text{ eV}$
1 atmosphere = $1.013 \times 10^5 \text{ N m}^{-2}$

The electromagnetic spectrum



$$[1\text{Hz} \equiv 3.00 \times 10^8 \text{ m} \equiv 4.14 \times 10^{-15} \text{ eV} \equiv 4.80 \times 10^{-11} \text{ K}]$$

Simple functional groups

| Compound type | Functional group |
|---------------------------|---|
| Alkene (double bond) | >C=C< |
| Alkyne (triple bond) | $\text{—C}\equiv\text{C—}$ |
| Alkyne (aromatic ring) |  |
| Halide | >C—X (X = F, Cl, Br, I) |
| Alcohol | >C—O—H |
| Ether | >C—O—C< |
| Carbonyl | >C=O |
| Aldehyde | >C—C(=O)H |
| Ketone | >C—C(=O)—C< |
| Ester | >C—O—C(=O)—C< |

| Compound type | Functional group |
|--------------------------|-------------------------------|
| Carboxylic acid | >C(=O)—O—H |
| Carboxylic acid chloride | >C(=O)—Cl |
| Amide | >C(=O)—N< |
| Amine | >C—N< |
| Nitrile | $\text{—C}\equiv\text{N}$ |
| Nitro | $\text{>C—N}^+\text{(=O)O}^-$ |
| Sulfide | >C—S—C< |
| Sulfoxide | >C—S(=O)—C< |
| Sulfone | $\text{>C—S(=O)}_2\text{—C<}$ |
| Organometallic | >C—M (M = metal) |

Contents

| | |
|---|------------------|
| <i>Preface</i> | <i>page</i> xiii |
| <i>Acknowledgements</i> | xv |
| <i>Notes for reference</i> | xvi |
| <i>Constants</i> | xvi |
| <i>Useful relationships</i> | xvi |
| <i>Electromagnetic spectrum</i> | xvii |
| <i>Simple functional groups</i> | xviii |
| | |
| 1 The bulk phases of matter | 1 |
| 1.1 Gases, liquids and solids | 1 |
| 1.2 Liquid crystals | 2 |
| 1.3 Phase changes | 4 |
| 1.4 Thermodynamic equilibrium | 8 |
| 1.5 Phase rule | 9 |
| <i>References</i> | 10 |
| | |
| 2 Monolayers: two-dimensional phases | 12 |
| 2.1 The gas–liquid interface | 12 |
| 2.2 Monolayer materials | 14 |
| 2.3 Monolayer stability | 16 |
| 2.4 Monolayer phases | 17 |
| 2.5 Monolayer compressibility and viscosity | 30 |
| 2.6 Electrical effects in monolayers | 31 |
| 2.7 Mixed monolayers | 35 |
| 2.8 Chemistry in monolayers | 37 |
| <i>References</i> | 37 |

| | | |
|------|---|-----|
| 3 | Film deposition | 39 |
| 3.1 | Deposition principles | 39 |
| 3.2 | Deposition speed | 43 |
| 3.3 | Molecular re-arrangement | 43 |
| 3.4 | First layer effects and epitaxy | 45 |
| 3.5 | Defects | 47 |
| 3.6 | Deposition onto rough or porous surfaces | 48 |
| 3.7 | Equipment for LB deposition | 49 |
| 3.8 | Experimental techniques | 55 |
| 3.9 | Post deposition treatments | 58 |
| 3.10 | Related thin film deposition techniques | 60 |
| | <i>References</i> | 63 |
| 4 | Monolayer materials | 65 |
| 4.1 | Fatty acids and related compounds | 65 |
| 4.2 | Simple substituted aromatic compounds | 69 |
| 4.3 | Dyes | 73 |
| 4.4 | Porphyrins and phthalocyanines | 75 |
| 4.5 | Fullerenes | 76 |
| 4.6 | Charge-transfer complexes | 77 |
| 4.7 | Polymers | 78 |
| 4.8 | Biological compounds | 83 |
| | <i>References</i> | 91 |
| 5 | Structure of multilayer films | 94 |
| 5.1 | Organization in long-chain materials | 94 |
| 5.2 | X-ray reflection | 98 |
| 5.3 | Neutron reflection | 104 |
| 5.4 | Electron microscopy | 106 |
| 5.5 | Infrared spectroscopy | 112 |
| 5.6 | Scanning tunnelling and atomic force microscopies | 121 |
| 5.7 | Surface analytical techniques | 124 |
| 5.8 | Film thickness measurements | 126 |
| 5.9 | Other methods | 127 |
| | <i>References</i> | 128 |
| 6 | Electrical phenomena | 131 |
| 6.1 | Basic ideas | 131 |
| 6.2 | Practical considerations | 134 |
| 6.3 | Quantum mechanical tunnelling | 139 |
| 6.4 | Space-charge injection | 141 |
| 6.5 | Schottky and Poole-Frenkel effects | 143 |
| 6.6 | Dielectric processes | 145 |

| | |
|--|-----|
| 6.7 Semiconducting multilayers | 150 |
| 6.8 LB film devices | 153 |
| <i>References</i> | 164 |
| 7 Optical properties | 167 |
| 7.1 Refractive index | 167 |
| 7.2 Ellipsometry | 168 |
| 7.3 The evanescent field | 170 |
| 7.4 Surface plasmon polaritons | 171 |
| 7.5 Optical waveguiding | 175 |
| 7.6 Dye layers | 179 |
| 7.7 Second-order nonlinear optical behaviour | 186 |
| 7.8 Third-order nonlinear optical effects | 194 |
| <i>References</i> | 194 |
| <i>Appendices</i> | |
| A Electronic energy levels in organic solids | 197 |
| A.1 Bonding in organics | 197 |
| A.2 Band theory | 203 |
| <i>Further reading</i> | 206 |
| B Interaction of electromagnetic radiation with organic thin films | 207 |
| B.1 Electromagnetic radiation | 207 |
| B.2 Interaction with solids | 208 |
| B.3 Linear optics | 209 |
| B.4 Nonlinear optics | 211 |
| B.5 Reflection and transmission from thin films | 212 |
| B.6 Absorption processes | 216 |
| B.7 Emission processes | 220 |
| <i>Further reading</i> | 221 |
| C Crystallography | 222 |
| C.1 The crystal lattice | 222 |
| C.2 Crystal systems | 222 |
| C.3 Miller indices | 224 |
| C.4 Distance between crystal planes | 225 |
| <i>Further reading</i> | 226 |
| <i>Materials index</i> | 227 |
| <i>Subject index</i> | 229 |

The bulk phases of matter

1.1 Gases, liquids and solids

The three most common states, or *phases*, of matter, *gases*, *liquids* and *solids* are very familiar (Walton, 1976). Phases that are not so well known are *plasmas* and *liquid crystals* (although these are both found in electrical and electronic devices in everyday use). All these states are generally distinguished by the degree of *translational* and *orientational order* of the constituent molecules. On this basis some phases may be further subdivided. For example, solids, consisting of a rigid arrangement of molecules, can be *crystalline* or *amorphous*. In an amorphous solid (a good example is a glass), the molecules are fixed in place, but with no pattern in their arrangement. As shown in figure 1.1, the crystalline solid state is characterized by long-range translational order of the constituent molecules (the molecules are constrained to occupy specific positions in space) and long-range orientational order (the molecules orient themselves with respect to each other). The molecules are, of course, in a constant state of thermal agitation, with a mean translational kinetic energy of $3kT/2$ (k is Boltzmann's constant, T is temperature; $kT/2$ for each component of their velocity). However, this energy is considerably less than that associated with the chemical bonds in the material and the motion does not disrupt the highly ordered molecular arrangement.

In the gaseous state, the intermolecular forces are not strong enough to hold the molecules together. They are therefore free to diffuse about randomly, spreading evenly throughout any container they occupy, no matter how large it is. The average interatomic distance is determined by the number of molecules and the size of the container. A gas is easily compressed, as it takes comparatively little force to move the molecules closer together.

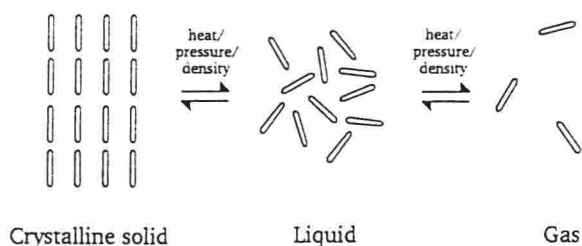


Figure 1.1 The three most common bulk phases of matter.

On the microscopic level, the liquid state is generally thought of as a phase that is somewhere between that of a solid and that of a gas. The molecules in a liquid neither occupy a specific average position nor remain oriented in a particular way. They are free to move around and, as in the gaseous state, this motion is random. The physical properties of both liquids and gases are *isotropic*; i.e., they do not depend upon direction (direction-dependent properties are called *anisotropic*). Therefore, there is a similarity between liquids and gases and under certain conditions it is impossible to distinguish between these two states. When placed in a container, the liquid will fill it to the level of a free surface. Liquids flow and change their shape in response to weak outside forces. The forces holding a liquid together are much less than those in a solid. Liquids are highly incompressible, a characteristic that is exploited in hydraulic systems.

Almost all elements and chemical compounds possess a solid, a liquid and a gaseous phase. The gaseous phase is favoured by high temperatures and low pressures. A transition from one phase to another can be provoked by a change in temperature, pressure, density or volume.

1.2 Liquid crystals

The melting of a solid is normally a very sharp transition. As the material is heated, the order of the system abruptly changes from that of the three-dimensional order of the solid to the zero order associated with the liquid. However, it is not uncommon for an *organic* solid to pass through intermediate phases as it is heated from a solid to a liquid. Perhaps one in every few hundred organic compounds exhibits such behaviour. Such phases are known as *mesophases*. When such a state is formed, the translational order of the solid phase may be lost, but the orientational order remains. The resulting phase is termed a *thermotropic liquid crystal* (Collings, 1990). Sometimes a mesophase may display translational order but no orientational order; this is termed a *plastic crystal*. A very wide range of liquid crystal phases is now known. These are identified by the degree of short range translational order and by the shape of the molecules.

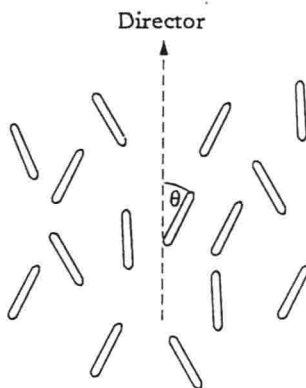


Figure 1.2 Arrangement of rod-shaped molecules in a liquid crystalline phase. Each molecule makes an angle of θ with the director.

The *nematic* (from the Greek word for thread) phase is the least ordered liquid crystal phase and is exploited extensively in electrooptic applications. This phase has no long-range translational order and only orientational order. There is only one nematic phase and, on heating, this will eventually become an isotropic liquid. A schematic diagram, showing the arrangement of rod-shaped molecules in a nematic phase, is given in figure 1.2. The molecules in the liquid crystal are free to move about in much the same fashion as in a liquid; as they do so they tend to remain orientated in a certain direction. The direction of preferred orientation is called the *director* of the liquid crystal. Each molecule is oriented at some angle θ about the director. The degree of orientational order is given by the *order parameter* S which is defined

$$S = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle \quad (1.1)$$

A value of $S = 1$ indicates perfect orientational order whereas no orientational order results in $S = 0$.

Smectic (from the Greek word for soap) phases are usually formed by thermotropic liquid crystals at lower temperature than the nematic phase. Besides the orientational order, smectic phases possess one-dimensional translational ordering into layers. The smectic phases can be further subdivided and, at present, twelve different types have been identified. These are designated S_A, S_B, \dots, S_K ; there are two smectic S_B phases – the *crystal B* and *hexatic* (for a discussion of this phase, see Tredgold 1994) S_B phases. Some of these mesophases (crystal B, S_E, S_G, S_H and S_I) have very long-range correlation of position over many layers and are more similar to crystalline solids.

The S_A phase is the least ordered of the thermotropic smectic phases. The molecules are arranged in disordered layers, each layer having a liquid-like

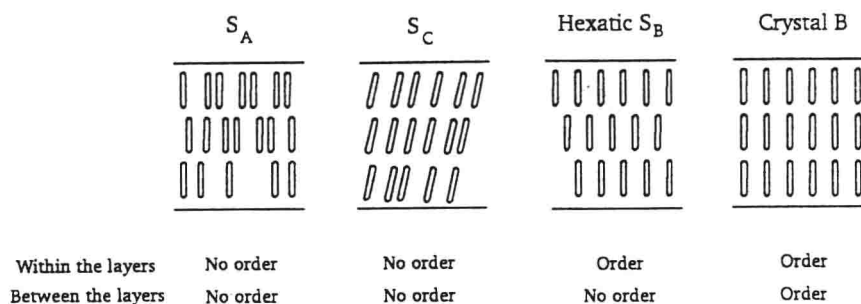


Figure 1.3 Different smectic liquid crystalline arrangements of rod-shaped molecules. S_C is a tilted version of S_A .

freedom of motion of its constituent molecules in two dimensions, with the director perpendicular to the layer planes. By contrast, in the S_C phase the molecules are tilted from this direction by about 35° . This tilt is correlated between molecules within each layer and from one layer to another. In the hexatic S_B phase, there is again ordering of orientationally aligned molecules into layers. The molecules are arranged in a hexagonal array but the translational order is short-range only. The orientation of the hexagonal net is, however, maintained over a long range and unlike the ordering of molecular positions, is correlated between layers. Two tilted variations of the S_B phase exist in which the tilt direction is constrained to point either towards one face of the hexagonal lattice (S_F) or towards one apex (S_I). The S_A , S_C , hexatic S_B and crystal B arrangements of rod-shaped molecules are contrasted in figure 1.3 (Lacey, 1994). Further details about these smectic liquid crystal phases are to be found in the book by Gray and Goodby (1984).

The final distinct type of liquid crystalline mesophase is the *cholesteric* or *chiral nematic*. The molecules in such a phase are arranged in a unique helical structure in which the director gradually rotates from one plane of molecules to the next. Such phases can exhibit vivid colour effects that change with temperature (as the pitch of the helix changes) and are exploited as temperature sensors. These molecules may also form smectic phases.

1.3 Phase changes

The science of thermodynamics allows the properties of the various phases of matter to be correlated. The *state* of any thermodynamic system (e.g., a fixed amount of matter) is specified by values of certain experimentally variable quantities called *state variables* or *properties*. Familiar examples are the temperature of a system, its pressure and the volume occupied by it. Those properties that are proportional to the mass of the system are called *extensive*; examples are the total volume and total energy of the