

The
Physical
Properties
of
Organic
Monolayers

Mitsumasa Iwamoto

Tokyo Institute of Technology

Wu Chen-Xu

Tohoku University



World Scientific

Singapore • New Jersey • London • Hong Kong

CONTENTS

CHAPTER 1	INTRODUCTION	1
1.1	Monolayer Structure and Monolayer Properties	2
1.2	Surface Pressure/Area Isotherm	3
1.3	Maxwell Displacement Current Measurement Technique	3
1.4	Molecular Dynamics of Monolayer Films	5
1.4.1	Orientalional Orders in Two-dimensional Systems	5
1.4.2	Interactions	8
1.4.3	State Equation and Piezoelectric Effect	8
1.4.4	Dielectric Constant	9
1.4.5	Phase Transition and Critical Phenomena	9
1.4.6	Dielectric Relaxation Phenomena	10
1.4.7	Pattern Formation	10
1.4.8	Optical Activity and Nonlinear Effect	11
1.4.9	Thermally Stimulated Phenomena	13
1.4.10	Electronic Properties at MIM Interfaces	14
	References	17
CHAPTER 2	POLARIZATION AND DIELECTRIC CONSTANT FOR 2D MEDIA	22
2.1	Polarization	22
2.2	Spontaneous Polarization	22
2.3	First Order Polarization and Dielectric Constant	23
2.3.1	Dielectric Anisotropy of Organic Monolayers	25
2.3.2	Dielectric Contribution by Molecular Orientation	28
2.3.3	Dielectric Constant	29
2.4	Nonlinear Polarization	31
2.5	Summary	34
	References	35
CHAPTER 3	MAXWELL DISPLACEMENT CURRENT METHOD	37
3.1	Maxwell Displacement Current	37
3.2	Maxwell Displacement Current by Monolayer Compression	38
3.3	MDC Generated across Organic Monolayers Consisting of Molecules with Dielectric Anisotropy	40
3.3.1	Molecular Structures and Experimental Results	41
3.3.2	Molecule-surface Interaction	44

3.3.3	Orientational Order Parameter for Biaxial Molecules	46
3.3.4	Comparison between the Two Directions	49
3.3.5	Simulation	55
3.4	Phase Transition of Chiral Phospholipid Monolayers by Maxwell Displacement Current Measurement	57
3.4.1	Maxwell Displacement Current of Chiral Phospholipid Monolayers	57
3.4.2	Symmetry of MDC Generation Influenced by Chirality in Mixed Phospholipid Monolayers	60
3.5	Maxwell Displacement Current by Photoirradiation	61
3.6	Evaluation of Liquid Crystal Alignment Using MDC Technique	65
3.7	Summary	74
	References	75
CHAPTER 4 MONOLAYERS VIEWED AS POLAR LIQUID CRYSTALS		78
4.1	Model and Internal Electric Fields	79
4.2	Polar Orientational Phase Transition in Smectic Monolayers	81
4.3	Change of Orientational Order Parameter at the Critical Point	85
4.3.1	Orientational Order Parameter	85
4.3.2	Normal-director Smectic Phase ($A/A_0 > a_c$)	86
4.3.3	Tilted-director Smectic Phase ($A/A_0 < a_c$)	87
4.4	Dielectric Properties Influenced by the Orientational Phase Transition	88
4.4.1	Orientational Order Parameter S_1	89
4.4.2	Dielectric Constant	89
4.5	Summary	92
	References	93
CHAPTER 5 DIELECTRIC RELAXATION PHENOMENA		95
5.1	Rotational Debye Brownian Motion Model	96
5.1.1	Dielectric Relaxation Equation for Monolayer Films	98
5.1.2	Dielectric Relaxation Time	100
5.1.3	Equivalent Circuit for Transient Relaxation Process	101
5.2	Relaxation Process at an Air-water Interface	102
5.2.1	Mean-field Approximation	102
5.2.2	Closed Packing and Molecule-surface Interaction	105
5.2.3	Relaxation Experiment of Monolayer Compression	107
5.2.4	Interaction Coefficient	109
5.3	Determination of Dielectric Relaxation Time	112
5.4	Summary	114
	References	115

CHAPTER 6	CHIRAL PHASE SEPARATION	117
6.1	Elastic Energy and Bragg-Williams Mixing Energy	118
6.2	Chiral Phase Separation	120
6.2.1	One-dimensional Periodical Solution	120
6.2.2	One-dimensional Chiral Phase Separation	125
6.3	Discrete One-dimensional CPS Solution	126
6.3.1	One-dimensional General Solution	126
6.3.2	One-dimensional Discrete Pattern	127
6.3.3	Line Tension	128
6.3.4	Pattern Formation	129
6.4	Summary	131
6.5	Appendix	132
	References	138
CHAPTER 7	NONLINEAR EFFECTS	140
7.1	SOS in Orientational Order Parameters for C_{∞} Monolayers	142
7.2	Chirality Representation	144
7.3	SHG-CD Effect	145
7.4	SHG-MDC Measuring System	145
7.5	Quantum Mechanical Analysis of Photoisomerization	150
7.6	Summary	153
	References	154
CHAPTER 8	THERMALLY-STIMULATED CURRENT	156
8.1	Thermally-stimulated Current	156
8.2	Depolarization due to Thermal Stimulation	158
8.2.1	Liquid Phase	159
8.2.2	Liquid-crystalline Phase	160
8.3	TSC Experiment	163
8.4	Phase Transition	163
8.5	Thermodynamics Approach to Monolayers	165
8.6	Summary	166
	References	167
CHAPTER 9	ELECTRONIC PROPERTIES AT MIM INTERFACES	168
9.1	Tunneling Current and Electronic Device Applications	168
9.2	Nanometric Interfacial Electrostatic Phenomena in Ultrathin Films	171
9.2.1	Electrically Insulating Ultrathin Films	172
9.2.2	Semiconductor Films	180

9.3 I-V Characteristic	186
9.3.1 PI LB Films	186
9.3.2 Semiconductor Films	192
9.4 Summary	196
References	197