



FUNDAMENTALS OF

LIQUID CRYSTAL DEVICES

SECOND EDITION

Deng-Ke Yang
Shin-Tson Wu



WILEY **SID** Series in **Display Technology**

FUNDAMENTALS OF LIQUID CRYSTAL DEVICES

Wiley-SID Series in Display Technology

Series Editors:

Anthony C. Lowe and Ian Sage

Display Systems: Design and Applications

Lindsay W. MacDonald and Anthony C. Lowe (Eds.)

Electronic Display Measurement: Concepts, Techniques, and Instrumentation

Peter A. Keller

Reflective Liquid Crystal Displays

Shin-Tson Wu and Deng-Ke Yang

Colour Engineering: Achieving Device Independent Colour

Phil Green and Lindsay MacDonald (Eds.)

Display Interfaces: Fundamentals and Standards

Robert L. Myers

Digital Image Display: Algorithms and Implementation

Gheorghe Berbecel

Flexible Flat Panel Displays

Gregory Crawford (Ed.)

Polarization Engineering for LCD Projection

Michael G. Robinson, Jianmin Chen, and Gary D. Sharp

Fundamentals of Liquid Crystal Devices

Deng-Ke Yang and Shin-Tson Wu

Introduction to Microdisplays

David Armitage, Ian Underwood, and Shin-Tson Wu

Mobile Displays: Technology and Applications

Achintya K. Bhowmik, Zili Li, and Philip Bos (Eds.)

Photoalignment of Liquid Crystalline Materials: Physics and Applications

Vladimir G. Chigrinov, Vladimir M. Kozenkov and Hoi-Sing Kwok

Projection Displays, Second Edition

Matthew S. Brennessoltz and Edward H. Stupp

Introduction to Flat Panel Displays

Jiun-Haw Lee, David N. Liu and Shin-Tson Wu

LCD Backlights

Shunsuke Kobayashi, Shigeo Mikoshiba and Sungkyoo Lim (Eds.)

Liquid Crystal Displays: Addressing Schemes and Electro-Optical Effects, Second Edition

Ernst Lueder

Transflective Liquid Crystal Displays

Zhibing Ge and Shin-Tson Wu

Liquid Crystal Displays: Fundamental Physics and Technology

Robert H. Chen

3D Displays

Ernst Lueder

OLED Display Fundamentals and Applications

Takatoshi Tsujimura

Illumination, Colour and Imaging: Evaluation and Optimization of Visual Displays

Tran Quoc Khanh and Peter Bodrogi

Interactive Displays: Natural Human-Interface Technologies

Achintya K. Bhowmik (Ed.)

Modeling and Optimization of LCD Optical Performance

Dmitry A. Yakovlev, Vladimir G. Chigrinov, Hoi-Sing Kwok

Addressing Techniques of Liquid Crystal Displays

Temkar N. Ruckmongathan

FUNDAMENTALS OF LIQUID CRYSTAL DEVICES

Second Edition

Deng-Ke Yang

Liquid Crystal Institute, Kent State University, USA

Shin-Tson Wu

College of Optics and Photonics, University of Central Florida, USA

WILEY

This edition first published 2015
© 2015, John Wiley & Sons, Ltd

First Edition published in 2006
© 2006, John Wiley & Sons, Ltd

Registered Office

John Wiley & Sons, Ltd, The Atrium, Southern Gate, Chichester, West Sussex, PO19 8SQ, United Kingdom

For details of our global editorial offices, for customer services and for information about how to apply for permission to reuse the copyright material in this book please see our website at www.wiley.com.

The right of the author to be identified as the author of this work has been asserted in accordance with the Copyright, Designs and Patents Act 1988.

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, except as permitted by the UK Copyright, Designs and Patents Act 1988, without the prior permission of the publisher.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print may not be available in electronic books.

Designations used by companies to distinguish their products are often claimed as trademarks. All brand names and product names used in this book are trade names, service marks, trademarks or registered trademarks of their respective owners. The publisher is not associated with any product or vendor mentioned in this book

Limit of Liability/Disclaimer of Warranty: While the publisher and author have used their best efforts in preparing this book, they make no representations or warranties with respect to the accuracy or completeness of the contents of this book and specifically disclaim any implied warranties of merchantability or fitness for a particular purpose. It is sold on the understanding that the publisher is not engaged in rendering professional services and neither the publisher nor the author shall be liable for damages arising herefrom. If professional advice or other expert assistance is required, the services of a competent professional should be sought.

Library of Congress Cataloging-in-Publication Data

Yang, Deng-Ke.

Fundamentals of liquid crystal devices / Deng-Ke Yang and Shin-Tson Wu. – Second edition.

pages cm – (Wiley series in display technology)

Includes bibliographical references and index.

ISBN 978-1-118-75200-5 (hardback)

1. Liquid crystal displays. 2. Liquid crystal devices. 3. Liquid crystals. I. Wu, Shin-Tson. II. Title.

TK7872.L56Y36 2014

621.3815'422–dc23

2014027707

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

Set in 10/12pt Times by SPi Publisher Services, Pondicherry, India

Contents

Series Editor's Foreword	xiii
Preface to the First Edition	xv
Preface to the Second Edition	xvii
1 Liquid Crystal Physics	1
1.1 Introduction	1
1.2 Thermodynamics and Statistical Physics	5
1.2.1 <i>Thermodynamic laws</i>	5
1.2.2 <i>Boltzmann Distribution</i>	6
1.2.3 <i>Thermodynamic quantities</i>	7
1.2.4 <i>Criteria for thermodynamical equilibrium</i>	9
1.3 Orientational Order	10
1.3.1 <i>Orientational order parameter</i>	11
1.3.2 <i>Landau–de Gennes theory of orientational order in nematic phase</i>	13
1.3.3 <i>Maier–Saupe theory</i>	18
1.4 Elastic Properties of Liquid Crystals	21
1.4.1 <i>Elastic properties of nematic liquid crystals</i>	21
1.4.2 <i>Elastic properties of cholesteric liquid crystals</i>	24
1.4.3 <i>Elastic properties of smectic liquid crystals</i>	26
1.5 Response of Liquid Crystals to Electromagnetic Fields	27
1.5.1 <i>Magnetic susceptibility</i>	27
1.5.2 <i>Dielectric permittivity and refractive index</i>	29
1.6 Anchoring Effects of Nematic Liquid Crystal at Surfaces	38
1.6.1 <i>Anchoring energy</i>	38
1.6.2 <i>Alignment layers</i>	39

1.7	Liquid crystal director elastic deformation	40
1.7.1	<i>Elastic deformation and disclination</i>	40
1.7.2	<i>Escape of liquid crystal director in disclinations</i>	42
	Homework Problems	48
	References	49
2	Propagation of Light in Anisotropic Optical Media	51
2.1	Electromagnetic Wave	51
2.2	Polarization	54
2.2.1	<i>Monochromatic plane waves and their polarization states</i>	54
2.2.2	<i>Linear polarization state</i>	55
2.2.3	<i>Circular polarization states</i>	55
2.2.4	<i>Elliptical polarization state</i>	56
2.3	Propagation of Light in Uniform Anisotropic Optical Media	59
2.3.1	<i>Eigenmodes</i>	60
2.3.2	<i>Orthogonality of eigenmodes</i>	65
2.3.3	<i>Energy flux</i>	66
2.3.4	<i>Special cases</i>	67
2.3.5	<i>Polarizers</i>	69
2.4	Propagation of Light in Cholesteric Liquid Crystals	72
2.4.1	<i>Eigenmodes</i>	72
2.4.2	<i>Reflection of cholesteric liquid crystals</i>	81
2.4.3	<i>Lasing in cholesteric liquid crystals</i>	84
	Homework Problems	85
	References	86
3	Optical Modeling Methods	87
3.1	Jones Matrix Method	87
3.1.1	<i>Jones vector</i>	87
3.1.2	<i>Jones matrix</i>	88
3.1.3	<i>Jones matrix of non-uniform birefringent film</i>	91
3.1.4	<i>Optical properties of twisted nematic</i>	92
3.2	Mueller Matrix Method	98
3.2.1	<i>Partially polarized and unpolarized light</i>	98
3.2.2	<i>Measurement of the Stokes parameters</i>	100
3.2.3	<i>The Mueller matrix</i>	102
3.2.4	<i>Poincaré sphere</i>	104
3.2.5	<i>Evolution of the polarization states on the Poincaré sphere</i>	106
3.2.6	<i>Mueller matrix of twisted nematic liquid crystals</i>	110
3.2.7	<i>Mueller matrix of non-uniform birefringence film</i>	112
3.3	Berreman 4×4 Method	113
	Homework Problems	124
	References	125

4	Effects of Electric Field on Liquid Crystals	127
4.1	Dielectric Interaction	127
4.1.1	<i>Reorientation under dielectric interaction</i>	128
4.1.2	<i>Field-induced orientational order</i>	129
4.2	Flexoelectric Effect	132
4.2.1	<i>Flexoelectric effect in nematic liquid crystals</i>	132
4.2.2	<i>Flexoelectric effect in cholesteric liquid crystals</i>	136
4.3	Ferroelectric Liquid Crystal	138
4.3.1	<i>Symmetry and polarization</i>	138
4.3.2	<i>Tilt angle and polarization</i>	140
4.3.3	<i>Surface stabilized ferroelectric liquid crystals</i>	141
4.3.4	<i>Electroclinic effect in chiral smectic liquid crystal</i>	144
	Homework Problems	146
	References	147
5	Fréedericksz Transition	149
5.1	Calculus of Variation	149
5.1.1	<i>One dimension and one variable</i>	150
5.1.2	<i>One dimension and multiple variables</i>	153
5.1.3	<i>Three dimensions</i>	153
5.2	Fréedericksz Transition: Statics	153
5.2.1	<i>Splay geometry</i>	154
5.2.2	<i>Bend geometry</i>	158
5.2.3	<i>Twist geometry</i>	160
5.2.4	<i>Twisted nematic cell</i>	161
5.2.5	<i>Splay geometry with weak anchoring</i>	164
5.2.6	<i>Splay geometry with pretilt angle</i>	165
5.3	Measurement of Anchoring Strength	166
5.3.1	<i>Polar anchoring strength</i>	167
5.3.2	<i>Azimuthal anchoring strength</i>	169
5.4	Measurement of Pretilt Angle	171
5.5	Fréedericksz Transition: Dynamics	175
5.5.1	<i>Dynamics of Fréedericksz transition in twist geometry</i>	175
5.5.2	<i>Hydrodynamics</i>	176
5.5.3	<i>Backflow</i>	182
	Homework Problems	187
	References	188
6	Liquid Crystal Materials	191
6.1	Introduction	191
6.2	Refractive Indices	192
6.2.1	<i>Extended Cauchy equations</i>	192
6.2.2	<i>Three-band model</i>	193
6.2.3	<i>Temperature effect</i>	195

6.2.4	<i>Temperature gradient</i>	198
6.2.5	<i>Molecular polarizabilities</i>	199
6.3	Dielectric Constants	201
6.3.1	<i>Positive $\Delta\epsilon$ liquid crystals for AMLCD</i>	202
6.3.2	<i>Negative $\Delta\epsilon$ liquid crystals</i>	202
6.3.3	<i>Dual-frequency liquid crystals</i>	203
6.4	Rotational Viscosity	204
6.5	Elastic Constants	204
6.6	Figure-of-Merit (FoM)	205
6.7	Index Matching between Liquid Crystals and Polymers	206
6.7.1	<i>Refractive index of polymers</i>	206
6.7.2	<i>Matching refractive index</i>	208
	Homework problems	210
	References	210
7	Modeling Liquid Crystal Director Configuration	213
7.1	Electric Energy of Liquid Crystals	213
7.1.1	<i>Constant charge</i>	214
7.1.2	<i>Constant voltage</i>	215
7.1.3	<i>Constant electric field</i>	218
7.2	Modeling Electric Field	218
7.3	Simulation of Liquid Crystal Director Configuration	221
7.3.1	<i>Angle representation</i>	221
7.3.2	<i>Vector representation</i>	225
7.3.3	<i>Tensor representation</i>	228
	Homework Problems	232
	References	232
8	Transmissive Liquid Crystal Displays	235
8.1	Introduction	235
8.2	Twisted Nematic (TN) Cells	236
8.2.1	<i>Voltage-dependent transmittance</i>	237
8.2.2	<i>Film-compensated TN cells</i>	238
8.2.3	<i>Viewing angle</i>	241
8.3	In-Plane Switching Mode	241
8.3.1	<i>Voltage-dependent transmittance</i>	242
8.3.2	<i>Response time</i>	243
8.3.3	<i>Viewing angle</i>	246
8.3.4	<i>Classification of compensation films</i>	246
8.3.5	<i>Phase retardation of uniaxial media at oblique angles</i>	246
8.3.6	<i>Poincaré sphere representation</i>	249
8.3.7	<i>Light leakage of crossed polarizers at oblique view</i>	250
8.3.8	<i>IPS with a positive a film and a positive c film</i>	254

8.3.9	<i>IPS with positive and negative a films</i>	259
8.3.10	<i>Color shift</i>	263
8.4	Vertical Alignment Mode	263
8.4.1	<i>Voltage-dependent transmittance</i>	263
8.4.2	<i>Optical response time</i>	264
8.4.3	<i>Overdrive and undershoot voltage method</i>	265
8.5	Multi-Domain Vertical Alignment Cells	266
8.5.1	<i>MVA with a positive a film and a negative c film</i>	269
8.5.2	<i>MVA with a positive a, a negative a, and a negative c film</i>	273
8.6	Optically Compensated Bend Cell	277
8.6.1	<i>Voltage-dependent transmittance</i>	278
8.6.2	<i>Compensation films for OCB</i>	279
	Homework Problems	281
	References	283
9	Reflective and Transflective Liquid Crystal Displays	285
9.1	Introduction	285
9.2	Reflective Liquid Crystal Displays	286
9.2.1	<i>Film-compensated homogeneous cell</i>	287
9.2.2	<i>Mixed-mode twisted nematic (MTN) cells</i>	289
9.3	Transflector	290
9.3.1	<i>Openings-on-metal transflector</i>	290
9.3.2	<i>Half-mirror metal transflector</i>	291
9.3.3	<i>Multilayer dielectric film transflector</i>	292
9.3.4	<i>Orthogonal polarization transreflectors</i>	292
9.4	Classification of Transflective LCDs	293
9.4.1	<i>Absorption-type transflective LCDs</i>	294
9.4.2	<i>Scattering-type transflective LCDs</i>	296
9.4.3	<i>Scattering and absorption type transflective LCDs</i>	298
9.4.4	<i>Reflection-type transflective LCDs</i>	300
9.4.5	<i>Phase retardation type</i>	302
9.5	Dual-Cell-Gap Transflective LCDs	312
9.6	Single-Cell-Gap Transflective LCDs	314
9.7	Performance of Transflective LCDs	314
9.7.1	<i>Color balance</i>	314
9.7.2	<i>Image brightness</i>	315
9.7.3	<i>Viewing angle</i>	315
	Homework Problems	316
	References	316
10	Liquid Crystal Display Matrices, Drive Schemes and Bistable Displays	321
10.1	Segmented Displays	321
10.2	Passive Matrix Displays and Drive Scheme	322
10.3	Active Matrix Displays	326
10.3.1	<i>TFT structure</i>	328

10.3.2	<i>TFT operation principles</i>	329
10.4	Bistable Ferroelectric LCD and Drive Scheme	330
10.5	Bistable Nematic Displays	332
10.5.1	<i>Introduction</i>	332
10.5.2	<i>Twisted-untwisted bistable nematic LCDs</i>	333
10.5.3	<i>Surface-stabilized nematic liquid crystals</i>	339
10.6	Bistable Cholesteric Reflective Display	342
10.6.1	<i>Introduction</i>	342
10.6.2	<i>Optical properties of bistable Ch reflective displays</i>	344
10.6.3	<i>Encapsulated cholesteric liquid crystal displays</i>	347
10.6.4	<i>Transition between cholesteric states</i>	347
10.6.5	<i>Drive schemes for bistable Ch displays</i>	355
	Homework Problems	358
	References	359
11	Liquid Crystal/Polymer Composites	363
11.1	Introduction	363
11.2	Phase Separation	365
11.2.1	<i>Binary mixture</i>	365
11.2.2	<i>Phase diagram and thermal induced phase separation</i>	369
11.2.3	<i>Polymerization induced phase separation</i>	371
11.2.4	<i>Solvent-induced phase separation</i>	374
11.2.5	<i>Encapsulation</i>	376
11.3	Scattering Properties of LCPCs	377
11.4	Polymer Dispersed Liquid Crystals	383
11.4.1	<i>Liquid crystal droplet configurations in PDLCs</i>	383
11.4.2	<i>Switching PDLCs</i>	385
11.4.3	<i>Scattering PDLC devices</i>	387
11.4.4	<i>Dichroic dye-doped PDLC</i>	391
11.4.5	<i>Holographic PDLCs</i>	393
11.5	PSLCs	395
11.5.1	<i>Preparation of PSLCs</i>	395
11.5.2	<i>Working modes of scattering PSLCs</i>	396
11.6	Scattering-Based Displays from LCPCs	400
11.6.1	<i>Reflective displays</i>	400
11.6.2	<i>Projection displays</i>	402
11.6.3	<i>Transmissive direct-view displays</i>	403
11.7	Polymer-Stabilized LCDs	403
	Homework Problems	407
	References	409
12	Tunable Liquid Crystal Photonic Devices	413
12.1	Introduction	413
12.2	Laser Beam Steering	414
12.2.1	<i>Optical phased array</i>	415
12.2.2	<i>Prism-based beam steering</i>	417
12.3	Variable Optical Attenuators	419

12.4 Tunable-Focus Lens	423
12.4.1 Tunable-focus spherical lens	423
12.4.2 Tunable-focus cylindrical lens	426
12.4.3 Switchable positive and negative microlens	428
12.4.4 Hermaphroditic LC microlens	434
12.5 Polarization-Independent LC Devices	435
12.5.1 Double-layered homogeneous LC cells	436
12.5.2 Double-layered LC gels	438
Homework Problems	441
References	442
13 Blue Phases of Chiral Liquid Crystals	445
13.1 Introduction	445
13.2 Phase Diagram of Blue Phases	446
13.3 Reflection of Blue Phases	447
13.3.1 Basics of crystal structure and X-ray diffraction	447
13.3.2 Bragg reflection of blue phases	449
13.4 Structure of Blue Phase	451
13.4.1 Defect theory	452
13.4.2 Landau theory	459
13.5 Optical Properties of Blue Phase	471
13.5.1 Reflection	471
13.5.2 Transmission	472
Homework Problems	475
References	475
14 Polymer-Stabilized Blue Phase Liquid Crystals	477
14.1 Introduction	477
14.2 Polymer-Stabilized Blue Phases	480
14.2.1 Nematic LC host	482
14.2.2 Chiral dopants	483
14.2.3 Monomers	483
14.3 Kerr Effect	484
14.3.1 Extended Kerr effect	486
14.3.2 Wavelength effect	489
14.3.3 Frequency effect	490
14.3.4 Temperature effects	491
14.4 Device Configurations	496
14.4.1 In-plane-switching BPLCD	497
14.4.2 Protruded electrodes	501
14.4.3 Etched electrodes	504
14.4.4 Single gamma curve	504
14.5 Vertical Field Switching	507
14.5.1 Device structure	507
14.5.2 Experiments and simulations	508
14.6 Phase Modulation	510
References	510

15	Liquid Crystal Display Components	513
15.1	Introduction	513
15.2	Light Source	513
15.3	Light-guide	516
15.4	Diffuser	516
15.5	Collimation Film	518
15.6	Polarizer	519
	15.6.1 <i>Dichroic absorbing polarizer</i>	520
	15.6.2 <i>Dichroic reflective polarizer</i>	521
15.7	Compensation Film	530
	15.7.1 <i>Form birefringence compensation film</i>	531
	15.7.2 <i>Discotic liquid crystal compensation film</i>	531
	15.7.3 <i>Compensation film from rigid polymer chains</i>	532
	15.7.4 <i>Drawn polymer compensation film</i>	533
15.8	Color Filter	535
	References	536
16	Three-Dimensional Displays	539
16.1	Introduction	539
16.2	Depth Cues	539
	16.2.1 <i>Binocular disparity</i>	539
	16.2.2 <i>Convergence</i>	540
	16.2.3 <i>Motion parallax</i>	540
	16.2.4 <i>Accommodation</i>	541
16.3	Stereoscopic Displays	541
	16.3.1 <i>Head-mounted displays</i>	542
	16.3.2 <i>Anaglyph</i>	542
	16.3.3 <i>Time sequential stereoscopic displays with shutter glasses</i>	542
	16.3.4 <i>Stereoscopic displays with polarizing glasses</i>	544
16.4	Autostereoscopic Displays	546
	16.4.1 <i>Autostereoscopic displays based on parallax barriers</i>	546
	16.4.2 <i>Autostereoscopic displays based on lenticular lens array</i>	550
	16.4.3 <i>Directional backlight</i>	552
16.5	Integral imaging	553
16.6	Holography	554
16.7	Volumetric displays	556
	16.7.1 <i>Swept volumetric displays</i>	556
	16.7.2 <i>Multi-planar volumetric displays</i>	557
	16.7.3 <i>Points volumetric displays</i>	560
	References	560
	Index	565

Series Editor's Foreword

The first edition of this book marked a new departure for the Wiley-SID Series in Display Technology because it had been written primarily as a text for postgraduate and senior undergraduate students. It fulfilled that objective admirably, but the continuing advances in liquid crystal display technology over the intervening eight years have made necessary some additions to keep the book current.

Accordingly, the following new sections have been added: elastic deformation of liquid crystals in Chapter 1, polarisation conversion with narrow and broadband quarter-wave plates in Chapter 3, and measurement of anchoring strength and pretilt angle in Chapter 5.

With each chapter is designed to be self-contained, the first chapters cover the basic physics of liquid crystals, their interaction with light and electric fields, and the means by which they can be modelled. Next are described the majority of the ways in which liquid crystals can be used in displays, and Chapter 12, the final chapter of the first edition, deals with photonic devices such as beam steerers, tunable-focus lenses and polarisation-independent devices. In this second edition, four new chapters have been added: two on blue phase and polymer stabilised blue phase liquid crystals, which are emerging from the realm of academic research to show promise for very fast response display and photonic devices, a chapter which discusses LCD componentry, and a final chapter on the use of LCDs in 3D display systems.

As with the first edition, and following a standard textbook format, each chapter concludes with a set of problems, the answers to which may be found on the Wiley web site.

New electro-optic technologies continue to be developed, and some of them make inroads into the LCD market. Nevertheless, liquid crystal technology – the first other than the CRT to make a significant breakthrough into the mass market and which made possible flat displays and transformed projection display technology – continues to hold a dominant position. This second edition of *Fundamentals of Liquid Crystal Devices*, with its additions which include references to some very recent work, will ensure that this volume will continue to provide students and other readers at the professional level with a most useful introduction to the subject.

Anthony C Lowe
Braishfield, UK 2014

Preface to the First Edition

Liquid crystal displays have become the leading technology in the information display industry. They are used in small-sized displays such as calculators, cellular phones, digital cameras, and head-mounted displays; in medium-sized displays such as laptop and desktop computers; and in large-sized displays such as direct-view TVs and projection TVs. They have the advantages of high resolution and high brightness, and, being flat paneled, are lightweight, energy saving, and even flexible in some cases. They can be operated in transmissive and reflective modes. Liquid crystals have also been used in photonic devices such as laser beam steering, variable optical attenuators, and tunable-focus lenses. There is no doubt that liquid crystals will continue to play an important role in the era of information technology.

There are many books on the physics and chemistry of liquid crystals and on liquid crystal devices. There are, however, few books covering both the basics and applications of liquid crystals. Our main goal, therefore, is to provide a textbook for senior undergraduate and graduate students. The book can be used for a one- or two-semester course. The instructors can selectively choose the chapters and sections according to the length of the course and the interest of the students. The book can also be used as a reference book by scientists and engineers who are interested in liquid crystal displays and photonics.

The book is organized in such a way that the first few chapters cover the basics of liquid crystals and the necessary techniques to study and design liquid crystal devices. The later chapters cover the principles, design, operation, and performance of liquid crystal devices. Because of limited space, we cannot cover every aspect of liquid crystal chemistry and physics and all liquid crystal devices, but we hope this book will introduce readers to liquid crystals and provide them with the basic knowledge and techniques for their careers in liquid crystals.

We are greatly indebted to Dr A. Lowe for his encouragement. We are also grateful to the reviewers of our book proposal for their useful suggestions and comments. Deng-Ke Yang would like to thank Ms E. Landry and Prof. J. Kelly for patiently proofreading his manuscript. He would also like to thank Dr Q. Li for providing drawings. Shin-Tson Wu would like to thank his research group members for generating the new knowledge included in this book, especially Drs Xinyu Zhu, Hongwen Ren, Yun-Hsing Fan, and Yi-Hsin Lin, and Mr Zhibing Ge for kind

help during manuscript preparation. He is also indebted to Dr Terry Dorschner of Raytheon, Dr Paul McManamon of the Air Force Research Lab, and Dr Hiroyuki Mori of Fuji Photo Film for sharing their latest results. We would like to thank our colleagues and friends for useful discussions and drawings and our funding agencies (DARPA, AFOSR, AFRL, and Toppoly) for providing financial support. Finally, we also would like to thank our families (Xiaojiang Li, Kevin Yang, Steven Yang, Cho-Yan Wu, Janet Wu, and Benjamin Wu) for their spiritual support, understanding, and constant encouragement.

Deng-Ke Yang
Shin-Tson Wu

Preface to the Second Edition

Liquid crystal displays have become the leading technology in the information display industry. They are used in small-sized displays such as calculators, smart phones, digital cameras, and wearable displays; medium-sized displays such as laptop and desktop computers; and large-sized displays such as direct view TVs and data projectors. They have the advantages of having high resolution and high brightness, and being flat paneled, lightweight, energy saving, and even flexible in some cases. They can be operated in transmissive and reflective modes. Liquid crystals have also been used in photonic devices such as switching windows, laser beam steering, variable optical attenuators, and tunable-focus lenses. There is no doubt that liquid crystals will continue to play an important role in information technology.

There are many books on the physics and chemistry of liquid crystals and on liquid crystal devices. There are, however, few books covering both the basics and the applications of liquid crystals. The main goal of this book is to provide a textbook for senior undergraduate and graduate students. This book can be used for a one- or two-semester course. The instructors can selectively choose the chapters and sections according to the length of the course and the interest of the students. It can also be used as a reference book for scientists and engineers who are interested in liquid crystal displays and photonics.

The book is organized in such a way that the first few chapters cover the basics of liquid crystals and the necessary techniques to study and design liquid crystal devices. The later chapters cover the principles, design, operation, and performance of liquid crystal devices. Because of limited space, we cannot cover every aspect of liquid crystal chemistry and physics and all the different liquid crystal devices. We hope that this book can introduce readers to liquid crystals and provide them with the basic knowledge and techniques for their career in liquid crystals.

Since the publication of the first edition, we have received a lot of feedback, suggestions, corrections, and encouragements. We appreciate them very much and have put them into the second edition. Also there are many new advances in liquid crystal technologies. We have added new chapters and sections to cover them.

We are greatly indebted to Dr A. Lowe for his encouragement. We are also grateful to the reviewers of our book proposal for their useful suggestions and comments. Deng-Ke Yang would like to thank Ms E. Landry, Prof. P. Crooker, his research group, and coworkers for patiently proofreading and preparing his sections of the book. He would also like to thank Dr Q. Li for providing drawings. Shin-Tson Wu would like to thank his research group members for generating new knowledge included in this book, especially Drs Xinyu Zhu, Hongwen Ren, Yun-Hsing Fan, Yi-Hsin Lin, Zhibing Ge, Meizi Jiao, Linghui Rao, Hui-Chuan Cheng, Yan Li, and Jin Yan for their kind help during manuscript preparation. He is also indebted to Dr Terry Dorschner of Raytheon, Dr Paul McManamon of Air Force Research Lab, and Dr Hiroyuki Mori of Fuji Photo Film for sharing their latest results. We would like to thank our colleagues and friends for useful discussions and drawings and our funding agencies (DARPA, AFOSR, AFRL, ITRI, AUO, and Innolux) for providing financial support. We would also like to thank our family members (Xiaojiang Li, Kevin Yang, Steven Yang, Cho-Yan Wu, Janet Wu, and Benjamin Wu) for their spiritual support, understanding, and constant encouragement.

Deng-Ke Yang
Shin-Tson Wu

1

Liquid Crystal Physics

1.1 Introduction

Liquid crystals are mesophases between crystalline solid and isotropic liquid [1–3]. The constituents are elongated rod-like (calamitic) or disk-like (discotic) organic molecules as shown in Figure 1.1. The size of the molecules is typically a few nanometers (nm). The ratio between the length and the diameter of the rod-like molecules or the ratio between the diameter and the thickness of disk-like molecules is about 5 or larger. Because the molecules are non-spherical, besides positional order, they may possess orientational order.

Figure 1.1(a) shows a typical *calamitic* liquid crystal molecule. Its chemical name is 4'-n-Pentyl-4-cyano-biphenyl and is abbreviated as 5CB [4,5]. It consists of a biphenyl, which is the rigid core, and a hydrocarbon chain which is the flexible tail. The space-filling model of the molecule is shown in Figure 1.1(c). Although the molecule itself is not cylindrical, it can be regarded as a cylinder, as shown in Figure 1.1(e), in considering its physical behavior, because of the fast rotation (on the order of 10^{-9} s) around the long molecule axis due to thermal motion. The distance between two carbon atoms is about 1.5 Å; therefore the length and the diameter of the molecule are about 2 nm and 0.5 nm, respectively. The molecule shown has a permanent dipole moment (from the CN head), but it can still be represented by the cylinder whose head and tail are the same, because in non-ferroelectric liquid crystal phases, the dipole has equal probability of pointing up or down. It is necessary for a liquid crystal molecule to have a rigid core(s) and flexible tail(s). If the molecule is completely flexible, it will not have orientational order. If it is completely rigid, it will transform directly from isotropic liquid phase at high temperature to crystalline solid phase at low temperature. The rigid part favors both orientational and positional order while the flexible part disfavors them. With balanced rigid and flexible parts, the molecule exhibits liquid crystal phases.

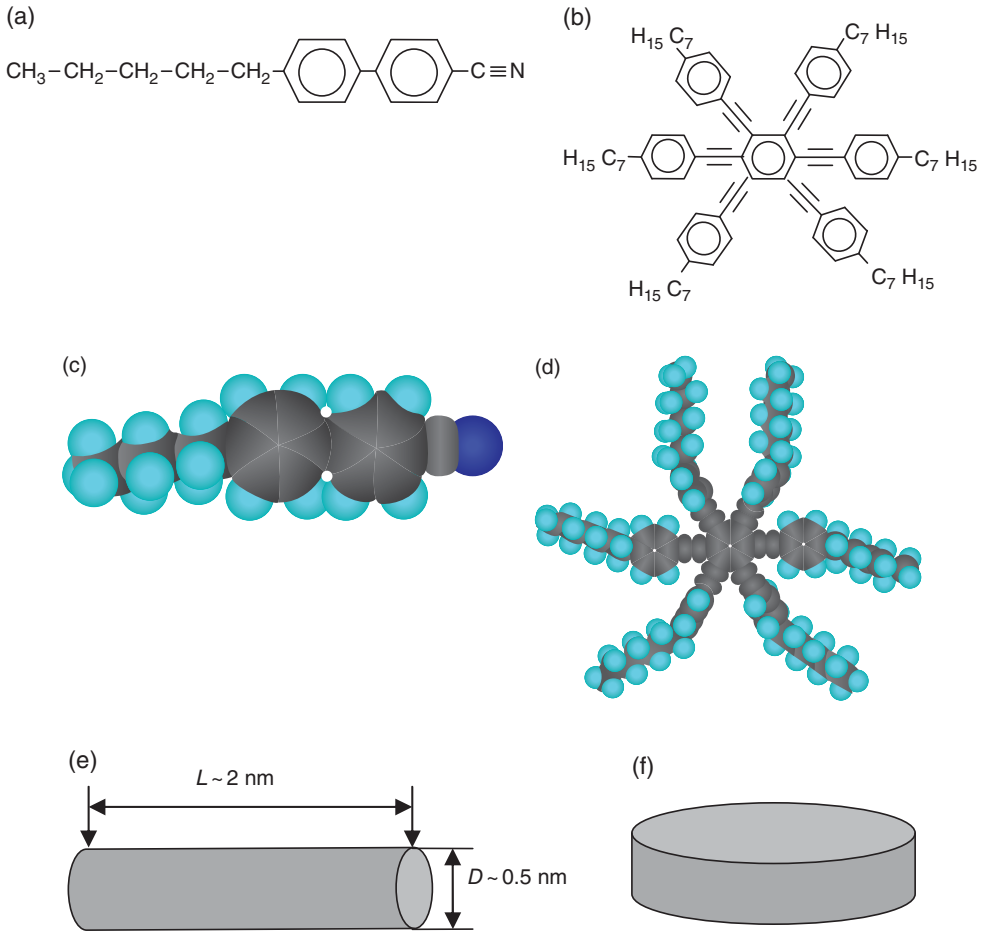


Figure 1.1 Calamitic liquid crystal: (a) chemical structure, (c) space-filling model, (e) physical model. Discotic liquid crystal: (b) chemical structure, (d) space-filling model, (f) physical model.

Figure 1.1(b) shows a typical *discotic* liquid crystal molecule [6]. It also has a rigid core and flexible tails. The branches are approximately on one plane. The space-filling model of the molecule is shown in Figure 1.1(d). If there is no permanent dipole moment perpendicular to the plane of the molecule, it can be regarded as a disk in considering its physical behavior as shown in Figure 1.1(f) because of the fast rotation around the axis which is at the center of the molecule and perpendicular to the plane of the molecule. If there is a permanent dipole moment perpendicular to the plane of the molecule, it is better to visualize the molecule as a bowl, because the reflection symmetry is broken and all the permanent dipoles may point in the same direction and spontaneous polarization occurs. The flexible tails are also necessary, otherwise the molecules form a crystal phase where there is positional order.

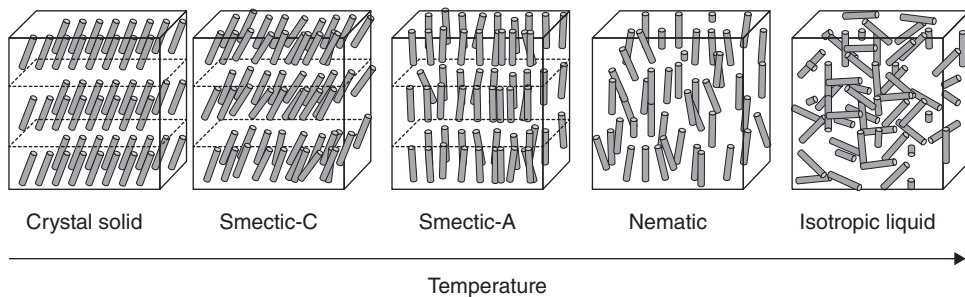


Figure 1.2 Schematic representation of the phases of rod-like molecules.

The variety of phases that may be exhibited by rod-like molecules are shown in Figure 1.2. At high temperature, the molecules are in the isotropic liquid state where they do not have either positional or orientational order. The molecules can easily move around, and the material can flow like water. The translational viscosity is comparable to that of water. Both the long and short axes of the molecules can point in any direction.

When the temperature is decreased, the material transforms into the *nematic* phase, which is the most common and simplest liquid crystal phase, where the molecules have orientational order but still no positional order. The molecules can still diffuse around, and the translational viscosity does not change much from that of the isotropic liquid state. The long axis of the molecules has a preferred direction. Although the molecules still swivel due to thermal motion, the time-averaged direction of the long axis of a molecule is well defined and is the same for all the molecules at macroscopic scale. The average direction of the long molecular axis is denoted by \bar{n} which is a unit vector called the liquid crystal director. The short axes of the molecules have no orientational order in a uniaxial nematic liquid crystal.

When the temperature is decreased further, the material may transform into the *Smectic-A* phase where, besides the orientational order, the molecules have partial positional order, i.e., the molecules form a layered structure. The liquid crystal director is perpendicular to the layers. Smectic-A is a one-dimensional crystal where the molecules have positional order in the layer normal direction. The cartoon shown in Figure 1.2 is schematic. In reality, the separation between neighboring layers is not as well defined as that shown by the cartoon. The molecule number density exhibits an undulation with the wavelength about the molecular length. Within a layer, it is a two-dimensional liquid crystal in which there is no positional order, and the molecules can move around. For a material in poly-domain smectic-A, the translational viscosity is significantly higher, and it behaves like a grease. When the temperature is decreased further, the material may transform into the *smectic-C* phase, where the liquid crystal director is no longer perpendicular to the layer but tilted.

At low temperature, the material is in the crystal solid phase where there are both positional and orientational orders. The translational viscosity becomes infinitely high and the molecules (almost) do not diffuse anymore.

Liquid crystals get the ‘crystal’ part of their name because they exhibit optical birefringence as crystalline solids. They get the ‘liquid’ part of their name because they can flow and do not support shearing as regular liquids. Liquid crystal molecules are elongated and have different

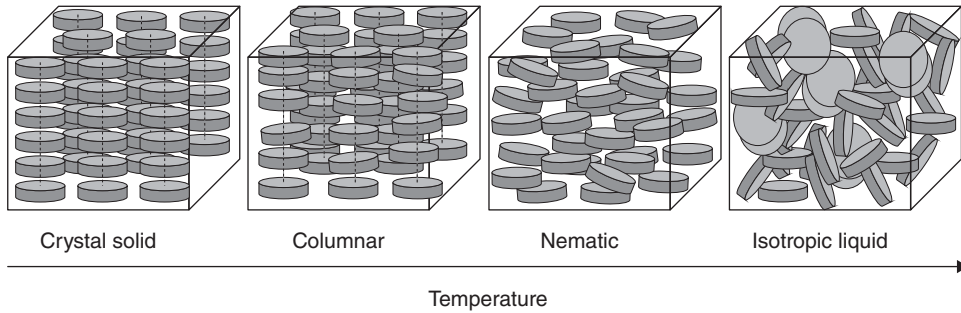


Figure 1.3 Schematic representation of the phases of disk-like molecules.

molecular polarizabilities along their long and short axes. Once the long axes of the molecules orient along a common direction, the refractive indices along and perpendicular to the common direction are different. It should be noted that not all rod-like molecules exhibit all the liquid crystal phases. They may exhibit some of the liquid crystal phases.

Some of the liquid crystal phases of disk-like molecules are shown in Figure 1.3. At high temperature, they are in the isotropic liquid state where there are no positional and orientational orders. The material behaves in the same way as a regular liquid. When the temperature is decreased, the material transforms into the nematic phase, which has orientational order but not positional order. The average direction of the short axis perpendicular to the disk is oriented along a preferred direction, which is also called the liquid crystal director and denoted by a unit vector \vec{n} . The molecules have different polarizabilities along a direction in the plane of the disk and along the short axis. Thus the discotic nematic phase also exhibits birefringence as crystals.

When the temperature is decreased further, the material transforms into the columnar phase where, besides orientational order, there is partial positional order. The molecules stack up to form columns. Within a column, it is a liquid where the molecules have no positional order. The columns, however, are arranged periodically in the plane perpendicular to the columns. Hence it is a two-dimensional crystal. At low temperature, the material transforms into the crystalline solid phase where the positional order along the columns is developed.

The liquid crystal phases discussed so far are called thermotropic liquid crystals and the transitions from one phase to another are driven by varying temperature. There is another type of liquid crystals, called lyotropic liquid crystals, exhibited by molecules when they are mixed with a solvent of some kind. The phase transitions from one phase to another phase are driven by varying the solvent concentration. Lyotropic liquid crystals usually consist of amphiphilic molecules that have a hydrophobic group at one end and a hydrophilic group at the other end and the water is the solvent. The common lyotropic liquid crystal phases are micelle phase and lamellar phase. Lyotropic liquid crystals are important in biology. They will not be discussed in this book because the scope of this book is on displays and photonic devices.

Liquid crystals have a history of more than 100 years. It is believed that the person who discovered liquid crystals is Friedrich Reinitzer, an Austrian botanist [7]. The liquid crystal phase observed by him in 1888 was a cholesteric phase. Since then, liquid crystals have come a long way and become a major branch of interdisciplinary sciences. Scientifically, liquid crystals are important because of the richness of structures and transitions. Technologically, they have won tremendous success in display and photonic applications [8–10].

1.2 Thermodynamics and Statistical Physics

Liquid crystal physics is an interdisciplinary science: thermodynamics, statistical physics, electrodynamics, and optics are involved. Here we give a brief introduction to thermodynamics and statistical physics.

1.2.1 Thermodynamic laws

One of the important quantities in thermodynamics is entropy. From the microscopic point of view, entropy is a measurement of the number of quantum states accessible to a system. In order to define entropy quantitatively, we first consider the fundamental logical assumption that *for a closed system (no energy and particles exchange with other systems), quantum states are either accessible or inaccessible to the system, and the system is equally likely to be in any one of the accessible states as in any other accessible state* [11]. For a macroscopic system, the number of accessible quantum states g is a huge number ($\sim 10^{23}$). It is easier to deal with $\ln g$, which is defined as the *entropy* σ :

$$\sigma = \ln g \quad (1.1)$$

If a closed system consists of subsystem 1 and subsystem 2, the numbers of accessible states of the subsystems are g_1 and g_2 , respectively. The number of accessible quantum states of the whole system is $g = g_1 g_2$ and the entropy is $\sigma = \ln g = \ln(g_1 g_2) = \ln g_1 + \ln g_2 = \sigma_1 + \sigma_2$.

Entropy is a function of the energy u of the system $\sigma = \sigma(u)$. The second law of thermodynamics states that *for a closed system, the equilibrium state has the maximum entropy*. Let us consider a closed system which contains two subsystems. When two subsystems are brought into thermal contact (energy exchange between them is allowed), the energy is allocated to maximize the number of accessible states, that is, the entropy is maximized. Subsystem 1 has the energy u_1 and entropy σ_1 ; subsystem 2 has the energy u_2 and entropy σ_2 . For the whole system, $u = u_1 + u_2$ and $\sigma = \sigma_1 + \sigma_2$. The first law of thermodynamics states that *energy is conserved*, that is, $u = u_1 + u_2 = \text{constant}$. For any process inside the closed system, $\delta u = \delta u_1 + \delta u_2 = 0$. From the second law of thermodynamics, for any process, we have $\delta \sigma = \delta \sigma_1 + \delta \sigma_2 \geq 0$. When the two subsystems are brought into thermal contact, at the beginning, energy flows. For example, an amount of energy $|\delta u_1|$ flows from subsystem 1 to subsystem 2, $\delta u_1 < 0$ and $\delta u_2 = -\delta u_1 > 0$, and $\frac{\partial \sigma}{\partial u_2} = \frac{\partial \sigma_1}{\partial u_2} + \frac{\partial \sigma_2}{\partial u_2} = \frac{\partial \sigma_1}{\partial u_1} \frac{\partial u_1}{\partial u_2} + \frac{\partial \sigma_2}{\partial u_2} = -\frac{\partial \sigma_1}{\partial u_1} + \frac{\partial \sigma_2}{\partial u_2} \geq 0$. When equilibrium is reached, the entropy is maximized and $\frac{\partial \sigma_1}{\partial u_1} - \frac{\partial \sigma_2}{\partial u_2} = 0$, that is, $\frac{\partial \sigma_1}{\partial u_1} = \frac{\partial \sigma_2}{\partial u_2}$. We know that when two systems reach equilibrium, they have the same temperature. Accordingly the *fundamental temperature* τ is defined by

$$1/\tau = \left(\frac{\partial \sigma}{\partial u} \right)_{N,V} . \quad (1.2)$$

Energy flows from a high temperature system to a low temperature system. The *conventional temperature* (Kelvin temperature) is defined by

$$T = \tau/k_B, \quad (1.3)$$

where $k_B = 1.381 \times 10^{-23}$ Joule/Kelvin is the Boltzmann constant. Conventional entropy S is defined by

$$1/T = \partial S / \partial u. \quad (1.4)$$

Hence

$$S = k_B \sigma. \quad (1.5)$$

1.2.2 Boltzmann Distribution

Now we consider the thermodynamics of a system at a constant temperature, that is, in thermal contact with a thermal reservoir. The temperature of the thermal reservoir (named B) is τ . The system under consideration (named A) has two states with energy 0 and ε , respectively. A and B form a closed system, and its total energy $u = u_A + u_B = u_o = \text{constant}$. When A is in the state with energy 0, B has the energy u_o , the number of accessible states: $g_1 = g_A \times g_B = 1 \times g_B(u_o) = g_B(u_o)$. When A has the energy ε , B has the energy $u_o - \varepsilon$, the number of accessible states is $g_2 = g_A \times g_B = 1 \times g_B(u_o - \varepsilon) = g_B(u_o - \varepsilon)$. For the whole system, the total number of accessible states is

$$G = g_1 + g_2 = g_B(u_o) + g_B(u_o - \varepsilon). \quad (1.6)$$

(A + B) is a closed system, and the probability in any of the G states is the same. When the whole system is in one of the g_1 states, A has the energy 0. When the whole system is in one of the g_2 states, A has the energy ε . Therefore the probability for A in the state with energy 0 is

$$P(0) = \frac{g_1}{g_1 + g_2} = \frac{g_B(u_o)}{g_B(u_o) + g_B(u_o - \varepsilon)}. \quad \text{The probability for A in the state with energy } \varepsilon \text{ is}$$

$$P(\varepsilon) = \frac{g_2}{g_1 + g_2} = \frac{g_B(u_o - \varepsilon)}{g_B(u_o) + g_B(u_o - \varepsilon)}. \quad \text{From the definition of entropy, we have } g_B(u_o) = e^{\sigma_B(u_o)}$$

and $g_B(u_o - \varepsilon) = e^{\sigma_B(u_o - \varepsilon)}$. Because $\varepsilon \ll u_o$, $\sigma_B(u_o - \varepsilon) \approx \sigma_B(u_o) - \frac{\partial \sigma_B}{\partial u_B} \varepsilon = \sigma_B(u_o) - \frac{1}{\tau} \varepsilon$. Therefore we have

$$P(0) = \frac{e^{\sigma_B(u_o)}}{e^{\sigma_B(u_o)} + e^{\sigma_B(u_o) - \varepsilon/\tau}} = \frac{1}{1 + e^{-\varepsilon/\tau}} = \frac{1}{1 + e^{-\varepsilon/k_B T}} \quad (1.7)$$

$$P(\varepsilon) = \frac{e^{\sigma_B(u_o) - \varepsilon/\tau}}{e^{\sigma_B(u_o)} + e^{\sigma_B(u_o) - \varepsilon/\tau}} = \frac{e^{-\varepsilon/\tau}}{1 + e^{-\varepsilon/\tau}} = \frac{e^{-\varepsilon/k_B T}}{1 + e^{-\varepsilon/k_B T}} \quad (1.8)$$

$$\frac{P(\varepsilon)}{P(0)} = e^{-\varepsilon/k_B T}. \quad (1.9)$$

For a system having N states with energies $\varepsilon_1, \varepsilon_2, \dots, \varepsilon_i, \varepsilon_{i+1}, \dots, \varepsilon_N$, the probability for the system in the state with energy ε_i is

$$P(\varepsilon_i) = e^{-\varepsilon_i/\tau} / \sum_{j=1}^N e^{-\varepsilon_j/k_B T}. \quad (1.10)$$

The *partition function* of the system is defined as

$$Z = \sum_{i=1}^N e^{-\varepsilon_i/k_B T}. \quad (1.11)$$

The *internal energy* (average energy) of the system is given by

$$U = \langle \varepsilon \rangle = \sum_i \varepsilon_i P(\varepsilon_i) = \frac{1}{Z} \sum_i \varepsilon_i e^{-\varepsilon_i/k_B T}. \quad (1.12)$$

Because $\frac{\partial Z}{\partial T} = \sum_i \left(\frac{\varepsilon_i}{k_B T^2} \right) e^{-\varepsilon_i/k_B T} = \frac{1}{k_B T^2} \sum_i \varepsilon_i e^{-\varepsilon_i/k_B T}$,

$$U = \frac{k_B T^2 \partial Z}{Z \partial T} = k_B T^2 \frac{\partial(\ln Z)}{\partial T}. \quad (1.13)$$

1.2.3 Thermodynamic quantities

As energy is conserved, the change of the internal energy U of a system equals the heat dQ absorbed and the mechanical work dW done to the system, $dU = dQ + dW$. When the volume of the system changes by dV under the pressure P , the mechanical work done to the system is given by

$$dW = -PdV. \quad (1.14)$$

When there is no mechanical work, the heat absorbed equals the change of internal energy. From the definition of temperature $1/T = \left(\frac{\partial S}{\partial U} \right)_V$, the heat absorbed in a reversible process at constant volume is

$$dU = dQ = TdS. \quad (1.15)$$

When the volume is not constant, then

$$dU = TdS - PdV. \quad (1.16)$$

The derivatives are

$$T = \left(\frac{\partial U}{\partial S} \right)_V, \quad (1.17)$$

$$P = - \left(\frac{\partial U}{\partial V} \right)_S. \quad (1.18)$$

The internal energy U , entropy S , and volume V are extensive quantities, while temperature T and pressure P are intensive quantities. The *enthalpy* H of the system is defined by

$$H = U + PV. \quad (1.19)$$

Its variation in a reversible process is given by

$$dH = dU + d(PV) = (TdS - PdV) + (PdV + VdP) = TdS + VdP. \quad (1.20)$$

From this equation, it can be seen that the physical meaning of enthalpy is that in a process at constant pressure ($dP = 0$), the change of enthalpy dH is equal to the heat absorbed $dQ (=TdS)$. The derivatives of the enthalpy are

$$T = \left(\frac{\partial H}{\partial S} \right)_P, \quad (1.21)$$

$$V = \left(\frac{\partial H}{\partial P} \right)_S. \quad (1.22)$$

The *Helmholtz free energy* F of the system is defined by

$$F = U - TS. \quad (1.23)$$

Its variation in a reversible process is given by

$$dF = dU - d(TS) = (TdS - PdV) - (TdS + SdT) = -SdT - PdV. \quad (1.24)$$

The physical meaning of Helmholtz free energy is that in a process at constant temperature ($dT = 0$), the change of Helmholtz free energy is equal to the work done to the system.

The derivatives are

$$S = - \left(\frac{\partial F}{\partial T} \right)_V, \quad (1.25)$$

$$P = - \left(\frac{\partial F}{\partial V} \right)_T. \quad (1.26)$$

The *Gibbs free energy* G of the system is defined by

$$G = U - TS + PV. \quad (1.27)$$

The variation in a reversible process is given by

$$dG = dU - d(TS) - d(PV) = -SdT + VdP. \quad (1.28)$$

In a process at constant temperature and pressure, Gibbs free energy does not change. The derivatives are

$$S = - \left(\frac{\partial G}{\partial T} \right)_P, \quad (1.29)$$

$$V = \left(\frac{\partial G}{\partial P} \right)_T. \quad (1.30)$$

The Helmholtz free energy can be derived from the partition function. Because of Equations (1.13) and (1.25),

$$F = U - TS = k_B T^2 \frac{\partial(\ln Z)}{\partial T} + T \left(\frac{\partial F}{\partial T} \right)_V$$

$$F - T \left(\frac{\partial F}{\partial T} \right)_V = -T^2 \left\{ \frac{1}{T} \left(\frac{\partial F}{\partial T} \right)_V + F \left[\frac{\partial \left(\frac{1}{T} \right)}{\partial T} \right]_V \right\} = -T^2 \left[\frac{\partial \left(\frac{F}{T} \right)}{\partial T} \right]_V = k_B T^2 \frac{\partial(\ln Z)}{\partial T}.$$

Hence

$$F = -k_B T \ln Z = -k_B T \ln \left(\sum_i e^{-\epsilon_i/k_B T} \right). \quad (1.31)$$

From Equations (1.11), (1.25) and (1.31), the entropy of a system at a constant temperature can be calculated:

$$S = -k_B \langle \ln \rho \rangle = -k_B \sum_i \rho_i \ln \rho_i \quad (1.32)$$

1.2.4 Criteria for thermodynamical equilibrium

Now we consider the criteria which can be used to judge whether a system is in its equilibrium state under given conditions. We already know that for a closed system, as it changes from a non-equilibrium state to the equilibrium state, the entropy increases,

$$\delta S \geq 0. \quad (1.33)$$

It can be stated in a different way that for a closed system the entropy is maximized in the equilibrium state.

In considering the equilibrium state of a system at constant temperature and volume, we construct a closed system which consists of the system (subsystem 1) under consideration and a thermal reservoir (subsystem 2) with the temperature T . When the two systems are brought into thermal contact, energy is exchanged between subsystem 1 and subsystem 2. Because the

whole system is a closed system, $\delta S = \delta S_1 + \delta S_2 \geq 0$. For system 2, $1/T = \left(\frac{\partial S_2}{\partial U_2} \right)_V$, and

therefore $\delta S_2 = \delta U_2/T$ (this is true when the volume of subsystem is fixed, which also means that the volume of subsystem 1 is fixed). Because of energy conservation, $\delta U_2 = -\delta U_1$. Hence $\delta S = \delta S_1 + \delta S_2 = \delta S_1 + \delta U_2/T = \delta S_1 - \delta U_1/T \geq 0$. Because the temperature and volume are constant for subsystem 1, $\delta S_1 - \delta U_1/T = (1/T)\delta(TS_1 - U_1) \geq 0$, and therefore

$$\delta(U_1 - TS_1) = \delta F_1 \leq 0. \quad (1.34)$$

At constant temperature and volume, the equilibrium state has the minimum Helmholtz free energy.

In considering the equilibrium state of a system at constant temperature and pressure, we construct a closed system which consists of the system (subsystem 1) under consideration and a thermal reservoir (subsystem 2) with the temperature T . When the two systems are brought into thermal contact, energy is exchanged between subsystem 1 and subsystem 2. Because the whole system is a closed system, $\delta S = \delta S_1 + \delta S_2 \geq 0$. For system 2, because the volume is not fixed, and mechanical work is involved. $\delta U_2 = T\delta S_2 - P\delta V_2$, that is, $\delta S_2 = (\delta U_2 + P\delta V_2)/T$. Because $\delta U_2 = -\delta U_1$ and $\delta V_2 = -\delta V_1$, $\delta S = \delta S_1 + (\delta U_2 + P\delta V_2)/T = \delta S_1 - (\delta U_1 + P\delta V_1)/T = (1/T)\delta(TS_1 - U_1 - PV_1) \geq 0$. Therefore

$$\delta(U_1 + PV_1 - TS_1) = \delta G_1 \leq 0. \quad (1.35)$$

At constant temperature and pressure, the equilibrium state has the minimum Gibbs free energy. If electric energy is involved, then we have to consider the electric work done to the system by external sources such as a battery. In a thermodynamic process, if the electric work done to the system is dW_e , $\delta S \geq \frac{dQ}{T} = \frac{dU - dW_m - dW_e}{T} = \frac{dU + PdV - dW_e}{T}$. Therefore at constant temperature and pressure

$$\delta(U - W_e + PV - TS) = \delta(G - W_e) \leq 0. \quad (1.36)$$

In the equilibrium state, $G - W_e$ is minimized.

1.3 Orientational Order

Orientational order is the most important feature of liquid crystals. The average directions of the long axes of the rod-like molecules are parallel to each other. Because of the orientational order, liquid crystals possess anisotropic physical properties, that is, in different directions they have different responses to external fields such as electric field, magnetic field and shear. In this section, we will discuss how to specify quantitatively orientational order and why rod-like molecules tend to parallel each other.

For a rigid elongated liquid crystal molecule, three axes can be attached to it to describe its orientation. One is the long molecular axis and the other two axes are perpendicular to the long molecular axis. Usually the molecule rotates fast around the long molecular axis. Although the molecule is not cylindrical, if there is no hindrance in the rotation in nematic phase, the fast rotation around the long molecular axis makes it behave as a cylinder. There is no preferred direction for the short axes and thus the nematic liquid crystal is usually uniaxial. If there is