# LIQUID CRYSTALS AND THEIR COMPUTER SIMULATIONS

Standing as the first unified textbook on the subject, *Liquid Crystals and Their Computer Simulations*, provides a comprehensive and up-to-date treatment of liquid crystals and of their Monte Carlo and Molecular Dynamics computer simulations. Liquid crystals have a complex physical nature, and, therefore, computer simulations are a key element of research in this field. This modern text develops a uniform formalism for addressing various spectroscopic techniques and other experimental methods for studying phase transitions of liquid crystals and emphasizes the links between their molecular organization and observable static and dynamic properties. Aided by the inclusion of a set of Appendices containing detailed mathematical background and derivations, this book is accessible to a broad and multidisciplinary audience. Primarily intended for graduate students and academic researchers, it is also an invaluable reference for industrial researchers working on the development of liquid crystal display technology.

CLAUDIO ZANNONI obtained his PhD in Chemical Physics from Southampton University in 1975 and has been Professor of Physical Chemistry (now Emeritus) at the University of Bologna since 1987. He has extensive experience in the field, having published some 300 papers and delivered over 350 lectures worldwide on computer simulations and molecular theories of liquid crystals. He is also past president (2012–2016) of the International Liquid Crystal Society. In 1998 he founded, and since then directs, the International School of Liquid Crystals in Erice.

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CAMBRIDGE UNIVERSITY PRESS

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UNIVERSITY PRESS

University Printing House, Cambridge CB2 8BS, United Kingdom

One Liberty Plaza, 20th Floor, New York, NY 10006, USA

477 Williamstown Road, Port Melbourne, VIC 3207, Australia

314–321, 3rd Floor, Plot 3, Splendor Forum, Jasola District Centre,
New Delhi – 110025, India

103 Penang Road, #05–06/07, Visioncrest Commercial, Singapore 238467

Cambridge University Press is part of the University of Cambridge.

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www.cambridge.org
Information on this title: www.cambridge.org/9781108424059
DOI: 10.1017/9781108539630



First published 2022

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

*Library of Congress Cataloging-in-Publication Data*
Names: Zannoni, Claudio, author.
Title: Liquid crystals and their computer simulations / Claudio Zannoni.
Description: New York : Cambridge University Press, 2022. |
Includes bibliographical references and index.
Identifiers: LCCN 2021058085 (print) | LCCN 2021058086 (ebook) |
ISBN 9781108424059 (hardback) | ISBN 9781108539630 (epub)
Subjects: LCSH: Liquid crystals. | Liquid crystals–Computer simulation. |
BISAC: SCIENCE / Physics / General
Classification: LCC QD923 .Z36 2022 (print) | LCC QD923 (ebook) |
DDC 530.4/29–dc23/eng20220208
LC record available at https://lccn.loc.gov/2021058085
LC ebook record available at https://lccn.loc.gov/2021058086

ISBN 978-1-108-42405-9 Hardback

To my wife, Nicoletta, for her support over all these years and for believing that I would finish this project even when I doubted it.

# Contents

# Preface

There are two main approaches to the theoretical study of liquid crystals: continuum and molecular.

The first, well covered in various good books [Chandrasekhar, 1992; de Gennes and Prost, 1993; Virga, 1994; Kleman and Lavrentovich, 2003; Stewart, 2004; Oswald and Pieranski, 2005, 2006; Barbero and Evangelista, 2006], considers anisotropic systems at macroscopic level and typically deals with optical and elastic properties as well as with many practical electro-optical applications of liquid crystals. At the continuum level, liquid crystals are assumed to exist and their properties (e.g. elastic constants and viscosities) to be known, insofar as they are needed to parameterize the relevant equations. Molecules, phase transitions and spectroscopic properties are not normally taken into consideration. In this line of work computer simulations typically refer to a determination of the preferred orientation (director) or of the ordering tensor field that minimize the elastic free energy under a variety of boundary conditions, while dynamics is normally related to the solution of hydrodynamics equations for anisotropic fluids.

The other main line of investigation deals with the molecular organization of liquid crystals and how their macroscopic behaviour can be understood in terms of constituent molecules (or colloidal particles, as appropriate) and their interactions, particularly with the help of computer simulation techniques. It is definitely this microscopic approach that we shall follow in this book, discussing in some detail the main types of liquid crystal phases as well as theoretical and computer simulation approaches. I believe that such a book does not exist at the moment and that it might be useful to have one. On one hand, books dealing with liquid crystals [de Gennes, 1974; Chandrasekhar, 1992; Chaikin and Lubensky, 1995; Collings and Hird, 1997; Khoo, 2007; Blinov, 2011] hardly talk of computer simulations, since they are focussed on other aspects or, possibly, because their development is relatively recent. On the other, good textbooks on computer simulations also exist [Frenkel and Smit, 2002; Berendsen, 2007; Allen and Tildesley, 2017], but none deals specifically with liquid crystals. This is a major problem, since computer simulations of liquid crystals need to go beyond the standard calculations of thermodynamics properties or radial distributions and should relate to relevant experiments in the field. In particular, this requires developing appropriate methodologies to calculate the anisotropic, tensorial, observables, order parameters, space and time correlation functions, director field and defects, that are characteristic

features of liquid crystals, and to make contact with what is actually measurable, e.g. from spectroscopic or diffraction experiments. Some of these aspects have been addressed in multi-author books [Luckhurst and Gray, 1979; Pasini and Zannoni, 2000; Lavrentovich et al., 2001; Pasini et al., 2005b], some of which I have co-edited. However, these books are now at least 15 years old, while very many new applications, e.g. all the predictive atomistic simulations of liquid crystals, have been developed more recently. It is also worth stressing that liquid crystals are an intrinsically interdisciplinary topic and many of the background tools needed for their understanding are drawn from different curricula, especially physics and chemistry, but also mathematics, biology, etc. A similar problem arises even within a single discipline when we wish to treat different anisotropic materials like low-molar-mass liquid crystals, polymers and membranes. At the moment, these topics are presented separately in reviews or book chapters. While these have the advantage of a detailed treatment of specific advanced topics, we aim here at a consistent approach that tries to amalgamate the various topics. For example, much of the background required to understand the application to liquid crystals of different spectroscopic techniques, such as Nuclear Magnetic Resonance (NMR), Fluorescence Depolarization (FD), Dielectric Relaxation (DR), X-ray, etc., is largely similar, even though the different fields have developed independently and often with a different jargon and notation for the same quantities, so that a unified treatment should now be timely. Such an approach, in terms of order parameters and correlation functions, is also key to predicting observables from computer simulations and comparing with experimental results. The book provides the basic conceptual and technical tools needed by a student towards the end of an undergraduate curriculum or at the beginning of a postgraduate course (in physics, chemistry, material sciences, engineering or mathematics), or more generally by someone starting research in liquid crystals. The book has grown from undergraduate and graduate courses that I have taught for a number of years at Bologna University as well as from lectures that I have given at a number of summer schools and at universities around the world, from Southampton to Kuala Lumpur. On the basis of this experience, I have made an effort to put together some of the contents useful for a fairly gentle introduction to liquid crystals at molecular level.

In summary, the organization of the book is as follows. The first part of the book introduces the various kinds of mesophases and their phase transitions from the thermodynamic point of view (Chapters 1 and 2) as well as in terms of order parameters (Chapter 3). The essentials of how various experimental techniques (Linear Dichroism (LD), FD, NMR, etc.) can be employed to determine order parameters are introduced. Pair correlations and their relation to various experimental quantities (elastic constants, X-ray scattering) are presented in Chapter 4, while the reorientational dynamics of molecules in liquid crystals is described in Chapter 6, with a detailed discussion of orientational correlation functions and of their properties. The calculation of these time dependent correlation functions using stochastic models (rotational diffusion in particular) is also presented. Connection with experiments providing information on dynamic properties is introduced with Linear Response Theory and some important cases (DR, ionic transport, thermal conductivity, viscosities) examined in some detail. Given the huge variety of liquid crystal phases, the systems are chosen with modelling and simulations in mind. Simulations are also viewed as a set of 'computer

experimental' techniques able to generate 'configurations', i.e. snapshots of the positions and orientations of a sample of $N$ molecules at equilibrium. The availability of these sets of configurations or of trajectories, i.e. of their time evolution, will, perhaps unconventionally, be assumed to be available, at least in principle. even in the first part of the book, so as to connect the various concepts introduced to characterize the liquid crystal phases to simulations. However, the details of how to perform the simulations will only be given in the second part of the book. Intermolecular and more generally particle–particle interactions are introduced in Chapter 5 and Molecular Field and Onsager theories, the most important approximate statistical mechanical approaches currently used, are discussed in Chapter 7. We then turn to computer simulation techniques. Both Monte Carlo (MC) and Molecular Dynamics (MD) methodologies are introduced in Chapter 8 and in Chapter 9, respectively, with special attention given to the calculation of anisotropic properties. The following chapters are devoted to the application of computer simulation techniques to liquid crystals at multiple length scale: Lattice (Chapter 10), Off Lattice Molecular (Chapter 11) and fully Atomistic models (Chapter 12). Most of the required mathematics is covered in a series of Appendices, hopefully making the book fairly self contained. Thus, spherical tensors, Wigner matrices, quaternions and other tools useful for dealing with rotations, which have normally to be extracted from books on angular momentum and quantum mechanics, are treated here with our applications in mind. Even simpler topics, like orthogonal basis sets, Dirac delta functions and Fourier transforms, typically treated in a physics curriculum, but not always in chemistry courses, are covered, with an eye to the practical user. The majority of chapters also have a detailed treatment of some 'simple' but relevant cases (sections) that can be read independently from the rest and could be used, e.g. for undergraduate courses. If the huge increase in computer performance and resources continues (it has been of a factor of the order of $10^5$ in the last 20 years), the vision is that computer simulations will become very widespread and used more and more by industry and by non-specialists in the field. Knowing the basic ingredients of computer simulations thus seem important even for potential users, rather than just for developers, even when dealing with materials as complex as liquid crystals.

In closing I wish to thank the many friends, students and colleagues that have helped providing advice and support. I am particularly grateful to Lara Querciagrossa, also for much essential help with the figures, and to Sergio Cataliotti who have both carefully read and corrected all the chapters. I am indebted to Andy Emerson, Alessandro Porreca and Riccardo Tarroni for some figures and to Matteo Babbi, Gianni Bendazzoli, Roberto Berardi, Martin Čopič, Raffaele della Valle, Juho Lintuvuori, Luca Muccioli, Silvia Orlandi, Guido Raos, Matteo Ricci, Lorenzo Soprani, Marco Mazza and Francesco Spinozzi for reading, correcting and commenting on some parts of the draft. All remaining errors are of course my responsibility. I am also very grateful to Oleg Lavrentovich for the beautiful image of a liquid crystal texture used for the cover and last, but certainly not least, to Roberto Berardi (unfortunately now prematurely deceased) and to Geoffrey Luckhurst for many essential discussions over the last few decades.

Part of this book was written at the Isaac Newton Institute, Cambridge, UK, and I am extremely grateful for the hospitality and for the stimulating atmosphere and the discussions with many colleagues that I thoroughly enjoyed there.