Soft Matter Physics

An Introduction

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Foreword by J. Friedel

With 256 Illustrations, 4 in Full Color

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Foreword

Introductions to solid state physics have, ever since the initial book by F. Seitz in 1940, concentrated on simple crystals, with few atoms per cell, bonded together by strong ionic, covalent, or metallic bonds. References to weaker bonds, such as van der Waals forces in rare gases, or to geometric or chemical disorder (e.g., alloys or glasses) have been limited.

The physical understanding of this field started well before Seitz's book and led to a number of Nobel prizes after the last war. Applications cover classical metallurgy, electronics, geology and building materials, as well as electrical and ionic transport, chemical reactivity, ferroelectricity and magnetism.

But in parallel with this general and well publicized trend, and sometimes earlier as far as physical concepts were concerned, an exploration and increasingly systematic study of softer matter has developed through the twentieth century. More often in the hands of physical chemists and crystallographers than those of pure physicists, the field had for a long time a reputation of complexity. If progress in polymers was steady but slow, interest in liquid crystals had lain dormant for forty years, after a bright start lasting through 1925, to be revived in the late 1960s based on their possible use in imaging techniques. The optoelectronic properties of the field in general are even more recent.

Maurice Kleman's initial research interests have been in the study of magnetoelastic effects in ferromagnetic crystals and films, a field where he was able to apply Kröner's techniques of infinitesimal dislocations to the study of inhomogeneous magnetism in walls, lines, and points, as initiated by P. Weiss and developed notably by L. Néel. When P.G. de Gennes started developing an interest in liquid crystals in Orsay, it was natural for Kleman to turn his own attention to this field, where many mesoscopic phenomena have to be attacked from somewhat similar points of view. True to his initial interests, Kleman kept as a main objective the understanding of the possible defects of such structures, a line of attack first explored by my grandfather G. Friedel and revived in the 1950s by Kleman's friend C.F. Frank. Kleman is now well known for his work in the general field of defects in soft matter, summarized in part in a little book on points, lines, and walls. The other author, Oleg D. Lavrentovich, studied in Kiev the structures of liquid crystal droplets, which he produced by a new method, with controlled surface anchoring conditions, which allowed him to recognize rather early the presence of a TGB phase as foreseen by analogy with superconductors of the second kind. After a long stay as a visiting scientist in Orsay with

Kleman, where he studied, with P. Boltenhagen, the splitting of oily streaks into focal conic domains, he has taken a position at Kent State University. Maurice Kleman and Oleg D. Lavrentovich now present us the results of their researches and teachings at the graduate and postgraduate levels in soft matter physics. Structure properties only are considered here.

As made clear in Chapters 1 to 4, soft matter is here mostly made of molecules weakly bound by intermolecular forces of various origins, excluding metallic, covalent, and ionic bonds. Thus soft matter can encompass biological matter, although not much of this is treated in this book, except for some properties of assembled DNA molecules. Because of the often complex and flexible forms of the molecules involved, entropy plays a leading role at the origin of various possible forms of "mesomorphic" phases of the liquid crystals, as well as of many easily produced distortions or defects. Extensions of similar concepts to liquid, amorphous, or quasicrystalline phases met in "strong" solids are stressed. To study simply the phase changes involved, one has first to define an order parameter with its characteristic phase and amplitude, smoothly varying in space and time. This approach, popularized by Landau, effectively neglects local atomic or thermal inhomogeneities but provides a general framework applicable to similar mesoscopic problems in superfluidity, magnetism, or phase changes in strong solids. The general concepts derived for analyzing phase changes in the main types of liquid crystals are thus compared with similar approaches for strong superconductivity or very anisotropic magnetism.

The two following chapters relate to possible static or dynamic distortions in liquid crystals: Chapter 5, on elasticity, gives a particularly clear presentation of a field where boundary conditions play a leading role; Chapter 6 presents many aspects of dynamics and viscosity.

Chapter 7, on fractals and growth phenomena, introduces the subject of surface effects, which is pursued further in Chapter 13. Here again, the two aspects of static and dynamical properties are clearly distinguished, even if the field treated could justify longer developments.

Finally, a large part of the book covers the problems of line and point defects in the various liquid crystal phases, as compared with classical strong crystals. This rich field, which covers much original work by the authors, is presented in a rather complete and original way. The two last chapters cover colloids and polymers in a clear, albeit summary, way.

Taken as a whole, this book provides a good introduction to the general background in the study of soft matter. The main concepts involved are presented in a clear and simple way. Short exercises at the end of each chapter together with a short bibliography help readers to broaden their knowledge. The core of the book concentrates on liquid crystals, their numerous phases and their possible static and dynamic conformations, with an emphasis on the role played by boundary conditions and especially free surfaces. But soft matter is not restricted to liquid crystals: Polymers and colloids are also considered, if more briefly. And the various concepts developed for the study of liquid crystals find their equivalents in some problems of "strong" matter: the role of lines and points defects in magnetism, various types of dislocations in liquids, amorphous or quasicrystalline phases; these various aspects are properly mentioned, though not treated to the same depth.

As rightly emphasized by the authors, a striking feature of soft matter is the specific role played by the *mesoscopic range*. In most cases, the direct molecular interactions are of short range. But the way to pave space with such molecules, of various forms, flexibilities, and viscosities, keeping a reasonably compact and stable arrangement, can lead to a variety of different solutions that might differ at long range only. In the search for such solutions, the concept of *coherence length* was first developed in similar problems of magnetism and superfluidity: This is a measure of the size of the mesoscopic range where a type of arrangement imposed on the border of a range is transmitted, with decreasing strength, to the other border. But from the study of soft matter, a new concept has emerged, that of *range of frustration*; in many cases, a local or especially stable arrangement of atoms or molecules cannot be extended far, because it creates too large intermolecular tensions. Examples referred to in this book are the double twist in cholesterics and the icosahedral packing of atoms in liquid, amorphous, or quasicrystalline phases. In such cases, the frustration range is limited by the development and suitable folding of disclination lines, as for instance in blue phases. Thus the nature and symmetry of short-range intermolecular forces can dominate not only the size of the network of dislocations but the long-range structure of the network. The authors have contributed greatly to the emergence of such a concept, and if anything, it could have been developed even further in this book.

Like most of their predecessors, the authors introduce the *line singularities* (dislocations, disclinations) by the Volterra process, then classify possible singularities (points, lines, walls) by the topological approach introduced by G. Toulouse and M. Kleman. The subject is treated in a progressive way, first in solids, then in smectics A, with their dislocations, disclinations, and specific focal conics, where the authors have recently added to our knowledge. Cholesterics and nematics are then treated in depth, with a discussion of liquid relaxation and the general importance of topological classification.

It is indeed rightly stressed that the Volterra process starts with a solid medium, while the topological approach assumes complete viscous *relaxation* of stresses on an at least partly liquid medium. As this relaxation increases from smectics to cholesterics and nematics, the passage through a Volterra process might look more and more artificial, and indeed it is a pity that no more has been done on the physical properties of disclinations in nematics, related to the noncommutativity of their topology: What is the equivalent of F.C. Frank's "kinks," produced by the crossing of two dislocations in a crystal, when two disclinations cross in a nematic?

However, liquid relaxation after a Volterra process in a frozen medium helps us to understand a number of characteristic features of the singular lines in liquid crystals: It reduces the stored energy of dislocations and disclinations and allows all these singular lines to be flexible and mobile; for disclinations, it fixes the orientation of the cut surface of the initial Volterra process, so as to minimize the energy; it allows the topological elimination of some lines by an escape into the third dimension, thus creating pairs of singular points; it also allows the characteristic rotation to be tangent to the disclination line, even a curved one. The Volterra process can finally explain in a natural way why a number of dislocation configurations can be maintained, although not predicted by topological arguments: This can refer, for instance, to slip at low temperatures in amorphous solids or in quasicrystals; it can also refer to boundary or initial conditions, which can maintain lines with a relaxed and continuous core, such as cracks in motion and disclinations in a tube of nematics with molecules perpendicular to the surface of the tube.

These remarks justify, I think, the plan followed by the authors, although liquid relaxation could have been introduced earlier in the book, for dislocations as well as for disclinations or focal conics. The continuous distribution of infinitesimal dislocations produced by such relaxations is precisely that first imagined by Volterra in continuous solids and which J.F. Nye, B.A. Bilby, and E. Kröner developed later in the context of flexion and torsion of solids, as recalled earlier in the book.

Some other comments could be made in the presentation of the book, if not in its substance

- The long-range Landau approach to phase changes neglects *short-range order* effects, which can be significant even in first-order transitions. Thus, as already pointed out in 1930 by G. Foëx, the short-range effects observed in the magnetic properties on both sides of a nematic isotropic transition do not necessarily imply a second-order phase transition at the equivalent of a Curie point in a ferromagnet; but their effects, known in the nematic phase since before the First World War as "swarms" (responsible for turbidity and correctly analyzed in the long-wave limit by P.G. de Gennes), as well as the equivalent effects observed by light scattering in G. Durand's group in the early 1970s in the isotropic phase, strongly reduce the latent heat and increase the temperature variations of the effective Landau parameters. Indeed, the large (optical) range of these fluctuations poses the question of the convergence of a Landau development, which in fact limits itself to very small groups of molecules. Similarly, short-range orientational order can exist in polymers without them showing a transition to a nematic phase, as shown, for example, by B. Deloche in molten polymers as well as in polymeric membranes, using resonance techniques. By skipping rather quickly over such effects, the authors might give too rigid a picture of a field where fluctuations are all important.
- Some "historical" references could have been usefully more fully developed. Thus to say that dislocations in solids began to be studied just before the Second World War probably refers to the fundamental work produced by J.W. Burgers and by R. Peierls in 1939; but the concept of dislocation and disclination lines in continuous solids dates from Volterra, before the First World War; and its transfer to crystals dates from the early 1920s, together with many applications to crystal plasticity. On the other hand, the "Cano" geometry of a tilt boundary of a smectic or cholesteric in a wedge is due to Grandjean using a mica crack and was most probably understood as presented in Figure 8.22 by G. Friedel in the early 1930s. Cano only added a specific way of aligning molecules in a definite direction along glass plates.

- Finally, research in soft matter has been helped by a transfer of concepts developed in strong solids, and this is made very clear in this book. Conversely, concepts developed in soft matter have been transferred to the study of strong solids or of biological materials. This is mentioned here in a number of cases, but it is not the main subject of this book. It can be hoped that another publication will cover in depth recent progress in these fields, where the authors have been active.

In conclusion, I am very happy to introduce a book that presents in a condensed but clear way many facets of a very rich and fascinating field.

Jacques Friedel
Paris, France
January 2001

Series Preface

Partially Ordered Systems

Many familiar materials have neither the precise order of crystalline solids nor the completely random structure of liquids and gases. Colloids such as milk, soap, and detergent solutions; liquid crystals, well known from flat electronic displays; gels; and many kinds of ultrastrong fibers are all partially ordered systems. Such systems have emerged as an important field of study not only from the point of view of basic physics, but also with practical applications in materials science and other disciplines.

This series includes research monographs and graduate-level texts that deal with condensed systems at microscopic, mesoscopic, or macroscopic scales that do not have full long-range spatial and orientational orders. These systems—some of which have also been called soft matter, complex fluids, or supermolecular fluids—include complex liquids with molecules or aggregates of molecules organized on long scales; liquid crystals, composed of monomers or polymers; colloids; molecular crystals; quasicrystals; granular materials; disordered systems; and aggregates. Books in the series cover all aspects of the materials, their structures, properties, and formation, as well as percolation and the formation of fractals and spatiotemporal patterns.

Lui Lam
San Jose, California

Preface

What Is Soft Matter? Scope of This Book

What we call "soft matter" covers a large variety of systems, from polymers to colloids, from liquid crystals to surfactants, and from soap bubbles to solutions of macromolecules. All of these materials are of increasing industrial importance. Although they have long been an eminent domain of research for chemists, physicists are now taking a keen interest in them. Soft matter systems indeed raise problems of physics of completely new types. What makes their unity is difficult to formulate precisely (one speaks of "complex systems," a qualification that at least does justice to their structural properties). We try to distinguish some characteristic proper to them all.

All systems that fall under the name of soft matter belong, with very few exceptions, to organic chemistry. In fact, when one speaks of colloidal gold, or of colloidal silica, reference is made more to a material texture than to the material itself, whereas *colloid science*, in the general understanding, addresses organic solutions characterized by dispersion or solution of one phase in another, such that interface phenomena are of great relevance. The term *colloid* is widely accepted, and even favored, but no clear unified definition of the concept has yet emerged.

This digression being made, let us note that the building blocks of soft matter are organic molecules with often complicated architectures, anisometric in shape, and bound by *weak interactions*. The stability range of these phases is, therefore, close to room temperature, and small changes in temperature are enough to induce phase transitions accompanied most usually by small latent heat or sometimes by chemical decomposition. This is to say that entropy, rather than enthalpy, is a quantity to be considered first and foremost. *Biological matter* (proteins, membranes, DNA and their associates, like viruses or microtubules) enter into the class of materials under this heading of soft matter when studied by physicists. An important characteristic of these materials is that they are not in equilibrium *in vivo*, but this fundamental property of living matter is completely outside the scope of this volume.

Soft matter, in particular *liquid crystals*, display phenomena of *order* of a very original nature, intermediary between those of crystalline solids and those of disordered phases. A considerable outgrowth of the theory of phase transitions, and of the theory of the order parameter singularities, has followed their discovery, with some remarkable features like the "phases with defects" (frustrated phases). The concepts that have been developed in this area have found applications in other parts of physics (quasicrystals, amorphous media, superfluids).

The specific nature of disorder in *polymers* has also required development of a completely new type of description of random media, the physics of *scaling laws*. Examples of new types of phase transitions (e.g., the sol–gel transition) have also encouraged new insights in the physics of tenuous media, using the notion of fractals.

Finally, let us stress the importance, at a fundamental as well as at an applied level, of their transport properties (diffusivity, viscosity), of their viscoelastic properties (e.g., flow under shear of liquid crystals, phase transitions under shear, plastic deformation of polymers), and of surface and interface phenomena (wetting, role of long-range forces), which define a large domain of renewal of *mesoscopic physics*, where we find the interplay of molecular and macroscopic concepts (hydrodynamics, rheology, capillarity). Not all of these topics will be covered in this textbook, which is essentially an *introduction* to the physics of soft matter.

Soft matter physics is *condensed* matter physics, and it goes hand in hand with solid state physics. One expects that a certain number of phenomena display neighboring, if not similar, aspects in both disciplines, to their mutual enrichment. We have therefore included in the introductory chapters a number of developments common to the whole of condensed matter physics, relating to stucture (atomic and molecular arrangements), cohesion (chemical bond), defects, and phase transitions. However, the reader should not expect that we have put the bases of both disciplines on an equal footing. For example, in our discussion of the interactions between atoms or molecules, we favor an exposition that emphasizes the chemical bond picture, not the infinite body electrons spatial configuration, which would fit better the description of phenomena in solid crystals. Therefore, a traditional classification like conductors versus insulators is hardly mentioned. The reader will also notice that we have put stress on the question of defects, extending it largely, this time, to the case of solids, in order to place it in a general perspective. The subject dates back to the beginning of the last century—liquid crystals are indeed the material for which the concept of defects was first developed—and has always looked particularly difficult to many students. Personal interest led us to develop this topic, but this is not the only reason. The general theory of defects has benefited from the discovery of many liquid crystalline phases; on the other hand, a new interest in the rheological properties of complex materials can benefit from our knowledge of the plasticity of solids. A number of concepts well investigated in this field for solids take their place in liquid crystals, with obvious differences: For example, the viscous relaxation of defects in a nematic yields situations that present less hysteresis than does solid friction in solids. Apart from this particular emphasis, we believe that all essentials are treated in a sufficiently detailed way to offer access to the whole subject of soft matter. The chapter on the hydrodynamics of nematics is introduced by a reminder of the standard hydrodynamics of isotropic fluids.

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Some technicalities: The list of references has been restricted on purpose to textbooks, review papers, and articles, when the subject they treat is not accessible in a review. Each chapter is accompanied by a few problems, generally with solutions, which either permit readers to test their understanding of the concepts developed in the chapter, or to extend some special points not treated in the body of the text. This is also the role of some appendices. We have also added a table of conversions of units.

Note added in proof:

In the color insert, please note that the scale bar in Fig. 3.14 should read "100 μm" instead of "100 ∞ m."

Acknowledgments

This textbook results from a collaboration between the two authors over many years, and from our individual experiences of teaching students at the graduate and upper undergraduate levels (MK, at École Polytechnique and DEA of Physique des Solides at Orsay and of Physique des Liquides in Paris; OL, at Chemical Physics Interdisciplinary Program, Kent State University, Ohio). MK wishes to thank Albert Libchaber, Rockefeller University, for welcoming him in his laboratory, where he found a pleasant and quiet atmosphere to work on this book. Thanks are also due to Loïc Auvray, Pascale Fabre, Jean-Baptiste Fournier, Paul Sotta, and André Thiaville, for discussion and help as members at different times of the teaching team of MK. OL is grateful to Sergiy Shiyanovskii, Victor Pergamenshchik, and Tomohiro Ishikawa, who have helped to teach his course. Claudine Fradin (of the Laboratoire de Physique des Solides, in Orsay) typed a large part of the initial draft: The authors want to thank her for her unfailing help, in spite of the distance.

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