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Soft Condensed Matter

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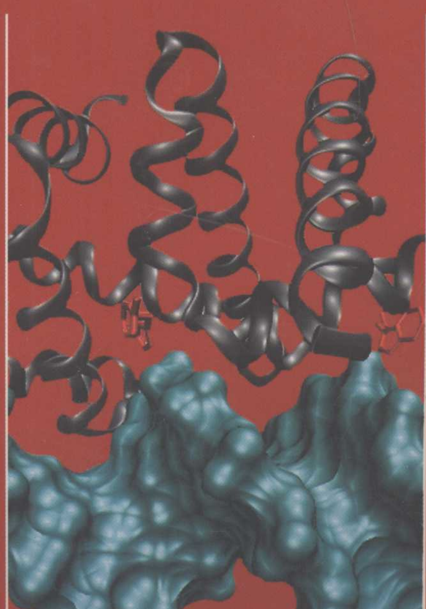

Richard A.L. Jones

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Preface

In writing this book I have attempted to give a unified overview of the various aspects of the physics of soft condensed matter—including colloids, polymers, and liquid crystals—at a level suitable for an advanced undergraduate or a beginning graduate student. I hope that the book will be found of value by students of chemistry, materials science, and chemical engineering, as well as those students of physics doing one of the increasing number of courses about soft matter in today's physics curricula.

As a background, a student should have an elementary knowledge of the properties of matter. The theoretical underpinning of soft matter physics is in statistical mechanics and thermodynamics, and some acquaintance with the basics of these subjects is also desirable. An appendix is included summarising some key results. I am aware that many students find statistical mechanics rather difficult conceptually, and I have tried to choose transparency over elegance in deriving results. One additional advantage of studying soft matter is that it provides many illuminating examples of the principles of statistical mechanics at work. In particular the role of entropy is central; for this reason I have stressed methods for calculating thermodynamic quantities which rely on directly calculating the entropy, rather than the more compact but less transparent routes via the partition function.

Writing a textbook in an area that is not already well provided with them has both the advantage and the disadvantage that a traditional canon of topics does not yet exist. The choice of topics I have made reflects, of course, my own personal interests, and no doubt others would disagree about what should and should not be included. I hope that my choice, at least, will give students an appreciation both of the breadth of application of this fascinating class of materials and of the unity of some of the physical principles that underlie their behaviour.

The origins of this book lie in a final year undergraduate physics course taught at Cambridge. I owe a great debt to my colleagues who taught the course before me: Professors Athene Donald, John Field, and Mick Brown. This course, entitled 'Materials', covered structural aspects of many materials, both 'hard' and 'soft', though as the research interests of the department evolved the 'soft' element of the course became increasingly emphasised. When I moved to Sheffield I took the opportunity to use some of this material in writing a course for fourth-year MPhys students exclusively devoted to soft condensed matter, and it is this course that formed the basis for this book.

I am grateful to my colleagues Mark Geoghegan and Martin Grell, at Sheffield, and Joe Keddie, at Surrey University, who read the manuscript and pointed out a number of errors and potential improvements. Jon Howse kindly supplied the cover image. I would also like to thank Dr Sönke Adlung and his colleagues at Oxford University Press for the combination of enthusiasm and professionalism which they brought to the project.

Most of all, I thank my parents, Robbie and Sheila, and my wife Dulcie. They gave me very practical assistance during the preparation of the manuscript, as well as supporting and encouraging me throughout the period of its writing.

Sheffield R.A.L.J.

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Introduction and overview

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1.1 What is soft condensed matter?

Soft condensed matter (or **soft matter**, for brevity) is a convenient term for materials in states of matter that are neither simple liquids nor crystalline solids of the type studied in other branches of solid state physics. Many such materials are familiar from everyday life—glues, paints, and soaps, for example—while others are important in industrial processes, such as the polymer melts that are moulded and extruded to form plastics. Much of the food we eat can be classed as soft matter, and indeed the stuff of life itself shares the qualities of mutability and responsiveness to its surroundings that are characteristic of soft matter. We are ourselves **soft machines**, in William Burroughs' apt phrase, and the material we are made of is soft matter.

In more precise terms, the materials we are discussing include **colloidal dispersions**, where submicrometre particles of solid or liquid are dispersed in another liquid, **polymer melts or solutions** in which the size and connectivity of the molecules lead to striking new properties, such as **viscoelasticity**, which are very different to those of a simple liquid, and **liquid crystals**, where an anisotropic molecular shape leads to states with a degree of ordering intermediate between a crystalline solid and a liquid.

What do these apparently disparate materials have in common? There are a number of features that they share which makes it worth considering them as a class. These include:

- The importance of **length scales intermediate between atomic sizes and macroscopic scales**. Colloidal particles are typically less than a micrometre in size, polymer chains have overall dimensions in the tens of nanometres, and the self-assembled structures formed by amphiphilic molecules have dimensions in a similar range. From the point of view of constructing theories, this means that one can (and should) use **coarse-grained** models that do not have to account for every detail on the atomic scale. These coarse-grained models emphasise **universality**; for example, many aspects of the behaviour of polymers derive not from the particular chemical details of the units that make up the chain, but simply from the topological implications that follow from the fact that the polymer molecule is a long, flexible curve in space which cannot be crossed by other chains.
- The importance of **fluctuations and Brownian motion**. Although typical structures in soft matter are larger than atomic sizes, they are small enough for **Brownian motion**—the fluctuations that take place in any thermal

system—to be important, and the typical energies associated with the bonds between structures and with the distortions of those structures are comparable in size to thermal energies. Soft matter systems should be visualised as being in a constant state of random motion; polymer chains in solution are continually writhing and turning, while the membranes formed by sheets of self-assembled amphiphilic molecules are not rigid plates, but are continually buckling and flexing under the influence of Brownian motion.

The propensity of soft matter to **self-assemble**. Related to the importance of Brownian motion is the fact that most soft matter systems are able to move towards **equilibrium**. But the equilibrium state of lowest free energy in a soft matter system is often not a state of dull uniformity; the subtle balances of energy and entropy in soft matter systems yield rich phase behaviour in which complex structures arise spontaneously. This **self-assembly** can take place at the level of molecules, but even more complexity occurs when ordering takes place **hierarchically**, with molecules coming together to form supramolecular structures (such as micelles), which themselves order at a higher level. In this way structures of tremendous intricacy and complexity are put together without external intervention, driven solely by the second law of thermodynamics.

We will see these themes recurring throughout the book.

1.2 Soft matter—an overview

The basic aim of condensed matter physics is to understand the collective properties of large assemblies of atoms and molecules in terms of the interactions between their component parts. In this book we will mostly be concerned with the structural and mechanical properties of soft matter, and the tools we will need are those of **statistical mechanics**. In Chapters 2 and 3 we review some of the concepts we will need, covering some material that will be familiar to many readers from elementary courses on the properties of matter, and introductory courses on solid state physics and thermal physics. At the macroscopic level, we need to be able to characterise the typical mechanical responses of solids and liquids; these responses can be understood at the microscopic level in terms of the role of bond energies and timescales for atomic or molecular motion. Elementary science stresses the distinction between solids and liquids, but we find cases that seem to stretch this definition: **viscoelastic** liquids, which seem to behave either like liquids or solids depending on the timescale at which they are probed, and **glasses**, which combine a liquid-like lack of long-ranged order with solid-like mechanical properties. **Phase behaviour** and **changes of phase** recur throughout the book; in Chapter 3 methods for treating both the equilibrium phase behaviour and the kinetics of phase transitions are introduced in the context of the unmixing of simple liquid mixtures. The methods introduced—in particular **mean field models** allowing one to calculate the free energy—are used again frequently in the book to deal with more complex systems. These two chapters thus provide a general framework in which the physics of more complex and specific systems covered in the later chapters can be dealt with in a unified way.

In Chapter 4, one specific class of soft matter is introduced—colloidal dispersions. This allows us to make some general points about the hydrodynamics of microscopic objects and Brownian motion, and gives one an opportunity to go into more detail about the forces that operate between surfaces at colloidal length scales. The discussion is mostly confined to the properties of hard, spherical, particles; the richness of behaviour found, for example, in suspensions of highly anisotropic particles such as clay platelets is not considered. However, even for spherical particles we find a wide range of behaviour: structural aspects include their assembly into colloidal crystals and aggregation into fractal structures, while in flow they display striking non-Newtonian effects such as shear thinning.

The properties of polymers are introduced in Chapter 5. Here we see a graphic illustration of the power of entropy in the random walk configurations taken up by long-chain molecules; understanding the role of this entropy allows us to understand the origin of the elastic properties of rubber. Combining this insight with an appreciation of how the topology of polymer molecules constrains their freedom to move allows us to construct a theory—**reptation**—that quantitatively accounts for the striking viscoelastic properties of polymer solutions and melts.

The formation of rubber from a melt of linear polymers involves **cross-linking**, and understanding this process, by which a liquid is turned into a material with a finite (but low) modulus, allows us to introduce in Chapter 6 another simple mathematical model that demonstrates how disparate physical systems can show a surprising degree of universality—**percolation**.

The next three chapters all consider aspects of **self-assembly** in soft matter. In Chapters 7 and 8, we consider self-assembly at the molecular level. In soft matter systems, we often find states of molecular order that are intermediate between the full three-dimensional order of a perfect crystal and the complete translational symmetry of a liquid. This intermediate order can be of two types. In Chapter 7 we consider **equilibrium** phases in which there may be only orientational order, or positional order only in one or two dimensions. These phases are known as **liquid crystalline** phases; some such materials are familiar to all of us as the basis of everyday display technologies for computers and calculators, but the variety of materials forming liquid crystalline phases is much wider, including a number of polymers. In Chapter 8 we consider crystallinity in polymers; here the reason for partial ordering is **kinetic** rather than thermodynamic. A fully crystalline state would have the lowest free energy, but such a state is inaccessible on experimental timescales, and it is the kinetics of the process of crystallisation which controls the intricate hierarchical structures that arise.

The theme of self-assembly is taken to another level in Chapter 9. Here we consider situations in which the units that come together to form ordered structures are not single molecules, but aggregates of molecules. The most familiar examples of such supramolecular self-assembly are found in soap molecules and similar amphiphiles, while analogous phenomena are to be found among polymers in **block copolymers**. Here liquid crystalline phases or even phases with full three-dimensional order are formed from units that are substantially bigger than molecular sizes.

The final chapter is rather different in its object to the others. Here I wish to introduce some of the areas of biology in which concepts drawn from the physics of soft condensed matter might prove of relevance. This chapter is much more tentative, but it seeks to highlight some important problems in molecular biology, such as the problem of **protein folding**, to which approaches from soft matter physics seem to offer promise. This chapter is inevitably incomplete and impressionistic, but with it I hope to be able to conclude the book with a sense of the potential of physics to make contributions in new and vital areas.

The constraints of brevity mean that many areas of soft condensed matter are treated only in rather a cursory way, while other areas (such as **foams**) are not covered at all. However, if I stimulate any reader to seek to read and think more deeply about any aspects of this fascinating branch of physics I will have achieved my aim.

Further reading

There are at present few books which cover the whole area of soft condensed matter physics. For a general introduction at a more descriptive level than this book, see Hamley (2000). Daoud and Williams (1999) is a collection of essays which give an excellent introduction to a number of aspects of soft condensed matter.