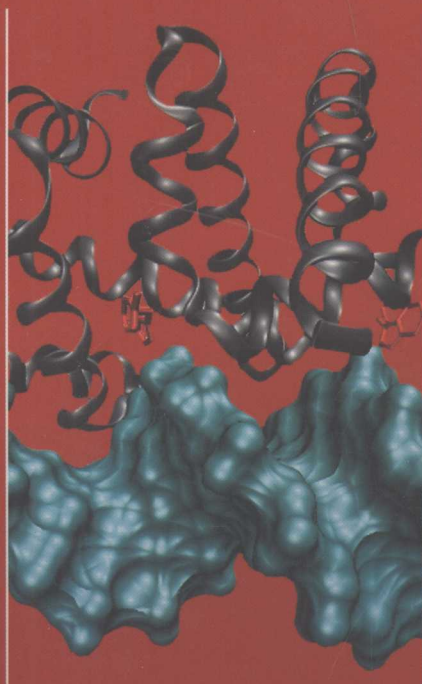


牛津大学 研究生教材系列

# Soft Condensed Matter

## 软凝聚态物质

Richard A.L. Jones



科学出版社

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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.

# 目 录

## 前言

<b>第 1 章 导论与概述</b> .....	1
1.1 什么是软物质? .....	1
1.2 软物质概述 .....	2
<b>第 2 章 凝聚态中的力、能量与时间尺度</b> .....	5
2.1 引言 .....	5
2.2 气体、液体和固体 .....	5
2.2.1 分子间力 .....	5
2.2.2 凝结与冻结 .....	8
2.3 黏性、弹性和黏弹性行为 .....	10
2.3.1 物质对剪切应力的响应 .....	10
2.3.2 在分子水平上理解物质的机械响应 .....	13
2.4 液体和玻璃 .....	16
2.4.1 实际形成玻璃系统 .....	16
2.4.2 形成玻璃的液体的弛豫时间和黏性 .....	17
2.4.3 实验玻璃转变 .....	18
2.4.4 理解玻璃转变 .....	21
<b>第 3 章 相变</b> .....	25
3.1 软物质中的相变 .....	25
3.2 液-液非混合性——平衡相图 .....	26
3.2.1 相间界面与界面张力 .....	31
3.3 液-液非混合性——相分离动力学 .....	32
3.3.1 相分离的两种机制 .....	32
3.3.2 失稳分解 .....	33
3.3.3 成核 .....	37
3.3.4 相分离后期的生长 .....	38
3.4 固-液相变——冻结与熔化 .....	41
3.4.1 固-液相变动力学——均匀成核 .....	42
3.4.2 固-液相变动力学——非均匀成核 .....	44
3.4.3 凝固——成长凝固锋面的稳定性 .....	45
<b>第 4 章 胶体分散体</b> .....	49
4.1 引言 .....	49
4.2 液体中的单个胶体颗粒——斯托克斯定律与布朗运动 .....	50

4.2.1	斯托克斯定律 .....	50
4.2.2	布朗运动与爱因斯坦方程 .....	50
4.3	胶体颗粒之间的力 .....	52
4.3.1	原子间力与颗粒间力 .....	52
4.3.2	范德瓦尔斯力 .....	53
4.3.3	静电双层力 .....	58
4.3.4	用枝接聚合物层稳定聚合物 .....	60
4.3.5	排空相互作用 .....	61
4.4	胶体的稳定性和相行为 .....	62
4.4.1	硬球胶体的结晶 .....	62
4.4.2	具有较长程排斥力的胶体 .....	65
4.4.3	具有弱吸引作用的胶体 .....	66
4.4.4	具有强吸引相互作用的胶体 .....	67
4.5	浓悬浮液中的流动 .....	68
<b>第5章</b>	<b>聚合物</b> .....	<b>73</b>
5.1	引言 .....	73
5.2	聚合物材料的种类 .....	73
5.2.1	聚合物化学 .....	74
5.2.2	立体化学 .....	75
5.2.3	结构 .....	76
5.2.4	共聚物 .....	76
5.2.5	物理状态 .....	77
5.3	随机行走与聚合物链的维度 .....	77
5.3.1	自由连接链及其高斯极限 .....	78
5.3.2	真实聚合物链——短程相关 .....	79
5.3.3	排除体积、温度与线团——小球相变 .....	80
5.3.4	聚合物熔体中的链统计学——弗劳里定律 .....	82
5.3.5	聚合物链尺度的测量 .....	82
5.3.6	界面上的聚合物——吸附链和枝接链 .....	84
5.4	橡胶的弹性 .....	85
5.5	聚合物中的黏弹性与蛇行模型 .....	86
5.5.1	聚合物黏弹性之表征 .....	86
5.5.2	线性黏弹性与玻尔兹曼叠加原理 .....	88
5.5.3	黏弹性性质的温度依赖性:时间-温度叠加 .....	88
5.5.4	黏弹性:单分散线性聚合物熔体的实验结果 .....	89
5.5.5	纠缠 .....	90
5.5.6	管道模型与蛇行理论 .....	91
5.5.7	对蛇行理论的修正 .....	93

<b>第 6 章 凝胶化</b> .....	95
6.1 引言 .....	95
6.2 凝胶的类别 .....	96
6.2.1 化学凝胶 .....	96
6.2.2 物理凝胶 .....	97
6.3 凝胶的理论 .....	97
6.3.1 逾渗模型 .....	97
6.3.2 凝胶的经典理论——弗劳里-斯托克迈尔模型 .....	98
6.3.3 逾渗模型中的非经典指数 .....	100
6.3.4 凝胶的弹性 .....	100
<b>第 7 章 凝聚态物质中的分子序——液晶</b> .....	104
7.1 引言 .....	104
7.2 液晶态入门 .....	105
7.3 丝状相——各向同性相转变 .....	107
7.4 液晶中的形变与拓扑缺陷 .....	111
7.4.1 丝状液晶的广义刚度与弹性常量 .....	111
7.4.2 边界效应 .....	112
7.4.3 向错、位错和其他拓扑缺陷 .....	113
7.5 液晶的电学和磁学性质 .....	114
7.6 弗里德里克斯转变与液晶显示 .....	116
7.7 聚合物液晶 .....	118
7.7.1 刚性聚合物 .....	118
7.7.2 螺旋-线团转变 .....	118
7.7.3 理想硬棒的各向同性相/丝状相转变 .....	122
7.7.4 真实溶致系统中的相转变 .....	126
7.7.5 热致液晶相 .....	126
<b>第 8 章 凝聚态物质中的分子序——聚合物晶体</b> .....	129
8.1 引言 .....	129
8.2 结构的等级 .....	129
8.3 链折叠晶体 .....	131
<b>第 9 章 软凝聚态物质中的超分子自组装</b> .....	136
9.1 引言 .....	136
9.2 双亲分子溶液中的自组装相 .....	136
9.2.1 油水为何不相混? .....	136
9.2.2 聚集和相分离 .....	137
9.2.3 双亲分子聚集体 .....	139
9.2.4 球状胶束与临界胶束浓度 .....	142
9.2.5 柱状胶束 .....	142



9.2.6	双层与膜泡	144
9.2.7	膜的弹性与涨落	145
9.2.8	双亲分子浓溶液的相行为	147
9.2.9	表面活性剂溶液中相复合体与微乳液	150
9.3	聚合物中的自组装	151
9.3.1	聚合物混合物中的相分离与聚合物/聚合物界面	152
9.3.2	共聚物中的微相分离	155
9.3.3	镶嵌共聚物的相图	156
<b>第 10 章</b>	<b>自然界的软物质</b>	<b>159</b>
10.1	引言	159
10.2	生命的成分和结构	160
10.3	核酸	161
10.4	蛋白质	165
10.4.1	蛋白质的一级、二级和三级结构	165
10.4.2	蛋白质折叠	167
10.4.3	蛋白质间相互作用:去折叠、集聚与结晶	170
10.4.4	蛋白质的误折叠、凝胶化和胶化纤维起源	172
10.5	多糖	173
10.6	膜	174
<b>附录 A</b>	<b>统计力学若干结果</b>	<b>178</b>
A.1	熵与热力学第二定律	178
A.2	能量、熵和温度	179
A.3	自由能和吉布斯函数	180
A.4	化学势	181
<b>附录 B</b>	<b>理想随机行走的分布函数</b>	<b>182</b>
B.1	统计权重的直接计算	182
B.2	无规行走与扩散方程	183
<b>附录 C</b>	<b>习题选解</b>	<b>185</b>
C.1	第 2 章	185
C.2	第 3 章	185
C.3	第 4 章	186
C.4	第 5 章	186
C.5	第 6 章	187
C.6	第 7 章	187
C.7	第 8 章	187
C.8	第 9 章	187
C.9	第 10 章	188
<b>参考文献</b>		<b>189</b>
<b>索引</b>		<b>193</b>

# Contents

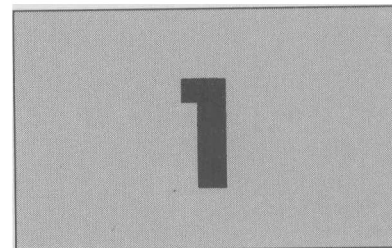
<b>1 Introduction and overview</b>	1
1.1 What is soft condensed matter?	1
1.2 Soft matter—an overview	2
<b>2 Forces, energies, and timescales in condensed matter</b>	5
2.1 Introduction	5
2.2 Gases, liquids, and solids	5
2.2.1 Intermolecular forces	5
2.2.2 Condensation and freezing	8
2.3 Viscous, elastic, and viscoelastic behaviour	10
2.3.1 The response of matter to a shear stress	10
2.3.2 Understanding the mechanical response of matter at a molecular level	13
2.4 Liquids and glasses	16
2.4.1 Practical glass-forming systems	16
2.4.2 Relaxation time and viscosity in glass-forming liquids	17
2.4.3 The experimental glass transition	18
2.4.4 Understanding the glass transition	21
<b>3 Phase transitions</b>	25
3.1 Phase transitions in soft matter	25
3.2 Liquid–liquid unmixing—equilibrium phase diagrams	26
3.2.1 Interfaces between phases and interfacial tension	31
3.3 Liquid–liquid unmixing—kinetics of phase separation	32
3.3.1 Two mechanisms of phase separation	32
3.3.2 Spinodal decomposition	33
3.3.3 Nucleation	37
3.3.4 Growth in the late stages of phase separation	38
3.4 The liquid–solid transition—freezing and melting	41
3.4.1 Kinetics of the liquid–solid transition—homogeneous nucleation	42
3.4.2 Kinetics of the liquid–solid transition—heterogeneous nucleation	44
3.4.3 Solidification—stability of a growing solidification front	45
<b>4 Colloidal dispersions</b>	49
4.1 Introduction	49
4.2 A single colloidal particle in a liquid—Stokes’ law and Brownian motion	50

4.2.1	Stokes' law	50
4.2.2	Brownian motion and the Einstein equation	50
4.3	Forces between colloidal particles	52
4.3.1	Interatomic forces and interparticle forces	52
4.3.2	Van der Waals forces	53
4.3.3	Electrostatic double-layer forces	58
4.3.4	Stabilising polymers with grafted polymer layers	60
4.3.5	Depletion interactions	61
4.4	Stability and phase behaviour of colloids	62
4.4.1	Crystallisation of hard-sphere colloids	62
4.4.2	Colloids with longer ranged repulsion	65
4.4.3	Colloids with weakly attractive interactions	66
4.4.4	Colloids with strongly attractive interactions	67
4.5	Flow in concentrated dispersions	68
<b>5</b>	<b>Polymers</b>	<b>73</b>
5.1	Introduction	73
5.2	The variety of polymeric materials	73
5.2.1	Polymer chemistry	74
5.2.2	Stereochemistry	75
5.2.3	Architecture	76
5.2.4	Copolymers	76
5.2.5	Physical state	77
5.3	Random walks and the dimensions of polymer chains	77
5.3.1	The freely jointed chain and its Gaussian limit	78
5.3.2	Real polymer chains—short-range correlations	79
5.3.3	Excluded volume, the theta temperature, and coil-globule transitions	80
5.3.4	Chain statistics in polymer melts—the Flory theorem	82
5.3.5	Measuring the size of polymer chains	82
5.3.6	Polymers at interfaces—adsorbed and grafted chains	84
5.4	Rubber elasticity	85
5.5	Viscoelasticity in polymers and the reptation model	86
5.5.1	Characterising the viscoelastic behaviour of polymers	86
5.5.2	Linear viscoelasticity and the Boltzmann superposition principle	88
5.5.3	The temperature dependence of viscoelastic properties: time-temperature superposition	88
5.5.4	Viscoelasticity: experimental results for monodisperse linear polymer melts	89
5.5.5	Entanglements	90
5.5.6	The tube model and the theory of reptation	91
5.5.7	Modifications to reptation theory	93
<b>6</b>	<b>Gelation</b>	<b>95</b>
6.1	Introduction	95
6.2	Classes of gel	96
6.2.1	Chemical gels	96
6.2.2	Physical gels	97

6.3	The theory of gelation	97
6.3.1	The percolation model	97
6.3.2	The classical theory of gelation—the Flory–Stockmayer model	98
6.3.3	Non-classical exponents in the percolation model	100
6.3.4	The elasticity of gels	100
<b>7</b>	<b>Molecular order in soft condensed matter—liquid crystallinity</b>	<b>104</b>
7.1	Introduction	104
7.2	Introduction to liquid crystal phases	105
7.3	The nematic/isotropic transition	107
7.4	Distortions and topological defects in liquid crystals	111
7.4.1	Generalised rigidity and the elastic constants of a nematic liquid crystal	111
7.4.2	Boundary effects	112
7.4.3	Disclinations, dislocations, and other topological defects	113
7.5	The electrical and magnetic properties of liquid crystals	114
7.6	The Frederiks transition and liquid crystal displays	116
7.7	Polymer liquid crystals	118
7.7.1	Rigid polymers	118
7.7.2	Helix–coil transitions	118
7.7.3	The isotropic/nematic transition for ideal hard rods	122
7.7.4	Transitions in real lyotropic systems	126
7.7.5	Thermotropic liquid crystal phases	126
<b>8</b>	<b>Molecular order in soft condensed matter—crystallinity in polymers</b>	<b>129</b>
8.1	Introduction	129
8.2	Hierarchies of structure	129
8.3	Chain-folded crystals	131
<b>9</b>	<b>Supramolecular self-assembly in soft condensed matter</b>	<b>136</b>
9.1	Introduction	136
9.2	Self-assembled phases in solutions of amphiphilic molecules	136
9.2.1	Why oil and water do not mix	136
9.2.2	Aggregation and phase separation	137
9.2.3	The aggregation of amphiphilic molecules	139
9.2.4	Spherical micelles and the CMC	142
9.2.5	Cylindrical micelles	142
9.2.6	Bilayers and vesicles	144
9.2.7	The elasticity and fluctuations of membranes	145
9.2.8	The phase behaviour of concentrated amphiphile solutions	147
9.2.9	Complex phases in surfactant solutions and microemulsions	150
9.3	Self-assembly in polymers	151
9.3.1	Phase separation in polymer mixtures and the polymer/polymer interface	152

9.3.2	Microphase separation in copolymers	155
9.3.3	Block copolymer phase diagrams	156
<b>10</b>	<b>Soft matter in nature</b>	<b>159</b>
10.1	Introduction	159
10.2	The components and structures of life	160
10.3	Nucleic acids	161
10.4	Proteins	165
10.4.1	Primary, secondary, and tertiary structure of proteins	165
10.4.2	Protein folding	167
10.4.3	Interactions between proteins: misfolding, aggregation, and crystallisation	170
10.4.4	Protein misfolding, gelation, and amyloidogenesis	172
10.5	Polysaccharides	173
10.6	Membranes	174
<b>A</b>	<b>Some results from statistical mechanics</b>	<b>178</b>
A.1	Entropy and the second law of thermodynamics	178
A.2	Energy, entropy, and temperature	179
A.3	Free energy and the Gibbs function	180
A.4	The chemical potential	181
<b>B</b>	<b>The distribution function of an ideal random walk</b>	<b>182</b>
B.1	Direct enumeration of the statistical weight	182
B.2	Random walks and the diffusion equation	183
<b>C</b>	<b>Answers to selected problems</b>	<b>185</b>
<b>C</b>	<b>Answers to selected problems</b>	<b>185</b>
C.1	Chapter 2	185
C.2	Chapter 3	185
C.3	Chapter 4	186
C.4	Chapter 5	186
C.5	Chapter 6	187
C.6	Chapter 7	187
C.7	Chapter 8	187
C.8	Chapter 9	187
C.9	Chapter 10	188
	<b>Bibliography</b>	<b>189</b>
	<b>Index</b>	<b>193</b>

# Introduction and overview



## 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

1.1	What is soft condensed matter?	1
1.2	Soft matter—an overview	2

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.