



Tom McLeish

SOFT MATTER

A Very Short Introduction

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Preface

Any addict, like myself, to the 'Very Short Introduction' series entertains a dream that one day they might be asked to contribute one. So it is with particular joy that I have been able to write this introduction to soft matter, and to acknowledge the attention to detail, patience, and advice from Jenny Nugee and Latha Menon at OUP, which have been outstanding. That is only one of the many privileges that this little book represents, however. To have witnessed, and to have been involved in a small way in the gestation and formation of an entire field of science is an experience not granted to many. Nor is the engagement with a topic that has the interdisciplinary reach of soft matter, from physics to chemistry, chemical engineering to biology. It is equally uncommon for a single field to bridge science going on in university and industrial laboratories with such ease of communication and collaboration. Finally the very place that soft matter holds in the recent history of science, and the way that it leads us back to our roots in the curiosity about the world immediately around us has led to fascinating discussions with historians and philosophers of science. To the many researchers across this rich and international community who have taught me patiently over the years, I am very grateful indeed.

I am also fortunate to have received the type of wisdom that only ever seems to reside in the first generation of pioneers within a

field. Particular gratitude is due to the inspirational advice of Prof. Pierre-Gilles de Gennes, Prof. Dame Julia Higgins, Prof. Walter Stockmayer, and above all Prof. Sir Sam Edwards. From the other end of the generational spectrum, those colleagues who have worked with me as post-doctoral fellows and PhD students have taught me far more than I them, for which I am extremely grateful.

The immediate context and inspiration of this book is the EPSRC Centre for Doctoral Training in Soft Matter and Functional Interfaces (“SOFI-CDT”), based at the universities of Durham, Leeds, and Edinburgh, and partner industries (<https://www.dur.ac.uk/soft.matter/soficdt/about/>). To the many staff and students who have grown the ‘SOFI’ community over the last few years I am very grateful, but particular thanks are due to the students who gave me their advice, diagrams, and editorial eyes on particular chapters: Peter Wyatt, Rebecca Fong, Vishal Makwana, and Vanessa Woodhouse.

I am grateful to my new academic home at the University of York for giving me the time and space to complete the project.

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Chapter 1

The science of softness

Lucretius, the Epicurean poet and philosopher of the 1st century BC, wrote a remarkable compendium of natural history (*De Rerum Natura*—On Natural Things), which introduces the power of conjecturing that all substances are composed of tiny, invisible ‘atoms’, or ‘seeds’:

Wine, we see, will flow on the instant through a sieve, but oil is hesitant and slow, either because its particles are larger, or else more hooked and tightly intertwined, and this is why they can’t be pulled apart so quickly into separate single atoms that seep through single openings, one by one.

The Epicurean tradition sought to explain the observable properties of material things as arising from the structure of their atoms. Though centuries before the experimental and theoretical methods of modern science provided incontrovertible evidence of the existence of atoms, and the larger and more complex molecules which they build, the ancient atomists had grasped a fundamental explanatory key to the world.

Lucretius, and others of the school such as Democritus, were particularly interested in the behaviour of matter as it deforms and flows. The sluggishness of honey is a visible clue, pointing to the invisible and underlying nature and interaction of its atoms.

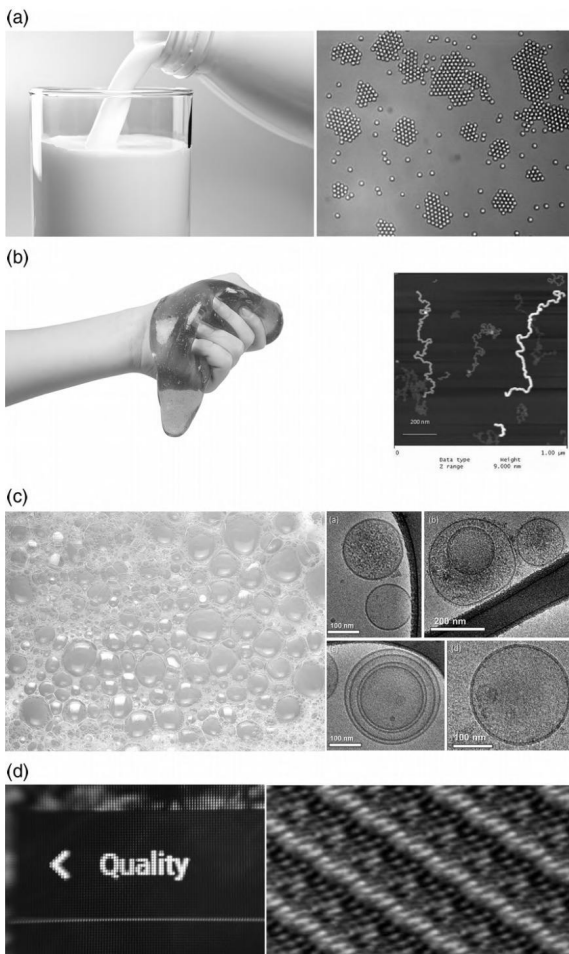
Whether human observers reflected scientifically on it or not, the technology of pliant and deformable matter has an even longer history than the atomic hypothesis. The inks used by the Babylonians of antiquity and the rubber latex of ancient Central America are as indicative of intriguing material properties as the wine and honey of classical Rome.

The Epicurians were also correct in suggesting that flow properties of materials are pointers to their underlying structures. Heraclitus, a much older pre-Socratic philosopher, is credited with the aphorism ‘everything flows’ (Greek, *panta rhei*—*παντα ρει*) as a metaphor for the continual dynamic change inherent in matter. The Greek for flow, *rhein*, has given us the name for the science of flow and deformation, *rheology*. The different rates at which fluids flow under the same force—the sluggishness of honey and the quickness of water—was, for the ancients, and is in today’s experimental laboratories, the fundamental characteristic of soft materials. Rheology has now been transformed into a highly quantifiable tool, accompanied by modern techniques such as microscopy and light scattering that allow direct visualization of the tiny structures within its materials of interest. ‘Soft stuff’, by definition, deforms and flows; hence rheology has also become part of the broader interdisciplinary field of *soft matter* that has emerged over the past three decades.

Soft matter science is special. It begins with the commonplace and familiar, yet it can take us to the frontiers of the exotic unsolved. Who would suspect that the slow drip of the hevea tree’s latex would connect to the 20th century’s theoretical physics of ‘field theories’? Or that the discovery of carbon-based inks in the ancient world would lead, via the work of a botanist peering at the constant motion of particles within plant seeds, to Einstein’s work on heat and to the final convincing proof that atoms exist? Who would have guessed that the ancient discovery of soap-making would lead to an understanding of the self-assembled structures

of the cells in living organisms themselves? This Very Short Introduction concerns deep ideas that pick up momentum on timescales of centuries yet also constitute some of the great cultural threads of our own time. The science of soft materials brings new insights into the world we see, hear, and feel around us. The lustrous whiteness of milk, the colourful swirls on soap bubbles, the stringy stickiness of melted cheese, the extraordinary extensibility of rubber, the switchable states of ‘liquid crystal’ displays—these everyday wonders may be familiar, but it is quite another thing to understand them. Such immediate sense impressions have nevertheless always been the starting point for science, so it will be those familiar properties that set the narrative of this book: the phenomenon of ‘soapiness’ leads to the science of ‘self-assembly’ and the experience of ‘sliminess’ to the idea of giant ‘polymer’ molecules (Figure 1 shows some different examples of soft matter, together with microscopic images of their underlying structures).

From the 1990s onwards, terms such as ‘soft matter’ and ‘soft matter physics’ began to appear with increasing regularity in conference announcements, review articles, and books. The new language reflected a cohering of previously much more fragmented scientific communities. ‘Soft matter’ had begun to subsume sciences that had previously gone by the names of ‘colloid physics’, ‘polymer physics and chemistry’, ‘liquid crystal science’, and more. The new term indicated not simply a merging of research programmes but that the whole represented more than the sum of those parts—the recognized emergence of a new field of science that drew on shared conceptual and experimental foundations. So materials falling under the labels of ‘colloids’, ‘polymers’, ‘liquid crystals’, ‘self-assembly’, ‘membranes’, ‘foams’, ‘granular materials’, ‘biological materials’, ‘glasses’, and ‘gels’ now find a common scientific home. Conversations between these sub-fields as well as within them are in consequence now commonplace.



1. (a) Milkiness; (b) sliminess; (c) soapiness; (d) pearlyness—the material manifestations of the soft matter examples of colloids, polymers, surfactants, and liquid crystals. In each case, the ordinary scale pictures are accompanied by microscopy images of the ‘mesoscopic’ or middle-sized structures underlying the soft materials: (a) colloids—particles; (b) polymers—strings; (c) foams—membranes; (d) liquid crystals—molecular rods.

Another contribution to the emerging history of soft matter science has been made by fruitful engagement between industries and universities. Many pioneering individuals have held posts in both, and many ideas and discoveries had their origin in industrial, rather than academic, laboratories. In the case of the science of plastics, for example, Du Pont in the USA and ICI in the UK were birthplaces for the synthesis of new materials and early theories of how the giant string-like molecules of ‘polymers’ are formed. Fundamental phenomena, for example the relation between the viscosity of melted plastic and the mass of their long-chain molecules, have often been first observed in industrial conditions. Even use of beams of sub-atomic neutrons—the technique known as ‘neutron scattering’—to elicit the first polymer structures was driven from these large industrial laboratories. Soft matter has illustrated how the fields of technology and science are far more closely entangled than the common phrase ‘technology transfer’ would suggest.

Furthermore, the nature of experiment and ways of theorizing in soft matter raises profound questions of where ‘fundamental’ scientific ideas really lie. The American physicist and Nobel Laureate Philip Anderson, in a landmark article entitled ‘More is Different’ published in the 1970s, described how structures can ‘emerge’ at length scales much greater than those of atoms and molecules, but which are just as ‘fundamental’. Soft matter provides many illustrations of Anderson’s claim that the notion of fundamental physics should not be tied to any one scale of length or energy, and that while ‘reductionism’ (the explanation of the behaviour of a system purely in terms of that of its smallest constituents) is an essential tool in science, it cannot be the whole story of how we understand the world. Nature is built from many components, but fundamental novelty arises also from the way they are assembled hierarchically. A few dozen atoms can build small molecules, which can in turn be assembled into giant ‘macromolecules’ or ‘nanoparticles’, whose properties now depend not on their tiny building blocks but on their shape and structure as a whole.

The development of soft matter science was propelled by a combination of communication within the scientific community (through conferences, research departments, and journals that attracted scientists from more than one sub-field), intrinsic conceptual overlap and commonality, and visionary leadership from a small number of pioneering scientists. Pre-eminent among those were two theoretical physicists working in the latter half of the 20th century, Pierre-Giles de Gennes in France (later a Nobel Laureate in physics), and Sir Sam Edwards in the UK. Both realized that broad conceptual frameworks and powerful theoretical techniques from other areas in physics could be applied to soft matter systems, and that as a result, simple and deep structures could be perceived beneath what had previously seemed a disparate collection of very complicated materials. The conceptual leaps were considerable: ideas from fields dominated by the structures of quantum mechanics required translation into systems dominated by thermal physics, whose tools and techniques appear at first sight to be quite distinct. The background of Edwards (a former student of American Nobel prizewinner Julian Schwinger) was quantum field theory—the physics of interaction of light with matter; while de Gennes (a former student of French physicist Jacques Friedel) had worked on superconductivity—the bizarre phenomenon of zero electrical resistance that appears in some metals at very low temperatures. The theoretical models they forged to describe the soft matter physics of polymers and liquid crystals respectively were written in the language of mathematics adapted from their earlier work, but the tangible soft matter examples opened up other, more visual and diagrammatic ways of understanding. These, rather than the formulas, will provide our conceptual ways into soft matter.

Chemistry proved as essential an ingredient to the new science of soft matter as ideas and techniques from physics, together with a renewed conversation between the two sciences. Chemists brought not only the careful synthetic construction of the

remarkable giant molecules and assemblies of soft materials but also ways of thinking about and characterizing the subtle forces between them. Arising from ancient technology, the imaginative leaps of individuals, and the cross-fertilization of ideas—including the final opening of a window onto the atomic world itself, imagined for so many centuries—it is not possible to tell a convincing story of the science of soft matter without visiting some more of its history in each case study.

Before we take deeper dives into some specific examples of soft matter, telling their stories, opening the experimental windows into their structures, and the theoretical concepts that have begun to turn the familiar into the understood, we first need to think a little more about what we mean by ‘soft matter’ itself, anticipating a handful of characteristics that are shared by the materials we term ‘soft’ and the science used to investigate them.

Characteristics of soft matter

The term ‘soft’ is used essentially in its everyday sense—but the compliance and mechanical subtlety of soft or weak solids, gels, and fluids is also the first clue to their internal structure and dynamics, for soft materials reflect a hidden inner world of constant motion.

Thermal motion

The ancient notion of atoms, and its modern development into the variously structured molecules of gases, liquids, and solids around us, is a good starting point but not quite enough to explain or understand ‘softness’. One of the most astonishing demonstrations that molecular ingredients alone are insufficient to determine material properties requires a rose and a container of the extreme coolant: liquid nitrogen (the gas that, apart from the 21 per cent of oxygen, comprises most of the rest of the air we breathe, liquifies at about -200°C). The lustrous rose’s petals

are indeed as ‘soft’ to the touch of a finger as any object we might imagine and as pliant. But now cool the flower to the temperature of the liquid nitrogen by submerging it in the nitrogen for a few seconds, and when we extract it by its stalk, while there is no visible change to its colour or shape, a sharp tap from a hammer will shatter the petals into so many shards, like a fragile piece of glass sculpture (see Figure 2).

The vital difference in the molecular structure of the flower at room temperature and at -200°C is not in the chemistry but in the *motion* of the molecules. Every one of these is in constant random motion, careering now in one direction, now in another, the chemical bonds between atoms vibrating and rotating this way and that. The higher the temperature, the faster all these motions are, on average, while instantaneous values of the random velocities vary hugely. This is the chaotic molecular motion that we call ‘heat’ on everyday scales.

The systematic study of this essential inner motion of matter was initiated by the early 19th-century botanist, Robert Brown, who



2. A rose, frozen in liquid nitrogen, shattering into shards on impact. Its softness is a function of its temperature, not just its molecular constituents and structure.

published a landmark pamphlet on it in 1828. He described his efforts at understanding the source of a constant ‘jiggling’ motion and diffusion of small particles suspended within pollen grains he had observed through his field microscope. In humble, but highly responsible, fashion, Brown explained all the many possible causes of the ceaseless motion (from magnetism to currents in the fluid) that he had systematically ruled out, yet he still found himself unable to account for its source. Although the correct explanation had to wait for an equally seminal paper by Einstein in 1905, as we shall see in Chapter 2, the thermal agitation is rightly called ‘Brownian motion’.

Every part of every material is subjected to Brownian motion, but where strong bonds tie the molecules or atoms to each other, such as in metals or minerals, the random thermal motions will not be able to excite large changes in structure. Shaking a steel climbing-frame in the local playground causes only a slight vibration. But applying the same force to and fro to the climbing net made of rope on the next-door apparatus will cause it to fluctuate wildly. Likewise at the molecular scale, the thermal kicks that jostle molecules around will have a greater effect on those joined by more compliant and weaker bonds. Here lies the molecular key to understanding ‘softness’. Soft materials exhibit large local rearrangements of their microscopic structural constituents under thermal agitation, while ‘hard’ materials suffer only small distortions under the same effects of heat.

There is a way of turning this idea of fluctuations and distortions from random thermal motion into numbers—a measure of ‘softness of matter’. The great 19th-century German scientist Ludwig Boltzmann gave us the ‘currency conversion’ formula we need to translate a temperature T (on the absolute scale where zero is -273°C) into the typical thermal energy of motion E_T that every microscopic particle will possess at that temperature. The ‘Boltzmann constant’ (a very small number when written in everyday units), written k_B , provides the conversion factor: just