1 Introduction

We are all familiar with cracks and the patterns they form. News of a drought brings to mind an image of dry earth forming a polygonal network of cracks on different scales. A stone thrown at a glass window makes a pattern of radial lines with superposed concentric cracks, reminiscent of a cobweb. Crack patterns are formed due to desiccation in the first case and due to external impact in the second case.

There is something fascinating about the patterns that artists and craftsmen often utilize. The typical batik fabric of South East Asia makes intelligent use of aesthetically pleasing cracks; glazed ceramic crockery with patterns of regular geometric cracks look very attractive. Often a coat of paint on metal artefacts or wooden furniture is designed so that it cracks without peeling off and has a pleasing visual effect. Paint cracks on the work of the Old Masters give them an air of living history. Spilt milk, egg or blood dries, cracks and flakes away, again each following its own characteristic pattern.

In spite of all this, comparatively few scientists have considered crack patterns as a subject that is serious, interesting and exciting enough to write a complete book on it. Engineers of course need to take crack formation induced by mechanical stress and fatigue very seriously, and a well-rounded curriculum exists addressing such issues. However, desiccation cracks, which are similar to mechanically driven cracks in some aspects, but quite different from them in others, deserve equal attention. A considerable amount of research has been done on this subject, and we feel that it is time a complete book be devoted to desiccation fracture.

Desiccation cracks can also be very useful. For example, photographs of the surface of Mars show patterns similar to desiccation cracks, which indicate the presence of water at some earlier time (see [1]). Patterns of cracks on composites are different from those on pure materials, and brittle and ductile materials show patterns with different characteristics [2, 3]. So crack patterns can provide an idea about the composition of the material. Patterns formed in drying drops of biofluids such as blood are being investigated for use as medical diagnostics [4].

Recently, very interesting experiments have been done, showing that cracks can be induced to grow in desired patterns by subjecting a system to mechanical

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excitation [5] or electromagnetic fields [6, 7] prior to drying, and precisely tailored cracks have been produced that may help in nanopatterning applications [8].

This book intends to bring together basic ideas, classical and modern theories, and the more recent experimental and theoretical aspects of desiccation crack patterns for readers of different disciplines. The subject should interest students and researchers from physics, earth sciences and engineering, possibly also chemists and biologists.

1.1 Why Study Drying Mud?

Why mud? Why drying? Drawn from many disciplines, serious scientists have approached their studies of nature through the investigation of desiccation cracks. Some examples of their results are shown in Figure 1.1. This is not simply whimsy, but rather reflects the value of desiccation fracture as a simple reliable model for investigating fracture in general. Contraction cracks may be the result of many distinct processes: drying, cooling, syneresis, stretching of a substrate or differential growth of biological tissue, to give a few examples. However, to a large degree, once the geometry and stress state of a system are set, one does not need to know which of these is the driving force in order to understand the resulting crack patterns. For the particular cases of drying and cooling the connection is even stronger, as there is an exact mathematical analogy between the flow and action of heat and moisture in elastic systems [9, 10]. Moisture is often easier to work with, especially when extreme temperatures are involved.

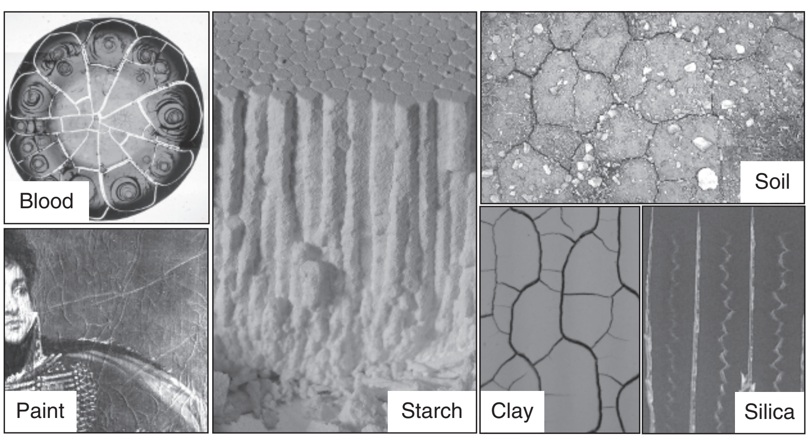

Figure 1.1 Examples of desiccation cracking in different media and under different conditions. Desiccation crack patterns are very rich and can show spirals, stripes, polygons, waves and columns, for example. The genesis of different crack patterns in thin layers is presented in Chapter 7, while columnar starch is discussed in Section 9.4. Blood droplet image courtesy of David Fairhurst; paint craquelure image courtesy of Ludovic Pauchard.

A practical approach to studying desiccation cracks can also be useful in two very different ways: either to prevent cracks or to make use of them. The primary may be to prevent cracks, which is the more traditional goal. But the study may also work in a positive sense to produce specific crack patterns for technological applications, or to use crack networks as a diagnostic tool that gives information about the composition of the cracking material or ambient conditions that caused cracks. This second application will feature prominently in this book.

Some demonstrated applications of the study of desiccation fracture include the following:

- **Industrial coatings:** There is a great interest in replacing paint solvents with environmentally friendly alternatives. These often lead to an increased tendency to crack during drying, and much work has attempted to prevent this [11]. Other industrial applications involve the colloidal films that are used as coatings on papers, for ink-jet printing and for modern high-performance ceramics (e.g. turbine blades in jet engines).
- **Photonics:** The manufacture of colloidal crystals, artificial opals and photonic materials often involves the preparation of a desired structure that is dispersed in fluid and the fixing of this structure by drying it out. Desiccation cracking is a notorious problem that limits the size of many photonic devices [12–14].
- **Geophysics:** Analogue experiments in geology can allow quantitative access to phenomena that occurred long ago in the Earth's past, on other planets, or over timescales inaccessible to humans. For example, dried starch columns are exact analogues of the columnar jointing of lava [15, 16], while the cracks that form in mud as it is repeatedly wetted and dried can help describe the millennia-long evolution of polygonal terrain in permafrost [17, 18].
- **Biophysical fracture:** Insight from desiccation crack networks has been applied to show that the head scales of the Nile crocodile develop as a fracture pattern [19], and to explain the ridges on the skin of cantaloupe [20]. There is also a long-standing question as to whether leaf venation patterns are equivalent to desiccation crack patterns [21].
- **Bespoke crack patterns:** Recently, it has been suggested that desiccation cracks and patterns may be used as templates for nanopatterning. The memory effect in pastes, induced by a gentle vibration of the paste prior to drying, can determine the orientation of the dried crack pattern [5]. Evaporative lithography can also be used to produce textured surfaces by locally varying the drying rate over a colloidal film [22, 23].
- **Forensics and medicine:** The pattern of cracks in dried blood droplets can be used in the diagnosis of illness [24] or to determine the time and conditions (temperature, relative humidity) at which the blood was spilled, for example in a homicide investigation [25]. In addition, the craquelure pattern in paintings can be used to help determine authenticity, age and authorship [26].

Desiccation fracture also allows a probe into the mechanical response of soft materials. Colloids, clays and polymer films are all relatively complex mixtures.

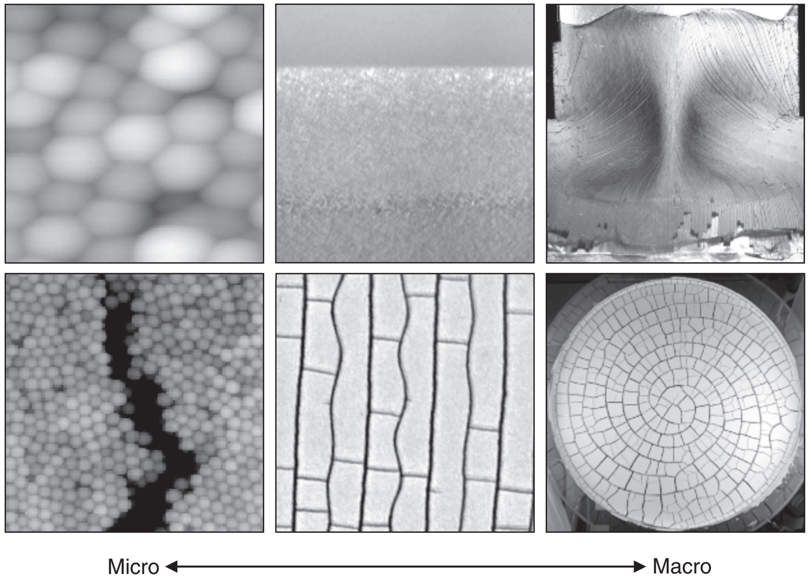

Figure 1.2 Drying dynamics from the microscale to the macroscale, and the connection between structure and fracture. In the top row, images focus on structural information. From left to right: an atomic force micrograph of dried colloidal spheres; a microscope image of a directionally drying colloidal dispersion, where colour changes reflect changes in structure [27]; and a digital photograph through crossed polarizers showing the pattern of birefringence in a dry film, resulting from anisotropy in the structure [28, 29]. The lower row focuses on the connection to fracture. From left to right: atomic force micrograph of a crack tearing through a drying colloidal film and causing structural damage; wavy cracks that follow from directional drying [30]; and curved cracks that are guided by a structural memory in a paste, induced by vibration prior to drying [5]. The effects of plasticity shown here are explored further in Chapter 8.

They are very far from the traditional topics of engineering, or materials science, where fracture mechanics was initially developed. Their behaviour also changes from fluid-like to solid-like as they dry, often very rapidly (e.g. gelation, aggregation, crystallization). Many of the topics we discuss, most explicitly in Chapter 8, try to make a connection between the microscale physics of interactions between the individual particles in a solid, and the macroscopic behaviour of that solid as it dries and breaks. A few examples are shown in Figure 1.2. As the physics of the microscale is intermediate between granular and atomic length scales, new concepts often need to be developed in order to make this connection possible.

1.2 Objectives and Organization of the Book

There are three goals of the work presented here: understanding, interpreting and controlling fracture. The prime concerns of this book are not about how to avoid fracture. Instead, they are about how to understand where fracture patterns come from; to interpret the fracture patterns that we see or find in our surroundings; and ultimately to be able to template or design situations that generate desired fracture patterns at our will.

We do not claim that all these goals have been achieved. Our aim is, however, to bring together the necessary tools for looking at the crack patterns that result from drying and to present the current state-of-the-art research into them. We have therefore structured this book in two roughly equal halves. In the first part, up to and including Chapter 6, we introduce a range of tools that are relevant to the study of desiccation and fracture. Through this we also try to highlight important applications or developments, as they come up. In the second half of this book, Chapters 7–9, we focus on more specialized topics, which are also the subject of ongoing research.

The first chapters, that is, Chapters 2 and 3, familiarize the reader with the basics of elasticity and fracture mechanics. The material in these chapters is applicable to fracture in general, whether from drying or from any other mechanical origin.

In Chapter 2 we describe the theory of linear elasticity, starting from the first principles of how springs behave and ending with a summary of how linear elasticity can be expressed in ways appropriate to a variety of different situations. We present the different elastic moduli that commonly arise, and show how they are defined and used.

Developing from this basis of linear elasticity, Chapter 3 outlines the theory of linear elastic fracture mechanics. A crack costs energy to grow, and this energy must come from relaxing the stress and strain around the crack. This balance is the Griffith criterion for fracture. Furthermore, a stress field will concentrate around rounded corners, to the point of diverging around a crack tip. The magnitude of this divergence was used by Irwin to give a stress-based formulation of fracture mechanics. We explore these two different critical conditions for fracture and show how they are equivalent to each other. We then look at a few more specialized topics, such as the cracking of a thin brittle film, and show how to modify the linear theory of fracture mechanics for non-linear situations such as plastic losses or dynamic effects. We close by introducing an important problem for this book: how does one predict the shape of a crack?

Chapters 4–6 relate to the additional concepts required for studying *desiccation* fracture in particular and introduce the materials in which desiccation cracks usually appear – colloids, pastes and clays.

Drying materials typically consist of a skeleton of solid particles and a pore space between them, which can be filled with either liquid, like water, or air. Chapter 4 introduces the set of ideas needed to consider stress and strain in such a multi-phase material and develops the linear theory of poroelasticity. This is a somewhat esoteric subject, but is included to understand how a driving force for fracture can arise internally, during drying, and to explain the important analogy between drying and cooling.

Chapters 5 and 6 turn to the forces and stresses that are relevant to the solid phase and the liquid phase of a multi-phase material, respectively. The interactions between colloidal particles and clay platelets are described in Chapter 5. The standard theory of colloidal stability, presented there, pairs the electrostatic repulsion of like-charged spheres, separated and screened by a dielectric electrolyte, with the van der Waals attraction felt between matter. We outline this theory and some of the more relevant extensions to it, such as solvation forces. In Chapter 6 we look at the fluid forces arising from capillary effects. We show how surface tension and the complex geometry of a drying porous soil, clay or network of colloidal particles give rise to capillary forces that tend to tear the solid phase apart.

In the second half of this book, Chapters 7–9, we discuss three special topics in depth: planar crack patterns; the effects of plasticity and viscoelasticity; and the means developed to control and interpret more exotic crack patterns.

In Chapter 7 we focus on describing, characterizing and understanding the origin of the many types of contraction crack patterns that can be found in thin, approximately two-dimensional films. We also outline some techniques for numerically modelling desiccation cracks and their patterns.

Chapter 8 deals with a more theoretical approach to understanding and modelling materials that exhibit plasticity and viscoelasticity, which are commonly encountered in the systems showing desiccation cracks. Here, we develop the connection between the macroscopic behaviour of cracks and the microscopic effects governing plasticity.

Finally, Chapter 9 is a collection of several interesting topics related to desiccation fracture in different ways. These include the effects of mechanical, electrical and magnetic stimuli; strategies for avoiding cracks; as well as possible ways of using cracks and designing tailor-made patterns. There is also a section on the spectacular geophysical patterns of columnar joints and polygonal terrain, both of thermal origin, and their relation to cracks in dried starch and mud.

1.3 Approach and Scope

This book is written from a physics perspective, but the questions and methods presented here are interdisciplinary. Work in the field of fracture patterns is currently pursued by physicists, earth scientists, soil scientists, chemical engineers, mechanical engineers, mining engineers, applied mathematicians and even biologists. Thus, a general introduction to each topic is necessary and is provided. Some of the materials in earlier chapters may be redundant to at least some readers. Any chapter can be skipped without losing much from later chapters, as references betweenrelevant sections highlight the more important connections when needed. It is expected, however, that most interested readers will not have command of all the topics covered, and so a broad explanatory tone is maintained throughout.

One common theme that runs through our presentation of material is a consideration of the thermodynamics, and in particular the free energy, of different situations. We derive the basic equations of linear elasticity by reference to the work of deformation, and the theory of fracture mechanics by the addition of a surface energy term to the free energy of an elastic solid, for example. This approach has many advantages, such as highlighting the similarity between poroelasticity and thermoelasticity, or allowing vector forces or tensor stresses to be derived directly from a scalar energy balance. Even though fracture is an inherently non-equilibrium phenomenon, where the final broken state cannot be predicted as the *global* minimum of some energy function, a driving force for fracture can still be shown to follow from the rate of change of the free energy, as an existing crack grows. Furthermore, there are rigorous methods to incorporate irreversible energy losses, either during fracture itself or due to plastic yielding of a drying paste, which preserve the strength of a fundamental thermodynamic approach.

It is assumed that a reader will have a good familiarity with calculus and differential equations. Tensor methods are essential to describe mechanical deformation accurately and concisely, but a primer is given in the appendices, as is a primer on fractals. There are three other appendices provided, which are rather longer discussions of some interesting topics related to Chapter 8.

Every chapter, save this one, ends with a section including a short list of suggested further reading. For the earlier chapters these are largely the most relevant textbooks on each subject. Since each of these chapters contains enough material that it could be (and has been) the topic of specialized textbooks, we had to be selective in what we included. The topics chosen here are mainly those that are most relevant to developing the story of desiccation cracks or their applications. However, for these topics we have tried to give as thorough a discussion as possible, showing the assumptions and physics that underlie the results, and highlighting their possible uses, limitations and extensions. For the special topic chapters, in which research is ongoing, the further reading contains additional pointers to particularly innovative publications or reviews.

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