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Fundamentals of Amorphous Solids : Structure and Properties

非晶态固体：结构和特性（英文版）

Zbigniew H. Stachurski

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Zbigniew H. Stachurski

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The Author

Prof. Dr. Zbigniew H. Stachurski
Australian National University
College of Engineering and Computer
Science
Research School of Engineering
0200 Canberra
Australia

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Preface

This book is intended primarily for students of materials science and related fields who want to acquire a fundamental understanding of the atomic arrangements in amorphous solids. A concomitant aim of the book is to provide an appropriate and consistent methodology and vocabulary for describing the atomic structure of amorphous solids.

The book may also be of interest to theoreticians, for this is a relatively new field of science, open to further evolution and requiring formal proofs of some of the concepts contained herein.

The first three chapters of this book focus mainly on the atomic arrangements in amorphous solids based on the ideal amorphous solid model used as geometrical foundation. Amorphous polymers and inorganic glasses have the most complex atomic arrangements whereas metallic glasses can be considered as being the simplest model of atomic arrangements in amorphous solids.

The twentieth-century may be called by science historians as the Renaissance of Materials Science because many new analytical methods were invented to discover and to ascertain the atomic arrangements in solids (for example, ranging from X-ray diffraction to high resolution transmission electron microscopy), thereby opening up the new science of structure–property relationships. Some of these relationships are described in this book.

The fourth chapter places the mechanical behaviour of amorphous materials in the general context of the mechanics of solids. In many instances, solutions from continuum mechanics of isotropic materials can be applied directly to homogeneous amorphous solids, as they are theoretically isotropic. The chapter presents these solutions in the light of mechanical behaviour of polycrystalline solids.

A good book should contain all the information that the reader is looking for, or at least it should point accurately to other sources where the information can be found. I believe this book has a coherent structure that conveys an important message about the distinction between ideal amorphous solid, ideal crystalline solids and that of real amorphous materials with the inevitable characteristic defects and imperfections in their atomic arrangements.

Many of my colleagues and friends have influenced my decision to write this book. In the first place, I wish to thank Professors Qinghua Qin, Richard Welberry and Witold Brostow for their encouragement. I am grateful to Professors

Jun Shen and Gang Wang who introduced me to the field of glassy metals, and Professors Kevin Kendall and Christian Kloc for their constant support. I wish to extend special thanks to Dr. Xiao Hua Tan for comments on the manuscript.

September 2014 *Canberra*

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Spheres, Clusters and Packing of Spheres

1.1
Introduction

Imagine, Design, Create, Explore

Theory of amorphousness is a science about the structural arrangement of atoms in amorphous solids. It is part of Materials Science, which includes the closely related theory of crystallography. Whilst theory of crystallography is well established, theory of amorphousness is beginning to emerge as a body of science in its own right.

Arrangement of objects leads to creation of patterns. The invention of a repeating pattern as a thoughtful and creative process has ancient beginnings, at first in art as discovered by archaeology and evidenced in mosaics existing in ancient buildings, and later in science as known from old manuscripts; for example the five ideal Greek solids. There are three types of patterns that can fill in Euclidean space contiguously, and to infinity. These are:

- patterns with translational symmetry that possess an underlying lattice
- patterns with fivefold rotational symmetry but without translational symmetry
- random patterns with no lattice and no rotational symmetry.

Two-dimensional examples of such patterns are shown in Figure 1.1. All three are used as conceptual models for atomic arrangements in solids.

Crystalline solids have been known and appreciated since antiquity. In modern times the intrinsic elements of symmetry in single crystals of minerals were given attention in 1822 by R. J. Haüy (pronounced $\overline{a}$-wee, $\overline{a}$ as in 'aside') in 'Traité de Cristallographie'. Shortly after, the theoretical treatments of W. H. Miller in 1839 on *hkl* notation, A. Bravais in 1845 on 14 lattices, A. Schönflies in 1892 and W. Barlow in 1898 on 230 space groups (with many contributions from others) resulted in a complete theory of geometrical crystallography. Perfectly regular and ordered structures of infinite extent are described by geometrical crystallography as perfect (*ideal*) solids, with positions and arrangements of all atoms defined precisely along specific lattices. Theory of crystallography provides a datum from which the ideal atomic arrangements (and defects) in real materials can be determined. By comparison, no such universal laws or rules are well known for the atomic structure in amorphous solids.

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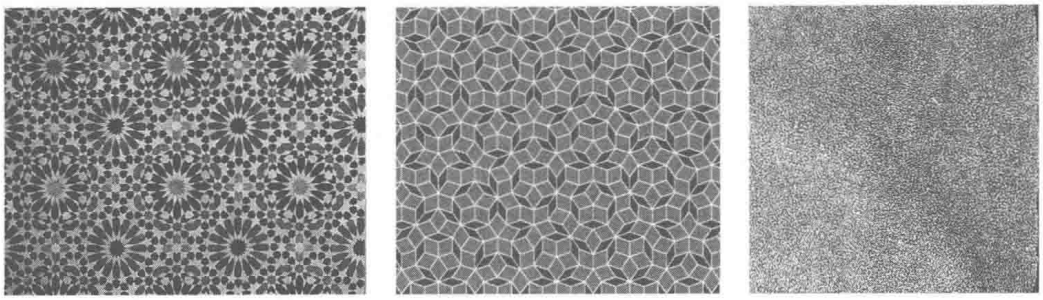

(a) (b) (c)

Figure 1.1 (a-c) Fragments of two-dimensional patterns representing the three formats of atomic arrangement in solids: crystalline (tiles from Morocco), quasi-crystalline (computer pattern generated by T.R. Welberry of ANU) and amorphous (Aboriginal painting by Ada Ross, Australia). (color plot at the end of the book)

In a historical perspective, it would be interesting to contemplate the following question: if Pythagoras were a statistician rather than deducing perfect harmony from ratios of pure numbers on strings, would we have had a theory of amorphousness in solid- state developed ages ago? Looking back in time, one can draw a direct line from the modern theory of geometric crystallography to the philosophy of pure numbers and rational ratios of antiquity. The René-Just Haüy description of packing of elementary blocks to form a single crystal with a simple relationship between its crystal faces and packing arrangement derives directly from the deductive Pythagorean notion of perfect harmony based on the relationship between the length of the string and perfect harmonic notes as 1 : 2, 2 : 3, 3 : 4, and son on. The relationship between atomic planes and crystal lattice is also expressed by simple ratios of whole numbers, the reciprocals of which are known as *Miller indices*. By comparison, relatively little is known about the structure of amorphous solids. Our knowledge of amorphous structures seems incomplete when compared with that of crystalline solids. In particular, the concept of an ideal amorphous solid as a datum and the corresponding theory have been lacking hitherto.

Until quite recently, amorphous solids were described as disordered crystalline solids, with some degree of order intermediate between a liquid and a solid. This was based on the understanding that glasses are free from the constraints that govern the arrangements of atomic clusters in crystalline materials, so there is a degree of ambiguity in the way that neighbouring clusters can be positioned and oriented.

A possible implication deriving from this view is that amorphous solids originate from the corresponding ordered crystalline state. In the field of geometric crystallography, a disordered crystalline structure implies the presence of defects which are defined relative to the perfectly ordered structure. Therefore, disordered materials are crystalline materials that, in principle, can be restored to the perfect crystalline state by the reversal of defects. It is conjectured that this cannot be done in amorphous materials and that a different approach and terminology

Figure 1.2 A view of the structure of solids along an undefined, somewhat arbitrary variable. The circles indicate the positions of the ideal (perfect) structures; the lines indicate the spectrum of structures in real solids. (color plot at the end of the book)

should be used to describe their structure, namely, *random* atomic arrangement. To emphasize this point, we note that in the field of statistics, when describing a set of *random* data, it would be unfitting to refer to that set as *disordered* data. Hence, it is proposed that amorphous structures, based on irregular packing of spheres, should be referred to as having a random arrangement of atoms rather than a disordered atomic arrangement. To promote this view, a drawing is shown in Figure 1.2 with the contemplated relative positions of the two types of solids and the envisaged discontinuity between the random and ordered types of atomic arrangements that must exist. The very small gap between the circle and the line on the crystalline side indicates that almost perfect single crystals can be grown. The larger gap on the amorphous side indicates that the structure of glasses may not be as close to the ideal amorphous solid as described later in this book. A discontinuity in the line near the middle is meant to indicate that even highly disordered crystalline solids are not the same as highly flawed amorphous glasses, and vice versa. This view is very close to that expressed by Kazunobu Tanaka *et al.* in the introduction to their book on 'Amorphous Silicon'.

A scientifically satisfactory explanation of the amorphous state continues to be a challenge, and for this reason, we advance and promote the theoretical concept of an *ideal amorphous solid* as a partial solution to this enigma. The right approach to a definition of amorphousness is through an appropriate geometric and topological model of the ideal amorphous solid, as described in this chapter.

However, the usage of the word 'disordered' appears in dictionaries to mean unpredictable, opposite to law and order. So, this seems to be also a matter of habit and semantics, rather than a question of pure logic. Nevertheless, an appropriate and consistent vocabulary conjures up a clear vision of the atomic arrangements and helps to define the field of science of amorphous solids, separate and distinct from the field of crystallography.

The study of atomic arrangements in amorphous solids was stimulated in the 1960s by theoretical work of J. D. Bernall on the structure of liquids, concurrent with experimental random packing of spheres by G. D. Scott. In the last few decades, research into atomic arrangements in amorphous solids has separated into two main streams: (i) more refined and detailed studies of packing of spheres and molecules and (ii) atomistic simulations by molecular dynamics (MD), including *ab-initio* methods. The understandings we gain from the two approaches are of different nature. In the latter approach, a unique definition of an amorphous

atomic structure cannot be achieved because in a simulated thermodynamic system with suppressed self-assembly tendencies every simulation, even repeated on the same system, must result in a different atomic arrangement. Modelling amorphous materials by these methods is equivalent to random packing with extreme cooling rates of the order of 10^{15} K s^{-1}. Nevertheless, these methods are successful and appropriate to simulate the structure of real amorphous solids with atomic arrangements containing imperfections. In the former case, simulations and geometrical modelling follow the methodology of representing atoms by hard spheres and creating representations of random atomic arrangement, naturally quite different from crystalline structures.

The earliest concept of atoms appears in a written record from Leucippus of Miletus (once an ancient Greek city on the western coast of Anatolia) and Democritus of Abdera (city–state on the coast of Thrace, its foundation attributed to Heracles), Greek philosophers of 5-4th century BC (Taylor, 1999). They conjectured that as matter is divided into smaller and smaller parts, there must be a limit to this division; namely atoms, the smallest indivisible objects. Otherwise, if there were no limit to the division, then the parts could be divided into "nothingness", and therefore, matter would not exist (*reductio ad absurdum* method of logic). Their theory envisaged atoms as invisible and indivisible particles, not as perfectly shaped as spheres but in the form of odd shapes with hooks and protrusions to render various properties of matter, such as taste, colour, fluidity and friction, as described by the Roman poet, Lucretius, in his *De Rerum Natura* (first century BC didactic poem on Epicurean philosophy). Coincidentally, modern view of atoms also shows electronic orbitals as having various shapes and protrusions, although the complete atom, encompassing all the orbitals, is imagined as having a spherical shape (Figure 1.3).

The concept of representing atoms by spheres has evolved gradually and over a long period of time. In 1611, Joannis Kepler drew hexagonal close packing of spheres to illustrate a compact solid (Kepler, 1611) and suggested that the hexagonal symmetry of snowflakes is due to the regular packing of the constituent particles. Some 50 years later, Robert Hooke wrote that crystals are composed of close packed 'spheroids'. At that time it was thought that spherical atomic particles must be close packed to form a rigid solid. Layers of round spherical objects,

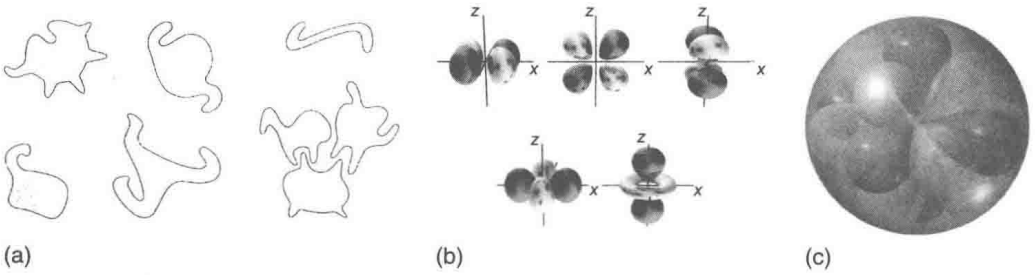

Figure 1.3 (a) Atoms of Leccipus and Democritus as depicted by Lucretius (Adapted from *Scientific American*). (b) Quantum mechanics view of electron clouds around atoms. (c) View of an atom as a sphere encompassing all electronic orbitals.