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# Crystal Engineering

How molecules build solids



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How molecules build solids

**Jeffrey H Williams**

Morgan & Claypool Publishers

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*As always, for Bruce Taylor Currie*



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# Preface

There are more than 20 million chemicals in the literature, with new materials being synthesized each week. Most of these molecules are stable, and the 3-dimensional arrangement of the atoms in the molecules, in the various solids may be determined by routine x-ray crystallography. When this is done, it is found that this vast range of molecules, with varying sizes and shapes can be accommodated by only a handful of solid structures.

This limited number of architectures for the packing of molecules of all shapes and sizes, to maximize attractive intermolecular forces and minimize repulsive intermolecular forces, allows us to develop simple models of what holds the molecules together in the solid. In this volume we look at the origin of the molecular architecture of crystals; a topic that is becoming increasingly important and is often termed, crystal engineering. Such studies are a means of predicting crystal structures, and of designing crystals with particular properties by manipulating the structure and interaction of large molecules. That is, creating new crystal architectures with desired physical characteristics in which the molecules pack together in particular architectures; a subject of particular interest to the pharmaceutical industry.

# Introduction: Crystal engineering

Chemists are busy people; there are over 20 million chemicals known in the literature, with many new molecules being synthesized each and every week. Most of these molecules are stable enough to be studied as they change state from solid to liquid, or solid to gas as the temperature is varied. And this huge number of molecules come in an appropriately wide variety of shapes and sizes. However, when it comes to how this huge diversity of molecules are packed together in solids, under the influence of the attractive electromagnetic forces that exist between all molecules, it is found that there are only a limited number of ways of ordering the stable packing of these variously sized and shaped molecules. This limited number of architectures for the packing of molecules to maximize attractive intermolecular forces and, consequently, minimize repulsive intermolecular forces, is the subject of this volume. We will look at the molecular architecture of crystals.

Looking at intermolecular interactions via a consideration of the detailed 3-dimensional arrangements of the molecules that constitute the solid, is not the usual route for studying intermolecular forces. However, the stable structure of a solid is the result of all possible interactions between the molecules that constitute that solid; that is, binary-interactions plus tertiary-interactions plus... N-body interactions, and I hope that my choice of the molecules reveals something of the contribution of these various terms that make up the intermolecular potential to the observed solid structure.

As the Nobel laureate Francis Crick said, ‘If you want to understand function, study structure’, and we will therefore consider the structure or internal architecture of a number of materials as determined by x-ray and neutron crystallography. Some of the 27 materials that I discuss in this volume have interesting and unusual bulk properties; for example, high-temperature superconductivity, birefringence, or laser activity. The data required to construct these 3-dimensional structures is stored in databases such as the Cambridge Structural Database ([www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)), which presently contains the structure of over 875 000 covalently-bonded crystals; with new structures being added continually. These structures represent data accumulated by studies on single-crystals and on powders over the period 1914 (when the first crystal structure was published) to the present day.

In our study, we will concentrate on the weak, non-bonding intermolecular forces that lead gases to condense into liquids, and liquids to transform into ordered solids as the temperature is lowered, or the pressure increased. It is these weak forces that cause covalently bonded organic compounds to crystallize in the manner they do, and it is the study and comparison of these crystal structures that allow us to comprehend the nature of the underlying intermolecular forces.

In one of the earliest conjectures about the architecture of solids; the Roman poet and philosopher Titus Lucretius Carus (c 99–c 55 BCE) said in his *De Rerum Natura*, ‘Those things, whose textures fall so aptly contrary to one another that hollows fit solids, each in the one and the other, make the best joining’. This qualitative observation of how macroscopic objects, or jigsaw puzzles fit together

has its modern counterpart in the observations of the Russian physicist Alexander I Kitaigorodsky who wrote, ‘The projections of one molecule get into the “hollows” of adjacent molecules, so that the molecules are closely packed with the minimum [number of] voids between them’; that is, as the crystallographer Jack Dunitz has said, ‘As far as the packing energy is concerned, empty space is wasted space’. Thus, we observe that molecules pack so as to avoid empty space; but why? What forces the molecules together to minimize intervening vacuum? This is what we will explore in this volume.

At the beginning of the last century, hardly anything was known about the arrangement of molecules in crystals. Indeed, the external point group symmetries of crystals had been determined from the examination of the symmetry of their external faces. As far as the internal structure of the crystals was concerned, the concept of space lattices had been introduced in the 18th century to explain the constancy of interfacial angles in differently shaped crystals of the same compound. The geometric theory of space lattices was complete by the end of the 19th century, culminating in the almost simultaneous recognition that there are only a finite number (230) of ways of combining elements of point symmetry with translational symmetry to form space groups. The mathematical theory of crystals may have been complete, but nothing was known about the underlying structure of the repeating units within those complex shapes.

This all changed with the discovery of x-ray diffraction by crystals. The first x-ray studies were of simple ionic crystals of high symmetry, such as the alkali halides (cubic), but it was not long before complex minerals, such as mica,  $\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$  (monoclinic) were being studied. With metals, the x-ray diffraction studies of the American physicist Albert Hull showed that the arrangement of atomic nuclei in many metallic crystals corresponds to the close-packed structures of spheres.

But for all the technical advances, questions about how organic molecules attracted or repelled one another took longer to be asked, and still longer to be answered. Such quantitative relationships as we have to explain the condensed phases came from experimental observations and ideas about the shape and size of molecules, although the nature of the molecular entities and of the forces acting among them were only approximately known. Today we still talk about van der Waals molecular volumes and van der Waals radii, and also about van der Waals forces without defining too closely what they mean.

In contrast to inorganic compounds, even simple organic compounds typically form crystals of low symmetry. Thus, crystals of anthracene examined by x-ray diffraction in 1920, were found to be monoclinic and thus intractable by the methods then in use. According to folklore, the idea for the ring structure of benzene came to German chemist Friedrich August Kekulé (1829–1896) in a daydream of 1865, in which he envisioned a snake eating its own tail. Kekulé’s daydream led him to propose that the structure contained a six-membered ring of carbon atoms with alternating single and double bonds. But questions still remained; for example, in what configuration was this ring? Was it puckered, bowed, or flat? Did the molecule have three distinct double bonds? Most chemists subscribed to the theory that benzene was flat, but it was not until British crystallographer Kathleen Lonsdale

(1903–1971) began her research in 1929 that the mystery was finally solved. Unlike benzene, hexamethylbenzene has just one molecule per unit cell, making it easier to distinguish the orientation of the molecule's central benzene ring. Lonsdale's x-ray crystallography experiments unequivocally demonstrated that the benzene ring was not only flat, but also had an evenly distributed cloud of electrons; there were no single or double carbon–carbon bonds. Because the benzene ring is the foundation of aromatic compounds, Lonsdale's discovery made it possible to advance the chemistry of aromatic molecules, and laid the basis for the modern form of organic chemistry, and for molecule and crystal design. As Lonsdale's head of department, Christopher K Ingold commented on her discovery, 'The calculations must have been dreadful... but one structure like this brings more certainty into organic chemistry than generations of activity by us [physicist] professionals'.

In quantum mechanics, there is no such thing as empty space. As far as the physics of intermolecular interactions is concerned, what matters is the nature and strength of the fields of force generated by the electrons and nuclei. In inorganic structures, the strong Coulombic fields exerted by the cations and anions were comparatively easy to understand, and atomic cohesion in such crystals seemed to present no fundamental problems. Similarly, as an obvious extension, it was soon realized that the interaction between molecules with permanent dipole moments, such as water, is subject to analogous Coulombic fields and may be attractive or repulsive, depending on the mutual orientation of the molecules. The nature of the cohesive forces among neutral non-polar molecules remained elusive for a longer time. For example, no theory based on classical mechanics and electrostatics could possibly reproduce the lattice energy of methane or the inert gases. This may be a small effect, but it is undoubtedly present, as witnessed by the condensation of these gases and the solidification of the liquid at sufficiently low temperature. The mysterious missing term, the dispersion energy, had to await the advent of quantum mechanics and Fritz London who first described dispersion interactions. Thus, explaining weak intermolecular interactions and pointing out that for these short-range forces to be effective, molecules must be in close contact; bumps into hollows, with as little empty space as possible. It was Kitaigorodsky's achievement, in the early-1960s, to put these concepts on a systematic footing beginning with a critical survey of organic crystal structures.

X-ray crystallography is not a difficult or obscure branch of science; on the contrary it is now a routine procedure, and measurements are today automated and the data analysis has become a *black-box* technology. This volume seeks to show that the beautiful and fascinating, detailed 3-dimensional pictures of closely-packed molecules tells us a great deal about molecular interactions, and the bulk behavior of solids. However, before we start exploring crystal architecture we will consider some of the basics of chemical structure, bonding and the nature of intermolecular forces. First, we will look at how atoms bond to form molecules and how electrons are distributed in those molecules. The reader will then discover that considerations of symmetry play a central role in classifying the structure of solids as well as in rationalizing the properties of crystalline materials.

Attentive readers will have noticed that it is barely a century since the very first crystal structure determination using x-ray diffraction, 1914. Not surprisingly, this anniversary generated a number of review articles. One of the most interesting is to be found at <http://cen.xraycrystals.org/introduction.html>, and comprises a set of highlights of crystallography over the last century as chosen by *Chemical&Engineering News*, the news magazine of the American Chemical Society.

# Acknowledgement

With this volume, *Crystal Engineering: How molecules build solids*, I should like to thank Dr Jeremy Karl Cockcroft, Chemistry Department, University College London, for all his help. I have known Jeremy Cockcroft since we both worked as experimental scientists at the Institute Laue-Langevin, Grenoble; where I was a solid and liquid-state physicist and Jeremy was a neutron crystallographer. Over the years, Jeremy has taught me a great deal about crystallography and about how a crystallographer looks at molecular interactions; and his help has been central in writing this volume. In addition, he has also got me back in the laboratory doing research. Earlier this year, I published my first technical paper in the peer-reviewed literature since 1993... back to the future.



# Author biography

## Jeffrey Huw Williams

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Jeffrey Huw Williams was born in Swansea, Wales, on 13 April 1956, and gained a PhD in chemical physics from Cambridge University in 1981.

Subsequently, his career as a research scientist was in the physical sciences. First, as a research scientist in the universities of Cambridge, Oxford, Harvard and Illinois, and subsequently as an experimental physicist at the Institute Laue-Langevin, Grenoble, which still remains one of the world's leading centres for research involving neutrons; particularly, neutron scattering. During this research career, he published more than sixty technical papers and invited review articles in the peer-reviewed literature. However, after much thought he left research in 1992 and moved to the world of science publishing and the communication of science by becoming the European editor for the physical sciences for the AAAS's *Science*.

Subsequently, he was Assistant Executive Secretary of the International Union of Pure and Applied Chemistry; the agency responsible for the world-wide advancement of chemistry through international collaboration. Most recently, 2003–2008, he was the head of publications at the *Bureau international des poids et mesures* (BIPM), Sèvres. The BIPM is charged by the Metre Convention of 1875 with ensuring world-wide uniformity of measurements, and their traceability to the International System of Units (SI). It was during these years at the BIPM that he became interested in, and familiar with the origin of the Metric System, its subsequent evolution into the SI, and the coming transformation into the Quantum-SI.

Since retiring, he has devoted himself to writing; in 2014, he published *Defining and Measuring Nature: The make of all things* in the IOP Concise Physics series. This publication outlined the coming changes to the definitions of several of the base units of the SI, and the evolution of the SI into the Quantum-SI. In 2015, he published *Order from Force: A natural history of the vacuum* in the IOP Concise Physics series. This title looks at intermolecular forces, but also explores how ordered structures, whether they are galaxies or crystalline solids, arise via the application of a force. Then in 2016, he published *Quantifying Measurement: The tyranny of number*, again the IOP Concise Physics series. This title is intended to explain the concepts essential in an understanding of the origins of measurement uncertainty. No matter how well an experiment is done, there is always an uncertainty associated with the final result—something that is often forgotten.