

In search of clarity

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Concepts that are ancient and pervasive do not lend themselves easily to precise definition. A layperson might think of 'crystal' as referring to table glass of high quality. But to a scientist, 'crystal' denotes solid matter in a more or less ordered form, whereas glass is considerably less ordered than a truly crystalline substance. Yet the Spanish, for example, have only one word (*crystal*) for both 'glass' and 'crystal'.

The dictionary definition of crystal is clinical, referring to "forms assumed by substances with a definite internal structure and external shape of symmetrically arranged plane surfaces". But the idea that crystals are cold and static has persisted since the time of ancient Greece — the term *crystallos* ('ice' or 'quartz') evolved from *cryos* ('cold') and *halas* ('salt'). As recently as the mid-1900s, the Nobel prizewinner Leopold Ruzicka dismissed crystals as "chemical cemeteries". Crystals were dead and so no chemistry could take place within them.

Physicists have taken a phenomenological approach. According to the International Union of Crystallography, a crystal is any solid that gives a discrete X-ray diffraction diagram. A crystal is thus defined not by what it is but by how it appears. But when an entity is defined by an observed property, its very existence depends on the method of observation. Crystals were first observed by eye, then by microscope, then by X-rays. What will be next?

The result of an X-ray structure analysis is a crystallographic unit cell and its constituent atoms. These supposedly identical building blocks are repeated along three principal axes (an arrangement known as periodicity) and crystallographers speak of

crystals as entities with long-range order. But this unit cell is an averaged measurement. No two unit cells are exactly the same and no unit cell looks exactly as it did a moment ago. If we are able to examine the contents of a single unit cell at a fixed point in time, will we change our definition of a crystal? The present definition was prompted by the discovery of quasicrystals. These have long-range order but lack the structural periodicity of classical crystals. Will there be other new forms of long-range order? Do sharp spots and a discrete diffraction pattern imply order? Already we know of giant biological crystals, such as ribosomes, that produce typical diffraction patterns despite their lack of strict periodicity. There is also evidence that if very intense X-rays are used, diffraction could be observed for non-crystalline materials. Indeed, crystallography today looks through a small window at what is potentially an expansive landscape.

Chemistry provides a more pragmatic definition of a crystal — bridging the divide between the austerity and accuracy of physics and the exuberance and excitement of biology. To a chemist, crystallization brings atoms, ions or molecules together to form a condensed phase that is characterized by some degree of order. A crystal is a manifestation of mutual recognition, a storage device for structural information and a victory of enthalpy over entropy. From the fluid state, in which molecules move randomly and ceaselessly, to the ordered cloister that is the crystal is a long journey, and one of the most remarkable reactions in all of chemistry. In this supramolecular reaction, it is weak intermolecular interactions, rather than strong covalent bonds, that are made and broken.

The emergence of a crystal from a fluid may seem magical, but closer inspection brings us nearer to discovering the energetic secrets of the process. There could be a gradual withdrawal of entropy and an ascendancy of enthalpy — a shift in the 'enthalpy-entropy balance' — just before the formation of the crystal nucleus, the free-energy maximum between the fluid and the crystal. Even as molecules begin to assemble through the mediation of weak intermolecular forces, giving rise to hydrogen bonds, electrostatic and van der Waals interactions, it is possible that the solute-solvent assemblage retains some 'wobble', so that the free energy of nucleation is reduced both by a favourable enthalpy of nucleation (formation of intermolecular bonds) and a less unfavourable entropy of nucleation (mobility of the solute-solvent cluster). In this way, order enters the putative crystal.

Crystal

Scientists differ from the public, and even among themselves, in their ideas of what constitutes a crystal. As these varying approaches testify, the definition of this form of matter is not as clear as its name suggests.

As in other chemical reactions, the products of the crystallization reaction are messy. So, rather than producing geometrically perfect constructs, the process yields crystals with defects, dislocations and incommensurate subdomains. Biological crystals contain so much water that different portions can have different flexibilities and mobilities. Metastable crystals and nanocrystals are kinetically trapped, whereas polymorphic crystals can be elusive. Even three-dimensional order is unnecessary — membrane protein arrays, for example, are ordered in only two dimensions, and fibres in only one.

But what of order, which seems to be a characteristic of all crystals? For most crystallographers it is long-range order that sets crystals apart from glasses and amorphous solids. But condensed-matter physicists have recognized that there is a structural continuum between ideal crystals and amorphous solids, and have quantified this concept with the order parameter. A variety of ordering can, in principle, be sampled as one moves along the reaction coordinate of crystallization. There is evidence that an amorphous phase might well be an intermediate stage en route to the formation of a more perfectly ordered crystal. Perhaps the Spaniards were right all along.

It seems that the issue is not how one defines crystal but how one should define order. Terms such as 'crystalline', 'amorphous', 'periodic', 'quasiperiodic' and 'aperiodic' only reveal our helplessness as we stumble around in small regions of a vast structural panorama. Scientists have long assumed that long-range order in a periodic crystal represents the lowest possible free energy for condensed phases, but no one has actually proved this. As chemistry moves towards systems of greater complexity and diversity, the meaning and scope of the term 'crystal' can only evolve and expand. ■

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FURTHER READING

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Beautiful demonstration: but not all crystals are as highly ordered as the Koh-i-Noor diamond.