

## An Unconventional View of the 'Closest Sphere Packings'

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If it is made a condition that the volume of the arrangement be finite, the close sphere packings may be regarded as arrangements of objects having the largest possible separations between neighbours. In this case the arrangement of the centres is considered, and the assumptions of a spherical shape and of mutual contact are not necessary. The motives for applying this viewpoint in crystal chemistry, and its fruitfulness, are discussed. The paper aims at a plausible understanding of crystal structures and their metrics.

### The three meanings of the 'close sphere packing' configuration

We consider a large number of any objects, randomly distributed within a large, fixed volume (e.g. rain drops, suddenly stopped and surrounded with walls). How are they to be arranged so that centres of neighbouring objects have largest possible separations? To solve the problem figuratively, we look for the shortest distance in the arrangement by imagining all centres of the objects to be blown up to like spheres, each object centre being coincident with a sphere centre. Upon expansion to a certain diameter, the spheres with the shortest separation will come into contact. By shifting them and possibly others we may break the contact. All spheres may then be blown up further until new contacts appear. The shift and blow-up procedure is then repeated. Apparently it has an end when we arrive at the most compact arrangement of the largest possible spheres in the given volume. The procedure shows that the problem of 'largest distances' is identical with the one of 'closest packing of spheres'. The closest sphere packing configuration (whatever this may look like) may thus appear for three different reasons:

(A) In our unconventional view, the configuration is determined by objects captured in a limited volume and tending to have largest separations between neighbours. The relative size, shape and eventual contact of the objects are unimportant, they may even be points. The space or volume belongs to all the objects and is not allocated to the individual particle.

(B) In the conventional view, the configuration is determined by the centres of attracting rigid spheres having a fixed diameter and tending to fit together as tightly as possible or to fill space as compactly as possible.

(C) In another conventional view, the configuration is determined by objects tending to have the highest possible coordination number (CN). The CN12 of the closest packings is the highest among points having all the same CN.

### The motives for applying the unconventional view in crystal chemistry

#### Formal motivation

Which one of the three views mentioned before is responsible for the realization of closest sphere packing positions in crystals? The views (B) and (C) imply direct postulates on the behaviour of atoms. View (A) can be suggested on the basis of the following four almost trivial statements (which also offer a basis for criticism)

- (1) atoms of different type attract each other,
- (2) atoms of the same type repel each other,
- (3) the forces act similarly in all directions and decrease rapidly with increasing distance,
- (4) atoms of the same type tend to be in equivalent positions.

From these statements, we draw the following conclusions. From (1) and (2) it follows that: (a) in crystals, the atoms remain in equilibrium positions, where attracting and repulsing forces equal each other. The volume of the configuration is thus limited and fixed and this is indeed one of the essential phenomenological properties of crystals (gases tend to expand to infinity). From (2) and (3) it follows that: (b) nearest neighbours of atoms of the same type should have largest possible separations. The conclusions (a) and (b) are identical with the conditions from which view (A) has been derived. With statement (4) in addition, of all close packings only the hexagonal two-layer and the cubic three-layer structure are to be considered, as these are the only packings with equivalent sites. A final conclusion may be stated: there should be a species of crystal in which the point configuration of atoms of one type is identical with the arrangement of sphere centres in the hexagonal two-layer or the cubic three-layer closest packing. Atomic separations may thereby be large compared with the atomic radius. Atoms of another type may be placed between atoms

of a cp set (*i.e.* a set of atoms of the same type in a closest sphere packing arrangement); thus view (*A*) may deal with 'long distances', whereas view (*B*) deals with 'contacting neighbours' only.

#### *Justification of the statements*

Many physical and crystal-chemical principles in the literature have bearings upon our statements. The statements 1, 2 and 3 qualitatively reflect Coulomb's law (attraction between charges of different, and repulsion between charges of the same sign). That atoms may be regarded as charged point masses and that Coulomb's law is a useful guide, is supported by infrared emission and absorption spectroscopy, which reveal dipole moments in practically all materials. Directed chemical forces and perhaps others may also occur. Directed forces, however, do not explain crystals, since in quartz glass and quartz crystal, for example, the coordination polyhedra due to them are believed to be essentially the same. Even if statements 1 to 3 consider only part of the whole play of forces, it is this part which suggests crystalline configurations [according to view (*A*)]. As a statement (5), we might say that directed chemical forces cause distortions in configurations satisfying statements (1) to (4). Statement (1) is related to Pauling's (1929) first rule (cation-anion attraction makes them nearest neighbours in polyhedra). Statement (2) and conclusion (*b*) are related to Pauling's third and fourth rule (cation-cation repulsion acts against sharing of elements between polyhedra). Statement (4) is related to Pauling's fifth rule (parsimony). Statement (4) is a simplified expression of the old Wiener-Sohncke principle [points are disposed around each point in the same way as around every other (Wiener, 1863; see Sohncke, 1879)]. The application of statement (4) produces arrangements of high symmetry; it is thus related to the 'philosophical doctrine' of Niggli (1926) and the perception of Fedorow (1904, 1920) (briefly: all crystals are either cubic or hexagonal, exactly or in a good approximation) and also to the 'symmetry principle' of Laves (1939, 1956, 1959, 1967). Statement 4 and its relatives and also the first part of statement 3 belong to a *simplex sigillum veri* reasoning, which is an evergreen in natural philosophy.

#### **Application to actual crystal structures**

Metals with closest packed structures are the standard example to demonstrate the atomic model of hard spheres having the packing tendency of view (*B*). To apply view (*A*), with reference to the electron-gas model, we say that the metal atoms split into cations and the electron gas. Repulsion among the cations forces them into a closest packed configuration, the electron gas acts as a 'glue' and keeps them together.

Repelling ions may also be kept together if two or more cp sets interpenetrate each other in such a manner that atoms of a different type become nearest neighbours. As these attract each other, an equilibrium with the

repelling forces may be set up. The structure of NaCl is a simple and unique example. There are two types of atoms and they appear in positions of cubic closest packings. Interpenetration with a shift of  $\frac{1}{2}$  in the cube diagonal results in a perfect coordination of every atom. In the alternative view (*B*) only the largest atoms build a cp set whereas the smaller atoms fill octahedral vacancies.

Another kind of interpenetration looks somewhat formal. We suppose that of two or more cp sets a certain fraction of points is coincident, and the charges there are summed up. The total charge requires atoms of another type in such positions; in the special case that equal positive and negative charges are coincident the position should be empty.

In the case of complex framework structures such as quartz and feldspar, a discussion of topology and cell metrics is possible with view (*A*) (Brunner, 1968), whereas the views (*B*) and (*C*) have no relation to such structures. As compared with the simple case of NaCl, the following generalizations are to be made: (*a*) atoms of the same chemical element of a compound may split into several interpenetrating cp sets (in the structure of an element, the atoms may split in two types,  $X^{\delta+}$  and  $X^{\delta-}$ ), (*b*) a cubic and a hexagonal cp set may interpenetrate each other (after a homogeneous deformation of both in order to obtain coincident lattice points; triclinic lattices may result as a best compromise), (*c*) locally some of the atoms may be displaced from their closest packed positions in order to arrive at a good coordination among chemically different nearest neighbours. Unfortunately, these generalizations may obscure the easy recognition of cp sets.

Other authors have already pointed out (but not explained) that closest packing positions may occur though the atoms do not touch. (Sasváry, 1958, 1960; Kleber, 1963; Patterson & Kasper, 1967; Ho & Douglas, 1968, 1969). It has been reported that triclinic cell parameters vary only within a restricted range (Brunner & Laves, 1967), and the work of Fedorow and of Niggli has been quoted before. Looking for an explanation of all these observations, it is very encouraging to believe in the physical reality of the ideas presented here.

#### **Remarks and historical details**

The concept 'space filling' inherent in the first of three principles of Laves (1939, 1956, 1959, 1967) is objectless for view (*A*). Nevertheless, it becomes adaptable if defined as an 'atomic concentration': the number of atoms contained in the volume of a sphere whose diameter is equal to the distance between neighbouring atoms. Identical numerical values are obtained, for structures of like spheres.

The literature on closest sphere packings can hardly be reviewed. For introductions see *e.g.* Wells (1962), Kleber (1963), Gehman (1963) [all for view (*B*) and Boerdijk (1952) [for view (*C*)]. Kepler (1611) and

Harriot\* are frequently referred to as the earliest references; the coordination number 12 of the closest packings, however, was already mentioned by Cardanus (1550). Though Barlow and Pope knew all three views of the sphere packings [Barlow (1884) for view (B), Barlow (1898) for (A) and (B); Barlow & Pope (1906) for (B) and (C)], all their structural suggestions were made with the emphasis on view (B). View (A) has never become popular in the crystallographic literature and seems forgotten today.

The controversy between views (A) and (B) is to some extent a controversy between two different atomic models. View (A) uses the model: 'atoms are centres of interaction whose diameters are negligible or of minor interest as compared to their separations'. This model originated in a theory by Boscovich (1758) and was widely accepted before the use of X-ray diffraction (see e.g. Beckenkamp, 1913). It is still alive in various modified forms: infrared spectroscopy for example deals with point masses interconnected by spring forces. View (B) is based on the model: 'atoms are material bodies which have a radius and can come into contact'. The change to this hard sphere model was initiated by the structural suggestions made by Barlow (1884, 1898) and Barlow & Pope (1906). It became sanctioned after the work of Bragg and Goldschmidt and is unavoidable in present crystallographic textbooks and introductions.

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\*T. Harriot, born 1560 and died 1621, quoted by Pauling (1962).