

Molecular Modeling of Four-Connected Zeolite Frameworks with Mathematical Beading

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Abstract

Mathematical beading is employed to build faithful and aesthetically pleasing physical models of 4-connected 3D nets such as diamond, silicates, zeolites, and hydrogen clathrates. In the cases of silicates and zeolites, the bead structures are the open packing models of hard spheres arranged according to their chemical topology. Spherical hard beads represent the oxygen anions while smaller positive cations hidden in the center of four large anions are ignored in the bead models.

In previous papers for the Bridges conferences, we demonstrated that mathematical beading can be used to build arbitrary fullerenes and topologically nontrivial graphitic structures. [1, 2] The essential feature underlying all these structures is that their chemical graphs are essentially 3-connected or trivalent—i.e., every vertex belongs to three edges. The bead model represents the chemical bond network of the corresponding molecule or structure. Another important feature of the bead models is that their three-dimensional shapes arise from a collection of open packed spherical beads held tightly together by a long fishing line. The simple fact that hard spheres occupy space mimics the important fact that the valence electron pairs surrounding each carbon core also occupy space and thus gives the local arrangement of chemical bonds approximately. [2]

One might ask whether the mathematical beading is useful for building physical models of more complicated structures with higher valencies or connectivities. The answer is positive. In the mathematical art exhibitions of two previous Bridges meetings held in Seoul and Baltimore, we presented several bead sculptures inspired by the inorganic structures with valencies up to twelve using the tubular beads. In this paper, we wish to show that mathematical beading can be systematically employed to build a rich family of inorganic materials called zeolites. Zeolites are porous aluminosilicates widely used in the chemical industry as ion exchangers, molecular sieves because the large pores and voids in the zeolite can trap small organic molecules and facilitate catalytic cracking or hydrocracking.

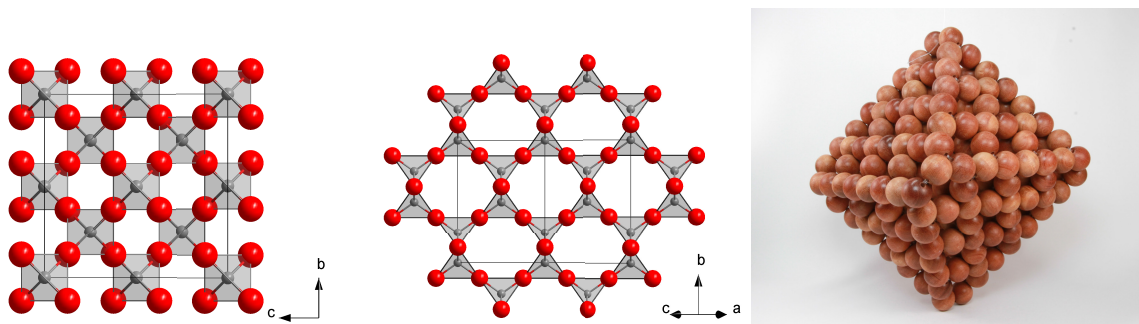


Figure 1: (a-b) Two different views of an idealized model of β -cristobalite, showing vertex-shared SiO_4 tetrahedra (Wikipedia), red spheres being oxygen atoms. (c) Bead model of β -cristobalite.

The basic structural unit for a zeolite framework or a silicate mineral is a tetrahedral TO_4 , with T is the cation located in the center of the tetrahedron (Si, Al, but also Ge, B, P, etc.) and four anions of oxygen are

located at vertices. Each tetrahedron can be connected to four other tetrahedra by sharing bivalent oxygen anions. Since the angle of T–O–T can vary widely, a very rich array of 3D structures comprising tetrahedral frameworks are possible. A simple example is the β -cristobalite, a high-temperature polymorph of silica (Fig. 1).

It is convenient to describe a zeolite framework topologically as a 4-connected net of tetrahedral cations and ignore shared oxygen anions as shown in Fig. 2. Many zeolite frameworks can be further viewed geometrically as close or open packings of secondary building units (SBUs) which are composed of suitable numbers of basic tetrahedral units. Examples of SBUs include cubes, prisms, truncated octahedron, dodecahedron, truncated cuboctahedron and so on. Four common zeolite frameworks containing the truncated octahedron or the sodalite cage, Sodalite (SOD), Linde Type A (LTA), Faujasite (FAU), hexagonal Faujasite (EMT), are shown in Fig. 2. [3]

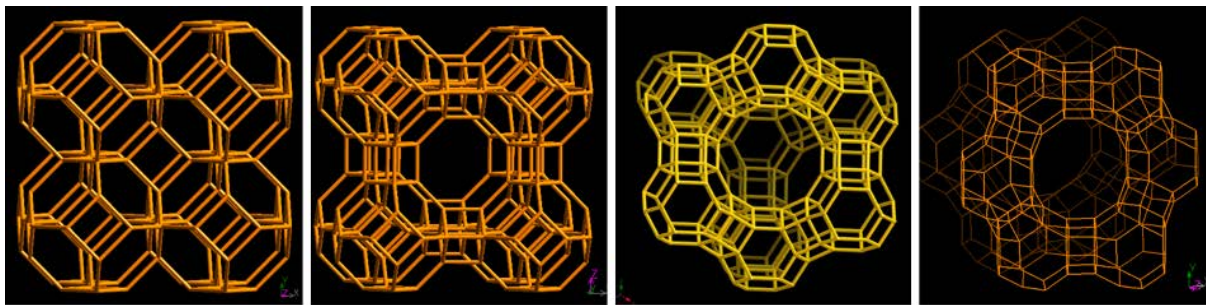


Figure 2 : Four Zeolite Framework Types: SOD (Sodalite), LTA (Linde-Type A), FAU (Faujasite), and EMT (Hexagonal faujasite). [3]

The sodalite structure is related to the uninodal 4-connected net formed by the uniform space-filling of truncated octahedra, with alternative names such as the bitruncated cubic honeycomb or Kelvin structure. The LTA structure is another zeolite based on sodalite cages, which can also be described as the cantellated cubic honeycomb formed by the space-filling of truncated octahedra, cubes, and truncated cuboctahedra in the ratio of 1:3:1. Alternatively, we can also view the sodalite cage as a supernode, which is connected to another supernode either through one of its square faces by a cube or through one of its hexagonal faces by a hexagonal prism. Cubes or hexagonal prisms here play the role of edges or links. Therefore, the LTA structure is simply a cubic lattice consisting of an open packing of sodalite cages by inserting a cube between two neighboring sodalite cages. On the other hand, the FAU structure corresponds to the open packing of sodalite cages through the hexagonal faces and thus creates a 4-connected diamond net of sodalite. It is also well known that there is an alternative arrangement of diamonds which has the ABAB... stacking and gives rise to the so-called 4-connected “lonsdaleite” net. [3] In the case of open packing of sodalite cages, this kind structure is called the hexagonal faujasites or EMT.

We describe a novel approach to make the three-dimensional physical models of zeolite frameworks with the figure-eight stitch technique of mathematical beading. [1] The same technique previously used to construct arbitrary fullerenes can be applied to model essentially any of the zeolite frameworks. However, it is important to understand that beads in the bead model of a zeolite structure represent oxygen anions or the edges of the corresponding zeolite 4-connected graphs, while the tetrahedral cations are not shown in the bead model, which is analogous to the interpretation of the bead models of fullerenes in which beads represent carbon-carbon bonds, instead of carbon atoms. In the case of trivalent graphitic structures, the microscopic repulsion among valence shell electron pairs are correctly described by the hard-sphere repulsion of spherical beads, and the attraction due to the tiny positive atomic cores is mimicked by the fishing line that tightly holds all beads together. Atomic cores are not shown in the bead model, though. A similar interpretation applies to the bead models of zeolite frameworks. The radius of oxygen anions with an approximate value of 1.40 Å is typically several times larger than that of cations (radius of Si^{4+} : 0.25 Å). It is a good approximation to

consider four oxygen anions located at vertices of a tetrahedron as large hard spheres in direct contact with each other, while the small cations hidden in the central tetrahedral holes are ignored and their role to hold oxygen anions together is mimicked by fishing lines. Thus, the three-dimensional structure of a bead model of a zeolite framework is essentially the hard-sphere open packing of oxygen anions which are arranged according to the topology given by the corresponding 4-connected graph. To demonstrate the picture fully, in Figure 3 we show bead models of four zeolite framework types that are based on truncated octahedra, Sodalite, Linde-A, faujasite, and EMT.

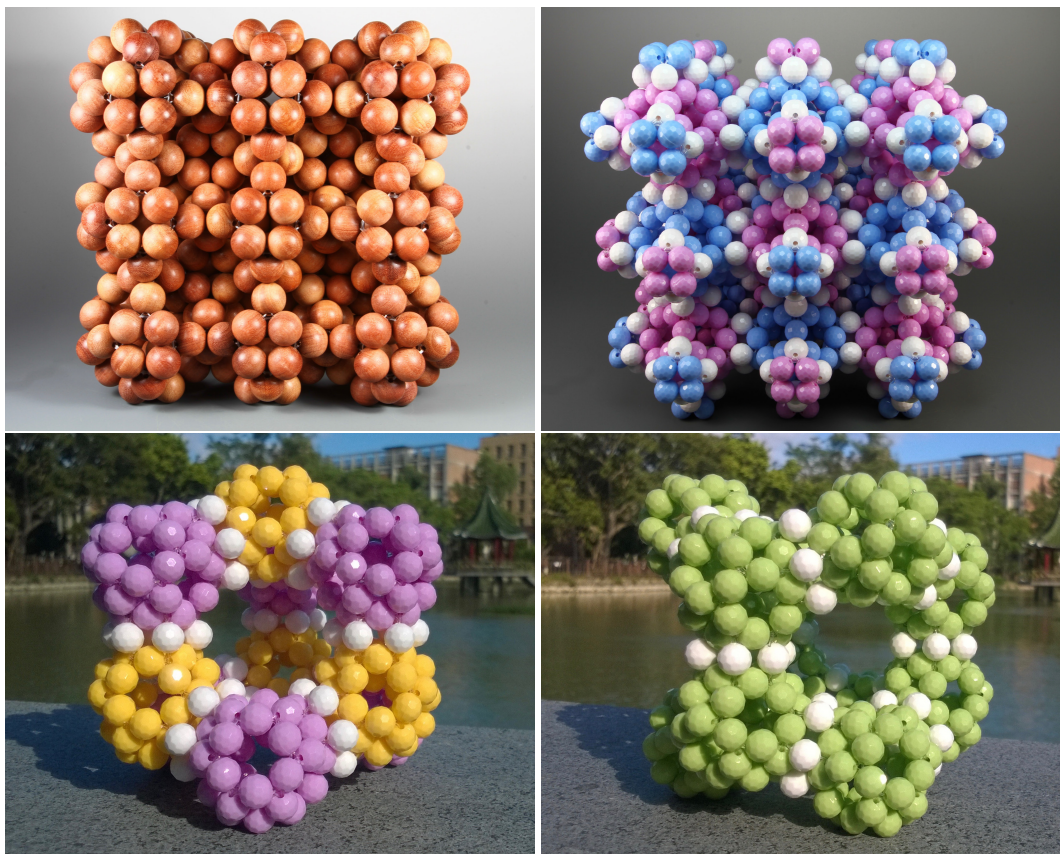


Figure 3 : Bead models of four zeolite framework types that contain sodalite cages. Top row: SOD (Sodalites) and LTA (Linde-type A structure); bottom row: FAU (Faujasite) and EMT (hexagonal faujasite) The colors in LTA and FAU are chosen so that no two adjacent sodalite cages have the same color.

At the time of this writing, the database of the International Zeolite Association [3] has listed 231 Zeolite Framework Types and their structural information. Each framework type is assigned a unique three-letter code such as SOD (Sodalite), MEP (Melanophlogite), and so on. The growth rate of newly discovered and synthesized zeolites is about seven new framework types per year. It is a challenging work to construct all these structures with beads since the beading is an inherently slow sequential process. Right now, we have succeeded in making bead models for more than thirty zeolite framework types. In Figure 4, we give some examples of these bead models based on SBUs other than sodalite cages. We believe that the mathematical beading is a general technique which can be used to build physical models for all other zeolite framework types listed in the zeolite database [3] or even prospective zeolite structures theoretically hypothesized. [4]

In conclusion, we show that the same beading technique, which was originally used for constructing the 3-connected 3D nets including arbitrary fullerenes and many 3D graphitic structures, can be extended to the construction of physical models of many 4-connected 3D nets such as zeolites and silicate minerals. The

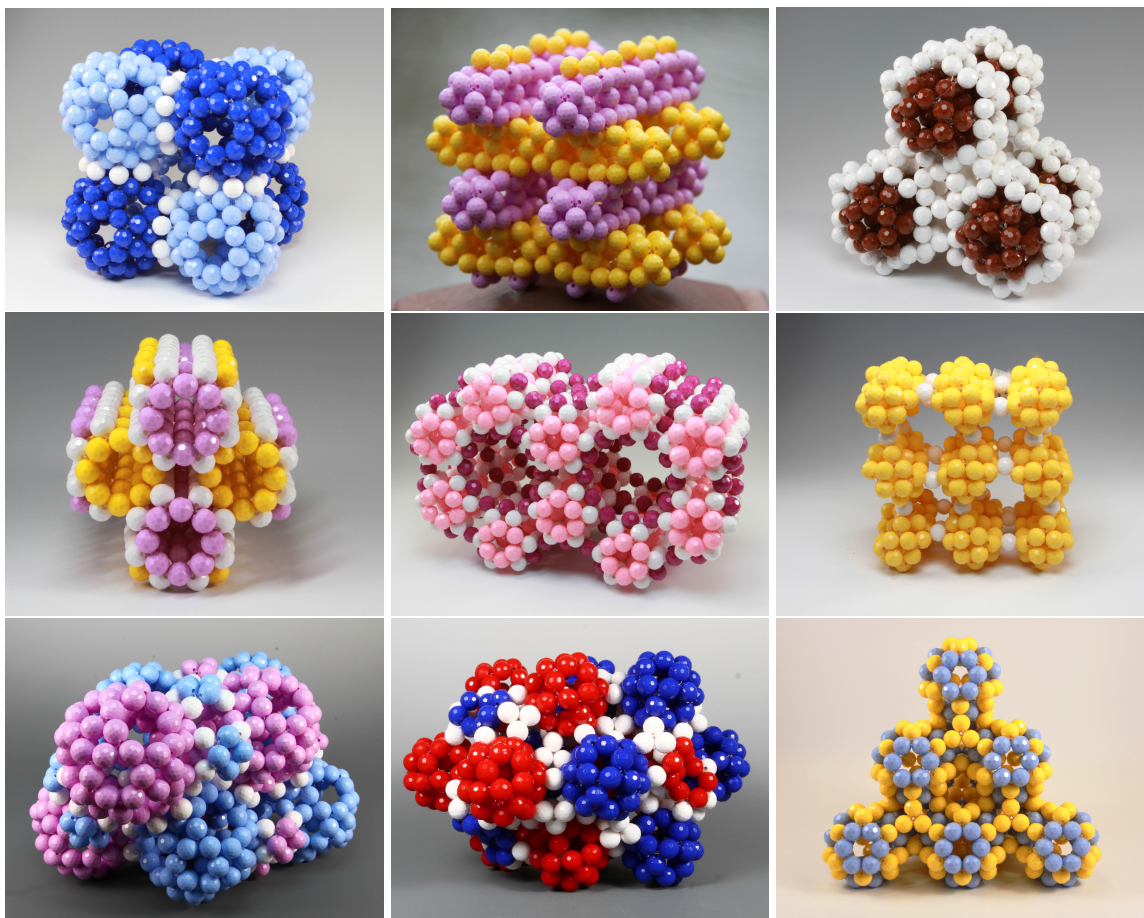


Figure 4: Assorted bead models of some zeolite frameworks: First row: RHO, BEC, SSF; Second row: ATN, LTL, SAS; Third row: KFI, MEP (Clathrate type I), MTN (Clathrate type II). The colors in the bead models are chosen so that their geometric features can be perceived more easily, even though all these beads represent oxygen anions.

bead models of these porous zeolite inorganic structures are structurally faithful because they correspond to the coarse graining in the form of hard spheres open packing of oxygen anions. More importantly, these bead structures are not only intellectually meaningful, but also aesthetically pleasing sculptures inspired by 4-connected zeolite materials.

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References

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