Designing Beaded Sculptures Inspired by Clathrate Hydrates

Yuan-Jia Fan[1], Bih-Yaw Jin[1], and Chia-Chin Tsoo[2]

[1]Department of Chemistry, National Taiwan University, Taipei, Taiwan; byjin@ntu.edu.tw
[2]National Center for High-Performance Computing, Hsinchu, Taiwan; c00cct00@narl.gov.tw

Abstract

Application of the mathematical beading to the construction of sculptures of several water cluster architectures based on clathrate hydrates and related Kelvin's and Weaire-Phelan's foam is presented. These nanostructures can be viewed as three-level hierarchical frameworks which are composed of primary tetrahedral hydrogen-bonded water pentamers, secondary cage-like units and final three-dimensional architectures. In this paper, we discuss the structure and general construction procedures for a few clathrate hydrates and also give some examples of bead models for structurally related Kelvin's and Weaire-Phelan's foams.

Introduction

In 1811 Humphry Davy discovered that what had been thought of as solid chlorine in fact contained a lot of water molecules. More than a decade later, his assistant Michael Faraday used analytical chemistry to confirm the chemical composition of this material as $Cl_2 \cdot 10\,H_2O$. More precise experiments later showed that the composition of this chlorine-containing hydrate was quite close to that of $Cl_2 \cdot 8\,H_2O$. Since then, hydrates containing a variety of different gaseous molecules, including inert gases and small hydrocarbons such as CH_4, have been reported. In the twentieth century, the structures of these gas hydrates were elucidated by using X-ray diffraction [2]. Typically, in all these materials, the water molecules are first connected by hydrogen bonds to form cage-like structures, which are then stacked into periodic tetrahedral frameworks. Small guest molecules are enclosed in cages and become clathrate hydrates.

In this paper, we show that the angle weave technique used in mathematical beading can be utilized for constructing faithful physical models corresponding to the hard-sphere loose packing models of this family of nano structures. Spherical beads in the resulting models stand for hydrogen bonds in clathrate hydrates, while the oxygen atoms that hold them together are mimicked by strings. Moreover, by using colored beads, we can create the same hydrate structure with its structural properties highlighted as well as adding to the aesthetic value of the work. The result is a colorful bead sculptures, which are inspired by the rich variety of tetrahedral calthrate hydrates found in the nanoworld.

Structures of Clathrate Hydrates

Structures of clathrate hydrates can be viewed as a three-level hierarchical framework. At the lowest level, every water molecule is tetrahedrally coordinated to four other water molecules to form a water pentamer through four hydrogen bonds which may be depicted as $O-H\cdots O$ as in Figure 1(a). Depending on the sizes and shapes of enclosed guest molecules, these primary structures are linked into various polyhedral cages such as dodecahedron, tetrakaidecahedron and so forth, with oxygen atoms at vertices and hydrogen atoms at edges. Finally, these cages are stacked into periodic space-filling frameworks which will be described later. In Figure 1(b) and (c), we give a list of five polyhedral cages designated by the nomenclature ($\prod_i {n_i}^{m_i}$), where n_i is the number of edges in face type i, and m_i is the number of faces with n_i edges. Notice also that, except for the cage $4^2 5^6 6^3$, which contains four-membered rings, the other four polyhedral cages have essentially the same structures as those of small fullerenes, C_{20}, C_{24}, C_{28}, and C_{36}, respectively. In Figure 1(b) and (c),

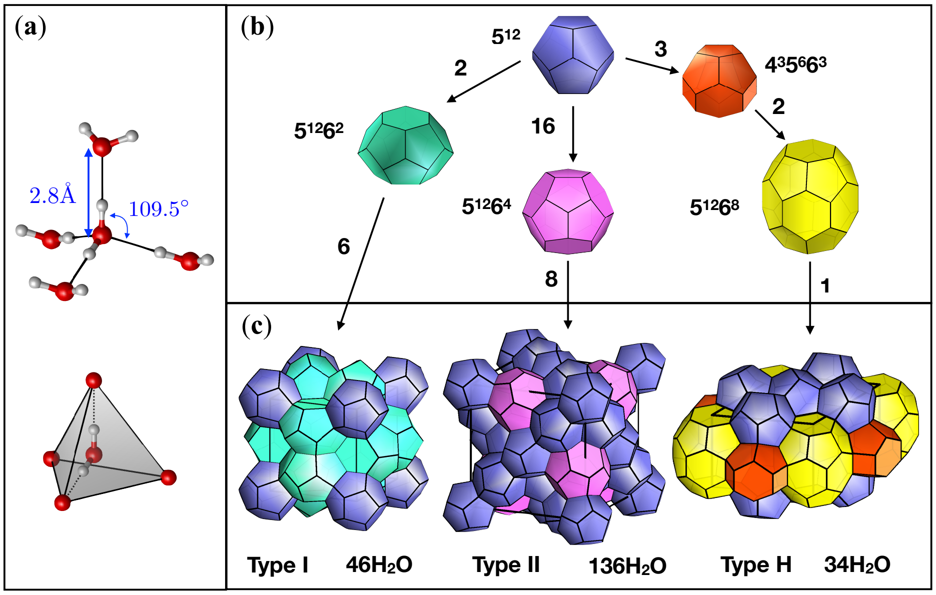


Figure 1: *Hierarchical organization of three different clathrate hydrates*

we give a brief hierarchical organization of the three most common clathrate hydrates: Type I, Type II, and Type H, respectively [2].

Type I clathrate hydrate consists of two different kinds of polyhedra: pentagonal dodecahedron (5^{12}) and tetrakaidecahedra ($5^{12}6^{2}$). These polyhedra are then stacked in a cubic arrangement according to the space group $Pm\overline{3}n$ with nine dodecahedra adopted the body-centered cubic structure and twelve tetrakaidecahedra lying on the six faces of a unit cell. Each dodecahedron is surrounded by twelve tetrakaidecahedra and shares a common pentagonal face with each of them. Tetrakaidecahedra can also be considered as forming three non-intersecting groups of infinitely long columns in parallel with the edges of the cubic unit cell. Along each column, two neighboring tetrakaidecahedra share a same hexagonal face. The three perpendicular two-fold rotation (C_2) axes of each dodecahedron are oriented in the direction of the edges of the cubic unit cell. The orientation of the dodecahedron at the center of a unit cell can be obtained by a rotation around one of C_2 axes by 90° relative to those on the corners of the unit cell as shown in Figure 2(a). It is worth noting that using the geometry of Type I hydrate as the starting structure, one can arrive at the Weaire-Phelan structure which gives a better solution for the “Kelvin problem”, i.e. the optimal partition of the space into cells of equal volume with the least area of surface between them, than the previous best-known solution based on the truncated octahedron proposed by Lord Kelvin himself.

Type II clathrate hydrate also contains two types of polyhedra: the 16-faced hexakaidecahedra ($5^{12}6^{4}$) together with smaller dodecahedra. The spatial arrangement is given by the cubic space group $Fd\overline{3}m$. The larger hexakaidecahedra share their hexagonal faces and form a diamond-like 3D network. Each of these hexakaidecahedra is surrounded by twelve dodecahedra. In this way, space filling of these two types of polyhedra is achieved. Each unit cell of Type II hydrate contains sixteen pentagonal dodecahedra and eight hexakaidecahedra. Type H clathrate hydrate has significantly larger cavities and can be formed in the presence of larger guest molecules. This type of clathrate hydrate has a hexagonal structure of space group $P6/mmm$. Each unit cell of Type H contains three types of cages, two small ones of different types (5^{12} and $4^{3}5^{6}6^{3}$), and one larger polyhedron ($5^{12}6^{8}$) as shown in Figure 1(c).

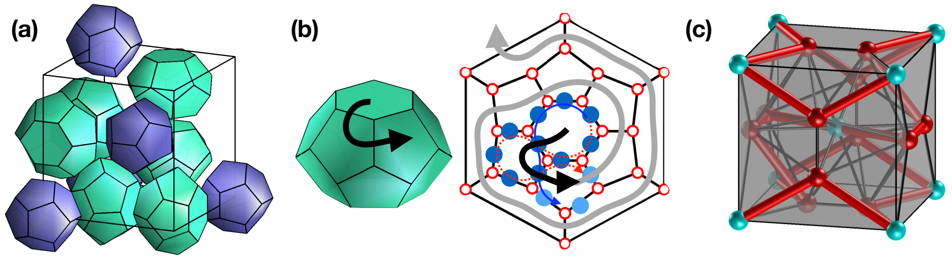


Figure 2: *(a) Structure of Type I hydrate with central dodecahedron revealed; (b) Angle weave that follows a spiral face-Hamiltonian path on the tetrakaidecahedron and its Schlegel diagram; (c) a Hamiltonian path (red) that traverses every polyhedral cage of a single unit cell.*

Bead Models of Clathrate Hydrates

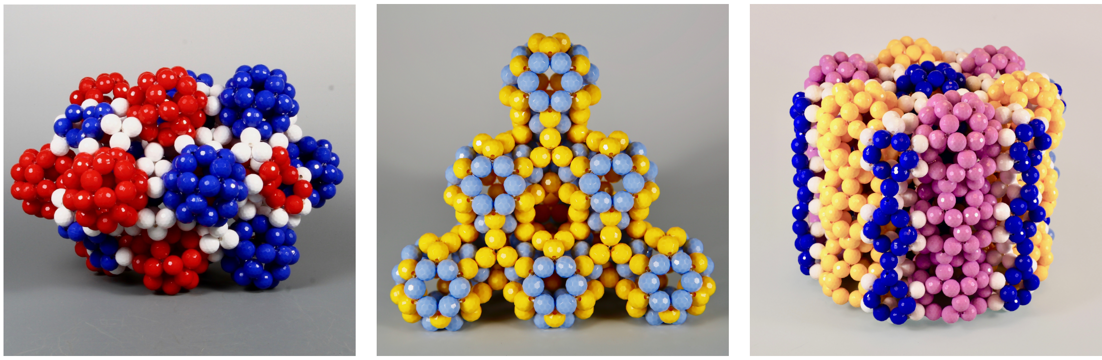
In this section, we apply the angle weave technique of mathematical beading, which is illustrated in Figure 2(b) in the case of the tetrakaidecahedron, to the construction of bead sculptures of a unit cell of Type I clathrate hydrate [1, 3]. The construction procedure of the beaded sculpture of a clathrate hydrate involves two different interweaved stages corresponding to the second and third levels in their structural hierarchy. At the lower level of the beading process, one needs to construct each individual polyhedral cage sequentially by using the angle weave technique, which involves the creation of an n-member ring that consists of n beads with two ends of the thread crossed at a particular bead, pointing to the adjacent ring (face) that will be made next. Figure 2(b) gives a particular face-Hamiltonian path, which is equivalent to a vertex-Hamiltonian path on its dual, starting from one hexagon and ending at the other hexagon for the tetrakaidecahedron. Moreover, it can be shown that the Hamiltonian path can start from and end at arbitrarily chosen faces for any of the five polyhedral cages as shown in Figure 1(b), which enable us to enter and leave a polyhedron in many ways.

At the next level of the hierarchy, one needs to bead polyhedral cages one after another sequentially until the whole intended sculpture corresponding to the clathrate hydrate is complete. When one starts to bead a new cage, which is usually connected to several existing cages, one usually needs to follow a different face-Hamiltonian path with different start and end faces in order to complete the remaining unfinished faces. Figure 2(c) shows a Hamiltonian path that visits all 21 polyhedra (nodes) of a single unit cell, with the central node connected to all twelve nodes on the faces but not to the eight nodes on the corners of the cube. The same technique can be easily applied to the construction of a unit cell of Type II and Type H clathrate hydrates. One might expect that there exists a face-Hamiltonian path which traverses all faces on a clathrate hydrate exactly once, however the proof is beyond the scope of the paper.

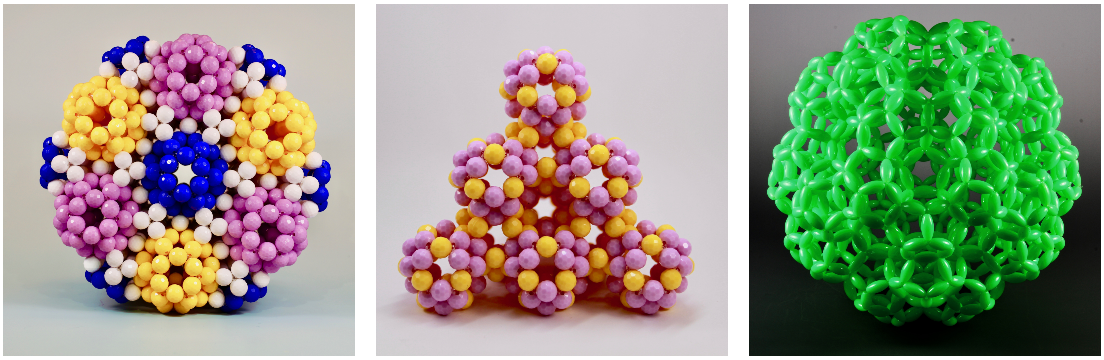
Figure 3 lists the bead models for Type I, II, and H clathrate hydrates together with two other bead models for the Type VII clathrate hydrate, which is topologically equivalent to Kelvin's foam, and the icosahedral water cluster (or simply the water buckyball), respectively. In constructing these beaded sculptures corresponding to different types of clathrate hydrates, we always try to choose finite portions of crystals with overall shapes and symmetries such that they are not only consistent with the underlying crystal structures, but also offer aesthetic pleasing appearances. For instance, the beaded sculpture of the Type I clathrate hydrate is represented by two interpenetrating colored cubes, each consisting of eight dodecahedra located at corners of a cube connected by twelve tetrakaidecahedra as shown in Figure 3(a).

Conclusions

In conclusion, we showed that the method of mathematical beading can be utilized systematically for constructing the sculptures inspired by clathrate hydrates, which are nanoscale crystalline water-based solids



(a) *Type I clathrate* **(b)** *Type II clathrate* **(c)** *Type H clathrate, side view*



(d) *Type H clathrate, top view* **(e)** *Type VII clathrate* **(f)** *Icosahedral water cluster*

Figure 3: *Bead models of several clathrate hydrates. (a) Also known as the Weaire-Phelan foam; (e) also known as the Kelvin's foam; (f) Hypothetical icosahedral clathrate structure consisting of* 60 *dodecahedra located at vertices of a truncated icosahedron.*

containing small gaseous molecules trapped inside their hydrogen-bonded cages. The bead models of these clathrate structures corresponds to the hard-sphere open packing of hydrogen bonds. Clathrate hydrates are structurally similar to tetrahedral zeolites, which we have discussed in a previous Bridges conference [3]. The main difference is that the role of tetrahedral SiO_4 is replaced by the tetrahedral hydrogen-bonded water pentamers $(H_2O)_5$. Also, the polyhedral cages that contain five-membered rings such as pentagonal dodecahedron occur much more frequently in many clathrate hydrates than in zeolites. These bead structures are not only intellectually meaningful physical models, but also aesthetically pleasing sculptures.

Acknowledgements

We acknowledge the financial support from the Ministry of Science and Technology, Taiwan, R.O.C.

References

[1] B.-Y. Jin, C. Chuang, C.-C. Tsoo. "Constructing Molecules with Beads: The Geometry of Topologically Nontrivial Fullerenes", *Bridges Conference Proceedings*, Pecs, Hungary, Jul. 24-28, 2010, pp. 391–394. http://archive.bridgesmathart.org/2010/bridges2010-391.html

[2] E. D. Sloan, C. A. Koh. *Clathrate Hydrates of Natural Gases*, 3rd ed. Marcel Dekker, 2008.

[3] C.-C. Tsoo, B.-Y. Jin. "Molecular Modeling of Four-Connected Zeolite Frameworks with Mathematical Beading", *Bridges Conference Proceedings*, Jyväskylä, Finland, Aug. 9-13, 2016, pp. 375–378. http://archive.bridgesmathart.org/2016/bridges2016-375.html