# Network Motif of Water

M. Matsumoto, A. Baba*, and I. Ohmine

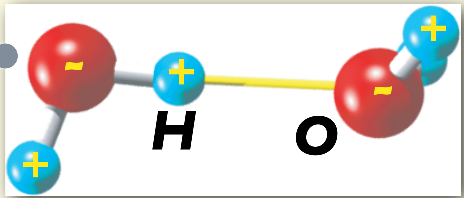
Department. of Chemistry, Faculty of Science, Nagoya University

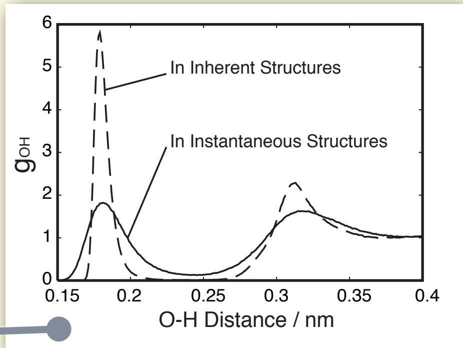
*Department of Earth and Planetary Sciences, Faculty of Science, Kobe University

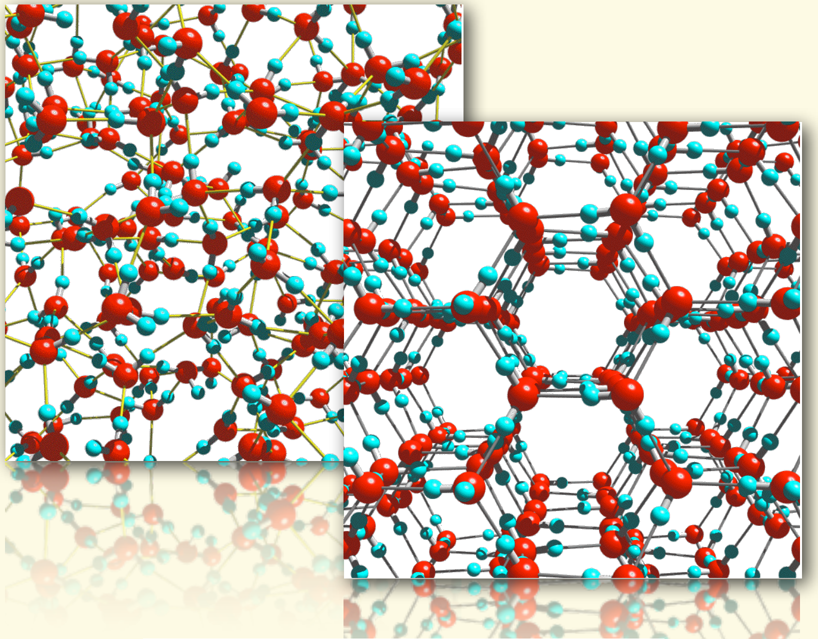
- **"The network is water."**
  - The network has effective control over the total properties of water.
  - Network is principal; collectivity in structure and dynamics involves the anomalies of water.
  - Anomalies of water become remarkable especially at subzero temperature.
  - There must be some kind of intermediate-range order in supercooled water.
- Network motif of water, "**vitrite**", is proposed.
  - Vitrites are the building blocks of supercooled liquid water and ice.
  - Their aggregation stabilizes the structure.
- Applications for vitrite analysis.

# Hydrogen Bond is Discrete

- Intermolecular electrostatic interaction (25kJ/mol per a bond)
- Discrete connection
  - Almost isolated 1st peak in oxygen-hydrogen radial distribution function (RDF).
  - **Graphical representation** is reasonable.
  - Interconnection between water molecules constructs a percolated network.



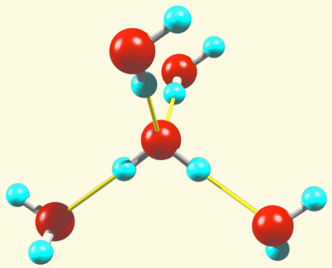



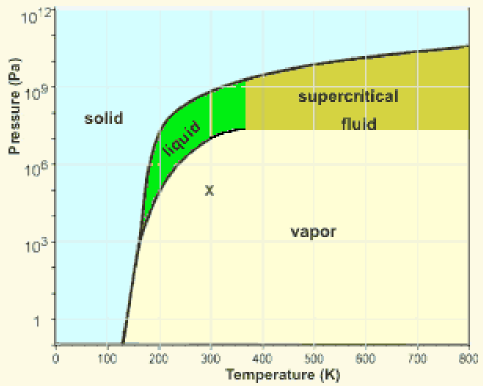
HBN of liquid water and ice

# Water is a Network-Forming Material

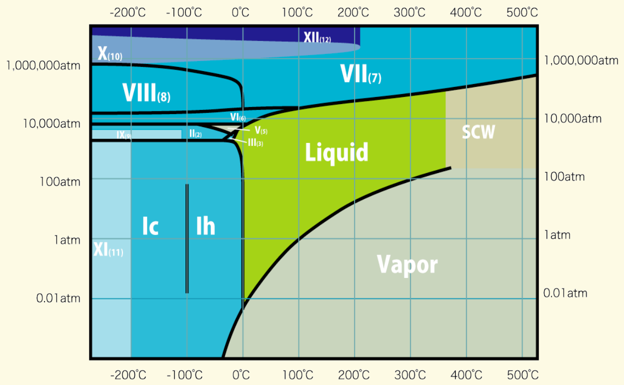
- Network with strict rules
  - Geometrical preference: Tetrahedral local configuration
  - Topological preference: 4-connected network
- All the ice phases obey the rules.
  - Even fluid phases obey them loosely.
- Ice phases are distinguished by the network topology.



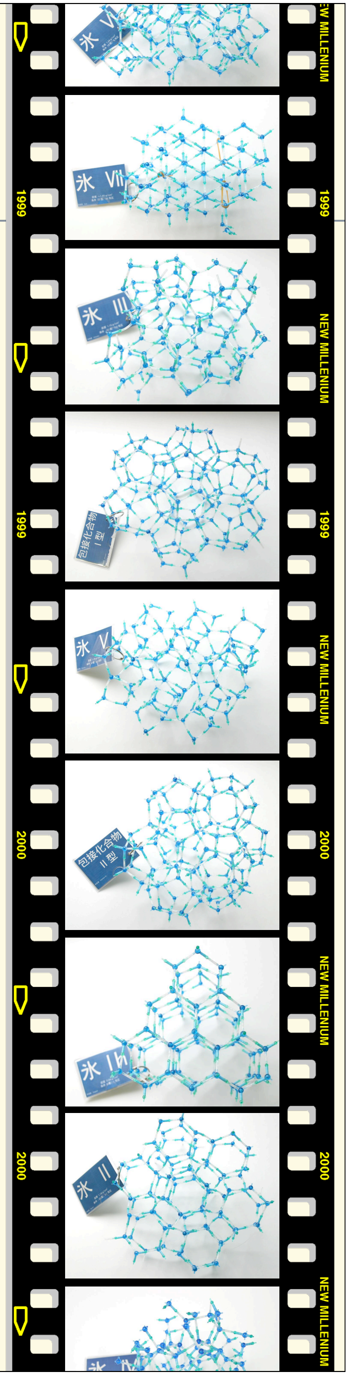
**Tetrahedral local configuration obeying the ice rule.**




**Phase diagram of simple liquids**




**Phase diagram of water**

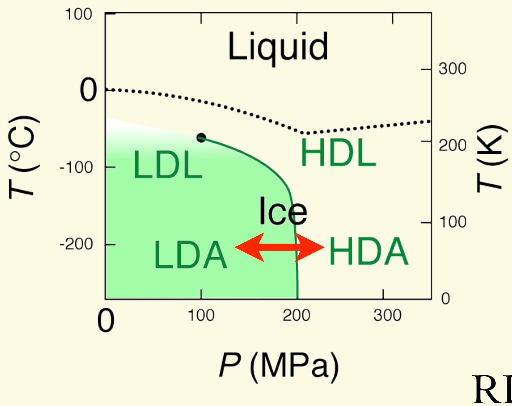


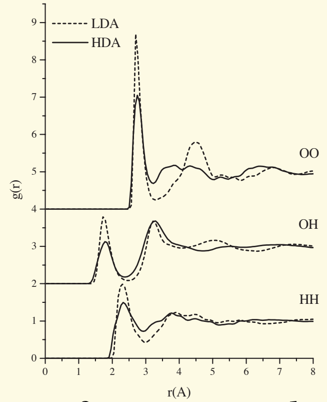
# "Polyamorphism"

O.Mishima, J.Chem.Phys. 100, 5910 (1994).
O.Mishima and H.E.Stanley, Nature 396, 329 (1998).

## Polyamorphism of water

- First-order phase transition between two amorphous phases.

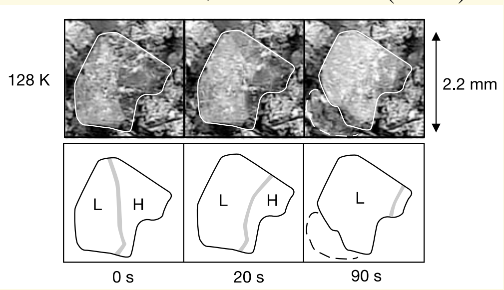



RDF of two amorphous phases differ clearly.

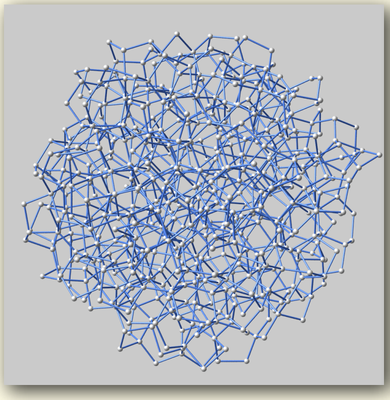
- *in situ* observation of coexistence

O. Mishima and Y. Suzuki, Nature 419 (2002) 599.

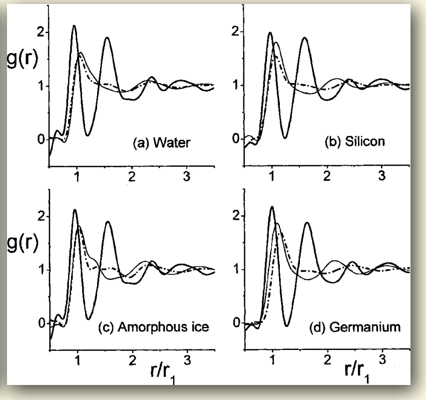



## Other materials

- Si, SiO2, Ge, etc. : Polyamorphism is commonly observed in network-forming materials with tetrahedral local order (TLO).



Continuous Random Network =Structure model of LDA

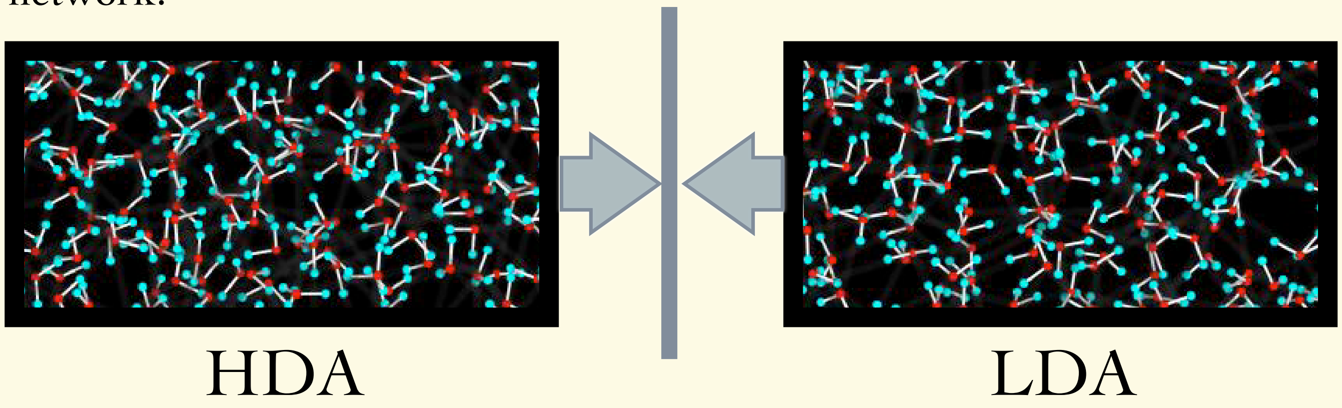



RDF scaled by the position of the 1$^{st}$ peak. Thick: LD; thin: HD; dashed: VHD.

C. J. Benmore et al, Phys. Rev. B 72 (2005) 132201.

# Can Two Amorphous Structures Coexist?

- Polyamorphism is a plausible cause of water anomalies.
- 1st order phase transition = coexistence
  - There must be articulate difference in structure.
  - Ordered phase (LDA) has the clue.
  - Local structure is not quite different.
  - There must be some **self-organizing** intermediate-range order (IRO) in the network.




Two amorphous phases are indistinguishable by eye.

# What is IRO in Supercooled Water?

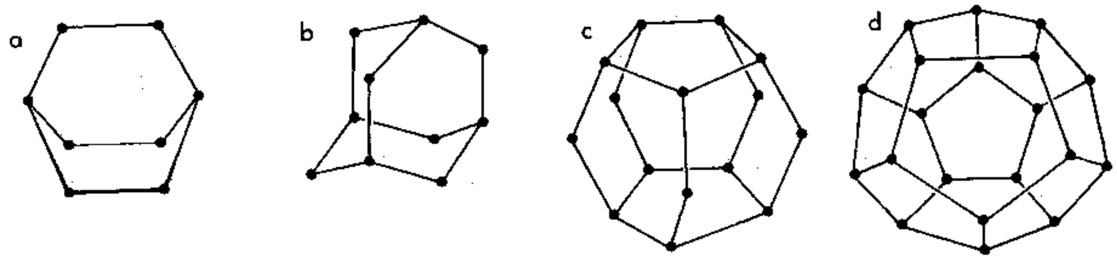
- "Density becomes low when water molecules in locally tetrahedral configuration accrete."
  J. R. Errington, et al, Phys.Rev.Lett. 89, 215503 (2002).
- "Large-sized cluster of 4-coordinated water molecules spreads."
  HIdeki Tanaka, Phys.Rev.Lett. 80, 113 (1998)
- "Voids distribute homogeneously; pre-peak emerges in structure factor."
  S.R. Elliott, J. Chem. Phys. 103 (1995) 2758.
- "Quasi-crystal structure emerges."
  M.F.Chaplin, Biophys. Chem. 83, 211 (1999).
- "Ice-like local structural units increase."
  Hajime Tanaka, Europhys. Lett., 50 (2000) 340.

- They all seem to be the **results** by IRO. The origin remains unexplained.
  - Why can 4-coordinated molecules get together?
  - What is the order in amorphous?
  - Why void appears?
  - Quasi-crystal? Micro-crystal? Non-crystal? Can we tell the difference?
- <u>What is the real origin of IRO in water?</u>

# Virtual Structure of Supercooled Water

F.H.Stillinger, Science 209, 451-457 (1980).

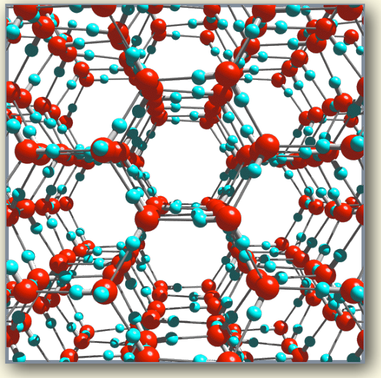
- "Model building reveals that the hydrogen bond angles naturally present in them to share edges and faces without the introduction of mutual strain. Consequently, they (**unstrained polyhedra**) are able to link up with one another more readily than a strained and an unstrained polyhedron can, on the average. As a result, the ideal unstrained structures find it advantageous to clump together; they experience a mean attraction for one another."
- "As their concentration rises, they will aggregate under the influence of the cited mean attraction to form larger and larger clumps or clusters."



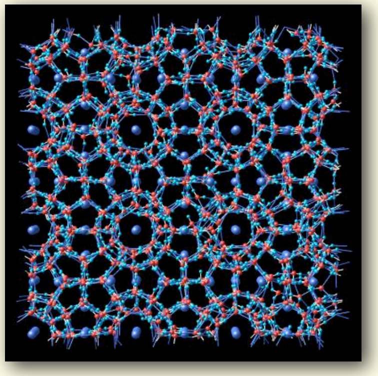
# Structural Units

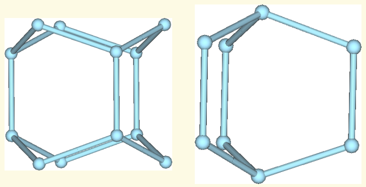
**Ice crystal is built of few kinds of structural units.**

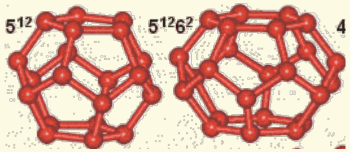
Ice Ih



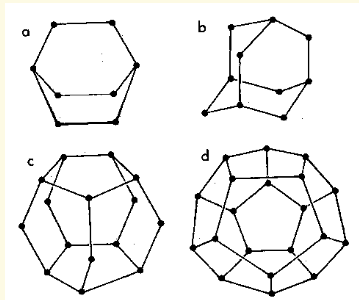
Methane Hydrate



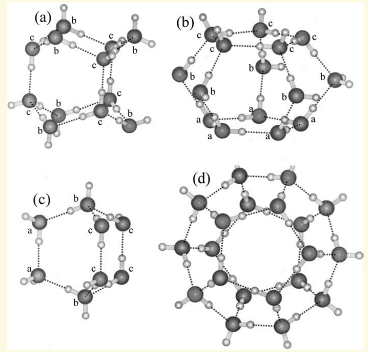




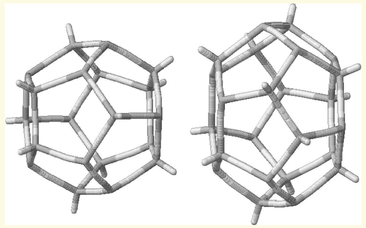

**Structural unit <u>candidates</u> in supercooled liquid water**



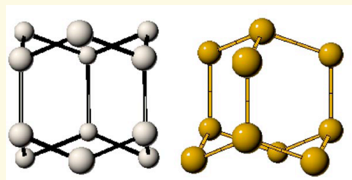

F.H.Stillinger, Science 209, 451-457 (1980)




M. F. Chaplin, Biophys. Chem. 83, 211 (1999).



G.-J. Guo, Y.-G. Zhang, and Y.-J. Zhao, J. Chem. Phys. 121,1542 (2004)



Units in liquid Si. P. Beaucage and N. Mousseau, Phys. Rev. B, 71, 094102 (2005).

# Exhaustive Search of Structural Units

- Such **stable structural units** in supercooled liquid water have been advocated in many papers since Stillinger first proposed.
- We need not **assume** the existence of such unit structures, because we already have all the trajectory information. **Just find them**.

- How shall we define the structural units?
  - All the empirical structural units are **hollow, compact graphs**.
  - Topology is essential for water.
  - Topological matching is much easier than geometrical matching.
  - Network topology in intermediate-range ( i.e. "**Network Motifs**" ) should be exhaustively searched, classified, and counted.

## How shall we define the structural units?

M. Matsumoto et al, J. Chem. Phys. , in press (2007).

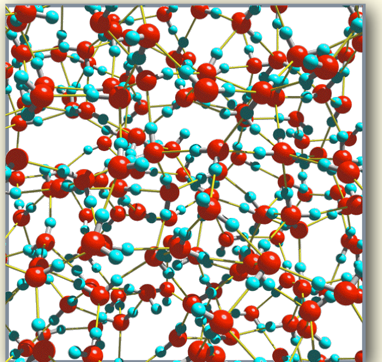
- Our definition for a unit graph for water.

A)**Quasi-polyhedron covered by rings. Each edge is shared by two rings.**

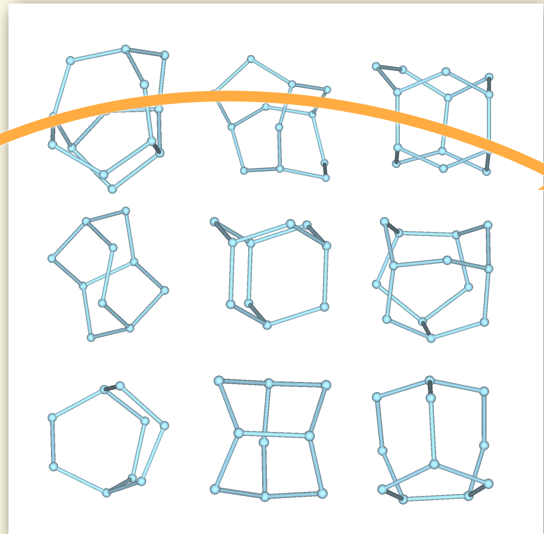
B)**Each vertex is shared by two or three rings.**

C)**Euler's formula for planar graph: Ring−Edge+Vertex=2**

- A and C guarantee the hollow compact structure.
- B is the property of the network with tetrahedral local order.
- We call them the "**fragments**" or the "**vitrites**"

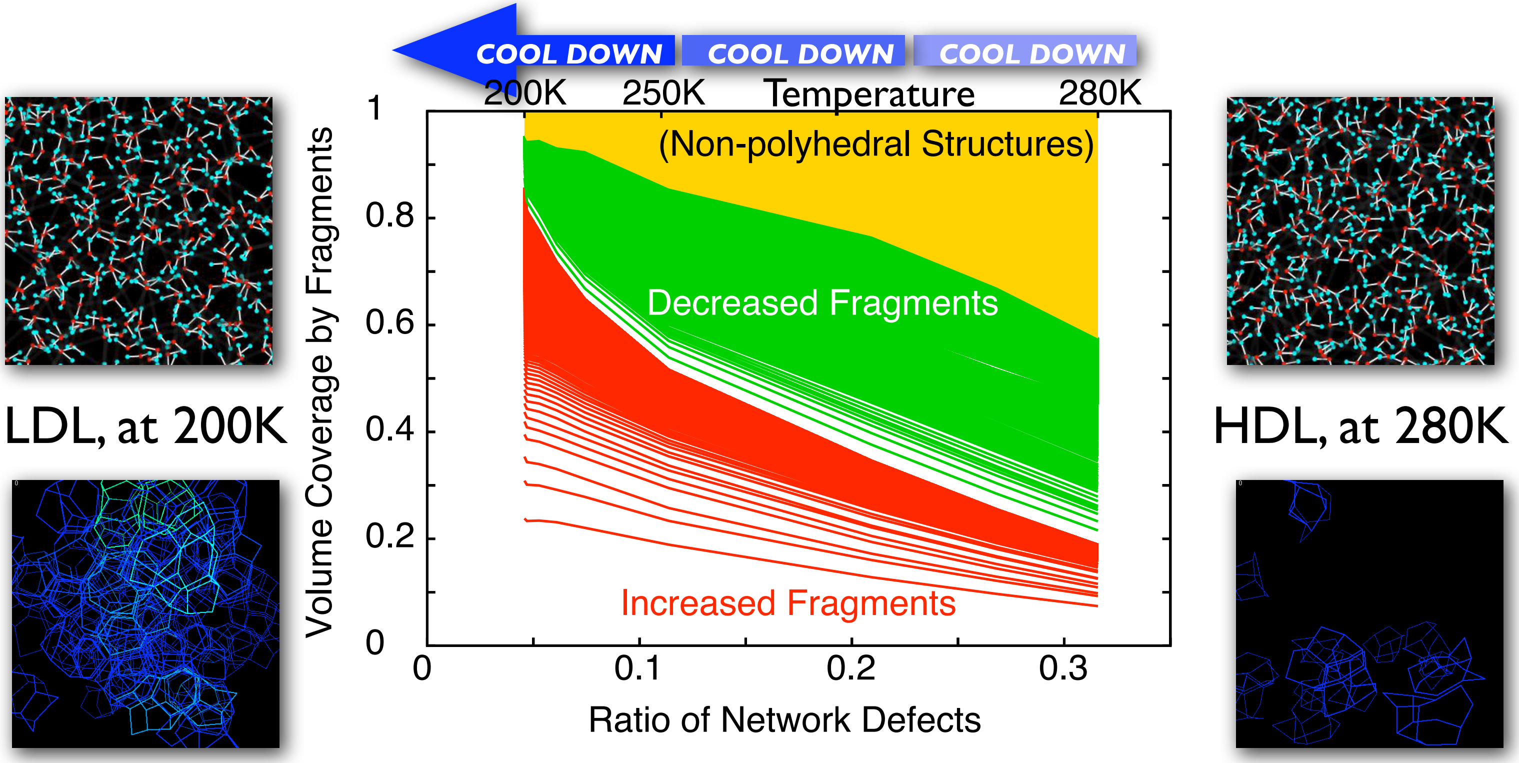


"raw" structure



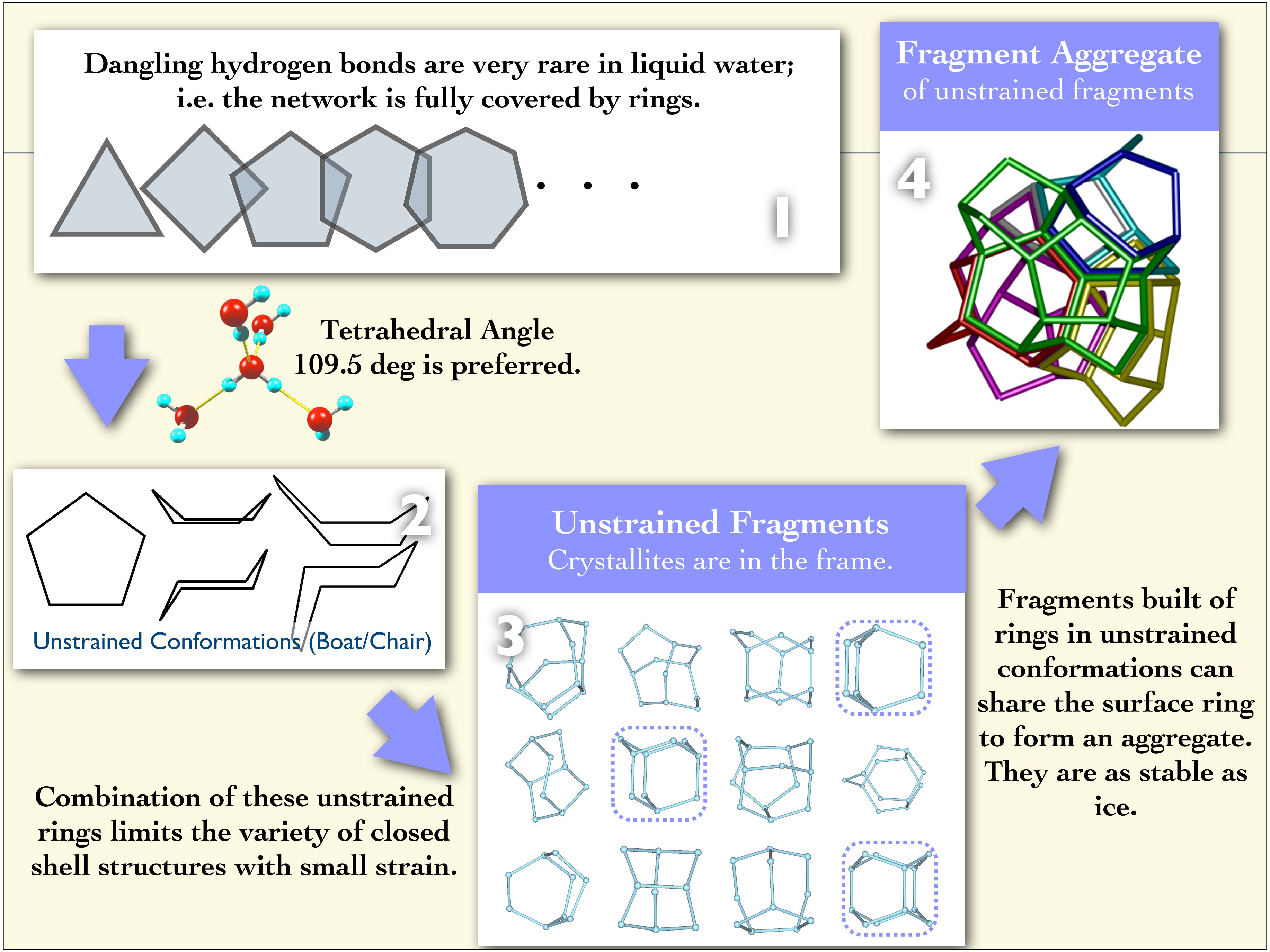
tiled by fragments

# Temperature Dependence




* Band widths between the lines indicate the number of different fragments.
* At 3000atm, Red portion is almost constant at about 0.2-0.3.

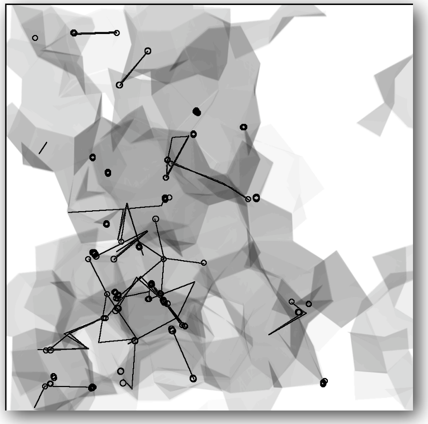
- Red part (= unstrained fragments) increases by cooling.
  They finally fill the whole space at low temperature limit.


Dangling hydrogen bonds are very rare in liquid water;
i.e. the network is fully covered by rings.
1
Tetrahedral Angle
109.5 deg is preferred.
Fragment Aggregate
of unstrained fragments
4
2
Unstrained Conformations (Boat/Chair)
Unstrained Fragments
Crystallites are in the frame.
3
Fragments built of rings in unstrained conformations can share the surface ring to form an aggregate. They are as stable as ice.
Combination of these unstrained rings limits the variety of closed shell structures with small strain.

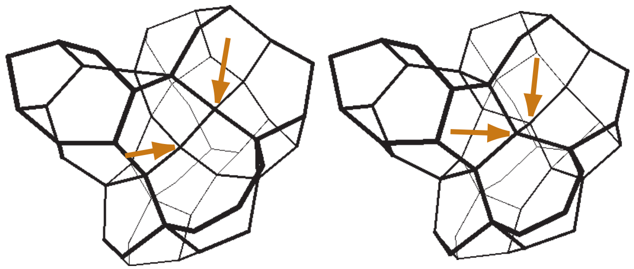
# Structural and Dynamic Heterogeneities

- In supercooled liquid water, HB network rearrangements occur heterogeneously.
- It is found that HBN rearrangements mostly occur outside the fragment aggregates.

**Fragment aggregation and network rearrangements**
Only the surface rings of the fragment aggregate are drawn with polygons. Blank area is filled with fragment aggregates. Black lines indicate the hydrogen bonds which are rearranged in 10 ps. Black dots indicate the network defects (water molecules not having four HBs). HBN rearrangements and network defects are expelled from fragment aggregates. (220K, 0 atm)



A casual rearrangement of HB affects the stability of rings and fragments sharing the bond. Only the rearrangements suppressing the total strain will be accepted.

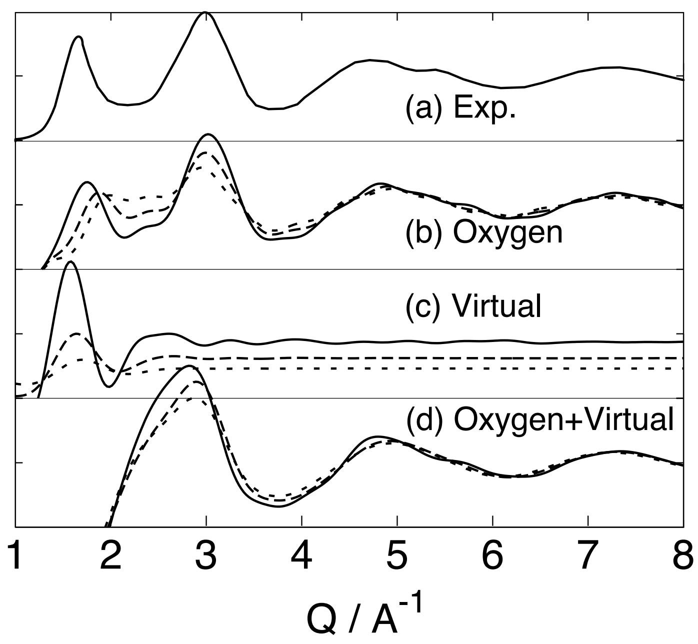


# Application 1: Assignment of FSDP

- First sharp diffraction peak (FSDP, aka pre-peak) of x-ray structure factor is commonly observed in glasses with tetrahedral local order.
- This peak is not attributed to any real-space partial pair distribution functions. Instead, it is considered to correspond to the **correlation length among cavities**, which exist in an amorphous network.
- When virtual atoms are put at the center of each fragment, FSDP in the total structure factor vanishes and the shape of the remaining peaks are similar for all the temperatures, i.e. the peak comes from **fragment-fragment correlation.**

$$g_{ff}(r) = \frac{V}{4\pi r^2 N_f^{\,2}} \left\langle \sum_i \sum_{j \neq i} w_i w_j \cdot \delta(r - r_{ij}) \right\rangle$$

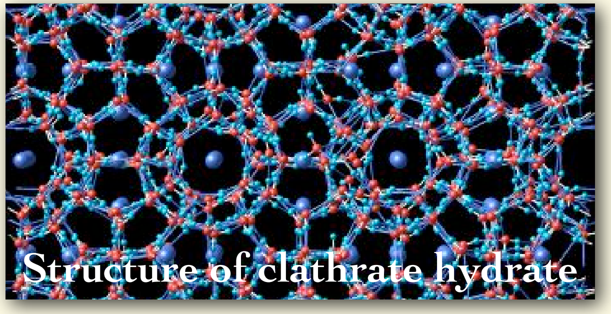
$$S_{ff}(k) = x_f + x_f^{\,2} \rho \hat{g}_{ff}(k)$$



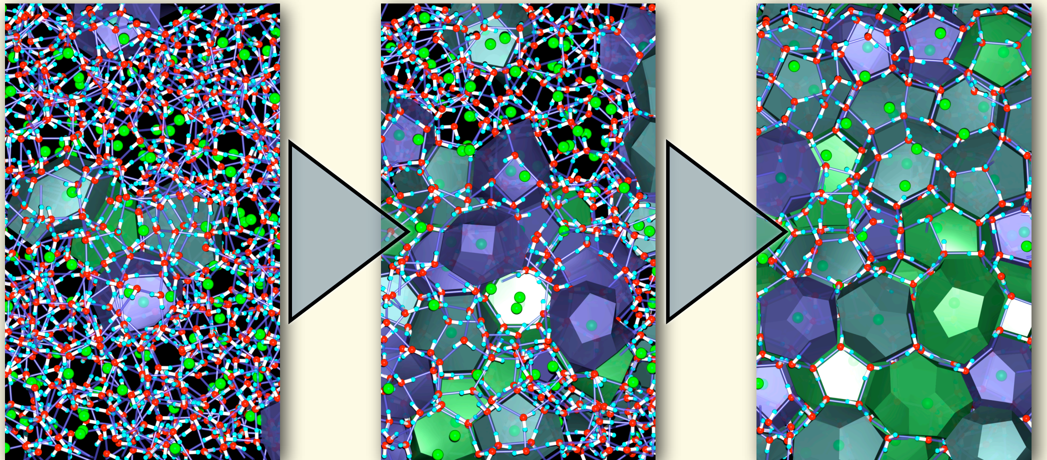

(a) X-ray structure factor of LDA. (b) Simulated O-O SF. (c) SF of virtual atoms placed at each fragment. (d) Total SF of oxygen and virtual

# Application 2: Methane Hydrate Formation

- In initial condition, methane molecules are forcibly mixed in water under high pressure.
- On early stage, the methane molecules are just dissolved in  water; there is no stable hydration shell constructed.


Structure of clathrate hydrate

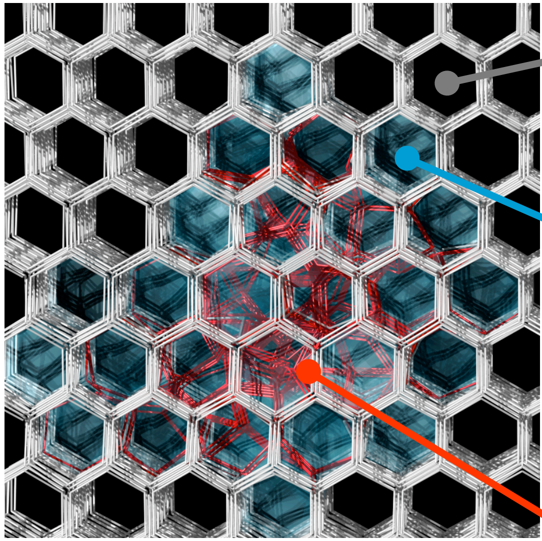
- Polyhedral cages (detected as fragments) gradually appear and share their surface rings to fill the volume. Composition of the cage sizes also changes gradually, reflecting the structure change from type II to I.



Crystallization process of methane hydrate. (from left to right: 1, 16, 160ns)
Green spheres indicate the methane molecules. Polyhedra from blue to green indicates 12- to 14-hedra, respectively. Y. Kitaoka et al, unpublished data(2007).

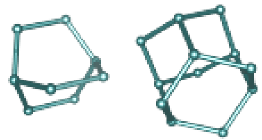
# Application 3: Homogeneous Nucleation toward Melting

- Fragments actually exist in the vicinity of liquid-ice interface at melting.
- Local structure in ice, at surface, and in liquid region can be clearly distinguished by the appearance frequency of the fragments.

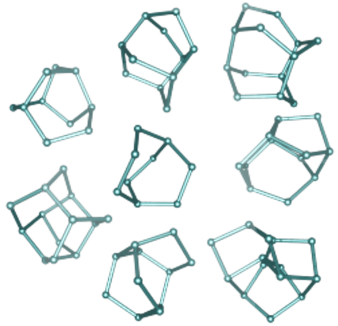


Fragments in molten nucleus inside ice crystal. Special types of fragments wet the solid-liquid interface to reduce the surface tension.

**White wireframe**: 2 types of **crystallites** in crystal ice Ih.



**Blue transparent polyhedra**: Major 8 types of **vitrites** at the single surface layer. All of them are built mostly of 5- to 7-membered rings.



**Red wireframe**: large variety of **vitrites** in the entangled network are observed, while none of the above fragments appears.

# Other Applications

**Fragment analysis will be useful when network topology matters.**

- Surface melting of ice.
- Ice nucleation from liquid water.
- Structure of hydration layers on the proteins.
- Structure of liquid water in the vicinity of interface/surface.
- Liquid-liquid coexistence in network-forming materials.
- etc.

# Vitrite Database

http://vitrite.chem.nagoya-u.ac.jp/cgi-bin/vitrite.cgi

- Vitrites (network motifs of water) are collected in a topology database.
- Two ways of search
  - Narrowing search by topological indices.
    - e.g. number of rings in a vitrite, topological volume, etc.
  - Topological search by exact graph matching algorithm.
- Analysis plugins
  - You can also add new analysis algorithm (e.g. radius of gyration, symmetry, etc.) as a plugin.
- HTTP/XML API is provided.
  - DB is accessible directly from your analysis program.