Molecular Dynamics of Water below Freezing
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Introduction

Fragment Analysis

Applications
No free water in the cell.

Water is not a mere solvent. It works with biomolecules complementarily.
- Fast proton transfer inside the proteins.
- Protein finds its native structure in water.
- Gel supports the body.

Water has many anomalous properties.

Life must have been utilizing (anomalous) properties of water as much as possible.

Anomalous Properties?
1. Water has unusually high melting point.
2. Water has unusually high boiling point.
3. Water has unusually high critical point.
4. Water has unusually high surface tension and can bounce.
5. Water has unusually high viscosity.
6. Water has unusually high heat of vaporization.
7. Water shrinks on melting.
8. Water has a high density that increases on heating (up to 3.984°C).
9. The number of nearest neighbors increases on melting.
10. The number of nearest neighbors increases with temperature.
11. Pressure reduces its melting point (13.35 MPa gives a melting point of -1°C).
12. Pressure reduces the temperature of maximum density.
13. D2O and T2O differ from H2O in their physical properties much more than might be expected from their increased mass; e.g. they have increasing temperatures of maximum density (11.185°C and 13.4°C respectively).
14. Water shows an unusually large viscosity increase but diffusion decrease as the temperature is lowered.
15. Water's viscosity decreases with pressure (at temperatures below 33°C).
16. Water has unusually low compressibility.
17. The compressibility drops as temperature increases down to a minimum at about 46.5°C. Below this temperature, water is easier to compress as the temperature is lowered.
18. Water has a low coefficient of expansion (thermal expansivity).
19. Water's thermal expansivity reduces (becoming negative) at low temperatures.
20. The speed of sound increases with temperature (up to a maximum at 73°C).
21. Water has over twice the specific heat capacity of ice or steam.
22. The specific heat capacity (CP and CV) is unusually high.
23. Specific heat capacity; CP has a minimum.
24. NMR spin-lattice relaxation time is very small at low temperatures.
25. Solute have varying effects on properties such as density and viscosity.
26. None of its solutions even approach thermodynamic ideality; even D2O in H2O is not ideal.
27. X-ray diffraction shows an unusually detailed structure.
28. Supercooled water has two phases and a second critical point at about -91°C.
29. Liquid water may be supercooled, in tiny droplets, down to about -70°C. It may also be produced from glassy amorphous ice between -123°C and -149°C [74] and may coexist with cubic ice up to -63°C [137].
30. Solid water exists in a wider variety of stable (and metastable) crystal and amorphous structures than other materials.
31. Hot water may freeze faster than cold water; the Mpemba effect.
32. The refractive index of water has a maximum value at just below 0°C.
33. The solubilities of non-polar gases in water decrease with temperature to a minimum and then rise.
34. At low temperatures, the self-diffusion of water increases as the density and pressure increase.
35. The thermal conductivity of water is high and rises to a maximum at about 130°C.
36. Proton and hydroxide ion mobilities are anomalously fast in an electric field.
37. The heat of fusion of water with temperature exhibits a maximum at -17°C [15].
38. The dielectric constant is high and behaves anomalously with temperature.
39. Under high pressure water molecules move further away from each other with increasing pressure.
40. The electrical conductivity of water rises to a maximum at about 230°C and then falls.
41. Warm water vibrates longer than cold water.
Most of the Anomalies Concern HB

- **Light and dissociative nature of proton in water**
  → Fast proton transfer, collective dynamics of water, etc.

- **Strong hydrogen bonding**
  → High boiling and melting points, large surface tension, etc.

- **4-coordinated HB network**
  → More than 10 kinds of ice polymorphs, liquid water is denser than ice, etc.

- **Orderliness in supercooled water**
  → Water expands when it cools below 4°C, many physical properties of water seem to diverge when it is supercooled, etc.
Anomalies of Supercooled Water

They are related to the polyamorphism of water.

Two distinct forms of the amorphous ice:
- Low-density Amorphous (LDA): Ordered
- High-density Amorphous (HDA): Disordered

Transition from HDA to LDA by Pressure Release
Anomalies of Supercooled Water

Computer simulation reproduces the polyamorphism of water.

What’s the matter with liquid water?
Polyamorphism also predicts the existence of two forms of liquid.

- Low-density Liquid (LDL): Ordered, high viscosity (ice-like)
- High-density Liquid (HDL): Disordered, low viscosity

Liquid water around $T_m = 273^\circ C$ is a heterogeneous mixture of two different ingredients.

Difference in structure is related to the difference in mobility.
Heterogeneity in Supercooled Water

- Hydrogen bonds make a well-percolated network.
- The structure looks random and homogeneous at a glance.

-20K below Tm

Only the hydrogen bonds are drawn.
Long exposure photography elicits the structural / dynamical differences in several nm scale.

-20K below Tm

Only the hydrogen bonds are drawn.
A one-component liquid seems to possess two regions with different properties.

a) **Ordered**, open structure with slower network rearrangements. RDF is similar to LDA.

b) **Disordered** part with fast rearrangements. RDF is similar to HDA.

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**Inset:** RDF by neutron diffraction
Water has **two distinct amorphous ice phases**.

Water has **two liquid structures**.
- Structured and destructured.

Supercooled liquid water seems to be a **heterogeneous mixture** of two liquids.

At atmospheric pressure, normal liquid water (**HDL**) **turns into LDA** by rapid supercooling; if the cooling rate is not enough, the fluctuation induces ice nucleation.
Introduction

Fragment Analysis

Applications
Structure of *Amorphous* Ice?

*Orderliness* in Liquid?
Structured Water Everywhere

- Liquid water is said to become “structured” in various environments,
  - e.g. at low temperature,
  - in amorphous ice,
  - near the hydrophobic wall,
  - in the quasi-liquid layer (QLL) of ice surface,
  - at the liquid-solid interfaces, etc.

LDA-like “Structured Water” may appear at:

- Melting of ice
- Crystal growth
- Ice Nucleation
- Surface water of a protein

In *ice*, all the water molecules are 4-coordinated *w/ regular angle* (109.5°).

Also in *liquid water*, 70% of water molecules are 4-coordinated.

Either not-4-coordinated or large deviation from 109.5° raises the potential energy.

Number of such defective water molecules decreases when supercooled. The network of supercooled water (LDA) approaches to the *ideal 4-coordinated random network* with regular angles.
Structure of Amorphous Ice

- **CRN** = Continuous Random Network (Zachariasen, 1932) model for Silicon and Germanium.
- 4-connected, tetrahedral network in short range; Random in long range.
- You can also build the CRN by hand.

- You cannot add new nodes freely. You will feel strong restriction.
- i.e. This structure is not totally random. **Intermediate-Range Order**.
- Configurational entropy of CRN is 0.93 $k_B$.

*How can we characterize this structure?*
In case of crystal, if one knows the unit structures, one can find them by **pattern matching**.

**Polyhedral Templates for hexagonal / cubic ice I (Wurtzite / diamond)**

**Nucleation of Silicon**

**Nucleation of water inside a nanopore**

**What is the template for amorphous ice?**
Stillinger (Great pioneer of MD)
“Model building reveals that the hydrogen bond angles naturally present in many of these polyhedra make it easy for them to share edges and faces without the introduction of mutual strain. Consequently, they 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.”

Let us define the “Polyhedra” and find them exhaustively!
General Definition of the “Polyhedron”


1. Two or three rings share a vertex.
2. Rings are not necessarily flat.
3. Consist of 3- to 8-membered rings.
4. Satisfy the Euler characteristics: \( F - E + V = 2 \)
   \( F \): number of rings, \( E \): number of edges, \( V \): number of vertices.

* They are not true polyhedra because rings are not flat.
We call them “(Quasi-polyhedral) Fragments”.
Finding “Fragments”


Define the Hydrogen Bond Network.

Look up rings.

Build compact polyhedra.

Put them in the database, classify, and count.
The network of Ice / LDA / CRN can be regarded as an aggregate of non-overlapping fragments.
When Water Cools,

Not classifiable as a fragment because of the entangled topology.

Interval between lines indicates the volume ratio occupied by a fragment type.

Locations of the Cryophiles

Locations of the Cryophiles
**Residual Distortion**

- **Magnitude of the bond angle distortion** from the regular angle, 109.5°, when the fragment is in its most relaxed form.
- Each fragment type has its unique RD.
- 4-membered ring increases RD.
- RD of a crystal fragment is zero.

RD of a fragment can be evaluated using the following formula:

\[ d = \frac{1}{N} \sum_{i}^{N} \left( \cos \theta_i + \frac{1}{3} \right)^2 \]

Where the summation sums over all \( N \) contained angles \( \theta_i \) between adjacent edges of a fragment.

- Note that \( \cos (109.5 \text{ deg.}) = -1/3 \), where 109.5 deg. is the angle forming the exact regular tetrahedral structure.

The minimal value of \( d \) is called the **“residual distortion”** of the network structure.

- Residual distortions of 4- and 5-membered rings are 1/9 and 0.0006, respectively.
- Residual distortion of 6- and 7-membered rings are zero when they are in boat or chair conformation.
- Rings larger than 7-member have many stable conformations with zero residual distortion.
- Residual distortion of a fragment is always larger than the average of residual distortions of its component rings because of the steric constraints, except for ice-I fragment where \( d \) values of the fragment itself and its component rings are all zero (Fig. 1(a-c)).

It is found that 90% of the hydrogen bond network at 200K under zero pressure is covered by the fragments whose RD values are less than 0.03.

**Built of 6-member rings in boat/chair conformations.**

**Built of bended 4- and 5-member rings.**

**Undistorted**

**Distorted**
Classes of the Fragments

Undistorted (RD=0)
**Crystal Fragments**

Least distorted (RD ≈ 0)
**Cryophilic Fragments**
5- to 7-rings

Distorted (RD >> 0)
**Thermophilic Fragments**
4-rings | irrelevant topology
HB network of water is well-percolated; The network is filled with rings.

Preference to the 4-coordination and regular angle 109.5°

Undistorted ring shapes: Pentagon and Boat/Chair Conf.

Limited variety of fragments by combination of these shapes

Least distorted Fragments (Cryophiles)

Aggregate of the Cryophiles

Combination of such fragments becomes stable because they can share the surface rings without introducing strain.
The network of Ice / LDA / CRN can be regarded as an aggregate of non-overlapping fragments.

Limited variety of fragments are less distorted, increase by cooling, and persist longer time than average. “Cryophiles”

Cryophiles can fill space by sharing the surface rings of similar shapes.
→Origin of the intermediate-range order in LDA.

Local order in LDA/LDL can be identified by these fragments.
Introduction

Fragment Analysis

Applications
Review the Structure of Water thru Fragments

1. Supercooled water
2. Water near the hydrophobic wall
3. Water near the hydrophobic molecule
4. Water of crystallization
5. Silicon at the crystal nucleation
6. Water at the crystal nucleation
7. Water at the ice growth
8. Water in the liquid nucleus at ice melting
Heterogeneity in water revisited.

- 10 ps per frame, 300 ps per 1 real second.
- Movie of long-exposure duration = 200ps.
- –20 K below Tm (supercooled)
- Cryophiles are drawn with thick lines.
Water near the hydrophobic wall

- 1 ps per frame, 30 ps per 1 real second.
- Movie of long-exposure duration = 20ps.
- At the Tm.
- **Hydrophobic wall made of argon** is put in the middle of the cell.
- Fragments with small RD are drawn with thick lines.
Water near the Hydrophobic Molecule

- 1 ps per frame, 30 ps per 1 real second.
- Movie of long-exposure duration = 20ps.
- At the Tm.
- Two methane molecules (black circles) are put in the cell.
- **Fragments with small RD are drawn with thick lines.**
The crystal of Vinblastine contains 19 water molecules in a unit. Among them, 15 water molecules localize and form a stable non-crystalline structure with 5-membered rings. It is found in our DB #6259 (Cryophile).
Right and wrong crystallites appear intermittently and independently.
Only the right nucleus grows up to be the crystal. The wrong one stops growing due to the geometrical frustrations.
“In general it is not the most stable but the least stable polymorph that crystallises first.” — Ostwald’s Step Rule (1897)

- **LDA**
  - Configurational entropy: $0.93 \, k_B$

- **Liquid Water**
  - Entropy by freezing can be estimated from the latent heat:
    \[ \Delta G = 0 = \Delta H - T_m \Delta S, \quad \therefore \frac{\Delta H}{T_m} = \Delta S \]
    \[ \Delta H = 80 \, \text{cal / g}, \quad \therefore \Delta S = 2.4 \, k_B \]
  - It is natural that LDA appears as the “Ostwald’s step” in the phase transition between ice and liquid water.
  - It will mediate between water and ice at the coexistence and decrease the surface energy by **wetting** the surface.

2. The initial nucleus with 5- and 7-membered rings appears. The nucleus wafts but live long.

3. The nucleus starts growing.


Ice Crystal Growth

- 1 ps per frame, 30 ps per 1 real second.
- Movie of long-exposure duration = 40ps.
- –10 K below Tm.
- **Ice slab** (basal plane) is put in the cell.
- **Cryophiles are drawn with thick lines.**

Initial position of the ice surface

Periodic Boundary

Periodic Boundary
1. Cracks, i.e. string-like defects, appear by chance. (Duration: 200ps～10ns)

2. Cracks merge, but the structure change is not frequent. Such cracks appear intermittently. (500ps)

3. Liquid “droplet” appears inside the large-scale cracks. Structure changes very quickly and the droplet starts growing. (200ps)

Homogeneous Ice Melting

1. Cracks, i.e. string-like defects, appear by chance.
   (Duration: 200ps ~ 10ns)

2. Cracks merge, but the structure change is not frequent. Such cracks appear intermittently.
   (500ps)

3. Liquid “droplet” appears inside the large-scale cracks. Structure changes very quickly and the droplet starts growing.
   (200ps)


Mochizuki, MM, and Ohmine, unpublished.

- **Melting droplet at the 3rd stage**
  - **2 types of the crystal fragments.**
  - **Monolayer of special fragments.** Only 8 kinds of fragment consist of 5- to 7-membered rings. Appear at the 2nd stage of melting.
  - **Liquid** consists of many kinds of fragments. No common member with the blue layer. Appear at the third stage of melting.
**Summary 3**

- **Fragments** can be used to describe the local structure and to say the difference directly.

- **Structured water mediates** liquid water and ice. It wets the interface and **reduce the surface energy**.
Grand Summary

- Water has many anomalous properties. We should know the anomalies to understand how life utilizes water.

- Anomalies of supercooled water is related to the polyamorphism.

- Low-density amorphous = structured water play an important role in anomalies and phase transitions at low temperature.

- Now we can detect such special structure in anywhere in the computer simulations by introducing fragment analysis.