Topological Building Blocks of Hydrogen Bond Network in Water

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The past ten years of research in supercooled liquid have produced major theoretical and experimental advancements. Anomalies of liquid water such as expansion below 4 degree C, for example, are now considered to reflect the properties of metastable forms of water.[1] The expansion accelerates below the melting point, and it is hypothecated to become the low-density amorphous ice if crystal nucleation does not intercept. This expanding "low-density liquid water" has structural similarities with the low-density amorphous ice (LDA).[2]

Structure of LDA is characterized by the tetrahedral local order and the intermediate-range order in the hydrogen bond network. Existence of intermediate-range order is assessed in terms of low configurational entropy, a distinct pre-peak in the structure factor, etc.[3,4] You can also ascertain the orderliness by yourself, by building the locally tetrahedral random network strucure with ball-and-stick model, that it is difficult to avoid defects and strains.[5] Such a structure, also known as continuous random network (CRN), has been studied for a long time as the model of tetrahedral semiconductors and its short-range order was assessed in terms of Voronoi polyhedra, coordination number, rings, etc. However, it is still unclear what kind of "intermediate-range" order exists in the "strong" glass structure.[6]

We introduce the basic three-dimensional units of the network, called fragments, to characterize the hydrogen bond (HB) network structure of water. A fragment is a compact network built of surface rings encapsulating a void. (Fig.1) Topological differences among normal liquid water, water at low temperature and water under high pressure are elucidated by their fragment statistics. Water at low temperature has almost defect-free network and is filled with stable fragments with small distortion. (Fig.2) It is found that there exists a certain way how fragments mutually aggregate. Well-formed aggregates heterogeneously constitute very stable network structures. HB network rearrangements occur scarcely inside these aggregated domains but take place in their surface areas. The heterogeneity of HB structure and rearrangement in water is thus explained in terms of the fragment structure and its rearrangements. The fragments analysis thus elucidates the intermediate-range order in water HB network, and will be also useful for understanding the structure of liquid water in the vicinity of surfaces, hydrophobic molecules, and biomolecules.

The true origin of expansion in liquid water and the relation with two-state behavior will also be discussed in terms of topological analyses.

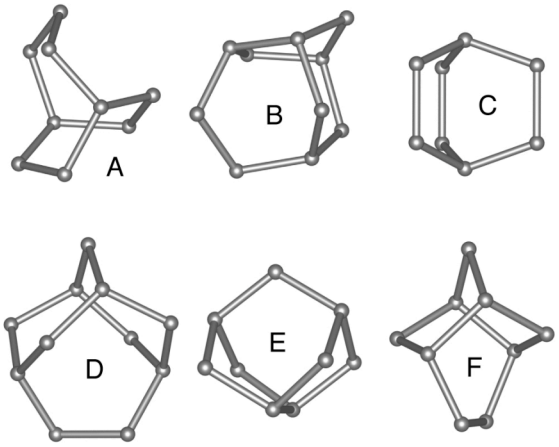

Figure 1: Six typical fragments in liquid water are illustrated. A ball and stick correspond to a water molecule and a hydrogen bond, respectively.

Figure 2: Fragments found in the deeply supercooled water. They fill the whole hydrogen bond network.

References

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