Why Does Water Expand When It Cools?

Masakazu Matsumoto*

Nagoya University Research Center for Materials Science, 1 Furo-cho, Chikusa-ku, Nagoya, Aichi, 464-8602 Japan

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The origin of the density anomaly of water is often explained in terms of the mixture model, in which the low-density ordered ''icelike'' component dominates by cooling. However, such an explanation based on heterogeneity conflicts with microscopic observations by computer simulation. Actually, heterogeneity in structure exists and a microscopic density fluctuation is observable; still, it is found that the density decreases quite homogeneously irrespective of the differences in local structure. Our finding of two linear correlations, the bond length against temperature and contraction against angular distortion, recovers the density anomaly of water without invoking heterogeneity.

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Only water expands when it cools above its melting point. The expansion continues far below the melting point to −45 °C, where the density becomes much lower than hot water at its boiling point. This unique property affects ocean currents governing global climate. Why does water expand that much?

There is a long history of arguments on the density anomaly of water. Since Whiting first proposed the mixture model of liquid water consisting of ''normal'' and ''icelike'' components, the mixture model was accepted and developed by many researchers [1,2].

Early mixture models, including cluster and interstitial models, overestimated the difference between both components [2,3], and were regarded as improbable, by the prosperity of molecular simulations in the 1970s [4]. On the other hand, the mixture model has returned recently to the mainstream in the context of water polyamorphism [5]; in this context, there are two structurally different (nano-) domains that coexist heterogeneously in supercooled liquid water: one is the ''high-density amorphous ice (HDA)''-like disordered mobile part and the other is the ''low-density amorphous ice (LDA)''-like immobile ordered part, and the latter dominates and reduces the density below the temperature of maximum density (TMD) [6–8]. This explanation sounds plausible but is not verifiable unless LDA- or HDA-likeness is declared.

One should be careful to use these metaphors, such as icelike, LDA-like, HDA-like, etc., because they have implications; microscopically an ''icelike'' structure may not have the macroscopic property of ice. For example, every water molecule in ice has four coordinates, and therefore a four-coordinated water molecule in liquid is often considered to represent the ''icelike'' part [9], while local density in a four-coordinated water molecule is not always low like crystal ice [7]. Malenkov found that water molecules with a larger local volume are more mobile than those with a smaller local volume, while increased density of the entire system leads to increased mobility of molecules [10]. This paradox suggests that division into two categories, i.e., an icelike ordered low-density domain and a normal high-density domain, might be too simplified to explain the reality.

When water cools, four-coordinated water molecules increase on average, tetrahedrality and heterogeneity accentuate, density decreases, approaching the hypothetical second critical point. These tendencies seem to correlate, but they need not always be explained at a time in a context of polyamorphism [11].

Computer simulation is a powerful tool to investigate these hypotheses on the basis of the all molecular configurations. In this Letter, a consistent picture on negative expansivity will be drawn based on the network geometry and topology explored by computer simulations.

Replica exchange molecular dynamics simulation is performed in a wide range of temperatures between 200 and 360 K under zero pressure, in which the Nose-Poincare-Andersen thermo-barostat is employed [12]. In the simulation, the TIP4P/2005 water model is used [13]. TIP4P and its successors are reliable models for reproducing the physical properties as well as structure over a wide temperature or pressure range [14]. All the data are reconfirmed by using several water models [15].

The definition of a hydrogen bond (HB) is usually given arbitrarily, and therefore the average HB length also depends on the energetic or geometrical threshold. In this Letter, HB is decided by the molecular configuration in the inherent structures [16], in which the connectivity is determined without arbitrariness [17]. Inherent structures are used only to define the network topology, and all other analyses are performed using instantaneous structures. [18] For example, average bond length is calculated as the average instantaneous distance between a pair of oxygen atoms which are determined as bonded in the inherent structure. Perception algorithms of rings and more complicated topologies are given in a previous paper [19].

Local density is considered to play an important role in liquid water. There are several ways of defining the local density at a molecular scale. In the present work, the volume of a Voronoi polyhedron (VVP) is employed as a fair decision of the volume occupied by a single molecule

[20]. Another definition of local density based on an intermediate-range structure will be introduced in the latter part of this Letter.

There are three factors affecting volume change of network-forming liquids, namely, change in bond length, network topology, and bond angle. The basic property of these factors will be covered next, and what is occurring in supercooled liquid water will be summarized.

An HB network can be regarded as a random network where oxygen atoms and HBs correspond to the network nodes and edges, respectively. It is therefore natural to represent the bond length by the average oxygen-oxygen distance at both ends. In Fig. 1(a), average bond length is plotted against temperature. It indicates that the O-O distance extends linearly, while the first peak position of O-O radial distribution function moves only a little, reflecting the anharmonic potential function of hydrogen bonding.

To exclude thermal expansion by bond extension, reduced specific volume $v_{\rm red}$ is defined as follows:

$$v_{\rm red} = v/L_{\rm avg}^3, \tag{1}$$

where v is the volume per molecule (i.e., specific volume) and $L_{\rm avg}$ is average bond length. Reduced specific volume decreases monotonically and rapidly by 20% by heating in the whole temperature range [Fig. 1(b)]. This drastic contraction should be attributed to angular distortion or topological change in the network.

There have been many arguments on the determination of the ordered domain in liquid water [9,19,21–23], but there seems to be a consensus that the ordered domain has an LDA-like network structure, plenty of four-connected water molecules (C4 hereafter) [6,22], lower mobility [24], and an intermediate-range order. We here employ the coordination number (i.e., number of HBs at a molecule) as the simplest local topological index. When the ordered domain (abundant with C4) is much less dense than the disordered domain (abundant with C3 and C5), and when the former increases at low temperatures (i.e., the temperature range below the room temperature where density anomalies become obvious), water would expand heterogeneously when it cools. Let us examine the relationship between coordination number and VVP.

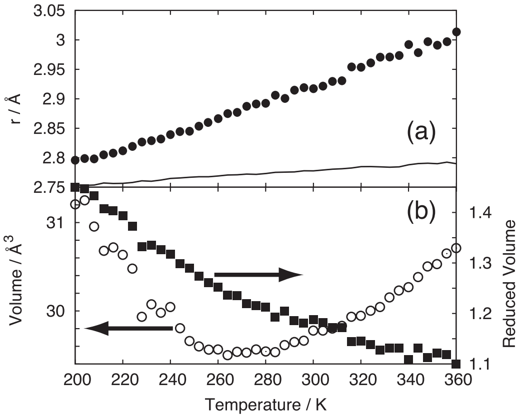

FIG. 1. (a) Average bond length is plotted against temperature using filled circles. First peak position of oxygen-oxygen radial distribution function is drawn with a solid line. (b) Volume change against temperature is plotted with open circles (left scale). Filled squares (right scale) indicate the reduced specific volume.

By heating from 200 to 300 K, C3 and C5 increase from almost zero to 15 and 13%, respectively (Fig. 2), and C2 and C6 is negligible below the room temperature. Thus, C4 dominates at low temperatures. On the other hand, local volume strongly depends on the coordination number. The VVP of C3 is 4 and 5.8% larger than the average at 200 and 280 K, respectively, while that of C5 is 10 and 7.2% smaller at the same two temperatures (Fig. 2). It should be stressed that deviation of the local volume of C3 and C5 is much larger than the standard deviation of the average VVP; i.e., the difference in local density is clearly captured by differences in coordination number, while the VVP of four-coordinated water molecules is not large but almost equal to the average. The contribution of C3 and C5 to the average specific volume, $v^{\rm ex}$, can be calculated by the following formula:

$$v^{\rm ex} = v_3^{\rm ex} x_3 + v_5^{\rm ex} x_5, \tag{2}$$

where $v_3^{\rm ex} = v_3 - v_{\rm avg}$ is the excess volume of C3, v_3 and $v_{\rm avg}$ is the VVP of C3 and average volume per molecule, respectively, and x_3 is the mol fraction of C3. Under ambient pressure, $v_3^{\rm ex}$ and $v_5^{\rm ex}$ are comparative values with opposite signs and x_3 and x_5 are also comparative.

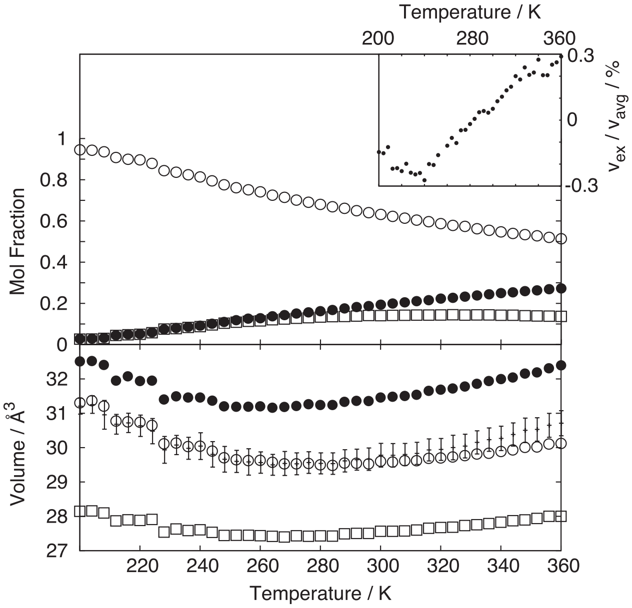

FIG. 2. Upper panel: Composition of C3, C4, and C5 is plotted against temperature with filled circles, open circles, and squares, respectively. Lower panel: VVP for different coordination numbers is plotted against temperature. Symbols are the same as the upper panel. Bars indicate the average volume per molecule and its standard deviation. Inset: Contribution of VVP of C3 and C5 to average volume.

Finally, the contribution of C3 and C5 to volume is completely cancelled (Inset in Fig. 2). A change in the composition of coordination number does not affect the total density.

Hence, the angular distortion of the network is the last realm to conquer. In a previous paper, average angular distortion d of a given network was defined as the deviation from the tetrahedral angle in the following formula [19]:

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

where θ_i and N are the ith-containing angle between the bonds and the total number of containing angles, respectively. Network topology determines the lower bound of d under the condition of fixing all the bond length to unity, which we call residual distortion (RD). RD is a simple measure of the frustration of the tetrahedral network. d is zero for a perfect ice structure. In liquid water, the d value of the total network increases monotonically against temperature.

A strikingly simple relationship between the reduced volume and angular distortion is found. In Fig. 3, it is clearly shown that the reduced specific volume v_{red} changes linearly against d. Thus, the volume change of liquid water is reproducible simply and quite precisely as the product of this tendency of contraction and thermal bond extension over the entire temperature range.

Let us examine this relationship microscopically. It was shown in our previous papers that the network of liquid water consists of many polyhedronlike structures, i.e., vitrites [19,25,26]. A vitrite is a void cell enclosed by rings and is the building block of the water structure at low temperature and low pressure. Hexagonal and cubic ice I, LDA ice, and clathrate hydrates can be uniquely and exclusively tessellated into vitrites. The volume of a vitrite can be calculated by spanning a membrane onto each ring (Fig. 4). The specific volume of a vitrite is an alternative of VVP reflecting the intermediate-range order of water.

The specific volume and the angular distortion of each type of vitrite was tracked over the whole temperature range. It was found that every vitrite is in the form of its maximum volume when it is least distorted and contracts linearly with a similar contraction ratio when heated (Fig. 5).

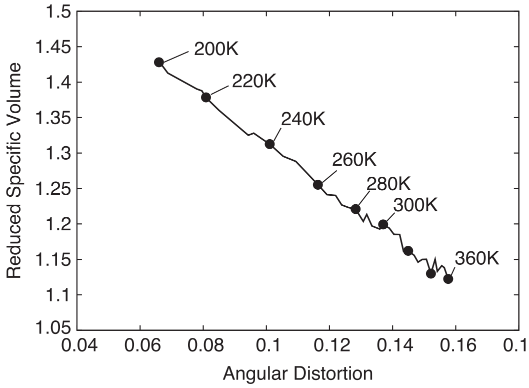

FIG. 3. Correlation between angular distortion and reduced specific volume is plotted with a solid line for different temperatures. Dots are placed every 20 K as a visual guide.

While the tendency of contraction is common to all vitrites, specific volume at its least distorted shape differs from vitrite to vitrite. In general, frustrated vitrite has a small specific volume (i.e., high density) [19]. One may therefore still think that the composition change of unfrustrated or frustrated vitrites might be responsible for the thermal contraction.

To evaluate the contribution from each vitrite to the volume change, all the vitrites that appeared in liquid water were classified into two categories by whether the RD (frustration) was larger than 0.015 or not. As we mentioned in a previous paper, vitrites do not cover the whole liquid water network at around room temperature where an entangled network region remains [19]. The volume of the uncovered part was calculated by subtracting the volume of vitrites from the total volume. Frustrated vitrites are found to have about 10% smaller specific volume than the average. On the other hand, the specific volume of the network regions covered by unfrustrated vitrites is very close to the average below its melting point, 250 K [27], similarly to the case of the coordination number. Thus, local frustration is coupled to local density, but the thermal contraction continues homogeneously, irrespective of the differences in local structure. The local density of the unfrustrated stable structure is almost the same as the average density below the melting point, in agreement with previous studies on VVP and coordination number [7,10,28]. At higher temperatures, the part covered by unfrustrated fragments has a rather higher density than the average because it has a well-interconnected HB network.

In summary, liquid water expands quite homogeneously when it cools to approach its low-density form. HB extension is responsible for thermal expansion of water and angular distortion in the network is responsible for thermal contraction. Supercooling of liquid water involves structural (and concomitantly dynamical) heterogeneity. Water molecules with a lower coordination number have lower

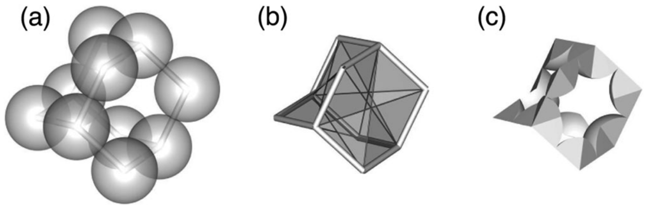

FIG. 4. Scheme to determine the volume and specific volume of a vitrite. (a) Determine the vitrite. (b) Place an additional node at the center of mass of each surface ring, and triangulate the ring. (c) Obtain the intersection of spheres and the polyhedron. Volume of a vitrite is defined as the volume of the polyhedron constructed in (b), and number of particles in a vitrite is represented by the total solid angles of the spheres clipped by the polyhedron depicted in (c).

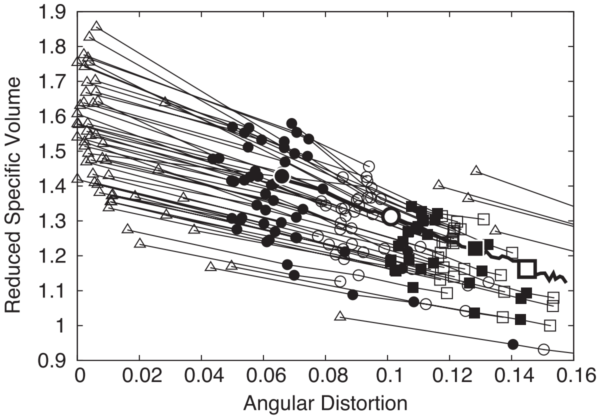

FIG. 5. Reduced specific volume v_{red} is plotted against angular distortion d. Thick line is overall average specific volume against average angular distortion in Fig. 3. Each thin line indicates the d-v_{red} correlation of a type of vitrite found in liquid water. Filled circles, open circles, filled squares, and open squares indicate the average d-v_{red} values at 200, 240, 280, and 320 K, respectively. (Overall average is indicated by large marks.) Triangles indicate v_{red} of isolated vitrites at their least frustrated shapes. Every vitrite contracts linearly with a common gradient against angular distortion.

local density. Vitrites with a large RD (i.e., frustration) have higher local density. Although such local structural differences yield more than 10% difference in local density, the thermal contraction proceeds equally at any place regardless of the structure. Thus heterogeneity and anomaly in density are not directly related [11].

Adjectives such as ‘‘icelike’’ and ‘‘LDA-like’’ are misleading because they imply low density. They actually declare the orderliness in structure and not the density. ‘‘Tetrahedrally ordered’’ would be a reasonable alternative to specify a group of four-coordinated, less mobile, less distorted water molecules.

Note that present results depend on the reproducibility of medium-range structure of liquid water by simulation. For further confirmation, direct observation of medium-range structure by experiments and high precision molecular simulation are wanted.

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*matto@nagoya-u.jp

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