

Cooperative Origin of Low-Density Domains in Liquid Water

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We study clusters formed by water molecules possessing large enough tetrahedrality with respect to their nearest neighbors. Using Monte Carlo simulation of SPC/E water and Voronoi tessellation, we find that regions of lower density than the bulk are formed by accretion of molecules into clusters exceeding a minimum size. Clusters are predominantly linear objects and become less compact as they grow until they reach a size beyond which further accretion is not accompanied by a density decrease. The results suggest that the formation of “icelike” regions in liquid water is cooperative.

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Water is an unusual liquid [1–3]. At low enough temperatures and pressures, it expands when cooled, becomes less viscous when compressed and more compressible when cooled, and its already large isobaric heat capacity increases sharply upon cooling. Because of its essential role in biology, atmospheric phenomena, geology, and technology, there is widespread interest in understanding the molecular origin of water’s anomalous properties [1].

Perhaps the best-known anomaly of liquid water is its ability to expand when cooled at constant pressure (negative thermal expansion). This phenomenon can be understood qualitatively in terms of the formation of localized molecular arrangements having a lower local density than the bulk. Molecules in these transient low-density configurations must, on average, adopt more structured arrangements than the bulk liquid [4]. Such local, transient, structured arrangements are often described as “icelike.” While the soundness of this picture is not in dispute (freezing in water is accompanied by a 7.7% decrease in density), its details are not well understood. The size, shape, and lifetime of icelike clusters have not, to our knowledge, been determined. Here we investigate a basic geometric aspect of this problem. We ask the question: what is the shape and size of clusters whose density is lower than the bulk density? We use Monte Carlo simulation of the shifted force extended simple point charge (SPC/E) model of water [5,6] to answer the question.

We first introduce an orientational order parameter q [7,8]. It measures the extent to which a molecule and its four nearest neighbors adopt a tetrahedral arrangement, such as exists in hexagonal ice (Ih), and has been used recently as an effective order parameter for crystallization in an aqueous system [9]:

$$q = 1 - \frac{3}{8} \sum_{j=1}^3 \sum_{k=j+1}^4 \left(\cos\psi_{jk} + \frac{1}{3} \right)^2. \quad (1)$$

In the above equation, ψ_{jk} is the angle formed by the lines joining the oxygen atom of a given molecule and those of

its nearest neighbors j and k (≤ 4). If a molecule is located at the center of a regular tetrahedron whose vertices are occupied by its four nearest neighbors, $\cos\psi_{jk} = -1/3$. Thus, in a perfect tetrahedral network, $q = 1$. If, on the other hand, the mutual arrangement of molecules is random, as in an ideal gas, the six angles associated with the central molecule are independent, and the mean value of q vanishes:

$$\langle q \rangle = 1 - \frac{9}{8} \int_0^\pi \left(\cos\psi + \frac{1}{3} \right)^2 \sin\psi \, d\psi = 0. \quad (2)$$

We study clusters formed by molecules whose orientational order parameter q exceeds a certain value q_c . Specifically, if two molecules have q values larger than q_c and are separated by a distance smaller than r_c , they belong to the same cluster. At any given thermodynamic state point, we chose the location of the first minimum in the O-O pair correlation function as the value for r_c .

Other metrics for orientational order in liquids exist. Bond-orientational order parameters, and, in particular, the Q_6 member of this family [10], are useful for describing orientational order as measured by the correlations among angles formed by “bonds” between a central molecule and its nearest neighbors. For water, however, this is not an entirely satisfactory measure of orientational order. We found it to be less sensitive to density than q . A modified Q_6 based on four nearest neighbors should yield information analogous to q but less sensitive to tetrahedrality, because Q_6 is not normalized to detect perfect tetrahedrality.

State points studied in this work span the temperature range $220 \leq T \leq 300$ K, at atmospheric pressure. An initial set of isothermal-isobaric simulations was performed to calculate the densities corresponding to 220, 240, 260, 280, and 300 K at atmospheric pressure. The results reported here correspond to subsequent (N , V , T) simulations at the calculated densities: 0.9748 g/cm³ at 220 K, 0.9843 (240 K), 0.9797 (260 K), 0.9744 (280 K), and 0.9653 (300 K). This indirect way of imposing isobaric conditions was adopted because the geometric analysis on

which this work is based involves the calculation of distances and volumes whose natural fluctuation is greatly amplified by volume fluctuations in (N, P, T) simulations.

Figure 1 shows the cluster size distribution at $T = 240$ K for various choices of q_c . The curves for $q_c = 0.7$ and 0.75 indicate the presence of a large, system-spanning cluster (the number of molecules in the simulation cell is 256). As q_c increases, however, smaller clusters are seen. They are formed by molecules that adopt a progressively more tetrahedral arrangement with their four nearest neighbors. It is on these clusters composed of molecules having a high degree of tetrahedrality that we focus our attention.

Figure 2 shows the average volume per molecule in a cluster as a function of the cluster size (number of molecules in the cluster), at 220 and 240 K (the temperature of maximum density is 240 K). The cluster volume is the sum of the Voronoi volumes of the molecules belonging to the cluster [11,12]. Normalization by the number of molecules yields the average volume per molecule in the cluster. The horizontal line corresponds to the bulk specific volume (note that this is minimum at 240 K). In each case, only the high- q_c curves (0.85, 0.9) rise above the bulk specific volume. Significantly, we find that only those clusters that exceed a threshold size attain a specific volume larger than the bulk. Furthermore, we see that the specific volume of small clusters and individual molecules that adopt highly tetrahedral arrangements with their four nearest neighbors is *smaller* than the bulk value. This means that the formation of icelike regions having a density lower than the bulk is cooperative: it requires the concerted action of several molecules in a

way that extends beyond an isolated central water molecule and its four nearest neighbors.

At 220 K, the specific volume for clusters composed of molecules with $q_c \geq 0.85$ reaches a plateau value. This means that clusters become looser when they grow until they reach a critical size, beyond which further accretion is not accompanied by a density decrease. This saturation effect can be seen for all values of q_c examined, whenever it is possible to observe large enough clusters. In the $q_c = 0.9$ case, the curvature at 220 K is consistent with volume saturation, but we did not observe large enough clusters of such highly structured nature for this effect to occur. At higher temperatures, we could observe only the initial growth of the $q_c = 0.9$ curve.

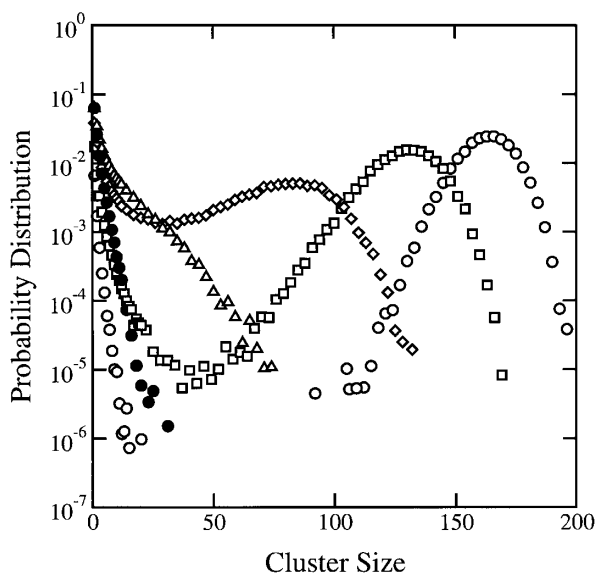


FIG. 1. The cluster size distribution at $T = 240$ K for various choices of q_c : 0.7 (empty circles), 0.75 (empty squares), 0.8 (empty rhombi), 0.85 (empty triangles), 0.9 (solid circles).

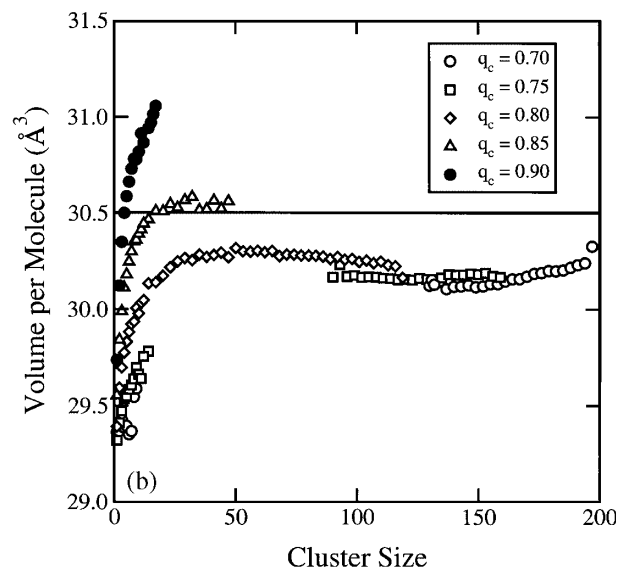
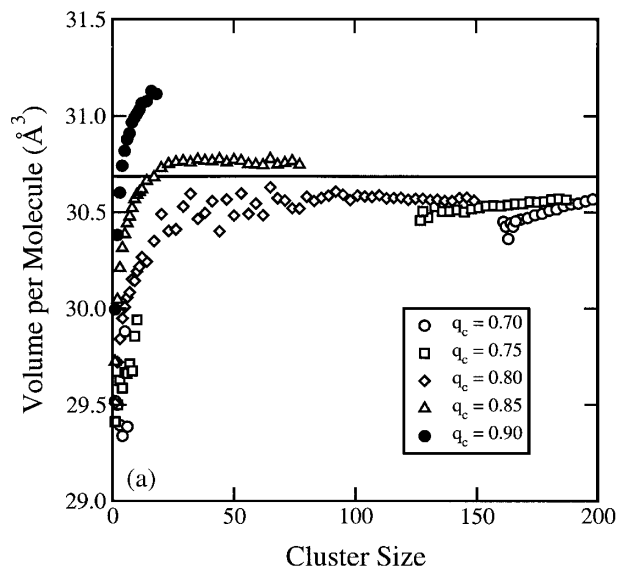


FIG. 2. The average volume per molecule in a cluster as a function of the cluster size at $T = 220$ K (a) and 240 K (b), for various choices of q_c . The horizontal line is the mean (bulk) volume per molecule for the entire simulation cell.

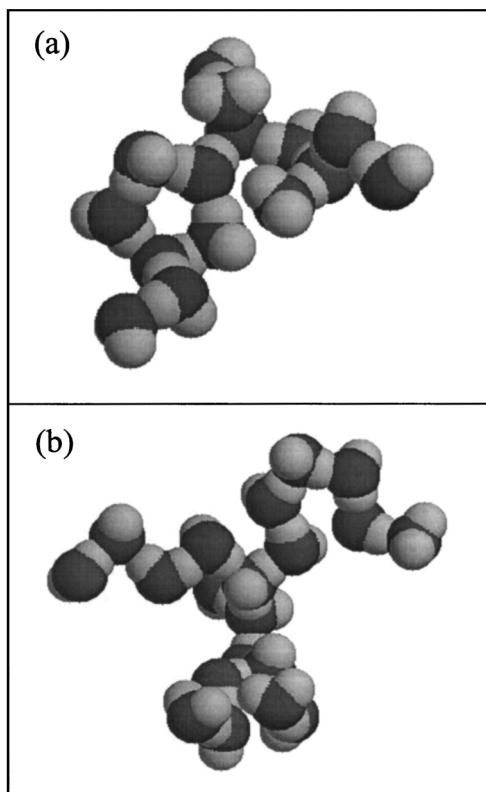


FIG. 3. Snapshots of two representative water clusters from a simulation at $T = 240$ K using $q_c = 0.85$; (a) 15- and (b) 20-membered cluster.

Figure 3 shows snapshots of a 15- and a 20-membered water cluster ($q_c = 0.85$, $T = 240$ K, $\rho = 1$ g/cm³). These are typical of many observations and show that low-density regions in liquid SPC/E water consist of linear or ramified clusters. We see no evidence of three-dimensional, clathratelike objects. Pentagonal and hexagonal rings, one of which is shown in Fig. 3(a), form in sufficiently large clusters. Although hydrogen bonds are not invoked in the definition of a cluster, it can be seen that clusters are, in fact, spontaneously held together by hydrogen bonds.

Extensive statistics on clusters such as those shown in Fig. 3 were collected, and the analysis yielded the results shown in Figs. 4 and 5. The quantity plotted in Fig. 4 is the number of bonds per cluster normalized by the minimum number of bonds, as a function of the cluster size. Calculations are shown for $T = 220$, 240, 260, 280, and 300 K. A bond in this context connects two molecules belonging to the same cluster and separated by a distance less than r_c . The minimum number of bonds in a cluster composed of n molecules is $n - 1$, corresponding to a linear arrangement. In accord with the images of Fig. 3, it can be seen that the clusters are predominantly linear objects: even 80-membered aggregates have barely 8% more bonds than a strictly linear object of the same number of molecules. Ring statistics at $T = 220$, 240,

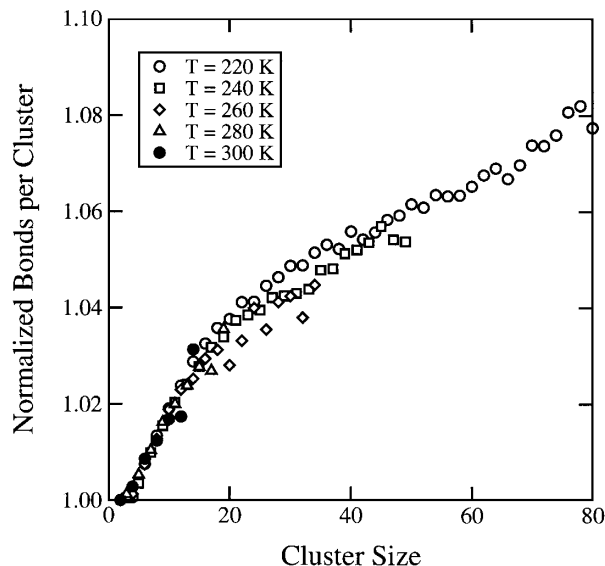


FIG. 4. The number of bonds per cluster normalized by $(n - 1)$, the number of bonds in a linear cluster of that size (n is the number of molecules in the cluster), as a function of the number of molecules in a cluster. The clusters were identified using $q_c = 0.85$ and data were collected at the different temperatures shown.

260, 280, and 300 K are shown in Fig. 5. It can be seen that on average one in every two 30-membered cluster contains a six-membered ring, and every 50-membered cluster contains on average one such ring. Virtually identical results (not shown) were obtained for five-membered rings. Smaller, highly strained rings are virtually never seen. Although the number of clusters of a given size depends on temperature, their geometric characteristics

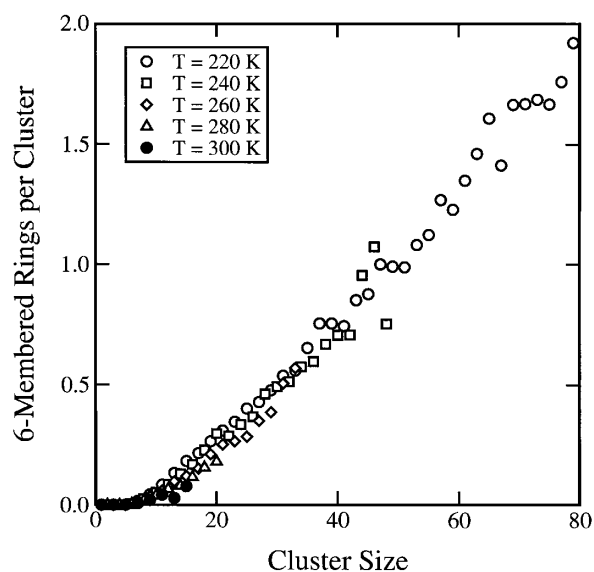


FIG. 5. The average number of six-membered rings per cluster as a function of cluster size. The clusters were identified using $q_c = 0.85$ and data were collected at the different temperatures shown.

show little sensitivity to temperature changes. Six-membered rings have been shown recently to play a key role in the nucleation of ice from supercooled water [13].

There is substantial literature on so-called mixture models of water [14]. In this approach, molecules are also assigned to one of two categories, often referred to as liquidlike and icelike. The former have a smaller specific volume and a larger enthalpy. The present analysis implies that these concepts do not apply locally. Molecules with a highly ordered local environment, as measured by their tetrahedrality with respect to their four nearest neighbors, only acquire a larger-than-average specific volume when they accrete onto a sufficiently large cluster of tetrahedrally arranged molecules. Icelike character, in other words, is cooperative. It is interesting to note that clusters similar to the ones reported here have been recently found to be responsible for the transitions between potential energy minima in supercooled SPC/E water [15].

X-ray diffraction measurements [16] and computer simulation [17–20] have provided molecular-level insight into water's density maximum. Comparison of the center-of-mass pair correlation function for thermodynamic states with the same density but different temperature revealed an increase in the number of so-called interstitial molecules at the expense of hydrogen-bonded molecules upon heating across the temperature of maximum density (interstitial molecules form closely packed arrangements with a central molecule and its hydrogen-bond-acceptor neighbors). The present study suggests that molecular-level understanding of the mechanism by which water expands upon cooling remains incomplete. In particular, the formation of low-density domains is cooperative and cannot be explained solely in terms of structural changes occurring at the nearest- or next-nearest neighbor level.

While the present analysis clarifies the static aspects associated with the formation of low-density regions in cold liquid water, the lifetime of clusters such as those shown in Fig. 3 is important and remains to be investigated. It would also be interesting to identify unambiguously the clusters responsible for water's negative thermal expansion. Both these issues are the subject of our ongoing investigations.

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