

Structure of the first- and second-neighbor shells of simulated water: Quantitative relation to translational and orientational order

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We perform molecular dynamics simulations of water using the five-site transferable interaction potential (TIP5P) model to quantify structural order in both the first shell (defined by four nearest neighbors) and second shell (defined by twelve next-nearest neighbors) of a central water molecule. We find that the anomalous decrease of orientational order upon compression occurs in both shells, but the anomalous decrease of translational order upon compression occurs *mainly in the second shell*. The decreases of translational order and orientational order upon compression (called the “structural anomaly”) are thus correlated only in the second shell. Our findings quantitatively confirm the qualitative idea that the thermodynamic, structural, and hence dynamic anomalies of water are related to changes upon compression in the second shell.

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It is known both from experiments [1–4] and simulations [5–7] that the first shell of a central water molecule, usually defined by the first minimum of the oxygen-oxygen pair correlation function $g(r)$, can accommodate between four and five water molecules, depending on pressure [8]. The signature of this first shell, defined by the first maximum of $g(r)$, barely changes with pressure. In contrast, the properties of the second shell, which extends between the first and second minima of $g(r)$, are highly dependent on pressure, indicating that large structural changes occur in this shell upon compression [2].

The structural order of water has been quantified by two measures [9]: A local *orientational* order parameter q , which quantifies the extent to which a molecule and its four nearest neighbors adopt a tetrahedral local structure in the first shell, and a *translational* order parameter t , which quantifies the tendency of molecular pairs to adopt preferential separations. While q depends only on the four nearest neighbors of a central molecule in its first shell, t depends on all the neighbors of the central molecule.

Water in the *liquid* phase displays: (i) A thermodynamic anomaly (density decrease upon cooling or, equivalently, entropy increase with pressure); (ii) a dynamic anomaly (increase of diffusivity upon compression); (iii) a structural anomaly (decrease of both q and t upon compression) [9]. Several other liquids with local tetrahedral order [10] such as silica, silicon, carbon, and phosphorous also show waterlike anomalies. In the case of water [9] and silica [11], computer simulation studies show that the anomalies (i)–(iii) in the liquid phase are closely related. For example, in the case of water, the region of thermodynamic anomaly in the temperature-density (T - ρ) plane is enclosed by the region of dynamic anomaly, which in turn is enclosed by the region of structural anomaly [9].

Recent studies show that simple liquids interacting via spherically-symmetric potentials can exhibit waterlike anomalies [12–18], suggesting that strong orientational interactions in the first shell are not *necessary* for a liquid to show

thermodynamic, dynamic, and structural anomalies and thus pointing out the importance of the second shell of water [12]. In light of these findings, it remains unclear how much the strongly orientation-dependent first-shell interactions and the second-shell environment each contribute to water’s anomalies. To address these questions, we first modify the definition of first and second shells for the purpose of quantitative study. Then we define the orientational and translational order parameters within each shell and study their changes with T and ρ .

Computer simulations of different water models [7,8,19] reproduce similar structural changes in water upon compression despite small differences in structural details compared to experiments [e.g., peak height in $g(r)$] [20]. We perform constant volume isothermal (*NVT*) molecular dynamics simulation of 512 TIP5P (five-site transferable interaction potential) water molecules. Our simulations are performed using a cubic box with periodic boundary conditions. We control the temperature using a Berendsen thermostat. The TIP5P model reproduces the thermodynamic properties of liquid water over a broad region of the phase diagram [19] although it does not reproduce well the phase diagram of solid water [21]. However our study concentrates on the liquid or supercooled phase of water at low T without crystallization. In particular, we find that the TIP5P model reveals similar relations between the thermodynamic, dynamic and structural anomalies (see Fig. 1) as observed in [9] using the SPC/E model.

The first and second shells of water can be defined according to the first and second minima of $g(r)$. For this definition, the number of molecules in each shell will change with pressure and temperature [6,8]. But the orientational measures that most concern us are the tetrahedral arrangement of nearest neighbors, and bond orientational order in next-nearest neighbors of a central molecule. To see how these orders evolve across a broad range of state points, we must base our comparison on a fixed number of nearest and next-nearest neighbors. Moreover, the minima in $g(r)$ be-

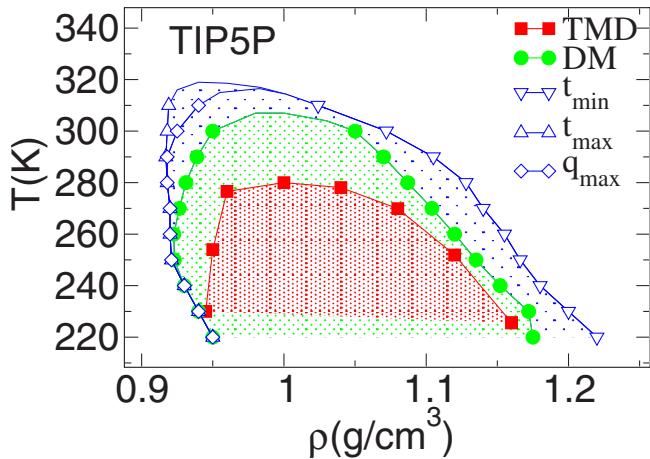


FIG. 1. (Color online) Anomalous regions in the T - ρ plane. (i) The density anomaly region is defined by the locus of density maxima (TMD), inside of which the density increases when the system is heated at constant pressure. (ii) The diffusion anomaly region is defined by the loci of diffusion maxima or minima (DM), inside which the diffusivity increases with density. (iii) The structural anomaly region is defined by the loci of translational order minima (t_{\min}) and maxima (t_{\max}), or orientational order maxima (q_{\max}), inside which both translational and orientational orders decrease with density (see Fig. 3).

come less obvious at high ρ , and $g(r)$ becomes almost featureless beyond the first peak at high ρ [see Fig. 2(b)]. Hence we choose a less ambiguous shell definition by denoting the nearest four and next-nearest twelve neighbors of a central water molecule as the first and second shells, respectively.

We first study the average effect of density on different shells by dividing $g(r)$ into three regions. We compute the average number of neighbors of a central molecule at a distance r as

$$N(r) \equiv 4\pi n \int_0^r r'^2 g(r') dr', \quad (1)$$

where n is the number density. We define r_1 and r_2 such that $N(r_1)=4$ and $N(r_2)=16$. Therefore, we can define three regions: $0 < r \leq r_1$ (first shell), $r_1 < r \leq r_2$ (second shell), and $r > r_2$, where r_1 and r_2 depend on T and ρ . We find that in general r_1 and r_2 decrease with ρ for different T due to the compression effect. Figure 2(a) shows $N(r)$ at $T=280$ K and $\rho=1.00$ g/cm³ ($n=33.4$ /nm³), where $r_1=0.32$ nm and $r_2=0.48$ nm.

Figure 2(b) shows $g(r)$ of TIP5P water at $T=280$ K for a range of density covering the anomalous regions of water of Fig. 1. Figure 2(c) shows the change upon compression, $\Delta g(r) \equiv g(r)|_{\rho} - g(r)|_{\rho_0}$, where $\rho_0=0.88$ g/cm³. Figure 2(d) shows the corresponding change, $\Delta N(r) \equiv N(r)|_{\rho} - N(r)|_{\rho_0}$. Figure 2(b) shows that as ρ increases, the first peak of $g(r)$ decreases, so $\Delta g(r) < 0$ at $r=0.28$ nm in Fig. 2(c). This effect of ρ on $g(r)$ is a result of having a fixed number of neighbors at $r \approx 0.28$ nm, normalized by n in the definition of $g(r)$. The change of the number of neighbors corresponding to the first peak of $g(r)$ is barely distinguishable [see Fig. 2(d)], i.e.,

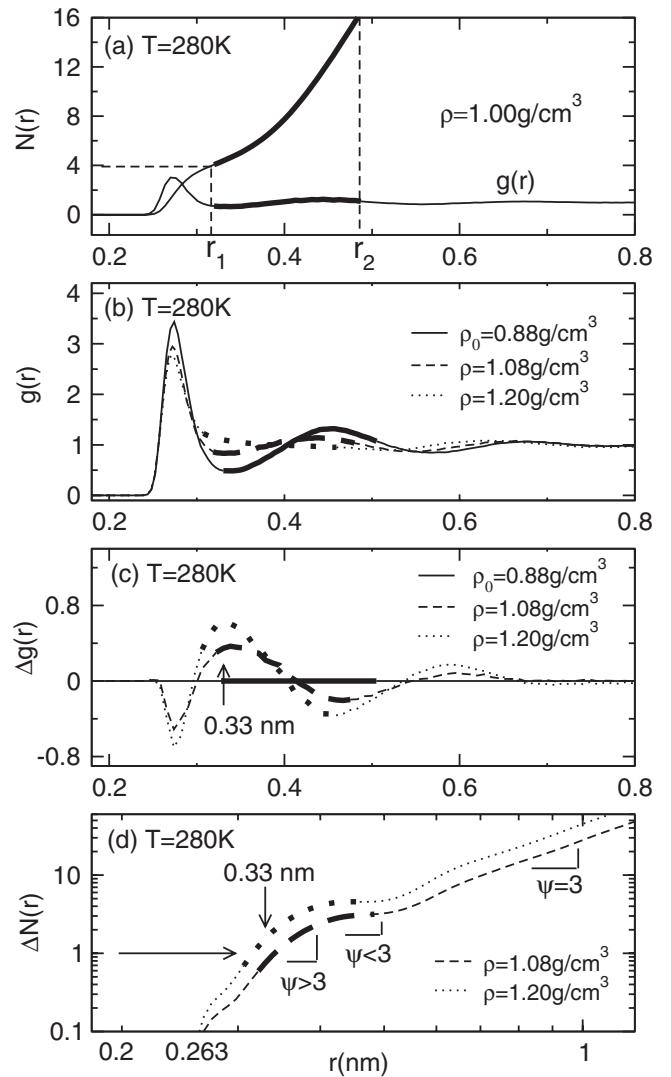


FIG. 2. (a) The number of neighbors $N(r)$ around a central water molecule. r_1 and r_2 correspond to the first and the second shell distances, defined such that $N(r_1)=4$ and $N(r_2)=16$. (b) Oxygen-oxygen pair correlation function $g(r)$. (c) Difference $\Delta g(r)$ between $g(r)$ at a given density and $g(r)$ at ρ_0 and (d) difference $\Delta N(r)$ between $N(r)$ at a given density and $N(r)$ at ρ_0 for TIP5P water. ψ characterizes the local slope. The bold portions of the curves correspond to water's second shell, $r_1 < r \leq r_2$, showing that the largest changes upon compression occur in the second shell.

$\Delta N(r) \approx 0-0.2$ for $r \approx 0.28$ nm. This suggests that the distance defined by the first peak of $g(r)$ is practically impenetrable and thus it roughly resembles a hard core. The main changes in $g(r)$ [Fig. 2(b)] and $\Delta g(r)$ [Fig. 2(c)] occur in the second shell ($r_1 > r > r_2$). As the density increases, hydrogen bond bending allows water molecules in the second shell to shift toward the first shell, filling the interstitial space [2]. The changes of $g(r)$ with pressure for $r > r_2$ are minimal.

Figure 2(d) shows in double logarithmic scale the relationship between $\Delta N(r)$ and r . The slope of the curve, ψ , characterizes the power law dependence $\Delta N(r) \propto r^{\psi}$. There are three main regimes in the behavior of $\Delta N(r)$ as shown by the different slopes $\psi > 3$, $\psi < 3$, and $\psi = 3$. The $\psi = 3$ regime at $r > r_2$ is mainly due to the density change, since $g(r) \approx 1$.

$[\Delta g(r) \approx 0]$ for $r > r_2$, so $\Delta N(r)$ behaves approximately as $\Delta N(r) \propto r^3 \Delta \rho$ with $\Delta \rho \equiv \rho - \rho_0$. Both the $\psi > 3$ and $\psi < 3$ regimes are located within the second shell. The increase of $\Delta N(r)$ for $r < r_2$ is not only due to density increase, but also due to the shift of water molecules from the second shell around 0.45 nm toward the first shell around 0.28 nm. Thus the regime where $\psi > 3$, for roughly $r < 0.4$ nm, is due to an increase of $g(r)$ [$\Delta g(r) > 0$], and $\psi < 3$ for roughly $0.4 \text{ nm} < r < r_2$ is due to the decrease of $g(r)$ [$\Delta g(r) < 0$]. Note that $\Delta N(r) = 1$ at $r \sim 0.33$ nm for $\rho = 1.08 \text{ g/cm}^3$, corresponding to the fifth neighbor [8], which is very close to the border of the first shell, where $\Delta g(r)$ has its maximum value. This fifth neighbor in the vicinity of the first shell of water can produce a defect in the tetrahedral network of water at high density. This defect leads to hydrogen bond bifurcation and offers paths with low energy barriers between different network configurations of water. It is also related to diffusion anomaly by lowering energy barriers for translational and rotational motions of water molecules [8].

The translational order parameter t is defined in Refs. [9,11,15,22]

$$t \equiv \int_0^{s_c} |g(s) - 1| ds, \quad (2)$$

where the dimensionless variable $s \equiv rn^{1/3}$ is the radial distance r scaled by the mean intermolecular distance $n^{-1/3}$, and s_c usually corresponds to half of the simulation box size, which is large enough to have $g(s_c) \approx 1$. We can decompose the translational order parameter t into t_1 , t_2 , and t_3 for each shell of water by integrating $|g(s) - 1|$ over the three different regions $0 < s \leq s_1$, $s_1 < s \leq s_2$, and $s > s_2$, where $s_1 = r_1 n^{1/3}$ and $s_2 = r_2 n^{1/3}$. Note that

$$t = t_1 + t_2 + t_3. \quad (3)$$

The orientational order q_i is used to quantify the tetrahedrality of the first shell, defined as [9]

$$q_i \equiv 1 - \frac{3}{8} \sum_{j=1}^3 \sum_{k=j+1}^4 \left[\cos \theta_{jik} + \frac{1}{3} \right]^2. \quad (4)$$

θ_{jik} is the angle formed between neighbors j and k and the central molecule i . The average value

$$q \equiv \frac{1}{N} \sum_{i=1}^N q_i \quad (5)$$

quantifies the orientational order of the system based on the molecules in the first shell. For perfect tetrahedral order, $q=1$; for an uncorrelated system, $q=0$.

Because the second shell of the hexagonal ice crystal forms an hcp lattice, the orientational order parameter for the second shell of water can be characterized by Q_{6i} , which quantifies the extent to which a molecule i and twelve of its neighbors adopt the local fcc, bcc, or hcp structures. This orientational order parameter [23] is often used for simple liquids [15,22,24] because they have fcc or bcc crystal structures. In order to compute Q_{6i} , we first define twelve bonds connecting each water molecule i with its twelve next-

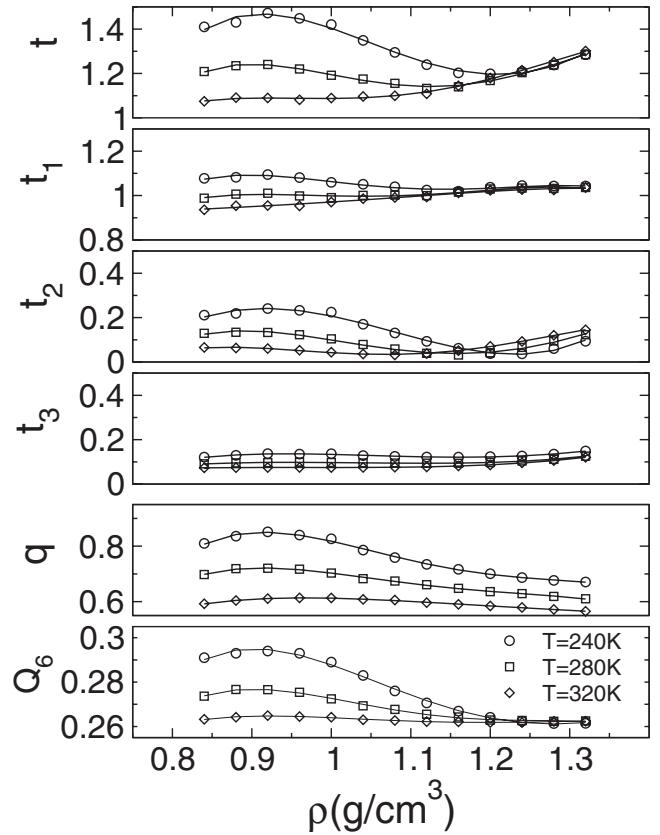


FIG. 3. Translational order parameters t ($=t_1+t_2+t_3$), t_1 (first shell), t_2 (second shell), t_3 and orientational order parameters q (first shell), Q_6 (second shell) of TIP5P water as function of density at different T . The anomalous decrease of orientational order upon compression occurs in both shells (q, Q_6), but the anomalous decrease of translational order upon compression mainly occurs in the second shell (t_2).

nearest neighbors in the second shell, and compute for each bond its azimuthal and polar angles (θ, φ) . Next we compute $\bar{Y}_{\ell m}(\theta, \varphi)$, the average of the spherical harmonic function over the 12 bonds of the molecule i . Finally we compute

$$Q_{\ell i} \equiv \left[\frac{4\pi}{2\ell + 1} \sum_{m=-\ell}^{\ell} |\bar{Y}_{\ell m}|^2 \right]^{1/2}. \quad (6)$$

For $\ell=6$, the average value

$$Q_6 \equiv \frac{1}{N} \sum_{i=1}^N Q_{6i} \quad (7)$$

quantifies the orientational order of the system based on the molecules in the second shell. Q_6 is large [23] for most crystals such as fcc (0.574), bcc (0.511), and hcp (0.485). For uncorrelated systems, $Q_6 = 1/\sqrt{12} = 0.289$.

Figure 3 shows the density dependence of all six order parameters at three temperatures covering the anomalous region of TIP5P water (see Fig. 1). Although t_1 is much larger than t_2 and t_3 , it is apparent that t_2 makes the most important contribution to the anomaly of t (decrease of t with increasing density), compared to t_1 and t_3 . t_1 also makes a small

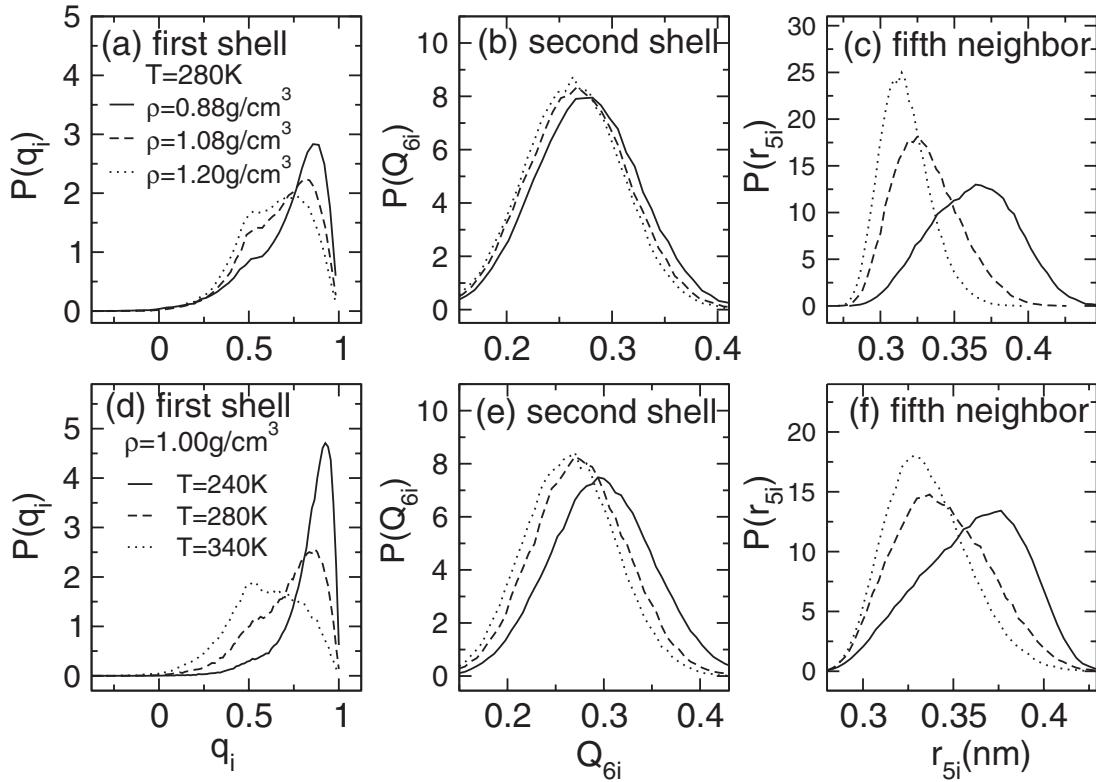


FIG. 4. Histograms of (a) the local orientational order q_i in the first shell, (b) Q_{6i} in the second shell, and (c) distance r_{5i} between a central water molecule i and its fifth neighbor of TIP5P water. (a), (b), and (c) show the changes for three different ρ at fixed $T=280\text{ K}$. (d), (e), and (f) show the changes for three different T at fixed $\rho=1.00\text{ g/cm}^3$. Upon compression or heating over the anomalous regions of the phase diagram, the fifth neighbor (and other interstitial water molecules in the second neighbor shell) shift towards first shell (see also Fig. 2 and [7]), corresponding to anomalous changes of structural order in the first and second shells, as quantified by Figs. 3 and 5.

contribution to the t anomaly at low $T=240\text{ K}$ due to a small decrease in the first peak of $g(r)$ upon compression. The anomalous behavior of t becomes weak at $T=280\text{ K}$ and disappears at $T=320\text{ K}$. The orientational order parameters q and Q_6 both show similar anomalous behavior. The distribution of individual q_i shifts from high q (icelike) at low ρ and T to low q (less tetrahedral) at high ρ and T as shown in Figs. 4(a) and 4(d), due to increased hydrogen bond bifurcation [8] as interstitial molecules move closely to the first shell [Figs. 4(c) and 4(f)]. Q_{6i} always has approximately normal distribution as shown in Figs. 4(b) and 4(e) because there is no direct bonding between a central water molecule and its second shell neighbors.

A useful way of investigating structural order in fluids is to map state points onto the t - q plane, a representation called the order map [9,15,24]. The order map for TIP5P water (i.e., using t and q) is shown in Fig. 5(a). This order map is similar to the one found in [9] using the SPC/E model. Its main characteristic is the correlation of the two order parameters in the anomalous regions where both q and t decrease with density, as shown by the isotherms collapsing onto a line. Recently an entropy-based measure of structural order in water [25] has revealed that the correlated order map is invariant to the choice of different measures, suggesting that such a correlation is a general feature of waterlike liquids. Figures 5(b)–5(h) show the different order maps obtained by considering the order parameters in different shells. The only one

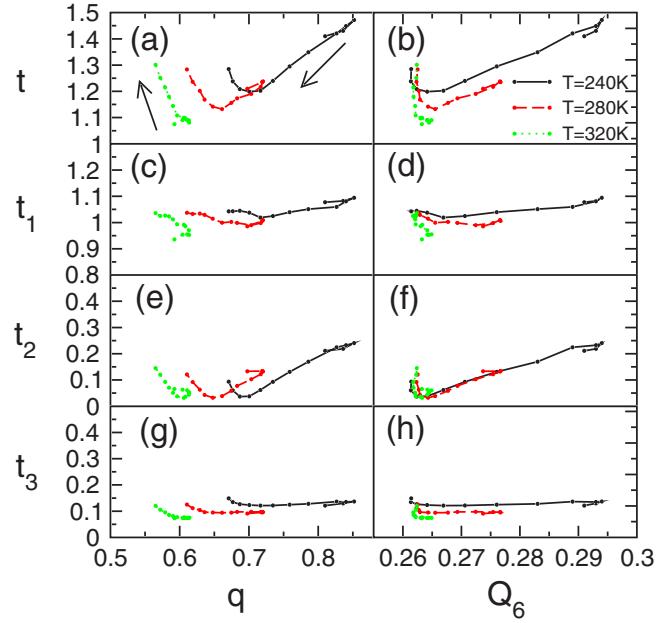


FIG. 5. (Color online) Order maps for TIP5P water. The arrows indicate the direction of increasing density from 0.84 g/cm^3 to 1.32 g/cm^3 . Only for the second shell order map, t_2 - Q_6 in (f), the isotherms collapse on a line and the decrease of translational and orientational orders is correlated.

that shows the states in the thermodynamically, dynamically and structurally anomalous regions collapsing onto a line, is Fig. 5(f) (i.e., the “ t_2 - Q_6 ” order map of the second shell), indicating that the changes in the second shell are related to anomalies of water.

The first shell “ t_1 - q ” order map in Fig. 5(c) is not correlated because t_1 has only small changes with increasing density due to the roughly impenetrable hard core at ≈ 0.28 nm, while q changes significantly with density. In the second shell, t_2 and Q_6 both change significantly and simultaneously with density so that they are well correlated. Our work quantitatively shows that the second shell is related to anomalies of water by its gradual shift towards first shell upon compression. In addition to water, other tetrahedral liquids such as silica, silicon, carbon and phosphorous [10] may also exhibit similar behavior, and a detailed, shell-based study of their order parameters may prove useful.

In summary, we performed molecular dynamics simulations of water to quantify structural order in both the first shell and the second shell of a central water molecule. We found that the anomalous decrease of orientational order upon compression occurs in both shells, but the anomalous decrease of translational order upon compression occurs *mainly in the second shell*. The decreases of translational and orientational orders upon compression (called the “structural anomaly”) are thus correlated only in the second shell. Our findings *quantitatively* confirm the *qualitative* idea that the thermodynamic, structural, and hence dynamic anomalies of water are related to changes upon compression in the second shell.

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