Structural and thermodynamic properties of different phases of supercooled liquid water

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Computer simulation results are reported for a realistic polarizable potential model of water in the supercooled region. Three states, corresponding to the low density amorphous ice, high density amorphous ice, and very high density amorphous ice phases are chosen for the analyses. These states are located close to the liquid-liquid coexistence lines already shown to exist for the considered model. Thermodynamic and structural quantities are calculated, in order to characterize the properties of the three phases. The results point out the increasing relevance of the interstitial neighbors, which clearly appear in going from the low to the very high density amorphous phases. The interstitial neighbors are found to be, at the same time, also distant neighbors along the hydrogen bonded network of the molecules. The role of these interstitial neighbors has been discussed in connection with the interpretation of recent neutron scattering measurements. The structural properties of the systems are characterized by looking at the angular distribution of neighboring molecules, volume and face area distribution of the Voronoi polyhedra, and order parameters. The cumulative analysis of all the corresponding results confirms the assumption that a close similarity between the structural arrangement of molecules in the three explored amorphous phases and that of the ice polymorphs Iᵥ, III, and VI exists. © 2008 American Institute of Physics.

[I. INTRODUCTION]

Understanding the origin of the anomalous behavior of water is in the focus of intensive scientific investigations for many years. Besides the well known density anomaly, water exhibits a set of other anomalous features both in thermodynamically stable and in supercooled liquid states. Thus, among others, the thermodynamic response functions, such as the heat capacity and isothermal compressibility increase rapidly with decreasing temperature, and either go through a maximum or diverge in the supercooled region of the phase diagram.¹-³

The possible explanations of the density anomaly proposed in the past century belong to two major groups, based on two different assumptions. The first type of explanation goes back to the mixture model of Röntgen,¹ and is based on the assumption that water is the mixture of two different types of structural elements. Among others, the popular iceberg model of the 1960s (Ref. 5) or the isobestic model of Robinson et al.⁶,⁷ belong to this family. However, there is now a growing consensus in the literature that the reason behind the density anomaly is not the presence of two different structural elements in water, but that of two different types of interaction between the water molecules. As it has been shown by Jagla, a simple model potential that corresponds to two equilibrium distances of the particles already leads to the density anomaly.⁸ Svishchev and Kusalik demonstrated that in water the distance of two neighboring particles also has two equilibrium values: besides the O–O distance of about 2.7 Å, corresponding to the hydrogen bonded pairs, the orientational pair correlation function g(r,Ω) has also another peak at the O–O distance of 3.5 Å in nontetrahedral directions.⁹ This peak reflects the presence of the interstitial neighbors, which are located at the cavities of the tetrahedral hydrogen bonding network of the molecules, and are forming closely packed structural units with their neighbors.¹⁰ Upon cooling, the fraction of the interstitial neighbors, and hence that of the closely packed structural units, decreases. This effect can compensate the increase of the density due to the lowering of the thermal motion of the molecules, and hence leads to the density anomaly.¹¹

In order to explain the anomalies occurring in supercooled water Speedy and Angell made the hypothesis that the liquid spinodal line of water is of anomalous shape.³,¹²-¹⁴ The liquid spinodal is the line that connects the points on the p-T plane beyond which the liquid state is no longer even metastable, and hence it gives the thermodynamic limit of

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the existence of the liquid phase. This line originates from the critical point, and normally goes to lower pressures with decreasing temperature. In their “stability limit conjecture” speedy and angell postulated that in water the slope of the spinodal changes sign in the negative pressure part of the phase diagram, and upon further decrease of the temperature it goes back to higher pressures, and reenters to the range of positive pressures in the supercooled region. The anomalous presence of this spinodal line in the supercooled region of water would then be responsible for the observed anomalies.3

An alternative explanation assumes that at least two different liquid phases of water exist in the supercooled region, and these two phases are separated by a line of a first order phase transition, which terminates in a second (liquid-liquid) critical point.15–17 Some arguments led to the assumption that this second critical point is at negative pressures.18,19 According to this explanation, the observed anomalies of supercooled water reflect the presence of this second critical point. In fact, several different phases of supercooled water, such as low density amorphous ice (LDA),20 high density amorphous ice (HDA),21 and very high density amorphous ice (VHDA),22 have been experimentally detected, however, the first order character of the phase transitions separating these forms of supercooled water has not been proved. Thus, a third possible explanation of the anomalies assumes that upon isobaric cooling the thermodynamic response functions of water go through a finite maximum, and hence this interpretation is free from singularities.23,24 A review discussing the possibilities of both the liquid-liquid critical point and the singularity free scenarios as well as their combination proposing only one liquid-liquid critical point between different phases of amorphous ice has recently been given by loerting and giovambattista.25

These theories only predict different behavior of water in extreme thermodynamic conditions, such as in deeply supercooled states and at negative pressures, which makes their experimental tests almost impossible. Such states can, on the other hand, be relatively easily accessed in computer simulations. However, since in a computer simulation the real system of interest is always replaced by an appropriate model, simulation results can strictly prove the validity of one or the other theory only for the particular model studied, although the verification of a theory for a given model certainly supports its applicability to the real system, as well. This support is stronger if the theory is proven to be valid for (i) several different models, and (ii) for models that reproduce the relevant properties of the real system better than others.

The validity of both the stability limit conjecture and the hypothesis of the liquid-liquid critical point has been intensively studied by computer simulation methods. The behavior of several simple, nonpolarizable water models, such as ST2,26 TIP4P,27 or SPC/E,28 was found to be incompatible with the stability limit conjecture.29–31 Further, these water models were shown to exhibit more than one supercooled liquid phases.32,33 In a series of studies we investigated the behavior of the polarizable BSV water model34 in this respect. We found that this model reproduces the temperature of maximum density of water far better than the conventional, simple nonpolarizable models,35,36 the isochor temperature difference of the x-ray scattering pattern of water,37 and also the temperature dependence of its thermodynamic response functions.38 Further, by performing Gibbs ensemble Monte Carlo simulations we showed that different supercooled liquid phases of BSV water can coexist, and hence they are separated by a first order phase transition.39 We found at least two liquid-liquid phase equilibria, and thus three different supercooled liquid phases, which can be identified as phases of LDA, HDA, and VHDA, respectively. Similar polymorphism was observed by Truskett et al. using a simple statistical mechanical model,40 by Brovchenko et al. for several simple, nonpolarizable water models,32,33 and by Morishita for a model of liquid Si.44 Analyzing the O–O partial pair correlation function we recently demonstrated, in accordance with earlier statistical mechanical models,45,46 that the local structure of the LDA, HDA, and VHDA phases of supercooled water shows very strong similarities with the ice polymorphs Ih, III, and VI, respectively.46 This result also resolved the seeming contradiction between the interpretation of the experimental data of soper and ricci47,48 and the computer simulation results of Saitta and Datchi49 obtained on low and high density water at temperatures well above any possible liquid-liquid phase transition. However, in this study we did not go beyond the analysis of the pair correlation function of the oxygen atoms.

In this paper we present a detailed analysis of the structural and thermodynamic properties of these three phases of supercooled water. Besides the pair correlation functions we investigate the characteristics of the local environment of the molecules, their ordering in the different phases, and analyze angular distributions. The results are compared to those obtained in the Ih, III, and VI ice polymorphs as reference systems. We focus our interest to two major points, namely, (i) the relation of the hydrogen bonded and interstitial neighbors in the different phases, and (ii) the question how the degree of ordering of the molecules changes when going from lower to higher density phases. The paper is organized as follows. In Sec. II details of the simulations performed are given. Then the obtained results concerning the pair correlation functions, angular distributions, local environment of the molecules, degree of ordering of the molecules, and thermodynamic properties of the systems are presented in Secs. III–VII, respectively. Finally, in Sec. VIII the conclusions of this study are summarized.

II. COMPUTER SIMULATIONS

Monte Carlo simulations of supercooled water have been performed on the canonical (N, V, T) ensemble at the temperature of 200 K at three different densities, i.e., 1.00, 1.12, and 1.24 g/cm3 using the polarizable BSV potential model.44 The above three thermodynamic states correspond to the LDA, HDA, and VHDA phases of supercooled BSV water, respectively (see Fig. 1). The edge length of the cubic simulation box of these systems has been 19.7166, 18.9856, and
and to site $A$ the dipole moment induced on molecule $j$ is expressed by the fractional charges of +0.499 centered on the O atom. The H atoms carry fractional positive charges on the O atom. The H–O–H angle is 104.52°.

The polarization of the molecules is described by induced point dipoles, located at the center of mass of the molecules, i.e., along the bisector of the O–H–O angle at the distance of 0.20 Å from the O atom. The (scalar) polarizability of the model is 1.444 Å$^3$, the length of the O–H bonds is 0.9572 Å, and the H–O–H angle is 104.52°.

The energy of the system has been calculated as the sum of the interaction energies of the molecular pairs and of the term coming from the polarization of the molecule,

$$U_{\text{POL}} = -\frac{1}{2} \sum_{i=1}^{N} \mathbf{\mu}_{\text{ind}}^{i} \cdot \mathbf{E}_{i}^{0},$$

where $\mathbf{E}_{i}^{0}$ is the electric field at the center of molecule $i$ due to the fixed point charges of the other molecules, and $\mathbf{\mu}_{\text{ind}}^{i}$ is the dipole moment induced on molecule $i$,

$$\mathbf{\mu}_{\text{ind}}^{i} = \frac{\alpha}{4 \pi \varepsilon_{0}} \sum_{j \neq i} \left( \frac{3 \mathbf{r}_{ij} \mathbf{\mu}_{\text{ind}}^{j} - \mathbf{\mu}_{\text{ind}}^{j}}{r_{ij}^3} \right) + \sum_{A=1}^{3} q_{A} \mathbf{r}_{i,A}^{\text{A}}.$$

Here, $\alpha$ is the polarizability of the model, $\varepsilon_{0}$ is the vacuum permittivity, index $A$ runs over the three charged sites of molecule $j$, $q_{A}$ is the charge of site $A$, whereas $\mathbf{r}_{ij}$ and $\mathbf{r}_{i,A}^{\text{A}}$ are the vectors pointing from the dipole induced on molecule $i$ (i.e., its center of mass) to the dipole induced on molecule $j$ and to site $A$ of molecule $j$, respectively. Since the dipole induced on a molecule depends on the dipoles induced on the other molecules, the full set of the induced dipoles can only be determined by an iterative procedure. At the beginning of the simulations all the induced dipoles have been set to zero, and in each simulation step this iteration stopped once the set of the $\mathbf{\mu}_{\text{ind}}$ values have changed less than 0.1% in one iteration step. Since one Monte Carlo step usually represent a rather small perturbation of the system, this convergence has usually been reached already in the first iteration step. All interactions have been truncated to zero beyond the center-center cutoff distance of 9.0 Å. The reaction field correction method has been applied, under conducting boundary conditions, to calculate the long range part of both the pairwise additive charge-charge interactions and the interactions related to the polarization of the molecules. The long range part of the Lennard-Jones interaction has been accounted for using the assumption that the O–O partial pair correlation function converges to unity beyond the cutoff distance.

In each simulation step a randomly chosen water molecule has been randomly translated by no more than 0.2 Å, and randomly rotated around a randomly chosen space-fixed axis by no more than 10°. About 30% of these steps have lead to a successful move. The systems have been equilibrated by performing $10^4 \times N$ Monte Carlo steps ($N$ being the number of the molecules). Then 200 sample configurations per system, separated by 100 $\times N$ Monte Carlo steps each have been saved for the analyses.

Besides the three supercooled liquid phases of water, we also simulated the Ih, III, and VI phases of ice as reference systems at 100 K. The ice simulations have been performed in the same way as the simulations of the supercooled liquid phases, with the only difference that, due to the symmetry of the different ice crystals, here the basic simulation box has been of rectangular shape, and the length of its edges, the cutoff distance beyond which all interactions are truncated to zero and the number of the water molecules has been changed accordingly in each phase. Thus, 192, 324, and 270 water molecules, 18.072 $\times 15.615 \times 22.068$ Å$^3$, 19.998 $\times 20.808$ Å$^3$, and 18.543 $\times 17.094$ Å$^3$, basic boxes, and 7.5, 9.0, and 8.5 Å interaction cutoff distances have been used in the simulation of the Ih, III, and VI polymorphs of ice, respectively.

### III. PARTIAL PAIR CORRELATION FUNCTIONS

The partial pair correlation functions obtained in the three phases of supercooled water are shown in Fig. 2. The behavior of these functions is in a good agreement with recent experimental data and with the oxygen-oxygen pair correlation function of TIP4P water as obtained at different pressures at 80 K. The main difference between the three sets of functions is the position of the second peak of the oxygen-oxygen pair correlation function $g_{OO}(r)$ in the higher density phases this peak appears at progressively lower distances, i.e., at 4.35, 3.75, and 3.35 Å in LDA, HDA, and VHDA, respectively. This change is in a good agreement with experimental results obtained for low and high density water well above any possible liquid-liquid critical point. We have recently shown that this shift reflects structural differences between the LDA, HDA, and VHDA phases that are highly analogous with those between the ice polymorphs Ih, III, and VI, respectively. The corresponding ice and supercooled liquid phases differ mainly in...
the long-range order of the molecules, while their local structure is very similar to each other. This structural analogy is illustrated in Fig. 3 by comparing the \( g_{\text{OO}}(r) \) functions of the corresponding ice and supercooled liquid phases. Thus, in LDA, just as in ice \( I_h \) the molecules are surrounded by four, tetrahedrally coordinated hydrogen bonded neighbors, and the fraction of the interstitial neighbors, located at the O–O distance of about 3.5 Å is very low. The presence of the tetrahedrally coordinated hydrogen bonded neighbors is characteristic of all the supercooled water phases and ice polymorphs; however, with increasing density the \( g_{\text{OO}}(r) \) function clearly increases around the position of the interstitial neighbors at 3.5 Å. This finding is in accordance with experimental data\(^{54,56}\) as well as with the results of Saitta and Datchi obtained at temperatures well above any possible liquid-liquid critical point,\(^{49}\) and is in a clear analogy with the fact that the high density ice polymorph VI is built up by two interpenetrating hydrogen bonded networks, where the molecules of one network occupy the interstitial positions of the other one.\(^{57}\)

It is also clear from Fig. 2 that the hydrogen bonding structure of the water molecules is remarkably insensitive to the changes in the density of the system. Thus, the first peak of the \( g_{\text{OO}}(r) \), and first two peaks of the \( g_{\text{OH}}(r) \) and \( g_{\text{HH}}(r) \) functions are all found to be very similar in the three different phases. The only noticeable difference is a slight decrease of the height of these peaks in the higher density phases. However, this change can simply be attributed to the fact that, by definition, the pair correlation function is normalized by the bulk phase density of the system, and therefore the same hydrogen bonding local structure results in lower peaks at higher densities. In accordance with this explanation, the coordination number of the first peak of \( g_{\text{OO}}(r) \) and \( g_{\text{OH}}(r) \) is found to be 4.1 and 2.0, respectively, in all the three phases of supercooled water. This result clearly indicates that neither the number of the hydrogen bonded neighbors, nor their distance from the central molecule, nor their orientation depends noticeably on the density of the system.

In order to investigate the origin of the increasing number of the interstitial neighbors in the higher density phases we have calculated the contribution of the \( i \)th topological hydrogen bonded neighbors of the molecules to the oxygen-oxygen partial pair correlation function. We consider a molecule to be the \( i \)th topological neighbor of the central one if the shortest path connecting these two molecules along intact hydrogen bonds involves exactly \( i \) consecutive bonds. Thus, the first topological neighbors are the hydrogen bonded neighbors of the molecules themselves; the second topological neighbors are the hydrogen bonded neighbors of the first topological neighbors, etc. In this analysis we define two molecules as being hydrogen bonded to each other if the distance of their O atoms is less than 3.3 Å, and, at the same
time, the distance of the (bonding) H atom of one molecule from the O atom of the other molecule is less than 2.45 Å. These limiting distances correspond to the first minimum position of the $g_{OO}(r)$ and $g_{OH}(r)$ functions at 1.00 g/cm$^3$, respectively.

The contributions of the $i$th topological hydrogen bonded neighbors of the molecules to $g_{OO}(r)$ are shown for $i=1$ in Fig. 4 as obtained in the three supercooled phases of water and in the three ice polymorphs considered. The contribution of the first topological neighbors covers completely the first peak of $g_{OO}(r)$ in every case. This indicates that, unlike in ambient liquid water, the distance range of the interstitial neighbors practically does not overlap with that of the hydrogen bonded neighbors at these low temperature states. In LDA the peak of the contribution of the $i$th topological neighbors appears at progressively larger distances with increasing values of $i$, namely, at 4.3 Å [i.e., at the position of the second peak of $g_{OO}(r)$] for $i=2$, at 6.4 Å [close the third peak of $g_{OO}(r)$] for $i=3$, and at 7.9 Å for $i=4$. Although these peaks are also present in HDA and VHDA, here these contributions are bimodal, having their other peak always at about 3.5 Å, i.e., at the distance characteristic of the interstitial neighbors. At this position in LDA the contributions of the third and fourth topological neighbors show only a small shoulder. In HDA these contributions already develop a clear peak, and also the single peak of the second topological neighbors appears at clearly lower distances (i.e., at 4.0 Å) than in LDA, indicating the appearance of a second peak at 3.5 Å that is not yet resolved from the other peak at 4.3 Å. In VHDA these two peaks are already resolved for $i=2$, and for $i=3$ the peak at 3.5 Å is almost as high as the other one. Further, a clear peak at 3.5 Å can still be observed for $i=4$, and some traces of it even for $i=5$. Very similar behavior is seen in the three ice polymorphs (Fig. 4).

This result indicates that the interstitial neighbors of the molecules are, at the same time, also distant neighbors in the hydrogen bonding network, in a clear agreement with the recent experimental finding that interstitial molecules in HDA and VHDA are also fully hydrogen bonded water molecules. This conclusion contradicts the idea that water is a mixture of two types of molecules, i.e., network forming and interstitial ones, and supports the view that it is characterized by two types of interactions instead.

**IV. ANGULAR DISTRIBUTION AROUND BONDING H ATOMS**

In order to emphasize the increasing role of the interstitial neighbors in the higher density phases of supercooled water we have calculated the cosine distribution of the angle $\gamma$ that is formed around a H atom by the vector pointing from this H atom to the O atom of the same molecule (along the intramolecular H–O bond) and the vector pointing from this H atom to its second nearest oxygen neighbor (excluding the intramolecular one). The first nearest intermolecular oxygen neighbor of a H atom is obviously the one to which it is hydrogen bonded, whereas the second nearest one is either an interstitial neighbor, or, in their absence, it belongs to the next neighbor molecule along the hydrogen bonded network.
Therefore, as it was pointed out by Saitta and Datchi, the distribution of \( \cos \gamma \) is a rather sensitive measure of the amount of interstitial neighbors that are present around the molecules.

The \( P(\cos \gamma) \) distributions obtained in the three supercooled liquid phases of water as well as in the three ice polymorphs considered are shown in Fig. 5. The distributions are always bimodal, having their first peak at about \( \cos \gamma = -0.35 \) (i.e., at \( \gamma = 110^\circ \)), and their second peak at about \( \cos \gamma = 0.45 \) (i.e., at \( \gamma = 63^\circ \)) in the supercooled liquid phases. The first peak is given by the interstitial, whereas the second peak by the hydrogen bonded neighbors of the molecules (see Fig. 3 of Ref. 49). The increase of the fraction of interstitial neighbors with increasing density is clearly evidenced. The change of the \( P(\cos \gamma) \) distributions in the three ice polymorphs shows a similar trend with increasing density, although, obviously, here these changes are considerably stronger than in the disordered phases. Considering the fact that the structure of the first coordination shell (i.e., that of the hydrogen bonded neighbors) is found to be insensitive to the variations of the density, we can conclude that the differences in the structure of the different phases of supercooled water concern solely the amount of the interstitial neighbors: the rise of the density at higher pressure states reflects the increasing amount of interstitial neighbors of the molecules.

V. LOCAL ENVIRONMENT OF THE MOLECULES

The local environment of the molecules in condensed phases can be very efficiently characterized by means of Voronoi analysis.\(^{58-60}\) In a three dimensional assembly of discrete seeds (e.g., particles) the Voronoi polyhedron (VP) of a given seed is the locus of the spatial points that are closer to this seed than to any other one. Thus, the volume of the VP, \( V \), is a measure of the space available for this central particle. Conversely, the reciprocal volume of the VP is a measure of the local density around this particle. The faces, edges and vertices of the VP are the locus of the spatial points that are equally far from two, three and four particles, respectively, and are closer to these particles than to any other one. Thus, faces of the VP define the neighbors of the particles: neighbors are the particles the VP of which share a common face with the VP of the central particle. (It should be noted that the list of neighbors given by this definition includes not only the nearest neighbors, but also neighbors of the second, and, in some cases, also of the third coordination shell.) To emphasize this point, here we refer to these neighbors as the Voronoi neighbors of the molecules. Further, the area of a face \( a \) gives information on the relative proximity of the given Voronoi neighbor: in general, closer Voronoi neighbors share larger faces of their VP. The vertices of the VP are the spatial points from where the distance of the nearest particle attains a local minimum: making an infinitesimally small step from such a vertex to any direction gets closer to at least one of the four particles sharing the given vertex. Therefore, VP vertices are the centers of the largest spherical cavities present in the system. The radius of such a cavity \( R_{	ext{cav}} \) is the distance of the vertex from the central particle. The sphericity of the local environment of the molecules can be characterized by the asphericity parameter \( \eta \), defined as

\[
\eta = \frac{s^3}{36 \pi \nu^2}. \tag{3}
\]

where \( s \) and \( \nu \) are the surface area and volume of the VP, respectively. The value of \( \eta \) is 1 for a perfect sphere, and takes larger values for less spherical objects.

In analyzing the local environment of the molecules in the three supercooled phases of water we performed Voronoi analysis on the sampled configurations, taking the O atoms of the water molecules as seeds in the analysis. The determination of the VP of the molecules as well as the calculation of their volume \( \nu \), surface area \( s \) and area of the individual faces \( a \) have been done as described in a previous paper.\(^{61}\) The mean volumes and standard deviations of the characteristics of the VP are summarized in Table I, whereas the distributions of the volume and asphericity parameter of the VP as well as of the area of the VP faces are shown in Fig. 6 for the three phases of supercooled water. Since the shift in the position of the VP volume distribution would only reflect the trivial fact that the density of the three systems are different, and this shift would hide the important differences between the three curves, here we show the volume distributions for the reduced volume of the VP \( \nu^* \), i.e., for the volume normalized to its mean value: \( \nu^* = \nu / \langle \nu \rangle \).
As is seen, in the higher density phases the volume distribution is narrower, and the distribution of the asphericity parameter is shifted to lower values of $\eta$. These findings reflect the presence of an increasing amount of interstitial neighbors. Since these neighbors are located at the cavities of the tetrahedral network around the central molecule, and thus make the local structure more closely packed, the increase of their number makes the local environment of the central molecule more and more spherical. The tetrahedral hydrogen bonded network of the water molecules does not correspond to a close packed arrangement. Instead, it is characterized by very close nearest (i.e., hydrogen bonded) neighbor distances and by the presence of relatively large cavities. Therefore, such a tetrahedral network exhibits relatively large fluctuations of the local density. These local density fluctuations are reduced in the presence of increasing amount of interstitial neighbors, because such neighbors occupy positions inside these cavities, making the system more homogeneous on the microscopic scale. This effect of the interstitial neighbors is reflected in the narrowing of the $P(\nu^*)$ distribution in the higher density phases.

Finally, the increasing amount of the interstitial neighbors of the molecules in the higher density phases can clearly be evidenced by the VP face area distributions $P(a)$. These distributions are found to be trimodal. The first, trivial peak at zero is simply given by the large number of distant Voronoi neighbors that share only a tiny face of their VP with that of the central molecule. The distributions show another peak above 5 Å$^2$. This peak is given by the nearest, hydrogen bonded neighbors of the molecules. The shift of this peak to lower $a$ values in the higher density phases already reflects the fact that the distance of these neighbors from the central particle deviates less from that of the other Voronoi neighbors because of the increase of the number of other close neighbor molecules (i.e., the interstitial ones). Finally, around the $a$ value of 3 Å$^2$ a third peak of the $P(a)$ distribution emerges with increasing density. This peak can be assigned to the interstitial neighbors: they are farther from the central molecule than the hydrogen bonded ones (the corresponding peak of which appears at higher $a$ values), but are clearly closer than the other Voronoi neighbors. Finally, the presence of two distinct peaks of the $P(a)$ distributions besides the trivial one at zero clearly evidences the fact that in water the molecules have two separate preferred nearest neighbor distances; a fact that can itself explain the majority of the water anomalies.\(^8\)

### VI. DEGREE OF ORDER OF THE MOLECULES

The quantification of the degree of order of the molecules in disordered phases is a nontrivial task, since such systems are characterized by short range order only, and this order vanishes at larger length scales. Complete characterization of the structural order of the molecules is usually done by using two order parameters, i.e., a translational one measuring the adoption of preferential separation of molecule pairs, and an orientational one, which quantifies the correlation of the angles formed by the nearest neighbors around a molecule.\(^{62-68}\) In this study, we adopted the order parameters proposed by Errington and Debenedetti.\(^ {66}\) The translational order parameter $t$ is thus defined as

$$t = \frac{1}{\xi_c} \int_0^{\xi_c} |g_{00}(\xi) - 1| d\xi,$$

whereas the tetrahedral order parameter $g$, being the rescaled version of that of Chau and Hardwick\(^ {62}\) is

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**TABLE I.** Mean values and standard deviations of the properties of the Voronoi polyhedra of the water molecules in the three supercooled liquid phases simulated.

<table>
<thead>
<tr>
<th></th>
<th>LDA</th>
<th>HDA</th>
<th>VHDA</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v$ (Å$^3$)</td>
<td>29.9 ± 2.9</td>
<td>26.7 ± 1.9</td>
<td>24.1 ± 1.5</td>
</tr>
<tr>
<td>$s$ (Å$^3$)</td>
<td>55.3 ± 3.8</td>
<td>50.4 ± 2.6</td>
<td>46.5 ± 2.1</td>
</tr>
<tr>
<td>$a$ (Å$^3$)</td>
<td>3.47 ± 3.41</td>
<td>3.22 ± 2.87</td>
<td>3.05 ± 2.47</td>
</tr>
<tr>
<td>$\eta$</td>
<td>1.67 ± 0.10</td>
<td>1.58 ± 0.08</td>
<td>1.53 ± 0.07</td>
</tr>
<tr>
<td>$R_{\text{cav}}$ (Å)</td>
<td>2.49 ± 0.26</td>
<td>2.33 ± 0.20</td>
<td>2.22 ± 0.16</td>
</tr>
</tbody>
</table>

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**FIG. 6.** Distribution of (a) the reduced volume, (b) the asphericity parameter, and (c) the area of the individual faces of the Voronoi polyhedra of the water molecules in the three supercooled liquid phases simulated. Solid lines: LDA, dotted lines: HDA, dashed lines: VHDA.
TABLE II. Translational and tetrahedral order parameters of water, as calculated in the three phases of supercooled water and three ice polymorphs simulated.

<table>
<thead>
<tr>
<th></th>
<th>Supercooled water phases</th>
<th>Ice polymorphs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LDA</td>
<td>HDA</td>
</tr>
<tr>
<td>t</td>
<td>0.508</td>
<td>0.495</td>
</tr>
<tr>
<td>q</td>
<td>0.704</td>
<td>0.671</td>
</tr>
</tbody>
</table>

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

(5)

In these equations ξ = rp^{1/3} (r being the distance of two O atoms), ξc is a numerical cutoff value, set to 2.3517 in the present calculations, and Θ_{jk} is the angle formed by the O atoms of the jth and kth nearest (oxygen-oxygen) neighbors around the O atom of the central molecule. In a completely disordered system (ideal gas) both of these order parameters are zero, their larger values indicate higher order. The highest possible value of \( q \) is 1, corresponding to the perfect tetrahedral arrangement of the molecules.

The values of the \( t \) and \( q \) order parameters are summarized in Table II as obtained in the three different phases of supercooled water as well as in the three ice polymorphs considered. The degree of order of the molecules in different states can be efficiently compared on the \((t,q)\) plane. The position of the simulated supercooled liquid and ice phases on this order map is shown in Fig. 7. For reference, the points corresponding to the perfect Iₜ, III, and VI ice crystals are also indicated.

Obviously, the highest order parameter values correspond to the perfect \((T=0\,\text{K})\) ice crystals. Further, due to the perfect tetrahedral arrangement of the oxygen atoms, the orientational order parameter of the perfect ice Iₜ crystal is exactly 1. The translational order parameter values calculated over the saved configurations of our simulated ice systems are considerably smaller than in the perfect crystal due to the thermal motion of the molecules. Further, the values of \( t \) are much closer to each other in the simulated than in the perfect ice crystals. On the other hand, the tetrahedral order parameter \( q \) does not change considerably upon going from the perfect to the simulated ice crystal, reflecting the fact that the tetrahedral arrangement of the nearest (hydrogen bonded) neighbors is only rather weakly affected by the thermal motion of the molecules. It is also clear that the relative positions of the three ice phases considered remain unchanged at finite temperature.

As is expected, the order parameters have lower values in the amorphous than in the crystalline phases. Further, the difference of the order parameter values corresponding to the different phases of supercooled water is much smaller than in the ice polymorphs. In particular, the value of the translational order parameter \( t \) resulted in almost the same in LDA, HDA, and VHDA (see Table II). Nevertheless, the relative position of the amorphous phases on the order map is again the same as that of the respective ice polymorphs, as is evident from the inset of Fig. 7. Thus, both VHDA and ice VI has the lowest, while both LDA and ice Iₜ the highest tetrahedral order in their own group of systems, and the translational order is slightly higher in these phases than in HDA and ice III, respectively. It should be noted that the path traversed both by the amorphous and by the crystalline phases on the order map with increasing density is similar to what was observed by Errington and Debenedetti upon isothermal compression,68 and by Giovambattista et al. upon isochoric cooling of glassy water at low enough temperatures. The obtained results stresses again our conclusion that in phase transitions from LDA to HDA and from HDA to VHDA supercooled water undergoes structural changes that are parallel with those occurring in the phase transition from ice Iₜ to ice III and eventually to ice VI.

VII. THERMODYNAMIC PROPERTIES

A. Pressure

The calculation of the pressure in a system described by a non pairwise additive force field is not a trivial task, since if periodic boundary conditions are applied—as in the case of the vast majority of computer simulations—the conventional way of deriving the pressure through the virial equation leads to incorrect results.69 This problem can be circumvented by using the test volume method for the pressure calculation. In this method the pressure is calculated as the derivative of the Helmholtz free energy \( A \) with respect to the volume \( V \).
\[ p = -\left( \frac{\partial A}{\partial V} \right)_{N,T} = \lim_{\Delta V \to 0} \left( \frac{\Delta A}{\Delta V} \right). \]  

In the calculation the volume of the system is isotropically changed by a factor of \((1+\xi)\), where \(\xi\ll1\), and the accompanying change in the free energy is calculated. Using the relation between the Helmholtz free energy and the canonical partition function \(Q\),

\[ A = -k_B T \ln Q = -k_B T \ln \int \exp(-\beta U) dq^N, \]  

the free energy change can be written as

\[ \Delta A = -k_B T \ln \frac{Q^*}{Q} = -k_B T \int \frac{\exp(-\beta U^*)}{V} ds^N \]  

\[ = -k_B T \ln((1+\xi)V) \exp(-\beta \Delta U) \} \right. \]  

where asterisks refer to the perturbed state, \(k_B\) is the Boltzmann constant \(\beta = 1/k_B T\), \(q^N\) and \(s^N\) are the absolute and scaled coordinates of the particles, respectively, \(\Delta U = U^* - U\), and the brackets \(\langle \cdots \rangle_U\) denote ensemble averaging in the nonperturbed state. In deriving Eq. (8) the relation between the original and perturbed volumes of the system

\[ V^* = (1 + \xi)V \]  

is also used. Substituting Eq. (8) to Eq. (6) the pressure can be given as

\[ p = \lim_{\xi \to 0} \frac{k_B T}{\xi V} \ln((1+\xi)V) \exp(-\beta \Delta U) \} \right. \]  

In determining the pressure in the three supercooled phases of water we have calculated the quantity \(-\Delta A/\Delta V\) with four different values of \(\xi\), i.e., 0.01, 0.005, 0.002, and 0.001, and extrapolated the obtained values to \(\xi = 0\) by fitting straight lines to the \(-\Delta A/\Delta V(\xi)\) data. This procedure is illustrated in Fig. 8, and the obtained pressure values are summarized in Table III.

The pressure of the LDA phase is found to be about zero. Considering also the fact that this state is located inside the liquid-vapor phase envelope of water (because the liquid branch of this envelope intersects the low density branch of the LDA-HDA phase envelope above 200 K,\(^{41}\) see Fig. 1), and hence this LDA phase is metastable not only with respect to ice but also with respect to vapor, we can conclude that the pressure of this phase is very likely negative. The pressure of the HDA and VHDA phases are found to be 5100 and 12400 atm, respectively.

B. Free energy and entropy

In a previous section we characterized the ordering of the molecules in the three supercooled phases through the translational and orientational order parameters. The degree of ordering can also be described by one single quantity, namely, the entropy of a given phase. In the canonical ensemble the calculation of the entropy requires the determination of the Helmholtz free energy of the system. In computer simulations the excess free energy of a homogeneous condensed phase relative to the ideal gas as the reference state can be obtained by the method of thermodynamic integration,\(^{73,74}\) by transforming the system from the ideal gas to the condensed state along a continuous path described by the coupling parameter \(\lambda\). The value of \(\lambda\) is changed between 0 and 1, where the \(\lambda = 0\) and \(\lambda = 1\) values correspond to the ideal gas and supercooled liquid states, respectively. The excess free energy of the supercooled liquid is calculated as

\[ A = \int_0^1 \frac{\partial A}{\partial \lambda} d\lambda. \]  

Using Eq. (7) the integrand of Eq. (11) can be written as

\[ \frac{\partial A(\lambda)}{\partial \lambda} = -k_B T \frac{\partial Q(\lambda)}{\partial \lambda} \exp(-\beta U(\lambda)) \]  

\[ \left\langle \frac{\partial U(\lambda)}{\partial \lambda} \right\rangle \]  

where the brackets \(\langle \cdots \rangle_\lambda\) indicate ensemble averaging at the TABLE III. Thermodynamic properties of the three supercooled liquid phases of water simulated.

<table>
<thead>
<tr>
<th></th>
<th>LDA</th>
<th>HDA</th>
<th>VHDA</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\rho) (g/cm(^3))</td>
<td>1.00</td>
<td>1.12</td>
<td>1.24</td>
</tr>
<tr>
<td>(\rho) (atm)</td>
<td>0 ± 270</td>
<td>5100 ± 800</td>
<td>12400 ± 1300</td>
</tr>
<tr>
<td>(U) (kJ/mol)</td>
<td>-47.2 ± 0.3</td>
<td>-48.5 ± 0.2</td>
<td>-48.9 ± 0.3</td>
</tr>
<tr>
<td>(A) (kJ/mol)</td>
<td>-27.4</td>
<td>-29.6</td>
<td>-29.8</td>
</tr>
<tr>
<td>(S) (J/mol K)</td>
<td>-98.8</td>
<td>-94.5</td>
<td>-95.6</td>
</tr>
</tbody>
</table>
\[ U(\lambda) = \lambda^4 U_1, \quad (13) \]

where \( U_1 = U(\lambda = 1) \) is the full potential energy of the supercooled state. The choice of this form of the \( U(\lambda) \) function is dictated by the fact that in three dimensions, for a potential containing \( r^{-12} \) repulsion term, the exponent 4 of \( \lambda \) in Eq. (13) is required to eliminate the singularity at the \( \lambda = 0 \) end of the integral of Eq. (11).\(^{25}\) Substituting Eq. (12) to Eq. (11) and using also Eq. (13) the full excess free energy of the supercooled phase can be calculated as

\[ A = \int_0^1 4\lambda^3 (U)_\lambda d\lambda. \quad (14) \]

As is seen from Eqs. (12) and (14), this calculation requires ensemble averaging at a given \( \lambda \) value, i.e., using \( U(\lambda) \) in the Boltzmann factor of Eq. (12). However, technically this is equivalent with using the full \( U_1 \) potential energy in the Boltzmann factor and performing the ensemble averaging at the temperature \( T' = T/\lambda^4 \).

The integrand of Eq. (14) has been evaluated at five different \( \lambda \) values per system, using a five point Gaussian quadrature (i.e., the \( \lambda \) values of 0.046 911, 0.230 765, 0.5, 0.769 235, and 0.953 089), by performing Monte Carlo simulations at the corresponding \( T' \) temperatures in the same way as described in Sec. II. The integration has been performed by fitting a fourth order polynomial to the obtained data points. This procedure is illustrated in Fig. 9, showing the integrand at each quadrature point as a function of the coupling parameter \( \lambda \), and the polynomial functions fitted to the three data sets. The obtained Helmholtz free energy values are collected in Table III. Having the excess Helmholtz free energy of the system the excess entropy can be calculated simply as

\[ S = \frac{U - A}{T}. \quad (15) \]

The potential energy and excess entropy values corresponding to the three supercooled water phases are also collected in Table III.

As is seen, the free energy values obtained in the three phases are rather close to each other. This is not surprising, since the three systems simulated are rather close to the corresponding branches of the liquid-liquid coexistence curves (see Fig. 1), and the two branches of such a coexistence curve correspond to the same Helmholtz free energy value along a given isotherm. Similarly, the potential energy of the three phases do not differ much from each other, being about 2.5%–3.5% lower in LDA than in the other two phases. This lower potential energy value is compensated by lower entropy in LDA: the entropy of this phase is found to be 4.6% lower than that of HDA, and 3.3% lower than that of VHDA. The order of the obtained entropy values, i.e., \( S_{\text{LDA}} < S_{\text{HDA}} = S_{\text{VHDA}} \) is in a clear agreement with that of the order parameters calculated in these phases (see Table II and Fig. 7), and reflects again the fact that the presence of a substantial fraction of interstitial neighbors is accompanied by a certain decrease of the order of the molecules, and thus by a certain increase of the entropy of the system.

VIII. SUMMARY AND CONCLUSIONS

In a previous paper we showed, on the basis of two sets of Gibbs ensemble Monte Carlo simulations, that the BSV polarizable potential model of water exhibits two liquid-liquid coexistence curves in the supercooled region.\(^{41}\) The presence of low and high density phases of supercooled water had recently been explored also by experimental methods.\(^{54,56}\) In fact, results of neutron scattering experiments performed both on liquid water at temperatures well above any possible liquid-liquid phase transitions,\(^{47,48}\) and also on different amorphous ices,\(^{54,56}\) clearly showed that upon going from low to high density phases of water the second peak of the oxygen-oxygen radial distribution function shifts to lower distances. Computer simulations performed at three different densities, corresponding to the LDA, HDA, and VHDA phases of supercooled water indicated that these structural changes can be understood in terms of the analogous transformations occurring in phase transition between ice polyphorms I, III, and VI, respectively.\(^{46}\)

Although this finding naturally leads to the assumption that there should be as many amorphous phases of supercooled water as ice polymorphs, such a conjecture cannot be adequately addressed on the basis of the present set of simulations. First, unlike the BSV and several conventional non-polarizable water models,\(^{33}\) ST2 water is known to exhibit three separate liquid-liquid phase equilibria, and hence four different supercooled liquid phases,\(^{32}\) one of which is presumably related to ice V. The existence of such a supercooled liquid phase has, on the other hand, never been shown for any other water model. The reason of this might be that such a phase exists only under such thermodynamic conditions (e.g., lower temperatures) that have not been explored yet for.
these models, or this phase might be metastable with respect to another supercooled liquid phase in the entire phase diagram. Similarly, new supercooled liquid phases (e.g., the one related to ice VII) might also exist at the very high pressure range that has not been accessed by computer simulations yet. Considering all these unexplored possibilities, however, the clear conclusion can be drawn from the present study that the existing supercooled liquid phases (polyamorphs) of water are in a very close structural relationship with certain ice polymorphs, i.e., LDA with ice I₆, HDA with ice III, and VHDA with ice VI.

Here we have reported results of a detailed investigation of the thermodynamic and structural properties of the LDA, HDA, and VHDA phases. We have evaluated the pressure through the test volume method, and the entropy by thermodynamic integration. The structural arrangement of the molecules has been investigated by the evaluation of various quantities, and compared with those obtained for the ordered phases of ice I₆, III, and VI. The obtained results clearly show that in the higher density phases the water molecules have more and more interstitial neighbors, which are, on the other hand, also distant neighbors along the hydrogen bonded network. The presence of the increasing amount of neighbors, which is evidenced both by the angular distribution of oxygen around a hydrogen atom, and by the appearance of a third peak in the Voronoi polyhedra face area distribution, lowers the degree of order, in particular, that of the translational order of the molecules. This effect is found to be similar to what happens upon going from lower to higher density ice polymorphs, namely from I₆ to III and VI. In particular, the study of the map of the translational and tetrahedral order parameters, as suggested by Errington and Debenedetti, proved to be a useful tool to stress the similarity of the amorphous phases with the corresponding ice polymorphs as far as the structural arrangement of the molecules is concerned. In conclusion, the present analysis gives a definitive confirmation of the hypothesis that, by increasing the density, phase transitions occur in the explored disordered systems that are accompanied by the same rearrangement of the molecules than the corresponding transformations of the I₆, III and VI ice polymorphs, and hence the occurrence of several different phases of supercooled water stems from the same physical origin than what is responsible for ice polymorphism.

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