Global minima for water clusters \((\text{H}_2\text{O})_n, n \leq 21\), described by a five-site empirical potential

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Abstract

Candidate global minimum structures are reported for \((\text{H}_2\text{O})_n\) clusters for \(n \leq 21\) described by the rigid-body TIP5P potential. These structures are compared with previously published results for the related TIP4P potential, and with ab initio calculations at the MP2 level. The variation of the energy gap from the putative global minimum to the next-lowest structure as a function of system size is analysed. Comparisons with previously reported structural trends in water clusters are made.

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1. Introduction

Water is perhaps the most intensively studied of condensed matter systems, due to its ubiquitous presence as a solvent in, amongst others, electrochemical and biochemical environments. Despite the development of increasingly sophisticated methods to describe the interactions in aqueous media [1], there is still a place for the use of simple, empirical potentials in this field. As both higher-level calculations and experimental data are available, small water clusters provide an interesting test for model potentials. Many such potentials are parameterised to reproduce certain bulk thermodynamic properties, but it seems logical that an accurate description of large numbers of molecules should be based on a good understanding of less extensive systems [2]. The determination of the low-energy cluster minima for these potentials provides information regarding the balance of different types of interaction within the model. The low-temperature properties of a system are also governed by the low-lying potential energy minima [3].

Putative global minimum structures for water clusters have been located for a number of empirical potentials, using various search methods. Kim et al. [4] applied simulated annealing to study the MCY potential, and many-body corrections thereto, for clusters in the range \(4 \leq n \leq 8\), reoptimising certain structures using ab initio techniques. Wawak and coworkers [5] also applied the diffusion equation method to the MCY potential for cluster sizes up to \(n = 8\), but failed to reproduce the previously located lowest-energy structures for the larger systems. Tsoo and Brooks [6] investigated the use of Gaussian density annealing with TIP4P clusters up to \(n = 8\), but these authors also experienced problems with the scaling of the algorithm to some of the larger sizes. Lee et al. [7] used simulated annealing to locate low-energy structures with the Cieplak, Kollman and Lybrand model for selected sizes up to \(n = 20\). As the aim of this approach was to produce starting points for further optimisation using DFT methods, and given the emphasis on the ‘fused cube’ morphology, it seems likely that the structures located for the larger system sizes were not true global minima in this instance. Niesse and Mayne [8] used a genetic algorithm to predict structures for the TIP3P potential up to \(n = 13\). Their results for \(n = 11–13\) were subsequently improved by Wales and Hodges [9] using the basin-hopping method. The latter authors also presented results for the TIP4P potential up to \(n = 21\). More recently, Kabrede and Hentschke [10] extended results for the SPC/E, TIP3P and TIP4P potentials to \(n = 25\), using both a genetic algorithm

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and basin-hopping. Hartke [11] applied the genetic algorithm approach for the TTM2-F potential up to n = 30, comparing structural trends with previous results for the TIP4P model. Kazimirski and Buch [12] applied a combination of methods to study selected cluster sizes up to n = 293 using the TIP4P and TTM2-R potentials, although their focus was on characterising trends in low-energy structures rather than locating true global minima.

Global optimisation of water clusters is significantly harder than optimisation of atomic systems with similar numbers of particles. This difficulty is, in part, because of the interaction between the translational and orientational degrees of freedom, which occurs for such molecular systems [9,11]. For this reason, there has as yet been no systematic extension of the above studies to numbers of water molecules in the high tens to hundreds in the same way as has been attempted with, for example, clusters described by the Lennard–Jones potential [13,14].

2. Methods

In this study, we have employed the TIP5P potential [15], which is the most recent addition to the family of rigid-body water models developed by Jorgensen and coworkers [16]. The principal distinguishing feature of this model compared to its predecessors is that the negative partial charge is shifted and separated in order to try and represent the lone-pairs on the oxygen atom with a greater degree of accuracy. There has been some discussion in the literature concerning the treatment of the long-range electrostatic interactions during the parameterisation of this model [17–19]. Given that there appear to be problems even with the use of more sophisticated methods beyond simple cutoffs, and the fact that we are particularly interested in the qualitative effects of introducing an extra interaction site on the low-energy structures, we have chosen to retain the parameters as originally published. For ease of reference, these values are reproduced in Fig. 1. Different parameterisations would likely give different global minima, especially as the size of the clusters increases, but given the many other sources of approximation we do not consider this to be a significant issue here.

In the TIP5P model, the interaction between two water molecules, a and b, is given by a Lennard–Jones term centred on the oxygen positions, plus electrostatic interactions between partial charges on the hydrogen and lone-pair sites:

\[
E_{ab} = \sum_{ij} \frac{q_i q_j \sigma^2}{4\pi\varepsilon_0 r_{ij}} + 4\epsilon \left[ \left( \frac{\sigma}{r_{OO}} \right)^12 - \left( \frac{\sigma}{r_{OO}} \right)^6 \right],
\]

where \(q_i\) and \(q_j\) are the partial charges on site \(i\) of molecule \(a\) and site \(j\) of molecule \(b\), respectively, \(r_{ij}\) is the Cartesian separation of the two sites, and \(r_{OO}\) is the distance between the two oxygens.

We have chosen to express the rigid-body orientational degrees of freedom in terms of angle-axis coordinates [20], rather than the Euler angle representation used previously [21,22,9]. The advantage of this new coordinate system is that it does not suffer from the problems associated with reduced dimensionality due to rotational axes becoming equivalent, which can occur with the use of Euler angles [5,22]. Experience suggests that such problems would not have manifested themselves significantly for the energy minimisation results reported here, but would have hindered further analysis, for example in the study of pathways between minima.

Searches for the global minima were conducted using the basin-hopping algorithm [13], which has previously been used in the study of various atomic and molecular clusters [13,9,23,24]. Due to the increased separation of the oppositely charged electrostatic sites, the TIP5P potential showed a greater propensity to undergo cold fusion than the previous members of the TIP family. Such events were detected and discarded from the Markov chains. The procedure developed in a previous study on protonated water systems [23], whereby a single high-temperature basin-hopping run is followed by multiple lower temperature runs from energetically diverse starting structures, was again employed here for cluster sizes \(n > 5\). For the smaller clusters, \(5 < n < 15\), five low-temperature starting structures were chosen, with a minimum of four of those runs converging to the same putative global minimum. For the larger clusters, \(16 < n < 21\), 10 low-temperature starting structures were chosen, with separation of the angular and translational degrees of freedom [9] again found to be beneficial. Except for \(n = 20\), at least four of the runs for each cluster size identified the same lowest-energy structure. The \(n = 20\) system proved to be particularly difficult, with many searches locating a group of structures around \(-877\ \text{kJ mol}^{-1}\), more than \(4\ \text{kJ mol}^{-1}\) above the global minimum candidate given below. We are still investigating why this occurred, but suspect that this system may have a particularly rough potential energy landscape with multiple funnel-like features.

3. Results

Putative global minima for the TIP5P potential and their energies are given in Tables 1 and 2. These structures are available for download from the Cambridge Cluster Database at http://www-wales.ch.cam.ac.uk/CCD.html.
For comparison, the previously located TIP4P minima [9] are also shown, together with the energies obtained when these structures are reminimised using the TIP5P potential. Two of the TIP4P structures, those for \( n = 13 \) and 17, lose a single hydrogen-bond upon reminimisation, and one, for \( n = 21 \), loses two. The remainder are topologically stable. For the purposes of this study, we define a hydrogen-bond to have \( r_{O-H} \leq 2.5 \text{ Å} \) and \( \theta \geq 110^\circ \), where \( \theta \) is defined in Fig. 3.

The smallest cluster size for which the new potential gives a different structure is \( n = 6 \), where the TIP5P global minimum is a planar ring whilst the TIP4P global minimum is a cage. A previous study by Mhin et al. [25] suggested that certain empirical water potentials, including TIP4P, overestimate the importance of two-body interactions relative to many-body interactions. This observation was taken as a factor in explaining why, in contrast to ab initio calculations, such potentials disfavour the single ring structure for the water hexamer, stabilising instead geometries with greater degrees of hydrogen-bonding. It is curious, therefore, that the TIP5P potential, despite having a greater binding energy for the water dimer than any of the potentials considered in [25], has as its global minimum the \( S_6 \) symmetry ring. For \( n = 8 \), in common with many previous studies on this system [26,27,21], we find that there are two low-energy cuboid structures of \( D_{2d} \) and \( S_4 \) symmetry. With the TIP5P potential we find that the \( D_{2d} \) minimum is lower in energy by 1.9 kJ mol\(^{-1}\). Thus, the TIP5P ordering agrees with that obtained from the TIP1P and TIP3P potentials, which is the opposite of that obtained for TIP2P and TIP4P [21]. The TIP5P separation is, however, somewhat larger than for the previous calculations. The gap to the next-lowest structure located for this system is large, of the order of 7 kJ mol\(^{-1}\), also in keeping with previous results.

For system sizes above \( n = 9 \), all of the TIP5P global minima are topologically distinct from their TIP4P counterparts. The two structures at \( n = 10 \) are both pentagonal prisms, but in the TIP5P case the hydrogen-bond donor–acceptor chains in the two five-membered rings are antiparallel, whilst in the TIP4P case they are parallel. It is noticeable that the more regular structures found for the TIP4P potential are not as favourable for the TIP5P potential. For example, the box-kite structures at \( n = 12 \) and 16,
when reminimised, lie 19 and 29 kJ mol\(^{-1}\), respectively, above the lowest-energy TIP5P structures located at these system sizes. It has previously been noted that TIP4P exaggerates the relative stability of fused cubic structures compared to those containing five- and six-membered rings [27]. Perhaps related to this decrease in regularity, the TIP5P global minima tend to have fewer hydrogen-bonds than the TIP4P global minima for a given number of molecules.

The potential energy density of minima near the global minimum for the TIP5P potential shows a significant and non-monotonic variation with system size. Such information can be useful in predicting magic number behaviour [28] and the appearance of low-temperature heat capacity plots [21]. In Fig. 2 we show the energy gap between the global minimum and the next-lowest structure as a function of \(n\). There are local maxima at \(n = 5, 9\) and 20. The water pentamer is probably too small a system to assign much significance to the large energy gap observed there. For \(n = 9\), all of the low-energy structures that we located are based on a cuboid with a single bridged edge. The lowest structure with an alternative geometry lies 15 kJ mol\(^{-1}\) above the putative global minimum. The reason why there is such a large gap in the energy spectrum is that the hydrogen-bonds in the global minimum are on average 3 kJ mol\(^{-1}\) stronger than in the next-lowest structure, although this effect is balanced somewhat by weaker non-hydrogen-bonding interactions. We have already commented upon the difficulties encountered in locating the putative global minimum for \(n = 20\). Given the large gap between this structure and the next-lowest minimum it seems that the basin of attraction for the global minimum must be rather small, to counterbalance the energetic driving force that would otherwise direct our searches to this structure. Visually, there is little to separate the lowest-energy structure from those immediately above it – all are amorphous polyhedral tubes with 32 hydrogen-bonds. The feature that again distinguishes the global minimum is that the hydrogen-bonds are better optimised, being on average 0.3 kJ mol\(^{-1}\) stronger than those in the next-lowest structure.

We observe that there seems to be significantly less correspondence between the global minimum structures for the TIP5P and TIP4P potentials in the size range considered here than there is between the TIP4P potential and the much more sophisticated TTM2-F potential [11]. The transition from all-surface structures to those containing interior water molecules is also different for TIP5P. We located no clathrate structures amongst the lowest 20 minima for sizes up to \(n = 19\). At \(n = 20\), the lowest clathrate structure is ranked 6th, and lies \(\sim 5\) kJ mol\(^{-1}\) above the all-surface global minimum. There are a further 6 clathrate structures in the lowest 20, although all are distinctly non-spherical in shape. At \(n = 21\), the TIP5P global minimum is a distorted dodecahedral clathrate. The low-energy spectrum of local minima at this size is dominated by clathrate structures, accounting for 14 out of the lowest 20, including the bottom 3 and 8 out of the lowest 10. The most favourable all-surface structure (ranked 4th) lies \(\sim 4\) kJ mol\(^{-1}\) above the global minimum. This represents quite an abrupt transition in structure, and it would be interesting to see whether the trend is maintained for \(n = 22\), or whether \(n = 21\) is a slight anomaly because of the availability of the favourable dodecahedral morphology. In contrast, previous results [11] for the TIP4P potential suggest that structures with interior molecules are relatively disfavoured even up to \(n = 22\).

4. Analysis

As the TIP models are effective pair potentials, we should examine more closely the results for the dimer systems if we wish to explain the observed structural trends for low-energy minima. Geometric parameters for \((\text{H}_2\text{O})_2\) for the two models considered in this study are given in Fig. 3. The oxygen–oxygen separation in the TIP5P minimum is somewhat smaller than that in the TIP4P structure. This compression is probably partly responsible for the fact that the densities of various ice phases are uniformly higher for TIP5P [29,30]. Whilst the angular variables at the minima are relatively similar for the two potentials, Mahoney and Jorgensen [15] showed that the energy variation with the tilt angle (equivalent to \(\phi\)) is significantly greater for TIP5P. In particular, these authors concluded that the
TIP5P model artificially favours tetrahedral arrangements of hydrogen-bonds. This phenomenon has been observed with other 5-site models of water [31]. In order to see what effect this enforced tetrahedrality has on the systems considered in this study we have calculated the angles between the hydrogen-bonds (specifically, the angles between the oxygen–oxygen vectors) formed by each water molecule. In Fig. 4 we show the average deviation from the ideal tetrahedral angle for the TIP4P and TIP5P global minima. According to this measure, the TIP5P structures are always equally or more tetrahedral than their TIP4P counterparts, even for identical topologies. We note that for TIP4P the \( n = 6 \) cage is particularly non-tetrahedral, as are the box-kite structures at \( n = 12 \) and 16. Of the larger clusters, the two structures at \( n = 19 \) are closest in terms of this descriptor. Hartke [11] has previously noted that the TIP4P global minimum at this size is slightly anomalous in that it is an isolated case of a clathrate structure.

We may also compare the structures predicted for the TIP5P potential with a series of recent calculations at the MP2 level [32–34]. The overstructuring of the TIP5P water dimer potential energy surface as a function of the tilt angle makes the agreement with MP2 results worse than for TIP4P [15]. We would expect this difference to be reflected to a certain degree in the cluster energetics, but we also note that the ab initio results in [15] are far from converged with respect to the basis set. For \( n = 6 \), Xanthos et al. [32] found formation energies for four different morphologies. As can be seen from Table 3, a prism structure was predicted to be the most favourable, with the cage structure almost isoenergetic. Other authors [35] have found that, in agreement with experimental results for this system, inclusion of vibrational zero-point corrections causes the energetic ordering of these two minima to be reversed. The relative ordering predicted by the TIP5P model is almost the opposite of that given by MP2, with the \( S_6 \) ring and book structures lying lowest. TIP4P gives better agreement, although the relative destabilisation of the ring is exaggerated. For \( n = 8 \), MP2 complete basis set (CBS) limit estimates [33] make the \( D_{2d} \) and \( S_4 \) structures practically isoenergetic, although the former was slightly lower in all calculations. The TIP5P potential reproduces this energy ordering, although the gap is overestimated, whereas TIP4P makes the \( S_4 \) structure more stable, but only by 0.1 kJ mol\(^{-1}\). For \( n = 20 \), structures belonging to four different morphologies that contribute low-lying minima have previously been examined [9,34]. For this system we performed additional basin-hopping runs, focussing on the orientational space associated with the different morphologies, for both the TIP5P and TIP4P potentials. The lowest energy structures located are given in Table 4. If we take the results from [34] to be representative of the relative stabilities of the different morphologies at the MP2 level, then it can again be seen that there is rather better agreement between the TIP4P predictions and MP2 than there is between TIP5P and MP2.

5. Conclusions

From a comparison of our results with those for the TIP4P potential, it appears that the TIP5P model exhibits a weaker driving force towards maximising the number of hydrogen-bonds. Instead, we see structures with smaller numbers of individually stronger hydrogen-bonds, and a greater preference for adopting tetrahedral arrangements of those interactions. As a consequence of this trend, the TIP5P potential does not appear to show the same preference for regular polyhedral structures, particularly those composed of fused cubes. From a comparison with ab initio results at the MP2 level, we see that the TIP5P potential gives generally worse agreement for the relative stabilities of different morphologies of clusters in the size range con-

![Fig. 4. Average deviation from tetrahedrality of the angle between hydrogen-bonds at a single molecule for TIP5P and TIP4P global minima. The average standard deviations in these values are 7° and 10° for TIP5P and TIP4P, respectively.](image)
sidered than does TIP4P. This result is probably related to the overstructuring of the TIP5P dimer potential surface.

We have seen that the TIP5P potential shows a different structural trend in terms of the transition (as a function of cluster size) to minima with interior water molecules. We further note that the TIP5P monomer dipole (2.29 D) is greater than that of TIP4P (2.18 D). Our results therefore seem not to support the previous suggestion that the reluctance of the TIP4P potential to form low-energy clathrate structures in the current size range is due to its inability to reduce unfavourable dipole interactions independently of the molecular geometry [11]. However, the elements of the quadrupole tensor are generally smaller in magnitude for the TIP5P monomer, which may complicate the analysis.

As a final point, we note that the low-energy minima discussed here are a byproduct of the search for the global minima. To the same extent that we cannot be sure that we have located the true, lowest-energy structures, we do not claim to have made an exhaustive survey of the low-energy spectrum. However, we are reasonably confident that our algorithm will have sampled most relevant regions of configuration space.

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