Classical Dynamics of Hydrogen Bonded Systems: Water Clusters

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Abstract

The minimum energy structures and the classical dynamics of $(H_2O)_n$ clusters, with $n = 3 - 6, 8$, have been investigated with the potential function of Cieplak, Kollman, and Lybrand. The potential is the sum of a pairwise additive part plus a polarization term calculated iteratively from the permanent and induced dipole moments. It is found, that at the minimum energy structures the polarization energy makes a contribution of about 13% in the total energy. Caloric curves and rms fluctuations of the oxygen-oxygen bond lengths show that the tetramer, with a tetragonal minimum geometry, and the octamer, with a cubic minimum geometry, are more stable clusters than the pentamer and hexamer. The geometries of absolute minima for the trimer, tetramer, and octamer agree with those predicted by other potentials. For the pentamer and hexamer the present potential predicts floppy type structures instead of cyclic ones, which are supported by other functions and ab initio calculations. The dynamics of water clusters is chaotic with a characteristic time for forgetting the initial conditions equal to the period of the stretching mode of hydrogen bond. Phenomena of coexistence appear for the hexamer and larger clusters for which classes of minima of different geometrical type exist. For all studied clusters the power spectra of the oxygen velocity autocorrelation function are characterized by two frequency bands; one around 30 cm^{-1}, torsional, and one at 200 cm^{-1}, stretching. Generally, no significant influence in the dynamics of the clusters is found by the inclusion of polarization interaction, although for the hexamer and octamer polarization energy results in interchanging the geometries of absolute minima.

1 Introduction

Studies on clusters have always been considered as filling the gap between our knowledge on molecules, systems with a limited number of degrees of freedom, and on macroscopic states of matter, which are described by statistical mechanics. The study of clusters allows one to apply techniques developed for systems with a relatively small number of degrees of freedom, such as methods of Molecular Dynamics and Nonlinear Mechanics, and to discover the way molecular properties determine the properties of the macroscopic states.

A detailed study of molecular dynamics at the classical mechanical approximation requires the determination of the structure of phase space. A systematic way to achieve that is first to locate the stationary points of the potential energy surface, then, to locate periodic orbits and other higher dimensionality classical objects, such as tori and reduced dimension tori, and to investigate the stability properties of the nearby trajectories.[1] This scheme can be accomplished in some extent for systems with a few degrees of freedom. However, dealing with clusters of several monomers the task of finding the minima of the potential energy surface is an important step towards the characterization of dynamics. This is supported by a topological theorem, which states that the topology of the energy manifold changes, and hence the dynamics, when we move from one stationary point to the other.[2]

Argon clusters have served as prototypical systems for studying the dynamics of small clusters, because of the good approximation of the potential function with pairwise potentials. It was shown very early that the dynamics is chaotic for small argon clusters,[3–6] whereas for a particular number of atoms, geometries with special stability exist.[7–10] It has been found that clusters with n = 7, 13, 19, 55, 147 are stable relative to local minima of higher energy and the explanation for this relies on their geometry; the above sizes have been named "magic number" clusters.[7,8,11,12] The lowest energy states observed from $n = 13$ up to $n = 33$ are characterized by a local icosahedral structure which allows the atoms to be packed into closed shells.

On the other hand, less stable structures have global minima that consist of a core Mackay icosahedron with the extra atoms clumped together on the surface.[7] Since, these atoms require less energy to be removed than those from a complete shell, the non "magic number" atom clusters have lower energy relative minima than the "magic" atom clusters.

Another unexpected result, which came out from early simulations of small argon clusters, was that microclusters can coexist in two distinct phases, a phenomenon in which both liquid-like and solid-like configurations are sampled for times long enough so that two different dynamical behaviors can be distinguished.[8,9,13,14] This was attributed to the great stability of the icosahedral structures and their large energy difference from the nearest accessible isomers.[13]

Covalent type clusters as Si_n, have been studied either by ab initio calculations[15,16] or by constructing potential functions fitted to macroscopic data.[17–19] Particularly stable configurations have also been observed for n = 4, 6, 10, 13, and 19. It seems, that the stability of the larger clusters is again a consequence of an ideal icosahedral arrangement of atoms, the same one that is met in Lennard-Jones clusters.[18] However, inferences on Si cluster structural trends must be taken with some caution, because of the inadequacies of the existing potentials to describe correctly and in a uniform manner the bonding properties of the silicon atoms in both the cluster and the bulk regime. On the other hand, Lennard-Jones potentials have been proved to be quite accurate for the description of any size of rare gas clusters.

Water molecular clusters are formed by hydrogen bonds which represent an intermediate case between the weakly bonded van der Waals systems ($\approx$ 0.3 kcal/mol) and those held together by strong covalent forces, ($\approx$ 100 kcal/mol).[20] Since, systems belonging to these two classes, like Ar_n and Si_n, have extensively and systematically been studied, the need for a detailed study of hydrogen bonded systems is apparent; $(H_2O)_n$ clusters are the most representative and important species of hydrogen bonded systems.

Small sized water clusters attained considerable theoretical attention in the past. However, there are no systematic studies of their stability and dynamical trends as happens for Ar clusters. Most of the effort was devoted to an as accurate as possible determination of the water-water interactions,[21–24] which provide the basis for the construction of accurate potentials capable of describing the liquid state. It became very early apparent, that water is far more complicated to model than the rare gases, and this property arises from the strength and the directionality of the hydrogen bond.

Also, the importance of non additive many body interactions for the description of the properties of both, small water clusters and liquid phase, has been a matter of investigation.[25–29]

The present paper is our first endeavor to study the detailed dynamics of hydrogen bonded systems with $(H_2O)_n$, $n = 3$, 4, 5, 6 and 8, being the realization systems. Using the relatively new potential function of Cieplak, Kollman, and Lybrand (CKL),[30] which allows the inclusion of polarization interactions, we try to answer the following questions:

What are the minimum energy geometries?

How the number of minima and their distribution in energy is associated with the size of cluster and their dynamical behavior?

Are there particularly stable configurations ("magic numbers")?

How easily the minima are visited when we run classical trajectories, and which minima can trap the trajectories for long periods of time?

Can we group the minima into classes according to their accessibility in the time evolution of the cluster?

More generally, can we observe localization effects which imply *structural selectivity*?

Do polarization interactions alter, and how, the static and dynamical properties of water clusters?

How the dynamics of water clusters is compared with those of argon and silicon clusters?

The organization of the present paper is the following. In Section 2, we present the potential as well as a brief review of the computational methods. In Section 3, low energy structures with the many body polarization terms off and on are presented for $(H_2O)_n$, $n = 3$, 4, 5, 6 and 8 clusters. The results of the simulations, caloric curves, root mean squares (rms) bond fluctuations, quenching of the visited configurations along the trajectory to their underlying potential minima, power spectra, and Maximal Lyapunov Exponents (MLE) are presented in Section 4. Section 5 summarizes the main conclusions of this work.

2 Potential Function and Cluster Dynamics Techniques

The potential function used is that of Cieplak et al.,[30] which is a modification of the Reimers, Watts, and Klein RKW2 potential for water-water interactions.[31] It is a 3-site model with charges placed on the two hydrogens ($q_H = 0.6$ e), and on the bisector of the $H-O-H$ angle at a distance 0.4913288 a_o from the oxygen ($q = -1.2$ e), and assumes rigidity of the individual water monomers. It was designed to incorporate many body interaction effects caused mainly by the second order induction energy. Its ability to reproduce properties of gaseous, liquid, and solid water was found to be satisfactory. However, its applicability to the cluster regime has not been tested.

The additive part of the potential, V_a, is a sum of the electrostatic interactions, oxygen-oxygen repulsions, Morse-type attractions between oxygens and hydrogens, and dispersion interactions.

The polarization term, V_p, is given by

$$V_p = -\frac{1}{2}\sum_j a_j \mathbf{E_j}\mathbf{E_j^0}, \tag{1}$$

where a_j are the polarizabilities of the oxygen and hydrogen atoms, and $\mathbf{E_j}$ is the electric field created at a given center by all other charges and induced dipoles belonging to any other molecule. $\mathbf{E_j^0}$ is the field created at a given center by the permanent charges only. V_p is evaluated through an iterative procedure at each time step. For completeness the potential is given in the Appendix.

We perform constant energy Molecular Dynamics calculations where the coupled Newton-Euler equations of motion for rigid bodies are integrated in time.[25] To avoid singularities inherent into the Euler angle representation of the reorientations of rigid bodies, we adopted the quaternion formalism.[32,33] As an integrator we used a variable time step, and variable order predictor-corrector algorithm described in the book of Shampine and Gordon.[34] The accuracy of the integration was checked by the conservation of the total energy, which was conserved up to the sixth decimal digit over as many as $1.8\text{x}10^5$ time steps. The variable time step integrator was proved to be more efficient compared to a fixed step Adams-Moulton predictor-corrector algorithm for the same degree of accuracy.

Our first task was to find the minimum energy configurations for each cluster examined. We adopted the Molecular Dynamics procedure as follows: trajectories are run with initial conditions to be either random structures or structures already known from the literature to be stable. Then, by quenching the kinetic energy several minima are approached. Our confidence about the located global minima is based on the several trials and examinations of different initial conditions which we have made.

The dynamics of the cluster is inferred by integrating first trajectories which start close to the absolute minimum configuration, with the total linear and angular momentum equal to zero, and for time equal to 437 ps. The first 125 ps were used for equilibrating the system, whereas averages were taken for the rest 312 ps. This time was much longer compared to previous calculations,[35] and we found it to be an adequate time interval to obtain converged mean values. Tests were made in the octamer for which integration over one ns did not show any substantial difference from the 312 ps runs.

Excitation of the cluster at higher energies was done by scaling the final velocities of the atoms with a constant factor, such as the total energy was increased by the constant amount of 0.5 kcal/mol. Some tests performed with smaller heating rates for the trimer and the octamer, and they did not alter the dynamical picture. The total energy range studied was up to the first fragmentation of the cluster.

With this procedure we were able to calculate the calorimetric equation of state for each cluster separately. Caloric curves with the polarization term included, were calculated for the trimer and the tetramer. Since, no significant differences were found, we did not extend these calculations to larger clusters. The implications from the omission of the polarization terms will be discussed in Section 4.

We performed quenches of the trajectory to the underlying local minima at specific energies and at time intervals of 0.5 ps. In this way, we were able to locate the most frequently visited local minima and metastable configurations, and to draw inferences about the topology of the potential surface.

Calculations with total rotational angular momentum, J, different than zero were also performed and they showed that there is a dependence on the initial conditions, and thus, non ergodic behavior should be expected when energy is stored in the rotational degrees of freedom. The clusters remained stable up to much higher temperatures and they experienced abrupt phase changes. Runs with different values of initial total angular momenta, evolved quite differently. However, the role of the cluster rotation as a whole is not systematically examined in this article.

It was found, that the root mean square (rms) bond length fluctuations, $\delta(E)$, was a more sensitive quantity to trace the structural changes of the cluster than the caloric curve, and it is given by

$$\delta(E) = \sum_{i<j}^{n} \frac{[< r_{ij}^2 > - < r_{ij} >^2]^{1/2}}{< r_{ij} >}, \tag{2}$$

where $<>$ means time average, and r_{ij} is the distance between the atoms i and j. The summation is over all molecules, n.

We have also calculated the oxygen atom velocity autocorrelation function, $C(t)$, at specific energies and the related power spectra, $I(\omega)$;

$$C(t) = \frac{< \mathbf{v_i}(t) \cdot \mathbf{v_i}(0) >}{< \mathbf{v_i}(0) \cdot \mathbf{v_i}(0) >}, \tag{3}$$

$$I(\omega) = \int_{-\infty}^{\infty} C(t) \exp(i\omega t) dt. \tag{4}$$

The local stability properties of the trajectories are estimated by computing the average rate of exponential divergence of two initially nearby trajectories according to the method of Benettin et al.;[36,37]

$$k(E) = \frac{1}{m\tau} \sum_{i=1}^{m} ln[D(t_i)/D_0], \tag{5}$$

where D is the distance in phase space of the two trajectories at time $t_i = i\tau$, which are initially separated by the distance D_0. τ is the period of time for which we integrate the pair of trajectories. k is called Maximal Lyapunov Exponent (MLE), and is expected to be a small number which tends to zero with time for regular motion, and a positive number for a chaotic trajectory. Although, there are other methods for characterizing a trajectory regular/chaotic, the MLE is one which can easily be applied to systems with many degrees of freedom.

Further analysis of the trajectories is done by examining time series of the bond lengths, bond and dihedral angles, and average kinetic energies of the clusters.

3 Minimum Energy Structures

3.1 Pairwise additive potential

We first search for minimum energy geometries predicted by the additive part of the potential. For the trimer the absolute minimum energy structure found, A0, is an almost equilateral triangle with sequentially bonded hydrogens; the equilibrium geometries are plotted in Fig. 1. All bonding hydrogens and oxygens lie on a plane and the angle between the OH and OO bond lengths is about 14 degrees. Both, ab initio calculations[24,26,38] and empirical potentials,[39] agree on the general features of this configuration, although they give different geometrical parameters. The double donor and double acceptor local minima (A3 and A4) reported by Reimers and Watts (RW)[39] are also predicted by the present potential, but they are found to lie at a somewhat higher energy, namely at 4.03 and 4.12 kcal/mol above the ground state compared to 3.7 and 4.0 kcal/mol found by the RW potential.

Apart from these we have identified two additional local minima (A1,A2) with energies lying between those of A0 and A3 minima. A1 is 0.75 kcal/mol above the absolute minimum with the same geometry for the oxygen atoms as the global structure, but with all the free hydrogens up, and the other is 2.98 kcal/mole having an intermediate structure between that of A0 and A3. These two local minima have also been found by the QPEN/B2 potential[40] and they lie 0.57 and 3.44 kcal/mol above the global minimum.

The most stable tetramer, B0 (Fig. 2), is a regular square, cyclic again with the free hydrogens at a trans position. The nearest lying relative minimum, B1, is a rectangle, slightly non planar with the free hydrogens at a cis position and lying at 0.56 kcal/mol above the ground state. The longer bond is between the oxygen atoms that carry the cis free hydrogens. This is the 4-1 local minimum of RW which was found to lie 0.7 kcal/mol above the global minimum, 4-0.

For both minima the angle between the OH and OO distances of the atoms which form the hydrogen bond, is 4 degrees. Comparing this value with the corresponding value of the trimer (14^0) we expect a stronger hydrogen bond for the square geometries. The consequencies of this conclusion to the structural stability of the water clusters is discussed later on.

The next two most frequently met local minima, B2 and B4, are non planar, with energies 1.33 and 1.77 kcal/mol respectively above the ground state B0, and differ only to the relative orientation of their non bonded hydrogens. Their geometries, and energy difference agree with the 4-2 and 4-4 structures of RW, but not in their absolute energies. B2 is also identified with the 4P structure of the potential of Kim, Dupuis, Lie, and Clementi (KDLC hereafter).[41] The B3 and B5 local minima are isomeric forms of the B2 and B4 but they are not frequently visited in the time evolution of cluster. The higher local minima B6, B7, and B8 (not shown in Fig. 2) are non planar quadrilateral configurations with different bonding patterns. B6 is the 4-5 structure of RW and has not been reported by KDLC. The highest energy local minimum, the B9 (Fig. 2), is at 3.94 kcal/mol and resembles the 4T′ structure of KDLC. The energies of the first up to ten local minima found here for all clusters studied are given in Table I in increasing order.

For the pentamer the global minimum C0 (Fig. 3), contrary to the common result of a cyclic ring configuration,[40–43] is predicted by the present potential function to be a rather floppy structure that can be formed from the B2 isomer of the tetramer, and with the fifth water molecule placed symmetrically on the top. It can be identified with the 5F structure of KDLC and with the 5-2 structure of Schröder.[40] Through quenching at different energies, we have located a total of 36 different minima spanning an energy range from 0.0 up to 4.1 kcal/mole. The energy spectrum of the local minima is dense when it is compared to that of the trimer and tetramer. The first relative local minimum, C1, lies 0.32 kcal/mol above C0 (Fig. 3a) and is of the same geometrical type as C0, although it follows a different bonding pattern. The lowest geometrically different configuration C14 (Fig. 3b), that consists of a triangle and a rectangle joined together, lies at 0.96 kcal/mol above the ground state, whereas the ring structure, C25, appears at even higher energies, at 2.11 kcal/mol. We have failed to locate any tetrahedrally coordinated structures. Nevertheless, the potential reproduces the tetrahedral properties of water liquid.[30]

The ground state of hexamer, D0 (Fig. 4), is of floppy character. Geometrically resembles the ground state of pentamer with the sixth water molecule accommodated at the free space between two oxygen atoms. This type of bonding pattern does not fit with any of those reported by KDLC, although the geometrical arrangement corresponds to that of the 6T and 6T′ structures with the 6T structure being the lowest in energy predicted by the MCY potential.[41] The cyclic hexamer of S_6 symmetry is believed to be the global minimum configuration by a number of investigators,[26] and this has recently been supported by ab initio calculations at the Hartree-Fock level.[44] However, it is expected that the configuration space of the hexamer is occupied by low energy near degenerate minima, which makes the definite identification of the absolute minimum a difficult task. The present potential predicts a staggered cyclic configuration which lies 6.0 kcal/mol above the ground state. An explanation for these differences will be given in Section 5.

The next two low lying local minima, D1 and D2, in contrast to what happens to the pentamer, are of a completely different structural type. They lie at 0.2 and 0.26 kcal/mol above the ground state and resemble the structures of prisms. They consist of two triangles placed the one on top of the other and they are sequentially bonded along the same direction for the former, and along the opposite direction for the latter. Prisms with different arrangement of hydrogen bonds were found at higher energies. Prisms have also been found by the MCY,[41] CCD,[41] and QPEN/B2[40] potential, which were either the ground state or very near to it. The "open book" structure (given by the MCY and CCD potentials) has been found by the present potential at 2.85 kcal/mol above the absolute minimum. The quenching studies showed that the configuration space is mainly occupied by two types of minima, the floppy and the prism. It is very dense in minima, although less than that of the pentamer, and becomes progressively denser with energy.

The lowest energy structure, E0 (Fig. 5), found for the octamer is a cube of S_4 symmetry. It consists of two squares the one on top of the other sequentially bonded along the same direction (like the B0 structure of the tetramer), and forming mutual vertical bonds with their trans free hydrogens. The first relative minimum, E1, is of D_{2d} symmetry at 0.03 kcal/mol higher in energy, and consists of two squares one on top of the other sequentially bonded along opposite directions and being vertically bonded by their trans free hydrogens. Both of these isomers have been previously reported[45] but with a reversed energy order. However, when the polarization term is included, we also obtain the D_{2d} geometry as the absolute minimum.

The second relative minimum, E2, is at 0.95 kcal/mol above the ground state. It can be obtained with the same way as the ground state, only now the two squares are bonded vertically with their cis free hydrogens. We find in the energy range up to 1.5 kcal/mole 8 cubes, E0-E7, which are formed systematically by combining two squares, with different bonding patterns and different relative orientations of their free hydrogens. At higher energies the configuration space is occupied either by distorted cubes or by less regular polyhedra with 12 or fewer bonds, (Fig. 5).

In Fig. 6 we show the energy spectrum for the minima of the trimer, tetramer, and pentamer and only part of that for the hexamer and octamer. Note, the absence of low lying isomers for the trimer, tetramer, and octamer (apart the D_{2d} minimum), and the high density of local minima in the pentamer and hexamer. The existence of gaps in the corresponding spectrum for rare gas clusters was attributed to magic numbers.[7] That the tetramer and octamer can be particularly stable relative to the pentamer and hexamer, is also verified by the dynamical calculations that follow.

In Fig. 7, we present the binding energy per molecule of the absolute minima as function of the size of cluster and for different potentials. All curves are almost parallel for clusters larger then the trimer, and there is no evidence for an increased stability of a particular size relative to neighboring ones in either case. However, this figure must be seen with some caution, since the minimum structures for the different potentials are not the same. In the same figure we plot the binding energy/bond instead of the binding energy/monomer produced from our results, and we see that *two peaks at $n = 4$ and $n = 8$ appear.* This is the first indication of the stability of those configurations with geometries which are based on the square tetramer.

3.2 Influence of polarization interactions

The minimum energy structures found when polarization interactions are included, are the same for the trimer, tetramer and pentamer as those located with the pair additive potential. However, for the hexamer and octamer the positions of the two lowest minima are interchanged with higher energy structures. In hexamer, the prism type configuration D2 (Fig. 4) becomes the lowest energy structure, whereas in octamer the D_{2d} configuration (Fig. 5) becomes the one with the lowest energy, in accord to the findings of the TIP3p,[45] EPEN,[46] CCD,[41] and MCY[41] potentials. The interchange of the S_4 and D_{2d} configurations in octamer and the corresponding change in the hexamer are not expected to influence the shape of their caloric and rms curves.

The polarization energy contribution was 12 to 14% of the total energy of the n-mers. Previously reported values for the trimer and tetramer are within this range.[26,27] In Table II the energies of a few minima of water clusters obtained with the polarization terms in the potential function, are stored.

4 Cluster Dynamics

4.1 Pairwise additive potential

The plot of the total energy, E, of the cluster versus its long time averaged kinetic energy, E_k, constitutes the caloric curve. The mean kinetic energy corresponds to a temperature which is given by the following expression

$$< E_k >= \frac{d}{2} k_b T, \quad d = \quad (6n - 6) \text{ if } J = 0, \tag{6}$$

$$d = \quad (6n - 3) \text{ if } J \neq 0, \tag{7}$$

where k_b is Boltzmann's constant, and d the number of degrees of freedom among which we assume equipartition of the total energy. J is the total angular momentum of the cluster. The curves derived from the simulations of the $n = 3$, 4, 5, 6, and 8 water clusters using pairwise additive potentials and zero total angular momentum, are presented in Fig. 8. The corresponding oxygen-oxygen rms bond length fluctuation curves as function of energy/molecule are shown in Fig. 9.

All caloric curves exhibit a low energy linear region which at an intermediate temperature changes its slope, marking thus, the onset of a phase change. At about the same temperature the rms bond length fluctuation curves show an abrupt increase of their amplitudes as the transition region is approached. Since, the transition energy is not well defined in the caloric curves, we adopted for the definition of the melting temperature, T_m, of the cluster, the temperature at which $\delta(E)$ shows its first large jump.

In Table III, we present the melting temperatures of the clusters. We can see that the T_ms for $n = 4$ and 8 are remarkably elevated relative to those of pentamer and hexamer. Therefore, in conjunction to the conclusion drawn from Figs 6 and 7, that represent static quantities, melting temperatures point out that the tetramer and octamer are more stable relative to pentamer and hexamer. This can be attributed to the structural stability of the square structures as the building element of the minimum energy configurations of $n = 4$ and 8 clusters.

It is tempting to assume that such a conclusion is rather independent from the particular potential function we used. Different potentials agree on the minimum energy structures found for the trimer, tetramer, and octamer, and admit that pentamer and hexamer have a high density minima with energies close to the global one. Therefore, we believe, that either potential function can produce distributions such as these of Fig. 6 and predict melting temperatures close to those of Table III. We have also included melting temperatures for n = 12, 20, and 35 clusters, obtained by other investigators and with different potential functions.

Details of our calculations for each separate cluster are now presented.

4.1.1 $(\mathbf{H_2O})_3$

In the rms bond length fluctuation curve (Fig. 9), we distinguish three almost linear regions. The first starts from low energies and extends up to -8.5 kcal/mole, the second with a larger slope goes up to -5.0 kcal/mol and the third one continues up to fragmentation. At the energies that correspond to the first linear region, the fluctuations are very small, at the intermediate one they start rising to higher values, and finally they increase at a lower rate.

We performed quenches to the nearest local minima along trajectories with energies from the three distinct regions, namely at E =-8.5 , E =-7.0, and E =-5.0 kcal/mol. The potential energies of the underlying local minima with respect to the time of visit are shown in Fig. 10 for the energies at -7.0 and -5.0 kcal/mol. Up to -8.5 kcal/mol, the cluster is found exclusively in the global potential well. At -8.5 the trimer has sufficient energy to break a bond and this is what we observe. One bond can open as much as 10 a_o and after a few ps it closes again. During the 312 ps of the simulation we have not recorded any substantial energy transfer to other bonds. Above -8.5 kcal/mol the change of the slope of the caloric curve and the abrupt jump at the bond length fluctuation curve are caused by the accessibility of the next local minima (A1 and A2). This implies the break of one bond and the simultaneous formation of a new one, although weaker. At E =-7.0 kcal/mole the cluster makes infrequent visits to the A1 and A2 local minima where it stays no more than 0.5 ps, which is the quenching time interval (Fig. 10a). At E =-5.0 kcal/mole the higher energy local minima A3 and A4 are accessed, but again the residence times are very short, (Fig. 10b). At all energies studied, the system spends most of its time in the global potential well.

The A3 and A4 local minima are obtained from the global A0 only through severe bond rearrangement, i.e. through the break of two hydrogen bonds. At E =-5.0, i.e. at 8.8 kcal/mole above the A0, the cluster has exactly the required amount of energy to perform such rearrangements. The process of energy transfer is very efficient and quick now. No jumps from one local minimum to another have been recorded at any energy. All excursions to other minima proceed through the well of the global minimum only. At energies from -5.0 kcal/mol and higher the system is free to move around the whole available configuration space, and it turns out, that there are no barriers to prevent such motions. This fact is apparent from the slower increase of the $\delta(E)$ curve at this energy range. The energetics of the transitions and the short residence times at the local minima imply the existence of shallow wells that are separated by low energy barriers.

4.1.2 $(\mathbf{H_2O})_4$

For the tetramer we observe a first small jump at E =-20.5 kcal/mol in the $\delta(E)$ curve and a larger one at E =-15.5 kcal/mol. Between the first and the second jump the fluctuations rise at a smaller rate, whereas after the second jump they increase rapidly until fragmentation occurs, without showing any tendency to level off. From quenching studies at E= -20.5 and -18.0 kcal/mol which lie below the second jump, we find the system to oscillate at increasingly higher frequencies between its two low lying trans and cis minima, B0 and B1 (Fig. 11a). The first small jump of the delta curve signifies exactly the onset of this transition. Remember, that a small OO bond length change is needed for the trans to cis transition to take place. This trans-cis oscillation is not evident in the caloric curve, because of the small potential difference.

The second jump is related to the accessibility of the first non planar configurations B2, and the B4 (they differ in the rearrangement of the free hydrogens). The B3 and B5 isomers are not frequently visited, and they have the same hydrogen bonding patterns as the B2 and B4. Quenches performed at distinct energies from the region of the $\delta(E)$ curve above the second jump, show that the main transition, even at the energies close to fragmentation, is the B0, B1 isomerization (Fig. 11d). The opening of the configuration space happens gradually and slowly, probably because the other higher local minima, B6-B9, are located at 1.5 kcal/mol above the B5 local minimum and they are not easily accessed.

From Fig. 6 we can see that there is an energy gap between these two classes of local minima, B0-B5 and B6-B9, which can explain the trapping of the trajectory at the lower energy wells. The dominant transitions are the B0,B1 and B0,B1,B2, as this is shown in Fig. 11.

The mechanism of the transition among the planar B0 and B1 to the non planar geometries B2-B4 is through the removal of a monomer at large distances, sometimes up to 16 a_o, thus, making two bonds to break simultaneously. When the monomer comes back is stabilized in a non planar configuration, and vice versa. As in the trimer, the residence times at the relative minima are very short and the frequency of the visits increases with energy. However, in tetramer the potential surface can be distinguished into three regions well separated one from the other with high barriers. The first one includes the lowest minima B0 and B1, where the system spends most of its time. The second one includes the B2, B3, B4, and B5 minima which are equivalent non planar configurations. The trajectory is not trapped here, but rather prefers to oscillate between this region and the one that includes the cis-trans minima. The third one consists of the B6-B9 non planar configurations which are temporarily visited only at higher energies and only from the well of ground state.

4.1.3 $(H_2O)_5$

The energy spectrum of the pentamer (Fig. 6) shows the largest density of local minima of all the clusters examined here. This is directly reflected to its melting point which is the lowest. The local minima distribution is rather uniform exhibiting no gaps between certain classes of configurations. Since, the most frequently visited low energy minima have comparable potential energies, no significant change in the slope of the caloric curve is detected. The onset of large fluctuations at the delta curve coincides with the transitions to the class of C1, C2, and C3 minima that are derived from the global one through the eruption of one bond and a simultaneous formation of a new one. This happens at about the energy of -25.5 kcal/mol. Below this energy quenches show (Fig. 12a) that the only transitions are between the isomeric forms of the ground state which are taken from different rearrangements of the free hydrogens (C5 and C8).

Quenching at an energy just above the transition region (Fig. 12b) shows the trapping of the cluster between the C0 and related isomers, and C1, C2, and C3 minima and also, some short excursions to the ring structure. Beyond that energy fluctuations rise more slowly in time. Quenches at two energies from this region, (Figs 12c and 12d) show that the trajectory tries to explore most of the available configuration space.

Although, we have not found any particularly stable excited configuration, it is important to note the increased number of visits to the ring structure with energy. Visits to the ring that accounted to the 1.5% of the total time at the transition energy, were increased to 10% at E =-18.0 kcal/mol. The potential of the pentamer can be characterized by the absence of significant barriers between the local minima. Once a transition to a low energy local minimum has been accomplished, and this happens at an energy where one bond breaks, the cluster starts the exploration of the configuration space.

4.1.4 $(\mathbf{H_2O})_6$

The rms fluctuations of the OO bond length curve for the hexamer shows three separate regions, each of them implying a different type of dynamics. The structural interconversion and their influence to the caloric and delta curves are found by quenching the trajectory at three energies, one from each separate region (Fig. 13). Both, caloric curve and $\delta(E)$ increase linearly with time until the energy of E =-31.0 kcal/mol is reached, where the first jump is observed. Up to this energy the cluster remains in the global well D0, (Fig. 13a).

Generally, the low energy local minima of the hexamer can be divided into two geometrical classes. Those that resemble the global minimum structure and are of floppy type, and those that resemble a triangular prism and are more rigid. The fluctuations suddenly increase when the cluster makes a transition to the prism type geometries D1 and D2, (Fig. 13b), and to the class of D3-D5 minima. The latter have the same floppy geometry as the global minimum, and a similar arrangement of the bonds, although different from that of the global minimum structure. The oscillations between the D3 and D5 minima occur, because of the two different equilibrium positions of the added sixth molecule at the space between two end oxygens; the one is at the middle and the other close to the one of them.

That the prisms may represent stable excited configurations, is justified by the long times the trajectory spends in such minima. This sort of coexistence between the floppy and the triangular prism configurations is reflected in the intermediate region of the caloric curve and to the absence of large variations in δ curve. At E =-29.0 kcal/mol, the system accesses other types of geometrically different configurations. No trapping in a particular configuration is observed, and we may assume that above this energy the cluster behaves like a liquid, (Fig. 13c).

The low melting temperature of the hexamer can again be explained from the high density of the low energy local minima. However, the fact that this density is lower as compared to that of the pentamer results in a higher melting temperature for the hexamer than the pentamer; but lower compared to the other clusters examined here. Additionally, since the lowest local minima are of different geometrical type than the global one, and a substantial bond rearrangement is needed for their accessibility, coexistence phenomena are observed. *This is the first cluster to exhibit trapping of the trajectory for a long time in excited configurations.*

4.1.5 $(H_2O)_8$

The caloric curve for the octamer shows a linear increase with energy up to $E = -46.0$ kcal/mol. The fluctuations rise also very slowly, suggesting that small sized rearrangements are taking place. This is rather surprising, because already at low energies, about -47.0 kcal/mol the cluster was found to make a transition from the E0 to E1 minimum, (S_4 to D_{2d}). The bonding pattern of these two configurations is quite different and transformation from one minimum to another can not be made by simple movements alone. Rather a more collective motion is required. However, the E0-E1 transition does not show up in the $\delta(E)$ curve probably because it happens only a few times (see for example Fig. 14a).

The onset of large scale fluctuations coincides with transitions to the space occupied from configurations different than cubes as well as distorted cubes. For example in Fig. 14b at times beyond 240 ps the cluster stays for significant time in the region where the minima, E20, E21, E22, and a higher one at -55.382 kcal/mol, are located. Looking at Fig. 14 we find many flat regions which correspond to quenching to regular cubic structures. We have identified 8 of them (E0 up to E7) which, as explained in Section 3, are produced by different combinations of two squares. All cubic configurations constitute stable local minima as is deduced from the long residence times, separated from the corresponding distorted cubic configurations by large barriers. The latter configurations may be rather considered as transitional structures where the cluster is trapped before making a transition to a stable cubic form.

We have performed quenches up to E=-38.5 kcal/mol, i.e. 22.6 kcal/mol above the ground state. Even at this energy the cluster remains for an appreciable time in certain cubic configurations, and the trajectory is far from being considered as ergodic. The cluster fragments without turning to a liquid. The total residence times of the cluster to its cubic and distorted cubic forms at E=-47, -45, -44.5, and -40 kcal/mol are 96.5%, 77% , 90%, and 45% of the total time of simulation, respectively. Therefore, we may conclude that the configuration space of the octamer constitutes of a large number of stable cubic structures, where the system can be trapped for a long time.

4.2 Power spectra and Maximal Lyapunov Exponents

In Figs 15 and 16 we present the power spectra of the n-mers taken at their melting temperature and at an energy near fragmentation, respectively. The power spectra have been obtained by taking the Fourier transform of the OO velocity autocorrelation function. Therefore, higher frequencies which are expected from the librational motions of the bonded hydrogens are not observed.

There are a few points to be noticed. First, for all n-mers except the trimer, there are two distinct well separated bands, one at low frequencies around 30 cm^{-1} and the other around 200 cm^{-1}. The range of low frequencies is attributed to torsional motions of the oxygen lattice, whereas, the higher frequency to stretching motions of the hydrogen bond. This has been verified by taking the power spectra of specific torsional angles and OO bond lengths.

Second, systematically the low frequency band has a higher intensity than the band at 200 cm^{-1}. This trend is also observed in the power spectra of $(H_2O)_{20}$[47] and at the bulk liquid.[48] Also, the lowest frequencies observed, agree with the harmonic frequencies calculated by Dykstra.[42]

Third, the two bands do no tend to overlap even at higher energies.

Forth, the distinct sharp and high intensity peaks at low frequencies found for the tetramer and octamer are again an indication of the stability of their low energy minima. Even at elevated temperatures, the peaks for the $n = 4$ and $n = 8$ clusters remain well defined.

Finally, note the absence of diffusion for the tetramer and octamer. The intensity of the zero frequency component, which is an indication that diffusion is taking place, is of the same order of magnitude for the trimer, pentamer and hexamer, whereas such a component is hardly seen in the tetramer and octamer.

The estimation of the rate of exponential divergence of two initially neighboring trajectories is a well established measure of the extent of instability in phase space at the region where the trajectory is located. The MLE not only distinguish regular from chaotic trajectories, but also provides a characteristic time in which the system forgets its initial conditions.[49] Usually, this parameter is computed for a range of energies of a specific system and for several initial excitation, thus, allowing to portrait the structure of phase space. Nevertheless, it is interesting to compare the MLE for the several clusters of water and with the pairwise additive potential.

In the present study we calculated the MLE for the trajectories we have examined but no systematic search has been undertaken for each particular cluster. In Figs 15 and 16 we plot the stochastic parameter defined in Eq. (5), as a function of time for the same trajectories used to calculate the power spectra. From these graphs we underline the following:

Convergence of the MLE is obtained after about 5×10^5 time au. The values for the trimer and tetramer are higher than those of the other clusters, and lower for the octamer. However, we point out that it is difficult to compare individual MLE, since these have been calculated for different energies relative to their absolute minimum. What we want to emphasize is that the range of variation of the MLE for all clusters in the Figs 15 and 16 is rather small. It varies between (0.0001, 0.0002) au^{-1}, and (0.00015, 0.00022) au^{-1} for the two cases studied.

The above values of the MLE corresponds to periods of time which are characteristic of one stretching vibrational hydrogen bond (≈ 200 cm^{-1}). Thus, we may conclude that for energies above the melting point irrespectively of the size of cluster randomization of the initial conditions occur at about one stretching vibrational period.

4.3 Influence of polarization interactions

To assess the significance of the many body forces on the dynamics, we have examined time series and power spectra of individual trajectories by including the polarization energy in the potential, V_p. Furthermore, we have calculated caloric and rms curves for the trimer and tetramer and imposing zero total angular momentum. The caloric curves for $n = 3$ and $n = 4$ together with their counterparts with no polarization are compared in Figs 17 and 18, respectively. These two curves are almost parallel to each other. The delta curves show the same trends indicating, that there is no significant changes in the behavior of the clusters by the inclusion of the polarization forces.

In Fig. 19 we present power spectra for the tetramer and octamer at two different energies and for the potential with polarization. Comparison of these results with those in Figs 15 and 16 again shows that, there are no indications of significant changes in the dynamics. The two bands which characterize all clusters remain, but we do find changes in the intensities of the lines.

The contribution of the polarization energy to the total energy of the absolute minima of the clusters is between 12 and 14% and it expected to be of similar size for other configurations. Therefore, it is not surprising that polarization interactions do not change the general trends in dynamics of the clusters. It turns out, that polarization energy has a tuning effect for some clusters, like in the hexamer and octamer where the geometry of the absolute minima changes.

Even in the case of the hexamer, where we find the more stable prism geometry to be the absolute minimum when polarization is introduced, calculations of the caloric and rms curves starting with the prism structure do not show any different behavior.

4.4 Influence of total angular momenta

The investigation of the cluster dynamics with respect to the total angular momentum requires a systematic work similar to the change of the total energy. However, we present some results which we obtained from trajectories with total angular momentum different than zero.

In Figs 20 and 21 we show the caloric curves and the rms of the OO fluctuations for the trimer and tetramer water clusters, respectively. We must say that these curves do not correspond to a constant J value for the whole energy range, since we heat the cluster by scaling the velocities at the end of each run at constant energy, and thus, the total angular momentum is also scaled by the same factor.

From the plots in Figs 20 and 21 it is seen that there is a dependence on the initial conditions. Specifically for the trimer we find two of the caloric curves (b and c) to have the same behavior as the curves with $J = 0$. When we substructed the amount of energy that corresponds to the three rotational degrees of freedom, assuming equipartition of the total kinetic energy, these two curves fall upon the caloric curve for $J = 0$. This is most apparent in the rms plots. On the other hand, curve (a) in Fig. 20 reveals that the rotational kinetic energy is not exchanged with the other degrees of freedom. Analysis of the trajectories showed that the cluster remained into the global well up to fragmentation. The abrupt change of the slope observed corresponds simply to the break of one bond, but by no means to a transition to another local minimum.

For the tetramer, we have computed two curves with different initial conditions labeled as a and b, where the cluster retained its square geometry (Fig. 21). The only transitions which the cluster performed, concerned the rearrangement of the non bonded hydrogens from their trans to cis position and vice versa.

Similar behavior has been found for the other clusters as far as the dependence on the total angular momentum is concerned. *These results demonstrate that for some initial conditions the rotational degrees of freedom are not strongly coupled with the internal degrees of freedom, which means that the phase space has a structure with regions showing different dynamical behavior.*

5 Discussion and Conclusions

In this work we have tried to answer several questions related to the structural stability and dynamical properties of water clusters, $(H_2O)_n$, and with $n = 3-6, 8$. The potential used is that of Cieplak et al. and is written as the sum of a pairwise additive part plus polarization interaction terms. The parameters in the potential function have been fitted to known properties of the dimer, liquid, and solid state water.

First, it is worth comparing the minimum energy geometries found by the present potential with those predicted by other potential functions. Agreement is obtained for the trimer, tetramer, and octamer, but the CKL potential does not give low energy minima for the cyclic structures of the pentamer and hexamer as other potentials do. It is found that the energies of the cyclic geometries are for the pentamer 2.1 kcal/mol and for the hexamer 6.0 kcal/mol above the ground state, or 1.77 and 5.44 kcal/mol respectively, when polarization terms are included. Nevertheless, there is still ambiguity about the minimum energy geometries of these clusters.

The most accurate ab initio calculations for the hexamer,[44] predict again a cyclic structure with S_6 symmetry as the minimum energy configuration, in accordance to the predictions of the Campell and Mezei potential.[26] However, the fact that different levels of optimization gave different configurations of the absolute minimum, suggests that the hexamer may possess many local minima very close in energy, and that still more accurate calculations are needed for the location of the global minimum configuration.

For the pentamer the central force pair potential of Stillinger and Rahman[22] favors a different geometry referred to as "cage".

In order to understand the different predictions of the CKL potential function, we have compared it with the widely used MCY potential. We find that the MCY[41] function is more attractive and contributes about 25% more in the total interaction energy at distances around 7 a_0. This explains why a ring structure with six hydrogen bonds for the hexamer is more stable than our structure with nine hydrogen bonds.

For the octamer the ambiguity on the global minimum structure is less. A cubic geometry for the absolute minimum with D_{2d} symmetry has been found from a number of potentials, and it has also been verified by Hartree-Fock calculations. A new configuration of S_4 symmetry has been recently reported to lie 0.26 kcal/mol above the D_{2d}.[45] All higher excitations are believed to lie 2-5 kcal/mol above these two minima. The pairwise additive part of the CKL potential does predict both minima However, with the S_4 minimum to be lower in energy by 0.03 kcal/mol than the D_{2d}.

the order of the minima is reversed when polarization interaction terms are included.

Examining the energy distributions of the minima for all clusters we find that the tetramer and octamer show energy gaps between classes of minima of different morphology. This has been associated with the trends of melting temperature obtained from the rms and caloric curves of the clusters. The latter have shown that both the tetramer and octamer are more stable with respect to large amplitude motions. On the other hand, these two clusters have low lying minima which are accessible with a relative small amount of energy; the trans-cis configurations for the tetramer, and the D_{2d} and S_4 configurations for the octamer.

The pentamer and hexamer are characterized by lower melting temperatures and this is attributed to the relatively large number of local minima with non regular, rather floppy geometries. Generally, the barriers between regular and non regular geometries are high, since the transition from one to the other requires the eruption of at least two hydrogen bonds. This is clearly seen in the hexamer, which is the first water cluster where coexistence phenomena are observed.

All the local minima were located by the quenching technique. Therefore, we can not claim that we have scanned the whole configuration space. But we believe that any new relative minima would not add much to our conclusions. One may also argue for the octamer that the low energy gap in the energy distribution of the minima may contain additional minima, not recovered by our calculations. We would not support such an argument, since the first excitations above the D_{2d} and S_4 local minima are obtained by a consistent and systematic way. For example the S_4 and D_{2d} minima consist of two squares placed the one on top of the other, with sequential hydrogen bonds along the same direction for the former and along the opposite direction for the latter. The two squares are held together by their free hydrogens at trans position. The next lying E2 and E3 local minima are obtained with the same way as the S_4 and

D_{2d}, but only now they are held together with the free hydrogens at the cis position. The E4 and E5 minima are held by three bonds offered by the top square and one bond by the bottom square, and so forth.

Generally, we can claim that polarization interaction terms do not change significantly the dynamics of water clusters. Their contribution in the minimum energies is about 13%, and the time average quantities such as the kinetic energy and the fluctuation of the bond lengths did not show qualitative changes for the trimer and tetramer. Differences in the dynamics may appear because of the change of the structure of absolute minimum to a different geometrical class as happens in the hexamer. In this cluster the trigonal prism becomes the lowest energy minimum.

One of the major findings of this work was that the tetramer and octamer constitute particularly stable structures. This conclusion was drawn first from the energy distributions of the local minima. Second, the binding energies per bond in the global minima of tetramer and octamer were elevated relative to those of neighboring clusters. This fact implies the structural stability of the tetragonal configurations, which can further serve as building elements for larger clusters. Third, we refer to the melting temperatures as defined previously in the text, which were higher for tetramer and octamer, relative to pentamer and hexamer. We believe, that such a conclusion could have been obtained with any other potential function that would be able to predict the same minimum configurations for tetramer and octamer, and the same local minima energy distributions.

And finally, the absence of appreciable diffusion in power spectra even at energies close to fragmentation for tetramer and octamer, and their sharp peak structure also work towards the same direction.

The above results are in the same line as the results for Ar and Si clusters. We mean that we can define the tetramer and octamer as "magic number" clusters for the same resons magic numbers have been defined for the other species.

The dynamics of the clusters as is revealed from the power spectra, MLEs, and the examination of several time series, demonstrate that there are two characteristic motions for all clusters larger than trimer. These are the stretching motions of the hydrogen bonds with characteristic frequencies around 200 cm^{-1}, and the torsional motions of two planes defined by oxygen atoms with characteristic frequencies around

30 cm^{-1}. Of course, there are frequencies which correspond to the bonded and non bonded hydrogen atoms and we have not analyzed them here, since the OO bond lengths are those which reveal major structural changes. What we want to emphasize is the transferable properties of small clusters to larger ones and even into the liquid phase, such as the two band frequencies in the power spectra. We believe that this is due to the fact that local type motions of the hydrogen bonds, i.e. stretching and torsional, dominate in the dynamics of the cluster.

In this work, we have tried to associate the cluster dynamics with the minimum structures supported by the potential function. By classifying the minima in classes according to their geometrical similarities, and we admit that this is a qualitative way, we hope to extract the dynamics of hydrogen bonded systems. The analysis which we presented in the previous sections seems to justify this expectation.

Finding specific geometrical objects which determine the dynamics of a system is a strategy which we have applied the last years.[1,50–52] For systems with a small number of degrees of freedom, where regular and chaotic regions coexist in the same energy manifold, the most important objects are stable and unstable periodic orbits. For large systems like the studied water clusters where the phase space is mainly chaotic, the location of stationary points allow for a systematic way of studying the dynamics.

We summarize the main conclusions of this work. The CKL potential predicts minima for the trimer, tetramer, and octamer in good agreement with other potential functions in the literature. For the pentamer and hexamer it gives rather high energy values of the ring structures, when they are compared to predictions of other potentials.

With respect to large amplitude fluctuations of the OO bond lengths the tetramer and octamer are found to be the most stable, whereas the pentamer and hexamer are less stable because of low lying relative minima of similar geometry.

The dynamics of water clusters is found to be chaotic with a characteristic time for forgetting the initial conditions equal to the period of the stretching mode of hydrogen bond. For all clusters but trimer we observe two bands of frequencies in the Fourier transform of the oxygen velocity autocorrelation function; one around 30 cm^{-1}, and one at 200 cm $^{-1}$. These frequencies are due to torsional, and stretching local motions of the hydrogen bond, and thus, should be independent of the size of cluster.

Generally, we do not find qualitative differences in the dynamics when polarizations terms are added into the potential function. On the other hand, they may change the absolute minimum, and in this case a minimum of different morphology may result in a different dynamical picture.

Rotational and internal degrees of freedom may stay decoupled for long times, something which is reflected in the caloric curves of the clusters.

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A Appendix: Potential Function for Water Clusters

The potential used in this work is that of Cieplak, Kollman, and Lybrand,[30] which is written as the sum of a pairwise part, V_a, and the polarization interaction term, V_p, which models the main part of the second order induction energy.

$$V = V_a + V_p, \tag{8}$$

$$\begin{aligned} V_a = {} & \sum_{i,j} \frac{q_i q_j}{r_{ij}} + \sum_{OO} A_{OO} \exp(-B_{OO} r_{OO}) + \sum_{OH} A_{OH} \exp[-B_{OH}(r_{OH} - r_{min})] \times \\ & \{\exp[-B_{OH}(r_{OH} - r_{min})] - 2\} - \sum_{OO} F \left[C_6 \left(\frac{g_6}{R_{sc}} \right)^6 \right], \end{aligned} \tag{9}$$

$$g_6 = 1 - \exp\left(-\frac{2.1}{6} R_{au} - \frac{0.109}{6^{1/2}} R_{au}^2 \right), \tag{10}$$

$$R_{sc} = r_{OO} (I_{H_2O}/I_H)^{2/3} = 0.94834673 \times r_{OO}, \tag{11}$$

$$F = 1 - R_{au}^{2.326} \exp(-R_{au}), \tag{12}$$

$$R_{au} = R_{sc}/0.529177, \tag{13}$$

$$V_p = -\frac{1}{2} \sum_j \alpha_j (\mathbf{E_j} \mathbf{E_j^0}), \tag{14}$$

$$\mathbf{E_j} = \mathbf{E_j^0} + \mathbf{E_j^{ind}} \tag{15}$$

$$\mathbf{E_j^0} = \sum_{i \neq j} \frac{q_i \mathbf{r_{ji}}}{\mathbf{r_{ji}^3}}, \tag{16}$$

$$\mathbf{E_j^{ind}} = \sum_{i \neq j} \mathbf{T_{ji}} \mu_\mathbf{i}^\mathbf{ind}, \tag{17}$$

$$\mathbf{T_{ji}} = \left(-\frac{\mathbf{1}}{\mathbf{r_{ji}^3}} + \frac{3\mathbf{r_{ji}} \otimes \mathbf{r_{ji}}}{\mathbf{r_{ji}^5}} \right), \tag{18}$$

$$\mu_\mathbf{i}^\mathbf{ind} = \alpha_i \left(\mathbf{E_i^0} + \sum_{\mathbf{k \neq i}} \mathbf{T_{ik}} \mu_\mathbf{k}^\mathbf{ind} \right), \tag{19}$$

$$\mathbf{r_{ji}} = \mathbf{r_j} - \mathbf{r_i}. \tag{20}$$

The summation is over all interacting molecules and charges or induced dipole moments. Equations (19) are solved by an iterative procedure.

The parameters are: $A_{OO} = 4.4 \times 10^6$ kcal/mol, $B_{OO} = 4.830$ Å^{-1}, $A_{OH} = 2.5$ kcal/mol, $B_{OH} = 3.00$ Å^{-1}, $r_{min} = 1.63781$ Å, $C_6 = 625.450$ kcal/molÅ^{-6}. The charges are on the two hydrogen atoms, $q_H = 0.6$ e, and on the bisector of the $H - O - H$ angle at 0.26 Å from the oxygen atom, $q = -1.2$ e. The polarizabilities are $a_H = 0.135$ Å^3, and $a_O = 0.465$ Å^3.

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TABLE I: Energies in kcal/mol for the absolute and a few relative minima of water clusters obtained with the pairwise additive potential.

$(H_2O)_3$	$-13.74, -12.99, -10.75, -9.71, -9.62$
$(H_2O)_4$	$-22.31, -21.75, -20.99, -20.85, -20.54$
	$-20.48, -19.03, -18.68, -18.55, -18.37$
$(H_2O)_5$	$-30.47, -30.15, -30.05, -30.03, -29.98$
	$-29.97, -29.96, -29.93, -29.90, -29.83, -29.81$
$(H_2O)_6$	$-40.29, -40.09, -40.03, -39.91, -39.65$
	$-39.58, -39.48, -39.36, -39.33, -39.32, -29.19$
$(H_2O)_8$	$-61.17, -61.14, -60.22, -60.02, -59.91$
	$-59.75, -59.73, -59.70, -59.30, -59.28, -59.23$

TABLE II: Energies in kcal/mol for the absolute and a few relative minima of water clusters obtained with the polarization terms in the potential function.

$(H_2O)_3$	-15.48 (A0), -14.61 (A1), -11.56 (A2), -11.49 (A3), -10.14 (A4)
$(H_2O)_4$	-25.66 (B0), -25.02 (B1), -23.07 (B2), -22.56 (B3), -21.94 (B4)
$(H_2O)_5$	-34.66 (C0), -32.88 (C25)
$(H_2O)_6$	-45.31 (D2), -45.24 (D1), -45.19 (D0), -39.87 (cyclic)
$(H_2O)_8$	-70.36 (D_{2d}), -70.30 (S_4)

TABLE III: Melting temperatures in K of various water clusters as are estimated from the OO rms bond length fluctuation diagrams (Fig. 9), and using the pairwise additive potential. The values for the clusters with more than 8 monomers have been taken from the literature.

	$(H_2O)_3$	$(H_2O)_4$	$(H_2O)_5$	$(H_2O)_6$	$(H_2O)_8$	$(H_2O)_{12}^a$	$(H_2O)_{20}^b$	$(H_2O)_{35}^a$
T_m	198	186	95	122	168	205	200	230

(a) I. P. Buffey, and W.A.Gebbie, *J. Chem. Soc. Faraday Trans.*, 86, 2357, 1990.

(b) P. M. Plummer, and J. S. Chen, *J. Phys. Chem.*, 87, 4190, 1983.

Figure Legends

1. Geometries of the minima of water trimer. The energies are given in Table I in increasing order. Two oxygen atoms are connected with a straight line when the interaction of the two water molecules is lower than -3.5 kcal/mol.

2. The geometries of the global minimum B0, and relative minima of water tetramer. Energies for the global minimum and the first nine relative minima are given in Table I.

3. Structures of the global and relative minima of water pentamer. Energies are given in Table I. The energies of the C14, C25, and C30, not included in Table I, are -29.51, -28.36, and -27.46 kcal/mol respectively.

4. Structures of the global and relative minima of water hexamer. Energies are given in Table I in increasing order.

5. Geometries of the global and relative minima of octamer. Energies are given in Table I. The energy of E11 is not included in Table I and is -59.15 kcal/mol.

6. Distributions of the relative minima of water clusters located in the energy range up to 4.5 kcal/mol above the absolute minimum. Notice the gaps in the distributions of the tetramer and octamer relative to those of the pentamer and hexamer. Only part of the minima is given for the hexamer and octamer.

7. Comparison of the calculated energies per molecule of water clusters with those predicted from the MMC,[42] and CCD[41] potentials. The curve which presents the binding energy per hydrogen bond shows the increased stability of the tetramer and octamer relative to other clusters. For completeness we have included the values of the heptamer, but no systematic search has been done for this system yet.

8. Plots of total energy per molecule with respect to the temperature of water clusters. The calculations have been performed with the pairwise potential V_a, and zero total angular momentum, J. Energies in kcal/mol.

9. Root mean square of the OO bond length fluctuations for water clusters as function of the energy/molecule. Energies in kcal/mol.

10. The energies of the relative minima of the water trimer found by the quenching technique, for a trajectory at (a) -7.07 kcal/mol total energy, and (b) -5.07 kcal/mol. The quenching is performed every 0.5 ps, and the line at the bottom of the graph corresponds to the absolute minimum (see text).

11. As Fig. 10 but for the tetramer. The total energies of the trajectories run are (a) -18.0 kcal/mol (below the melting temperature), (b) -15.0 kcal/mol (at the melting temperature), (c) -12.0 kcal/mol (above the melting temperature), and (d) -11.0 kcal/mol.

12. As Fig. 10 but for the pentamer. The total energies of the trajectories are (a) -27.1 kcal/mol (below T_m), (b) -25.1 kcal/mol (at T_m), (c) -21.1 kcal/mol (above T_m), and (d) -18.1 kcal/mol.

13. As Fig. 10 but for the water hexamer. The energies of the trajectories are (a) -34.1 kcal/mol (below T_m), (b) -31.1 kcal/mol (at T_m), (c) -26.1 kcal/mol (above T_m). Notice in plate (a) that in spite of 6.2 kcal/mol excess energy the trajectory does not visit any other minimum but the absolute one. Also, notice in plate (b) the trapping of the trajectory in the prism geometry regions at about 250 ps.

14. As in Fig. 10 but for the octamer. The energies of the trajectories are (a) -47.0 kcal/mol (below T_m), (b) -45.0 kcal/mol (at T_m), (c) -44.5 kcal/mol (above T_m), (d) -43.0 kcal/mol, (e) -42.5 kcal/mol, (f) -41.5 kcal/mol, (g) -40.0 kcal/mol, and (h) -38.5 kcal/mol. Flat regions correspond to trapping into cubic configurations.

15. Power spectra of water clusters obtained from the oxygen velocity autocorrelation function (Eqs (3,4)), and from trajectories with total energies which correspond to the melting point; $n = 3$, $E = -8.5$ kcal/mol, $n = 4$, $E = -15.0$ kcal/mol, $n = 5$, $E = -25.1$ kcal/mol, $n = 6$, $E = -31.1$ kcal/mol, and $n = 8$, $E = -45.0$ kcal/mol. The lower right frame shows the convergence

of Maximal Lyapunov Exponent as function of time and with reference trajectories the same which are used in the power spectra. The time is in atomic time units.

16. As Fig. 15 but for energies near the first fragmentation limit; $n = 3$, $E = -5.07$ kcal/mol, $n = 4$, $E = -11.0$ kcal/mol, $n = 5$, $E = -18.1$ kcal/mol, $n = 6$, $E = -22.1$ kcal/mol, and $n = 8$, $E = -38.5$ kcal/mol.

17. Comparison of the caloric and rms OO bond length fluctuations of the water trimer obtained without and with polarization interaction terms. Energies are in kcal/mol.

18. The same as Fig. 17 but for the tetramer.

19. Power spectra for the tetramer, (a) $E = -15.0$ kcal/mol, (b) $E = -11.0$ kcal/mol, and octamer, (c) $E = -47.5$ kcal/mol, and (d) $E = -40.4$ kcal/mol, obtained with the polarization interactions included in the potential function.

20. Comparison of the caloric and rms curves of the trimer cluster obtained from trajectories with different values of the total angular momentum and with the pairwise potential. Note, the different behavior of curve (a).

21. The same as Fig. 19 but for the tetramer cluster. The behavior of the curves (a) and (b) shows the trapping of energy in the rotational degrees of freedom.