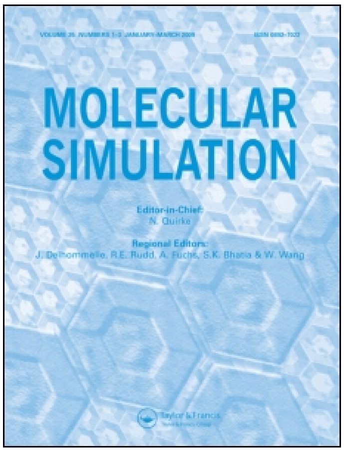

Molecular Simulation

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Methane in Water: An Ab Initio Study

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To cite this Article Site, L. Delle(2001) 'Methane in Water: An Ab Initio Study', Molecular Simulation, 26: 5, 353 — 365
To link to this Article: DOI: 10.1080/08927020108023018
URL: http://dx.doi.org/10.1080/08927020108023018

Molecular Simulation, 2001, Vol. 26, pp. 353–365
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METHANE IN WATER: AN *AB INITIO* STUDY

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(Received June 2000; accepted July 2000)

In preceding publications we discussed some properties of pure water in condensed phases using an *ab initio* approach. Here this study is used as a basis of comparison for analysing the behaviour of water as a solvent in the presence of an apolar molecule. Our analysis is focused on the process of organization of the hydrogen bonding network around the solute. For this purpose we perform some *ab initio* calculations for a system of 32 water molecules and one methane molecule at 300 K; in particular, the average molecular dipole moment of water is determined and the result is compared with that of pure water. Next the attention is switched to the methane molecule; related properties such as excluded volume and sphericity of its shape are illustrated and discussed. A comparison with results obtained using classical approaches suggests that some classical models of water can be considered to be still valid when they are used to analyse the water–methane system.

Keywords: Hydrophobic hydration; Molecular dipoles; Classical models

I. INTRODUCTION

The importance of analysing water as a solvent is evident since many chemical and biological phenomena are based on the process of solvation. Water is a peculiar liquid as it is characterized by a hydrogen bonding network which does not occur in other simple liquids; in previous publications [1, 2] we discussed the electrostatic properties of pure water

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*Present address: Max-Planck-Institute for Polymer Research, Theory Group, PO Box 3148, D-55021 Mainz, Germany. Tel.: +49 (0)6131 379 328, Fax: +49 (0)6131 379 340, e-mail: dellsite@mpip-mainz.mpg.de in condensed phases from an *ab initio* point of view, this kind of study can now be used as a basis of comparison for studying, through an *ab initio* approach, the properties of water as a solvent when the solute is a methane molecule. The crucial point of this work is to understand how the hydrogen bonding network rearranges itself in the presence of the solute and, above all, how this affects the electrostatic properties of water molecules; the information obtained by studying pure water can now be used to investigate the electrostatic aspect of the hydration process at molecular level. For this purpose, we performed some *ab initio* calculations for a methane molecule in liquid water. We took a configuration of 32 water molecules and one methane from a classical simulation, and used the positions as input for an *ab initio* molecular dynamics at 300 K. Our aim is to compare the average molecular dipole moment calculated for pure water with that calculated for water as a solvent while the analysis of structural properties such as the radial distribution function and the consequent comparison with results of previous work will give as an indication about the validity (in general) of our calculation; in particular the average molecular dipole of water will provide us with important information about the polarization induced by the solute. However limitations related to our calculation make the analysis valid only as an initial study. Once the comparison with pure water is performed, we extend the analysis comparing our results with those obtained for equivalent systems using classical models. Although our *ab initio* results must be considered only a basis for a more detailed investigation, the comparison with results obtained with classical models, as in case of pure water, will give a general indication of the validity of these models. The limitations related to our calculations consist in the fact that we can only analyse systems of a relatively small size and short time scale of simulation (compared with those of the classical simulation). At the current time, the massive computational expense required for this kind of calculation and the computational resources available to us do not allow us to perform calculations for larger system sizes and longer times. For example a standard run of molecular dynamics with a time step of 30 a.u. (1 a.u. = 0.0241888428 fs) on four processors each of 500 Mb, is able to complete 30 steps in 16 hours. However the advantage of the *ab initio* approach consists in the fact that the process of reorganization of the hydrogen bonding network and the subsequent induced polarization (if this happens), is described using an explicit treatment of the valence electrons. This allow us to understand how the charge distribution changes as the solute is introduced in the system, capturing in a direct way some relevant aspects of the microscopical process involved in the solvation.

II. THEORY AND SIMULATION DETAILS

The importance, in general, of a solvation process has been underlined before; in particular, in this work, we analyse the solvation of the methane since it represents a simple model for hydrophobic hydration. The role of hydrophobic interactions in a variety of processes such as protein folding, clathrate–hydrate formation, micelle and membrane formation is thought to be very important if not dominant. Therefore much attention is dedicated to the understanding of the essence and origin of these interactions. Two molecules of methane embedded in a water liquid environment represents a simple example of a system characterised by hydrophobic interactions. This system is used as a model system for understanding the role of the hydrophobic interactions in the process of protein folding. Because of the importance of such a process particular attention was paid to this system [3–7]; classically it is thought that two apolar solutes will associate in order to reduce their combined surface area [3], consequently classical calculations for this system were performed to obtain the free energy of the system as a function of the solute–solute distance. Currently this kind of study can only be done using a classical approach, the technical limitations of our investigation underlined in the previous section do not allow us to repeat the classical calculation with an *ab initio* approach. We will focus our attention on what in the literature is known as hydrophobic hydration, which refers to the study of a single solute molecule in a liquid environment; in this case attention is particularly focused on the properties of the molecules in the first hydration shell. Our aim is to understand the basic effects due to the presence of the apolar molecule in terms of structure and electronic polarization. We think that the *ab initio* approach can give a detailed description of the local microscopical properties and that this can turn out useful for understanding the nature of the hydrophobic interactions. For this reason we calculated the dipole moment of the water molecules which due to the small size of our system are located in the first hydration shell of the methane. We identify single molecules and the corresponding charge distribution using the method we addressed as the downhill method in Refs. [1, 2] which is based on the Bader's criterion for partitioning charge distribution in real space [8]. Comparison with results obtained for pure liquid water can allow us to understand how some basic molecular properties change in the presence of the apolar solute. It is commonly accepted that the methane molecule does not affect the polarization of the water molecules directly, but the large volume occupied constrains the water molecules to reorganize in such a way that the hydrogen bonding network corresponds to an equilibrium configuration. The main question is: does the process of reorganization affect the polarization of water molecules indirectly?

The answer to this question can solve different problems. From a general point of view this can give some important indications about the essence of hydrophobic effects. From a practical point of view it can give an indication of how good the classical models are in describing this phenomenon. In order to have a complete view, the study of the polarization effects are combined with the analysis of structural properties such as the solvent–solute radial distribution function and the study of the properties of the methane molecule in the liquid environment. The limitations related to the size of the system have as a consequence that the description of the second hydration shell is totally neglected, however we are interested in the local microscopic properties of the molecule in the first hydration shell, because we suppose that as a first approximation they are the ones which are mainly affected by the presence of the apolar solute.

II.1. Details of the Simulation

The system consists of 32 water molecules and one methane molecule with simple cubic boundary conditions. The distance between a point and its nearest image is 10.109397 Å; we use 32 molecules in order to have direct comparison with the system of pure liquid water analysed in Ref. [1]. The initial configuration for the *ab initio* molecular dynamics was taken from an equilibrated classical molecular dynamics simulation performed with the program *DL_POLY* [9]. For methane the initial classical configuration was taken as a tetrahedral structure centred on the carbon, with angle 109.45 degrees and carbon–hydrogen distance of 1.09 Å, the charge on the carbon is equal to $-0.572\,e$, the charge on each hydrogen is $0.1430\,e$ (see [10]) for the water molecules the SPC/E model has been used. We used the code FEMD [11, 12] which is based on a finite temperature – DFT approach; the core-valence interactions are represented with norm conserving, separable pseudopotentials. A soft Troullier–Martins pseudopotential is used to describe the oxygen ion [13]. A local pseudopotential is used for the hydrogen while a kinetic-energy filtered pseudopotential generated by Lee (*C_MH*) is used for the carbon of the methane molecule [14]. We used the BLYP gradient correction [15, 16] which has been shown from previous work [17] to be the most appropriate choice. The *ab initio* molecular dynamics was performed for 1.93 ps, with a time step of 30 a.u. We used a plane-wave cutoff of 60 Ry, the electron density is expressed on a grid in real space with a separation between grid points of 0.11232664 Å. The carbon–oxygen radial distribution function was calculated by averaging over data collected after an *ab initio* equilibration of 0.9 ps, the same was done for determining the distribution of the HCH angle and C—H distance within the methane molecule and the distribution of the angle between the vector joining the carbon with the oxygen and the bisector of the water molecule. The electron density of two instantaneous configurations (both configurations were taken after 1 ps, the interval between them is 0.5 ps) was analysed in terms of molecular dipoles.

III. RESULTS AND DISCUSSION

In this section we report the results obtained from the simulation of the water–methane system; we look at the properties of the water molecules as well as the methane molecule. The relevance of these results in the light of the results reported in previous work is discussed. The low solubility of methane in water has as a consequence that experiments do not give an important contribution to understanding the essence of the hydrophobic effects. This is a typical case in which simulation can supply the lack of knowledge due to the technical difficulties of the experiments. Most of the work about methane in water was performed using classical approaches, and we are not aware of any previous *ab initio* work; this means that it is important to understand whether the modification at molecular level with reference to the pure water environment is such that the classical models for water can still give a realistic description for this system. In the absence of experimental results, by "realistic description" we mean a description based on *ab initio* calculation which is commonly thought to be in principle more complete at microscopic level than a description based on classical calculation. The most common classical models of water [18] have a rigid structure and fixed charges localised on three or more sites, so that their dipole moment does not change during the simulation. When a methane molecule is introduced in the system, it creates a large amount of empty space around itself (see Fig. 1). Figure 1 represents an equicharge surface of value $0.03 \times e/(a.u)^3$ for an instantaneous configuration. The black circle at the centre of the figure represents the carbon of the methane. As it is possible to see from this value of the charge density, strong hydrogen bonds between water molecules are created, while a relatively large empty space is created around the solute. Whether or not this structural process can influence the polarization of the single molecules is an important issue. Using the

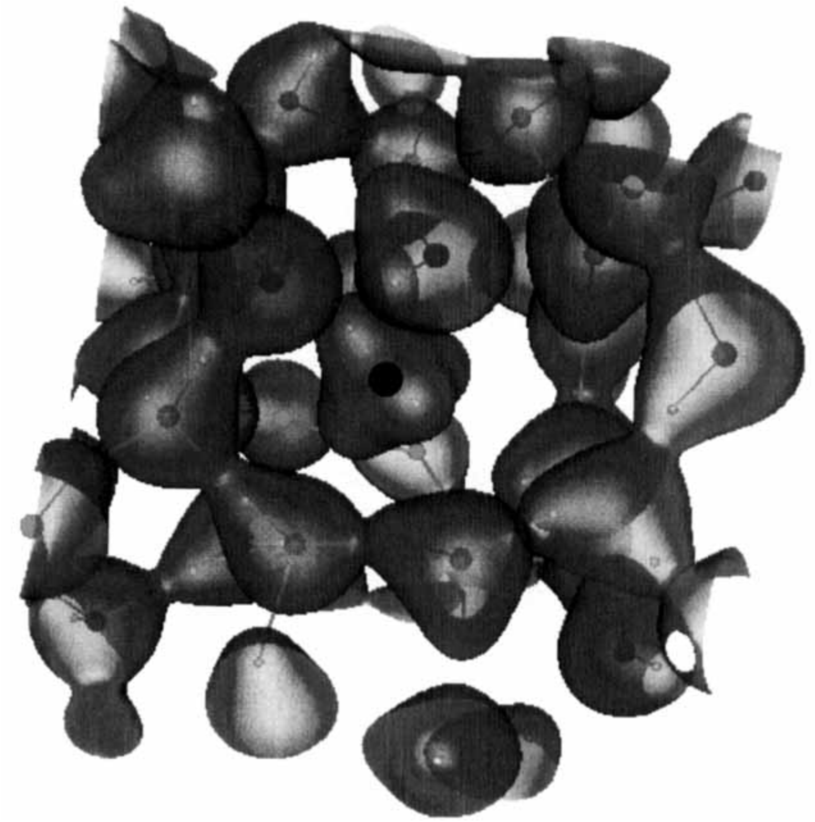

FIGURE 1 Electron density contour surface. This surface is drawn at $(0.03 \times e/a_0^3)$. The carbon of the methane is represented by the black circle at the centre of the figure. Note the large amount of empty space around the solute and the non-spherical shape of the methane. (See Color Plate I).

downhill method as we have done for pure water [1,2], we identified the charge distribution of single water molecules and then analysed it in terms of molecular dipoles. The value of the average dipole moment calculated for two instantaneous configurations (64 molecules) is 2.54 Debye (2.55 Debye for the first configuration, 2.53 for the second), which must be compared with the value of 2.55 Debye obtained for pure water using the same method (see [1] but above all [2]). Another important feature can be seen in Figure 2 where the carbon–oxygen radial distribution function is shown. As stated earlier, due to the technical limitations of our calculations we can describe only the first hydration shell, however within this range we notice that our result is consistent with those based on classical approaches (see for

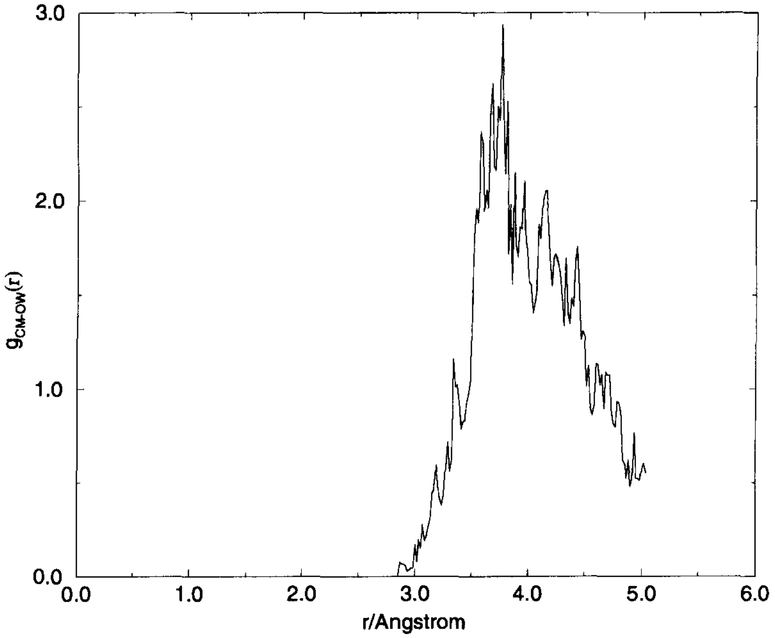

FIGURE 2 The oxygen–carbon radial distribution function. The function is calculated averaging on the data collected, after 0.93 ps, for 1 ps. The plot shows one peak at about 3.7 Å; this result is consistent with that obtained in Ref. [3] using a classical model.

example [3]). As for the case of pure water, some classical models such as SPC/E and TIP3P whose dipole moment is 8% lower than the value we obtained, can be considered to be still valid in describing the essential physics of water-methane system. For example in the case of TIP3P, the carbon–oxygen radial distribution function (see [3]) is consistent with the one based on the *ab initio* calculation and although the value of the dipole for this model is not large enough to state that it fully captures the molecular electrostatic properties, it is not small enough to state that it does not capture the essence of the macroscopic physics. Finally, Figure 3 shows the distribution of the orientation of the bisector of the HOH angle with respect to the carbon–oxygen vector; it tells us the average orientation of the dipoles of the water molecules. The shape of the distribution reflects the fact that the hydrogen bonding network forms a sort of smooth ordered structure around the solute and geometrically this means that most of the molecules cannot point radially to the carbon.

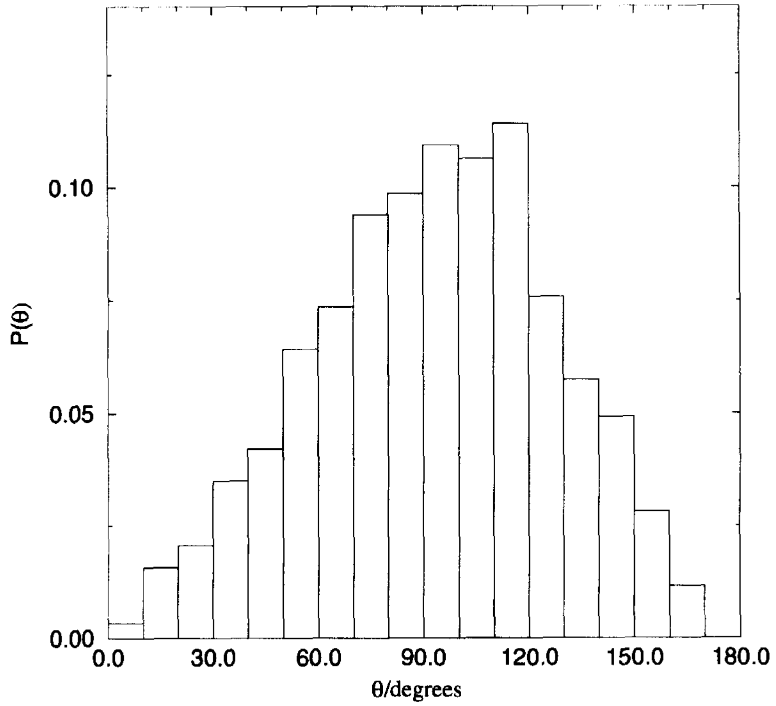

FIGURE 3 The distribution of the angle between the oxygen–carbon vector and the bisector of the HOH angle. The function is calculated by averaging over the data collected, after 0.93 ps, for 1 ps. The plot shows that most of the water molecules do not point to the carbon and this reflects the fact that a smooth hydrogen bonding network "surface" is formed around the solute.

III.1. Clathrate Hydrate Structure

Another feature (strictly related to Fig. 3) which is found in several works based on classical calculations concerns the clathrate hydrate structure (see [19–21]). The term "clathrate hydrate" indicates the structure of liquid water around a hydrophobic solutes. The usual clathrate-like structures are three dimensional lattices connected by tetrahedral hydrogen bonds, which form cages composed of 4-,5-,6-sided polygons (for more details see [19]). In our case although the size of the box of simulation is small, in Figure 4 we can observe a 4-sided and a 5-sided polygon. This fact suggests that the *ab initio* description of the local structure is in general satisfactory in spite of the limitations due to the size of the system and the number of molecules; it also represents a clear indication that classical models can capture in an appropriate way the

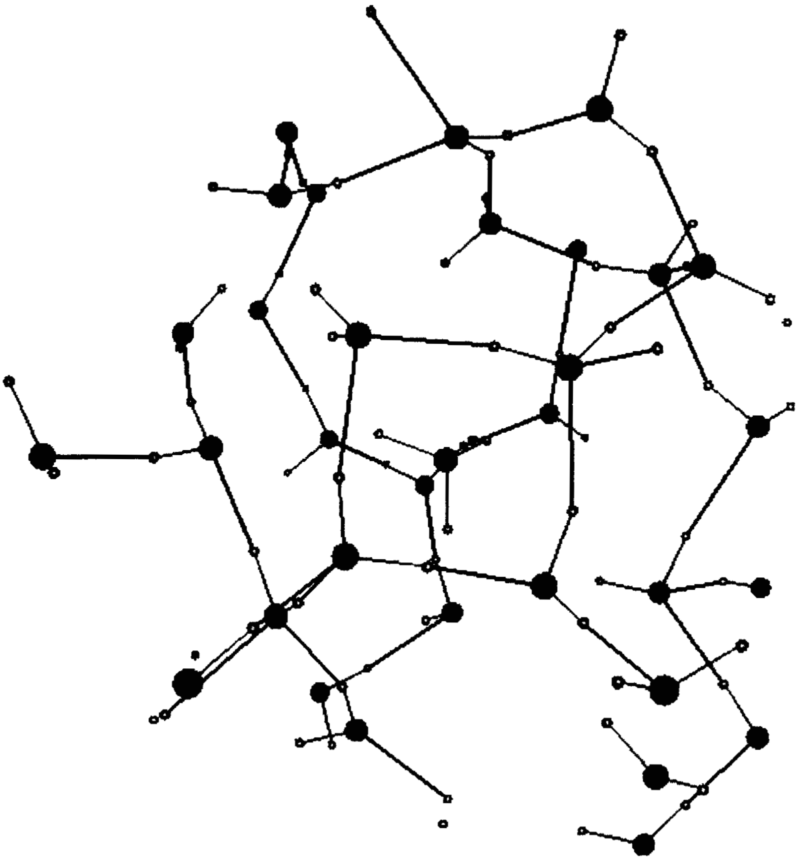

FIGURE 4 The plot shows an instantaneous configuration from the molecular dynamics run. The red spheres represent the oxygens the grey spheres the hydrogens, the green lines represent the water–water hydrogen bonds. Note the 4-sided polygon and the 5-sided polygon. These polygons are the basic unit in a clathrate structure. (See Color Plate II).

essence of the solvation process at molecular level although electrons are not explicitly considered. Finally we considered the properties of the methane molecule embedded in water; we dedicate to this subject the following subsection.

III.2. The Methane Molecule

In calculations for a water–methane system based on a classical approach, the methane is often treated as an apolar sphere (see for example [22]). This approximation is based on the hypothesis that the large empty space around the solute is the main effect and the electrostatic interaction between the methane and the water is not relevant. Figure 1 shows that the molecule is not exactly spherical, it is also flexible; for example a calculation of the instantaneous dipole in two configurations, produces the values of 0.241 Debye and 0.257 Debye. These results must be combined with those shown in Figure 5 where the distribution of the HCH angle is reported and with those shown in Figure 6 where the distribution of the C—H distances is reported. Although the classical approach based on a spherical methane is in general reasonable and the values of the dipoles we calculated are small, the results we found can be considered as an indication that the methane interacts directly with the water system. It is not clear how to quantify the importance of this interaction, but we can speculate that it could be rather important in the formation of a structure around the solute. When a spherical model is used, the solute creates the same conditions at each point around it, while a model which explicitly consider the molecule (like the one we used) breaks this symmetry so that the structure forming around the solute can be directly influenced.

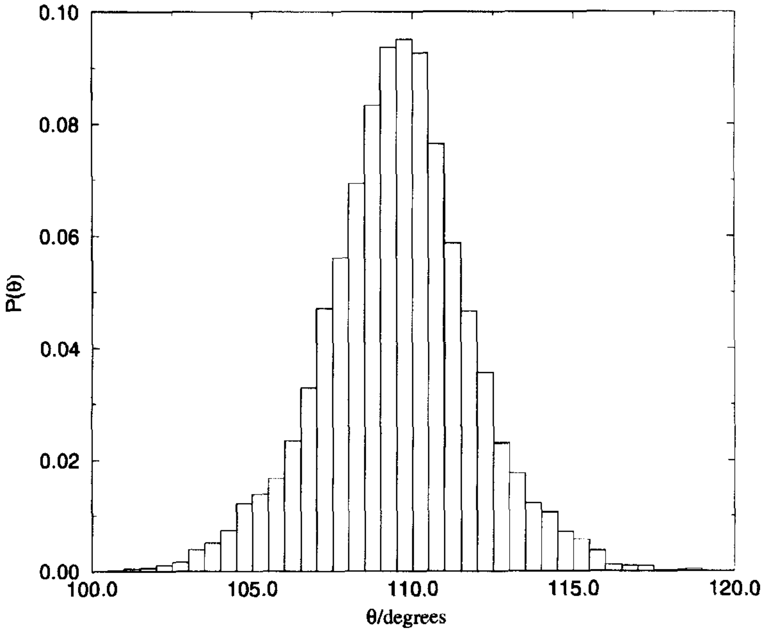

FIGURE 5 The distribution of the HCH angle (Θ) within the methane molecule. The function is calculated by averaging over the data collected, after 0.93 ps, for 1 ps. The plot shows a symmetric distribution centred on the value of 109.6 degrees.

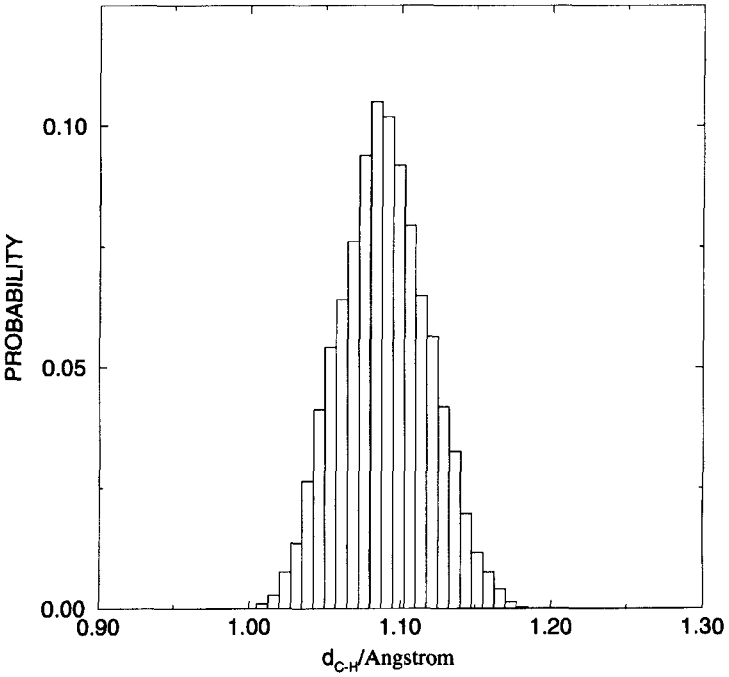

FIGURE 6 The distribution of the C—H distance within the methane molecule. The function is calculated by averaging over the data collected, after 0.93 ps, for 1 ps. The plot shows that the variation is small.

IV. CONCLUSION

We analysed, within an *ab initio* approach, electrostatic and geometrical properties emerging from the hydration process of a single methane molecule. The modifications of molecular properties with respect to the pure water occurring in the solvation process allows one to understand some important aspects of the solvent–solute interaction. We found (within the conditions and limitations of our approach) that there is no increase of polarisation for the single molecules which suggests that some classical models used for pure water (such as SPC/E and TIP3P) are equally valid if used in this environment. This conclusion is supported by the comparison of the *ab initio* and classical (TIP3P) oxygen–carbon radial distribution function; moreover the clathrate-like structure observed in the *ab initio* MD can be taken as an indication of the validity of classical models in describing the system at molecular level. On the other hand the approximation of the methane molecule with a uniform sphere seems to be questionable; not only is the electron density tetrahedral rather than spherical but the fluctuation of the HCH angle and the presence of a small dipole moment show that the hydrogens of the methane interact with the surrounding molecules of water. How important this interaction is in describing the solvation process is difficult to say but we think it could play an important role for the formation of a clathrate-like structure around the solute. However the limitation of the *ab initio* calculation suggests that this structure can be properly observed only in case of much larger system than the one we considered. The main result of this work is the indication that some classical models of water can be considered to be still valid when they are used for simulating the water–methane solvation process; this is a nontrivial conclusion, since a detailed analysis in this case can be performed only within a classical approach as the computational difficulties related to the *ab initio* analysis are massive. Apart from the computational difficulties, it must be also underlined that our analysis concerns only some particular (although relevant) aspects of the very complicated process of methane hydration; for this reason this work has to be considered simply an attempt to analyse connections between some molecular properties calculated with an *ab initio* approach and the properties calculated through a classical approach; however we believe that this analysis can be relevant for giving indications about the validity of classical approaches in the context of the methane hydration.

Acknowledgments

I would like to thank Professor R. Lynden-Bell and Dr. A. Alavi for a critical reading of the manuscript, Dr. M. Sprik for helpful suggestions, T. Somasundaram for preparing the classical configuration. I also thank EPSRC for financial support (grants GR/K20651 and GR/L08427) and the IFI for financial support for the Irish Centre for Colloids and Biomaterials.

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