Computer simulation of two new solid phases of water: Ice XIII and ice XIV

Maria Martin-Conde, Luis G. MacDowell, and Carlos Vega[a)]
Departamento de Quimica Fisica, Facultad de Ciencias Quimicas, Universidad Complutense, 28040 Madrid, Spain

Thirteen solid phases are known for water.[1] However, Salzmann *et al.*[2] have found experimentally two new solid structures which have been labeled as ice XIII and ice XIV, respectively.[2] They were obtained at moderate pressures (5000–12 000 bars) by cooling ice V (to obtain ice XIII) or ice XII (to obtain ice XIV) doped with HCl to induce the proton ordering. After cooling to 77 K, the new ices were decompressed at 77 K and studied by neutron diffraction[2] (they were mechanically stable at these conditions). The interest to study solid phases of water by computer simulation is growing.[3–6] Recently we have determined[7,8] the phase diagram for some of the most popular models of water, such as SPC/E,[9] TIP4P,[10] and TIP5P.[11] It has been found that only TIP4P is able to provide a qualitative description of the experimental phase diagram of water (ice II was more stable than ice I_h for the SPC/E and TIP5P models). Concerning density predictions[7,12] TIP4P and SPC/E overestimate the densities of ices by about 2%-3% and TIP5P by about 7%. The parameters of the TIP4P model have been modified to reproduce either the experimental melting temperature, TIP4P/Ice model,[13] or the temperature of maximum density of liquid water, TIP4P/2005 models.[14] Both models reproduce reasonably well the densities of the different polymorphs of water with an average error of about 1%. Two other models have been proposed recently to be used along with Ewald sums, namely, TIP4P-Ew (Ref. 15) and TIP5P-E.[16] The main goal of this work is to test the performance of the different water models for these two new solid phases. NpT simulations have been performed for ices XIII and XIV. The unit cell and the coordinates of the oxygens and hydrogens in the initial configuration were taken from Salzmann *et al.*[2] For ice XIII we used $3 \times 3 \times 2$ unit cells (with 28 water molecules per unit cell) so that the total number of molecules was 504. For ice XIV we used $3 \times 3 \times 5$ unit cells (with 12 water molecules per unit cell) so that the total number of molecules used was 540. We performed, for $T=80$ K and $p=1$ bar, anisotropic NpT Monte Carlo simulations (Parrinello-Rahman type[17] allowing both the shape and the relative dimensions of the unit cell to change). The Lennard-Jones (LJ) and the real part of the electrostatics (Ewald sums) were truncated at 8.5 Å. Long range corrections to the LJ part of the potential were included. Results were obtained from runs of 80 000 cycles (trial move per particle plus a trial volume change) after 20 000 cycles of equilibration. The results of the NpT runs are shown in Table I.

As it can be seen in Table I, TIP5P and TIP5P-E predict poorly the densities of ices XIII and XIV. The tetrahedral arrangement of charges of TIP5P models seems not appropriate to describe the distorted tetrahedral environment of water molecules in ices. The predictions of SPC/E, TIP4P, and TIP4P-Ew are better but still too far from the experimental value. The model TIP4P/2005 yields a significantly better density prediction, and finally TIP4P/Ice yields the best estimate of the densities of ices XIII and XIV. Trends found in this work are similar to those found previously for the other solid phases of water.[12] For ice XIV (orthorhombic) we found for the TIP4P/Ice model a unit cell of dimensions of 8.425, 8.188, and 3.965 Å to be compared with the experimental values of 8.350, 8.139, and 4.082 Å. For ice XIII (monoclinic) we found for the TIP4P/Ice model a unit cell of dimensions of 9.436, 7.386, and 10.234 Å and $\beta=109.76$ to be compared with the experimental dimensions of 9.242, 7.472, and 10.297 Å and $\beta=109.69$. The models with the best predictions, TIP4P/Ice and TIP4P/2005, have larger charges than the traditional TIP4P. This increase of the charge improves dramatically the description of the quadrupolar moment of water.[13,14,16] A good description of the quadrupole moment of water is required to describe correctly both the phase diagram and the density of ice polymorphs.

TABLE I. Densities of ices XIII and XIV at $T=80$ K and $p=1$ bar as obtained from NpT simulations and from experiment (Ref. 2). The experimental value of the density of H_2O was estimated from that of D_2O by assuming that no change in the parameters of the unit cell occurs by the isotopic substitution. Residual internal energies are also reported.

| Ice	Model	ρ (g cm^{-3})	U (kcal mol^{-1})
XIII	TIP5P	1.355	−12.88
XIII	TIP5P-E	1.358	−13.08
XIII	SPC/E	1.306	−13.96
XIII	TIP4P	1.286	−12.71
XIII	TIP4P-Ew	1.284	−13.87
XIII	TIP4P/2005	1.262	−14.16
XIII	TIP4P/Ice	1.244	−15.57
XIII	Experiment	1.251	⋯
XIV	TIP5P	1.394	−12.45
XIV	TIP5P-E	1.397	−12.66
XIV	SPC/E	1.360	−13.73
XIV	TIP4P	1.357	−12.78
XIV	TIP4P-Ew	1.351	−13.86
XIV	TIP4P/2005	1.332	−14.25
XIV	TIP4P/Ice	1.312	−15.67
XIV	Experiment	1.294	⋯

125, 116101-1
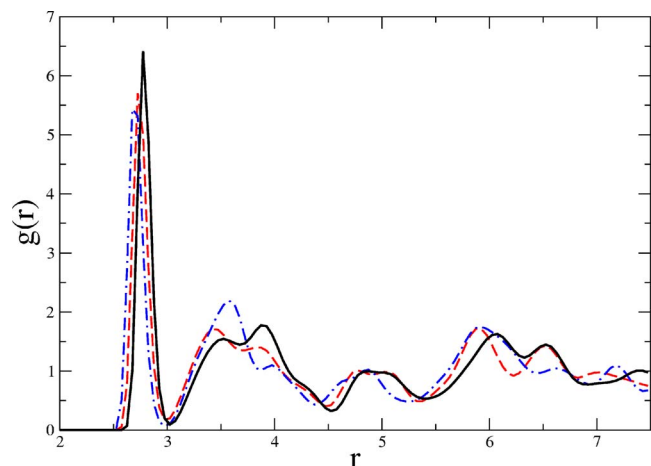
FIG. 1. (Color online) Oxygen-oxygen radial distribution function for ice XIII at $T = 80$ K and $p = 1$ bar. The distance between oxygen atoms is given in Å. Solid line: Results for the TIP4P/ice model. Dashed line: Results for the SPC/E model. Dashed-dotted line: Results for the TIP5P model.

The oxygen-oxygen radial distribution functions for ices XIII and XIV as obtained from computer simulation are shown in Figs. 1 and 2, respectively.

As it can be seen there are significant differences between the predictions of the TIP4P/Ice, SPC/E, and TIP5P models (similar differences were found previously for other proton ordered phases[12]). All TIP4P models yield rather
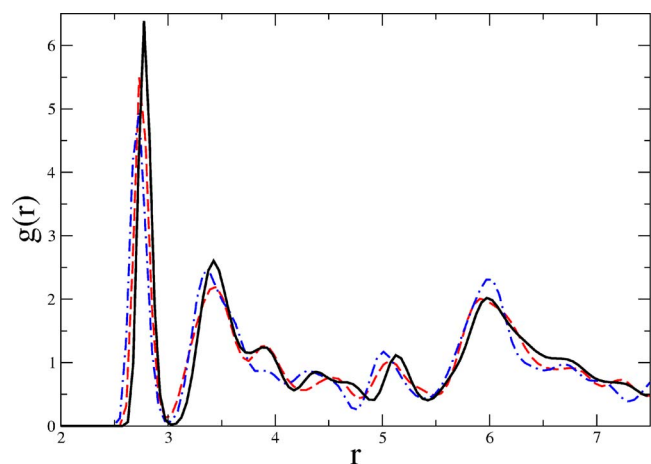

FIG. 2. (Color online) Oxygen-oxygen radial distribution function for ice XIV at $T = 80$ K and $p = 1$ bar. The rest of the notation is the same as in Fig. 1.

similar O–O distribution functions, the height of the first peak being the main difference between them. For this reason the results of TIP4P/Ice presented in the figures are representative of the TIP4P family. Since experimental results of the O–O correlation function are not yet available it is not possible to obtain conclusions on the quality of the results. We would like to mention that for ice I_h the O–O radial distribution function of the TIP4P model is in excellent agreement[18] with that reported from experimental measurements by Narten *et al.*[19] That gives us some confidence in the predictions of the O–O distribution function obtained by TIP4P models. It would be of interest to determine experimentally this function from diffraction experiments to test the predictions of the different water models.

a)Electronic mail: cvega@quim.ucm.es
[1] V. F. Petrenko and R. W. Whitworth, *Physics of Ice* (Oxford University Press, Oxford, 1999).
[2] C. G. Salzmann, P. G. Radaelli, A. Hallbrucker, E. Mayer, and J. L. Finney, Science **311**, 1758 (2006).
[3] M. D. Morse and S. A. Rice, J. Chem. Phys. **76**, 650 (1982).
[4] L. A. Báez and P. Clancy, J. Chem. Phys. **103**, 9744 (1995).
[5] S. W. Rick, J. Chem. Phys. **122**, 094504 (2005).
[6] A. Baranyai, A. Bartok, and A. A. Chialvo, J. Chem. Phys. **123**, 054502 (2005).
[7] E. Sanz, C. Vega, J. L. F. Abascal, and L. G. MacDowell, Phys. Rev. Lett. **92**, 255701 (2004).
[8] C. Vega, E. Sanz, and J. L. F. Abascal, J. Chem. Phys. **122**, 114507 (2005).
[9] H. J. C. Berendsen, J. R. Grigera, and T. P. Straatsma, J. Phys. Chem. **91**, 6269 (1987).
[10] W. L. Jorgensen, J. Chandrasekhar, J. D. Madura, R. W. Impey, and M. L. Klein, J. Chem. Phys. **79**, 926 (1983).
[11] M. W. Mahoney and W. L. Jorgensen, J. Chem. Phys. **112**, 8910 (2000).
[12] C. Vega, C. McBride, E. Sanz, and J. L. Abascal, Phys. Chem. Chem. Phys. **7**, 1450 (2005b).
[13] J. L. F. Abascal, E. Sanz, R. G. Fernández, and C. Vega, J. Chem. Phys. **122**, 234511 (2005).
[14] J. L. F. Abascal and C. Vega, J. Chem. Phys. **123**, 234505 (2005).
[15] H. W. Horn, W. C. Swope, J. W. Pitera, J. D. Madura, T. J. Dick, G. L. Hura, and T. Head-Gordon, J. Chem. Phys. **120**, 9665 (2004).
[16] S. W. Rick, J. Chem. Phys. **120**, 6085 (2004).
[17] M. Parrinello and A. Rahman, J. Appl. Phys. **52**, 7182 (1981).
[18] E. Sanz and C. Vega, (unpublished).
[19] A. H. Narten, C. G. Venkatesh, and S. A. Rice, J. Chem. Phys. **64**, 1106 (1976).