

RESEARCH NOTE

The range of meta stability of ice-water melting for two simple models of water

CARL McBRIDE, CARLOS VEGA*, EDUARDO SANZ, LUIS G. MACDOWELL
and JOSE L. F. ABASCAL

Departamento de Química Física, Facultad de Ciencias Químicas,
Universidad Complutense de Madrid, Ciudad Universitaria, 28040 Madrid, Spain

(Received 7 April 2004; revised version accepted 30 June 2004)

A number of crystal structures of water have been 'superheated' in Monte Carlo simulations. Two well-known models for water were considered; namely the TIP4P model and the SPC/E model. By comparing the fluid–solid coexistence temperature to the temperature at which the solid becomes mechanically unstable and melts it is possible to determine the typical range of temperatures over which it is possible to superheat the ice phases in conventional simulation studies. It is found that the ice phases can be superheated to approximately 90 K beyond the fluid–solid coexistence temperature. Beyond this limit they spontaneously melt. This limit appears to depend weakly both on the type of ice phase considered and on the chosen model. Obviously only rigorous free energy calculations can determine the equilibrium fluid–solid coexistence of a model. However, a 'rule of thumb' is that, by subtracting 90 K from the mechanical stability limit of the ice phase one is provided with a first guess as to the equilibrium fluid–solid coexistence temperature.

1. Introduction

Ever since the advent of statistical mechanical 'experiments' on fast computing machines it was realized that performing computer simulations of water would be of the utmost importance to the understanding of what must be one of the most important molecules known to man. Pioneering studies of such nature were performed by Barker and Watts [1] and by Rahman and Stillinger [2]. Since then, thousands of computer simulation studies have been carried out. However, the possibility of determining the water phase diagram by computer simulation has not received such widespread attention. This is surprising since the phase diagram for a number of molecular models such as spherocylinders [3, 4], linear tangent hard spheres [5, 6] and Gay–Berne [7, 8] models are well known. Although several studies have examined the vapour–liquid equilibria of different model potentials of water [9], the fluid–solid equilibria have been investigated in just a few cases [10]. Recently we have determined the phase diagram of two of the most popular model potentials of water [11, 12], namely the SPC/E [13] and the TIP4P [14] models (note that for a theoretical description, simpler models may be required,

based either on associating site potentials [15–17] or on polar convex bodies [18, 19]). In this way it was possible to show that the simple TIP4P model is able to provide a qualitatively correct view of the phase diagram of water. In order to determine the phase diagram, hundreds of NpT simulations were performed, leading to an equation of state for both the fluid and solid phases. It was also necessary to compute the free energy of the fluid phase (via thermodynamic integration) and the free energy of the solid phase (via Einstein crystal calculations [20]). Once a single point on the coexistence line was determined, Gibbs–Duhem integration [21] was used to obtain the full saturation line. Such calculations have allowed the authors to determine the phase diagram of the potential models TIP4P and SPC/E and to establish their ability to reproduce the experimental phase diagram of water [11]. It is fair to say that the determination of the phase diagram of a given model potential of water is a cumbersome task. One may naively wonder as to whether NpT runs could be sufficient in order to obtain directly the fluid–solid equilibria of a simple model. Unfortunately this is not possible. When a 'molecular liquid' is cooled to below the freezing temperature at constant pressure in an NpT simulation, one usually obtains a supercooled liquid.

*Author for correspondence. e-mail: cvega@quim.ucm.es

It is very difficult to observe in computer simulations the formation of a perfect crystal (also in experiments one often finds supercooled liquids).

What is the behaviour of the solid phase when heated at constant pressure? Experimentally, when a solid is heated at constant pressure it melts at the melting temperature, because the surface acts as a nucleation site. It is therefore not possible to superheat a solid above the melting temperature. This sounds good since it suggests a procedure to determine the melting temperature from computer simulations; one simply heats the solid until it melts. However, in practice this is not the case. In computer simulations (in contrast to real experiments) one may superheat the solid before it melts. This is well known for hard spheres [22] (with pressure being the thermodynamic variable in question) and for Lennard–Jones (LJ) particles [23, 24]. In NpT runs it is found that the solid melts at pressures below the equilibrium melting pressure (for hard spheres), or at temperatures above the melting temperature (for the Lennard–Jones system).

Since the rigorous phase diagram of water of two simple models is now available, it is possible, for the first time, to analyse the typical range of temperatures over which the solid phases of water (ices) can be superheated in a computer simulation before spontaneous melting occurs. The probability of melting once the ice is superheated obviously depends on the size of the system and on the length of the run. However, here our intention is to provide ‘ball-park’ figures of the stability range of the ice phases. The numbers obtained may prove to be useful when designing new potential models which lead to a better description of the phase diagram of water.

2. Simulation details

The initial solid configurations were constructed using crystallographic data (taken from [25] and references therein). In the case of the proton ordered ices (i.e. II and VIII), this is all that is required. However, for the proton disordered ices (i.e. I, VI and VII), while the oxygens were situated on the lattice points, the hydrogen atoms were located in disordered configurations such that the net dipole moment was zero as well as at the same time satisfying the ice rules [26]. This was done by using the algorithm of Buch *et al.* [27]. For ices III and V, which present a certain degree of proton ordering, the Buch algorithm was generalized in order to produce initial configurations having biased occupation of the hydrogen positions [28].

Anisotropic NpT Monte Carlo simulations (Parrinello–Rahman like) were used for the solid phases [29]. The pair potential was truncated for all phases at 8.5 Å. Standard long range corrections to the LJ energy

Table 1. Relation between the number of molecules in the simulation box and the ice structure simulated for both the SPC/E and the TIP4P models.

Ice	No. of molecules
I(Ih)	288
I(Ih)	432
II	432
III	324
V	504
VI	360

were added. Ewald sums were employed for electrostatic interactions.

The number of particles used in the simulations is presented in table 1 (chosen for each solid phase so as to allow for at least twice the cut-off distance in each direction).

The melting transition is monitored by following the progress of the structure factor of the system. The structure factor for the Bragg reflection of the planes hkl of the crystal is given by

$$F_{hkl} = \frac{1}{N} \sum_{i=1}^{i=N} f_i \exp(2\pi i(hx_i + ky_i + lz_i)). \quad (1)$$

The intensity of a given line is given by

$$I_{hkl} = |F_{hkl}|^2 = F_{hkl} F_{hkl}^*. \quad (2)$$

It should be mentioned that only oxygens were used when computing the structure factor in equation (1). The scattering factor f_i of oxygen was arbitrarily set to one. For each solid structure (ice I, II, III, V, VI) the combination of hkl values that provided the most intense line were used to detect the melting transition.

The runs were performed by taking an initial crystal-line configuration under thermodynamic conditions corresponding to that of the solid phase. This initial state was then simulated at intervals of 10 K with runs of 8×10^4 cycles per temperature. One cycle is defined as a trial move per particle (translation or rotation) plus a trial volume change. Each subsequent simulation was started from the final configuration of the previous run. When the structure factor was seen to fall to zero then the previous temperature was re-run up to three times in order to see whether this state too would melt.

3. Results

A typical fall in the structure factor of an ice phase is shown in figure 1 (in this case for the melting of TIP4P–ice V at $T = 310$ K and 0.5 GPa). As can be seen, once the structure factor falls below a certain value the

melting proceeds rapidly and irreversibly. Results for the other ice phases and models are similar.

Table 2 presents the first temperature for which spontaneous melting of ices was found (see the column labelled as T_{stab}). It should be noted that in all cases, simulation runs of up to 2.4×10^5 cycles were performed for a lower temperature (by 5 or 10 K) without success in melting the ice. In table 2, the melting temperatures of the corresponding ice phase for the TIP4P and SPCE models are also shown for comparison (column denoted as T_{coex}). The latter values are taken from [11] and were calculated by determining the free energies of the fluid and solid phases. ΔT (we shall denote this value as the

meta stability range) represents the difference between T_{stab} and T_{coex} and is also given in table 2. For TIP4P ice I the stability range depends only weakly on pressure (for the two pressures considered the range is about $\Delta T = 68$ K). The stability range of different ices for a certain model are slightly different, although these differences are never large. For the TIP4P, we may state that 80 K is the typical range of meta stability for the different ice phases. For the SPC/E model the meta stability range appears to be about 90 K (i.e. 10 K larger than that of the TIP4P). This is not surprising since the internal energies of the solids are always lower in the SPC/E model than in the TIP4P model (the hydrogen bonding is slightly stronger in the SPC/E model when compared with the TIP4P model). In any case, differences in the stability range of both models (SPC/E and TIP4P) are small. In this respect, the numbers presented here represent the typical values of the stability range that would be expected to be found in simulations of other realistic models of water. Although a systematic study of the system size dependence of T_{stab} has not been performed (see [30]), we have studied the behaviour of T_{stab} for ice Ih of the TIP4P model at $p = 0.1$ MPa for two system sizes: 288 molecules and 432 molecules. The 50% increase in system size delays the onset of melting by about 10 K.

Finally, figures 2 and 3 show the location of the stability temperature (symbols) of the different ices for both the TIP4P (figure 2) and for the SPC/E (figure 3)

Table 2. Results for the range of superheating for the various ices and models. T_{stab} is the temperature at which the system becomes unstable (spontaneous melting), while T_{coex} is the thermodynamic melting temperature.

Ice	P (GPa)	TIP4P			SPC/E		
		T_{coex}	T_{stab}	ΔT	T_{coex}	T_{stab}	ΔT
I (288)	0.0001	232	300	68	215	295	80
I (432)	0.0001	232	310	78	–	–	–
I	0.05	229	297	68	–	–	–
II	0.5	–	–	–	249	365	116
III	0.3	197	280	83	–	–	–
V	0.5	204	310	106	–	–	–
VI	2.0	270	350	80	–	–	–
VI	2.5	–	–	–	234	330	96

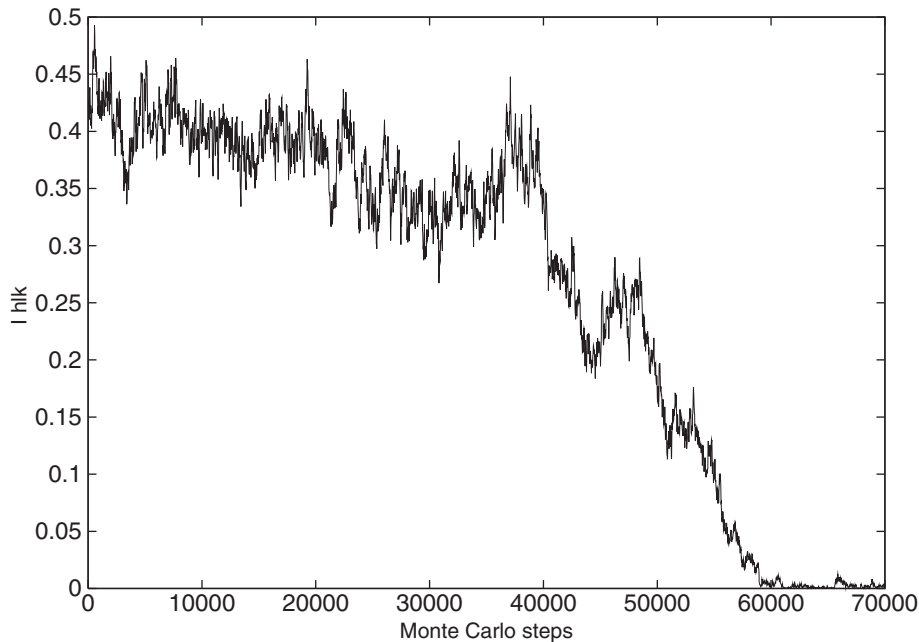


Figure 1. A plot of the intensity of the structure factor, I_{hkl} , for the TIP4P model of ice V at 310 K and 0.5 GPa. This plot is representative of the sudden fall in the intensity of the structure factor associated with melting.

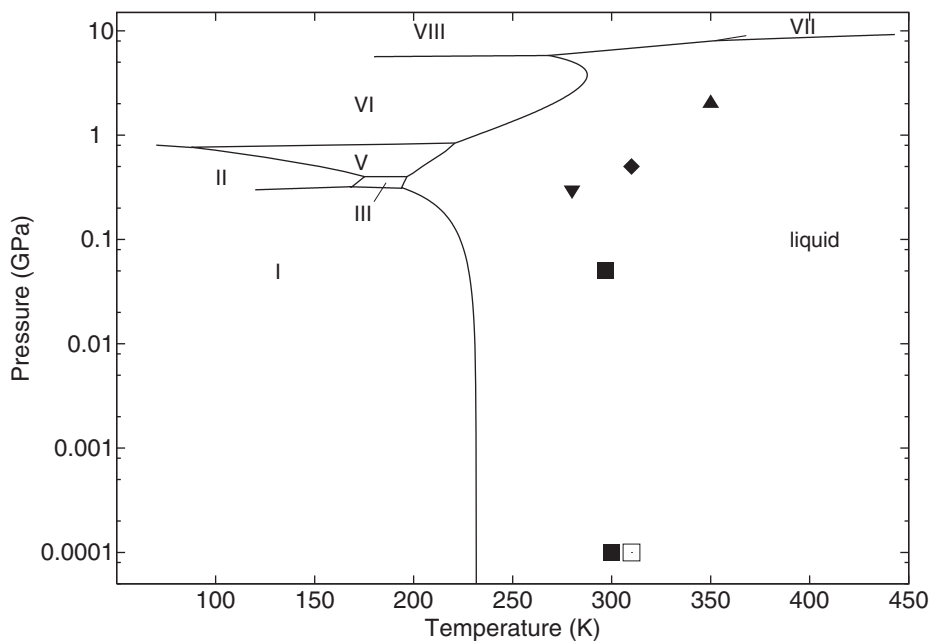


Figure 2. Plot of the phase diagram of water for the TIP4P model. Points are the temperatures at which the solid melted under constant pressure. ■ ice I (288 molecules), □ ice I (432 molecules), ▲ ice III, ◆ ice V and ▲ ice VI.

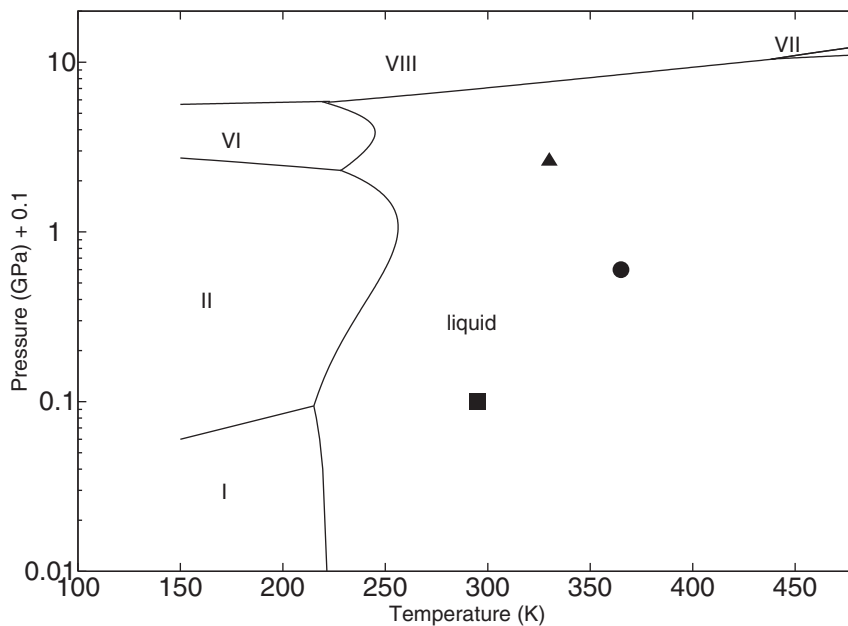


Figure 3. Plot of the phase diagram of water for the SPC/E model. Points are the temperatures at which the solid melted under constant pressure. ■ ice I, ● ice II and ▲ ice VI.

models. The phase diagram as obtained from free energy calculations is also shown (lines). It can be seen that the degree of superheating is of the order of 85 K. Interestingly the stability temperatures reflect the trends found in the equilibrium coexistence lines. This suggests that a first rough estimate of the melting temperature of ices can be obtained from the NpT simulations.

Although for the SPC/E model ice III and V (and also ice Ih!) are not thermodynamically stable phases (i.e. for any given p and T another ice always exists with lower Gibbs free energy) they are mechanically stable and it is possible to perform simulations of these phases [11]. The stability limit has been studied only for the thermodynamically stable phases of the TIP4P and

SPC/E models. However it is also possible to determine T_{stab} for ices which are metastable with respect to other solid structures. For example, for ice III in the SPC/E model at $p = 0.5$ GPa it was found that $T_{\text{stab}} = 270$ K, which is substantially lower than the value obtained for ice II (the thermodynamically stable phase of the SPC/E at this pressure) at the same pressure, having $T_{\text{stab}} = 365$ K.

Financial support from project numbers FIS2004-06227-C02-02 and BFM-2001-1017-C03-02 of the MCYT (Ministerio de Ciencia y Tecnología) is acknowledged. CM would like to thank the Comunidad de Madrid for the award of a post-doctoral research grant (part funded by the European Social Fund). ES would like to thank MEC for a predoctoral grant. L. G. MacDowell would like to thank the Universidad Complutense de Madrid and MCYT for the award of a Ramón y Cajal fellowship.

References

- [1] BARKER, J. A., and WATTS, R. O., 1969, *Chem. Phys. Lett.*, **3**, 144.
- [2] RAHMAN, A., and STILLINGER, F. H., 1971, *J. chem. Phys.*, **55**, 3336.
- [3] MCGROTHER, S. C., WILLIAMSON, D. C., and JACKSON, G., 1996, *J. chem. Phys.*, **104**, 6755.
- [4] BOLHUIS, P., and FRENKEL, D., 1997, *J. chem. Phys.*, **106**, 666.
- [5] WILSON, M. R., 1995, *Molec. Phys.*, **85**, 193.
- [6] VEGA, C., MCBRIDE, C., and MACDOWELL, L., 2001, *J. chem. Phys.*, **115**, 4203.
- [7] DE MIGUEL, E., and VEGA, C., 2002, *J. chem. Phys.*, **117**, 6313.
- [8] WILSON, M. R., 1997, *J. chem. Phys.*, **107**, 8654.
- [9] BOULOUGOURIS, G. C., ECONOMOU, I. G., and THEODOROU, D. N., 1998, *J. phys. Chem. B*, **102**, 1029.
- [10] BÁEZ, L. A., and CLANCY, P., 1995, *J. chem. Phys.*, **103**, 9744.
- [11] SANZ, E., VEGA, C., ABASCAL, J. L. F., and MACDOWELL, L. G., 2004, *Phys. Rev. Lett.*, **92**, 255701.
- [12] SANZ, E., VEGA, C., ABASCAL, J. L. F., and MACDOWELL, L. G., 2004, *J. chem. Phys.*, **121**, 1165.
- [13] BERENDSEN, H. J. C., GRIGERA, J. R., and STRAATSMA, T. P., 1987, *J. phys. Chem.*, **91**, 6269.
- [14] JORGENSEN, W. L., CHANDRASEKHAR, J., MADURA, J. D., IMPEY, R. W., and KLEIN, M. L., 1983, *J. chem. Phys.*, **79**, 926.
- [15] NEZBEDA, I., 1997, *J. molec. Liq.*, **73**, 317.
- [16] GIL-VILLEGAS, A., GALINDO, A., and JACKSON, G., 2001, *Molec. Phys.*, **99**, 531.
- [17] GALINDO, A., GIL-VILLEGAS, A., JACKSON, G., and BURGESS, A. N., 1999, *J. phys. Chem. B*, **103**, 10272.
- [18] JANECEK, J., and BOUBLÍK, T., 2003, *Phys. Chem. chem. Phys.*, **5**, 2391.
- [19] BOUBLÍK, T., 1992, *Molec. Phys.*, **76**, 327.
- [20] FRENKEL, D., and LADD, A. J. C., 1984, *J. chem. Phys.*, **81**, 3188.
- [21] KOFKE, D. A., 1993, *J. chem. Phys.*, **98**, 4149.
- [22] ALLEN, M. P., and TILDESLEY, D. J., 1987, *Computer Simulation of Liquids* (Oxford: Oxford University Press).
- [23] NORMAN, G. E., and STEGAILOV, V. V., 2002, *Dokl. Phys.*, **47**, 667.
- [24] LUO, S. N., STRACHAN, A., and SWIFT, D. C., 2004, *J. chem. Phys.*, **120**, 11640.
- [25] PETRENKO, V. F., and WHITWORTH, R. W., 1999, *Physics of Ice* (Oxford: Oxford University Press).
- [26] PAULING, L., 1935, *J. Am. chem. Soc.*, **57**, 2680.
- [27] BUCH, V., SANDLER, P., and SADLEJ, J., 1998, *J. phys. Chem. B*, **102**, 8641.
- [28] MACDOWELL, L. G., SANZ, E., VEGA, C., and ABASCAL, J. L. F., 2004, *J. chem. Phys.* (in press).
- [29] PARRINELLO, M., and RAHMAN, A., 1980, *Phys. Rev. Lett.*, **45**, 1196.
- [30] GAY, S. C., SMITH, E. J., and HAYMET, A. D. J., 2002, *J. chem. Phys.*, **116**, 8876.