Relation between the melting temperature and the temperature of maximum density for the most common models of water

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Water exhibits a maximum in density at normal pressure at 4° above its melting point. The reproduction of this maximum is a stringent test for potential models used commonly in simulations of water. The relation between the melting temperature and the temperature of maximum density for these potential models is unknown mainly due to our ignorance about the melting temperature of these models. Recently we have determined the melting temperature of ice I_h for several commonly used models of water (SPC, SPC/E, TIP3P, TIP4P, TIP4P/Ew, and TIP5P). In this work we locate the temperature of maximum density for these models. In this way the relative location of the temperature of maximum density with respect to the melting temperature is established. For SPC, SPC/E, TIP3P, TIP4P, and TIP4P/Ew the maximum in density occurs at about $21-37$ K above the melting temperature. In all these models the negative charge is located either on the oxygen itself or on a point along the H–O–H bisector. For the TIP5P and TIP5P-E models the maximum in density occurs at about 11 K above the melting temperature. The location of the negative charge appears as a geometrical crucial factor to the relative position of the temperature of maximum density with respect to the melting temperature. © *2005 American Institute of Physics.*
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I. INTRODUCTION

Water is an important molecule. It forms the matrix of life,[1] it is the most common solvent for chemical processes, it plays a major role in the determination of the climate on earth, and it also appears on planets, moons, and comets.[2] Hence the importance of improving our understanding of the behavior of this substance. More than thirty years ago, computer simulations of water started their road with the pioneering papers by Watts and Barker[3] and by Rahman and Stillinger.[4] Since then, thousands of simulation studies have been undertaken where water was involved either as the only component or as one of the components of the mixture. A key issue when performing simulations of water is the choice of the potential model used to describe the interaction between molecules. A number of different potential models have been proposed (see the review paper of Guillot[5] for a comprehensive review). It is probably fair to say that the potentials for water most commonly used in the past years have been the SPC,[6] SPC/E,[7] and TIP4P (Ref. 8) models. Two recently proposed models, namely, TIP5P (Ref. 9) and TIP4P/Ew,[10] also give promising results and are increasingly used nowadays.

Two properties of real water are specially indicative of its singular behavior. The first one is the fact that at constant pressure it exhibits a maximum in density when plotted as a function of temperature.[11] The temperature at which this maximum occurs is usually denoted as the temperature of maximum density (TMD). At normal pressure the TMD occurs at about 4 °C. The TMD line moves to low temperatures very quickly upon increasing pressure. For instance, for heavy water (D_2O) the TMD line crosses[12,13] the melting line of ice I_h at about $p=600$ bars, and is located inside the metastable region of the liquid for higher pressures until it crosses the stability limit line of the fluid phase at about 2100 bars. For water the TMD line crosses the melting line at about 269 K and 400 bars.[14] Water presents a number of other anomalies in the fluid phase at low temperatures (see the review paper of Debenedetti[13]). Usually the existence of the TMD is related to the behavior of some order parameters[15] or to the behavior of the entropy of water at low temperatures.[16,17] The possibility of a second critical point in liquid water at low temperatures[18] is partly responsible for the renewed interest in supercooled water over the last few years. The second special feature of water is the fact that at normal pressure its solid phase (ice I_h) is less dense than the liquid phase (silica and carbon are among the very few compounds that present this special feature). From the Clapeyron equation it follows that the melting line has negative slope in the p-T representation. A fundamental question about these two singular features of water is the following: is the existence of a TMD line related to the existence of a low-density solid? Intuitively one expects that they must indeed be related, since experimentally they appear simultaneously in real substances. However, a complete theoretical proof that one thing implies the other has, to the best of our knowledge, not been provided as yet.

For some models of water (TIP3P, TIP4P, SPC, and SPC/E) the parameters of the potential were chosen to reproduce thermodynamic and/or structural[19,20] properties of water at room temperature and pressure. For these potentials the

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TMD was not considered when determining the potential parameters. It was not even clear if these models indeed present a TMD at normal pressure. A search for the TMD for potential models of water has been performed by several groups.[9,10,18,21–36] The first report of a TMD in liquid water from computer simulations was made by Stillinger and Rahman.[21] These authors showed that the ST2 potential model (introduced by them) did show a TMD. That was confirmed and refined by Stanley and co-workers.[18,22] For the SPC/E model, Báez and Clancy,[23] Harrington et al.,[22] and Bryk and Haymet[24] showed the existence of a TMD. Another important work in the search of TMD is that of Jorgensen and Jenson[25] who studied the SPC, TIP3P, and TIP4P models using relatively long runs. They concluded that whereas TIP4P models did exhibit a clear TMD, the SPC and TIP3P did not apparently exhibit a TMD (at least for the range of temperatures considered). The temperature of maximum density for TIP4P and SPC/E found by these groups was 20–30 K below the experimental value. In the last years two promising models of water have been proposed, the TIP4P/Ew (Ref. 10) and the TIP5P.[9] In this case the TMD was explicitly considered in the fitting procedure used to determine the potential parameters. For this reason these models provided the best description of the experimental TMD line.

Once the existence of this TMD for the majority of water models had become clear, an interesting question is the relative location of the TMD curve with respect to the melting point of these models. Obviously this requires the determination not only of the TMD but also of the melting point. Some early work on the determination of the melting point of SPC/E and TIP4P was undertaken in the past decade. By studying the ice I_h-fluid interface Haymet and co-workers have estimated the melting temperature for TIP4P,[37] SPC,[38] and SPC/E models.[39] The melting temperature of the SPC/E has also been considered by Clancy and co-workers.[40,41] For the SPC/E model the estimate of the melting point of Haymet and co-workers[24,39] and that of Clancy and co-workers[40,41] are in conflict since they differ by 50 K. The melting temperature of the TIP4P model has been determined by Tanaka and co-workers[42,43] and by van der Eerden and co-workers.[44,45] Again the results of these two authors are in conflict. For the proton-disordered ice I_h their estimates of the melting point differ by about 40 K (191 K reported by van der Eerden and co-workers[44,45] and a value close to 230 K by Tanaka and co-workers[42,43]). The melting temperature of the TIP5P model has been determined quite recently by Koyama et al.[43] and by Nada and van der Eerden.[45] Fortunately in this case the estimates of the two groups are in agreement (although the Tanaka group considered a proton-disordered structure and the group of van der Eerden considered a proton-ordered structure). Recently we have performed extensive work on fluid-solid equilibria and solid-solid equilibria of the most common models of water.[46–53] In fact, we have recently determined the melting point of the proton-disordered ice I_h for the TIP3P, TIP4P, SPC, SPC/E, TIP4P/Ew, and TIP5P models of water. In addition to the free-energy calculations, which allow one to determine the fluid-solid equilibria of a certain model, we

also performed Hamiltonian Gibbs-Duhem integration allowing us to determine the melting point of a model starting from the melting properties of another model.[52] Our melting temperatures obtained from free-energy calculations were mutually consistent with those obtained from Hamiltonian Gibbs-Duhem integration. For TIP3P and TIP4P/Ew we have reported the first estimate of the melting point. For the SPC and SPC/E models our estimates agree well with those of Haymet and co-workers.[38,39] For the TIP4P our results agree with those of Karim and Haymet[37] and Tanaka and co-workers.[42,43] For the TIP5P our results agree well with those of Nada and van der Eerden[45] and with those of Koyama et al.[43] In summary for SPC, SPC/E, TIP4P, and TIP5P we have at least another author (sometimes two) who we agree with. For TIP3P and TIP4P/Ew our estimates are new. Recently we have proposed a new model (TIP4P/Ice) specially designed to describe solid phases of water.[53] Since this model was specially designed to describe the behavior of ices, it is of interest to establish the existence or absence of a TMD for this model. We shall study this problem in this work.

In this work we shall locate the TMD for the water potentials SPC, SPC/E, TIP3P, TIP4P, TIP5P, TIP4P/Ew, and TIP4P/Ice. For TIP4P/Ew and SPC/E we shall use results from other researchers. For the rest of the models we shall perform computer simulations to determine the TMD. It will be shown that all these potential models exhibit a maximum in density as a function of temperature at normal pressure. We shall analyze the location of the TMD temperature with respect to the melting temperature of ice I_h for the model.

II. SIMULATION DETAILS

In this work computer simulations of the fluid phase were performed to determine the TMD of several water models. The simulations were performed in an analogous way to that used previously by the authors to determine the melting temperatures of the water models. In our simulations, the Lennard-Jones (LJ) potential was truncated for all phases at 8.5 Å. Standard long-range corrections to the LJ energy were added. The importance of an adequate treatment of the long-range Coulombic forces when dealing with water simulations has been pointed out in recent studies.[54–58] In this work, the Ewald summation technique has been employed for the calculation of the long-range electrostatic forces. For the determination of the TMD 360 molecules of water were used in the simulations. Isobaric isothermal (NpT) Monte Carlo simulations were performed to determine the equation of state at $p=1$ bar as a function of the temperature. The simulation box was cubic and isotropic scaling was used.

Two important remarks should be made concerning studies searching for the TMD at a certain pressure. The first is that very long runs are needed to determine the TMD with accuracy. Here we typically used about $1-1.5 \times 10^6$ cycles to determine the TMD (a cycle is defined as a trial move per particle plus a trial volume change). Equilibration is extremely difficult for temperatures below or close to the TMD. For this reason even longer runs were performed at those temperatures. For temperatures well above the TMD, equili-

TABLE I. Equation of state at $p=1$ bar for common water models. For each model the first column is the temperature and the second one is the densities (in g/cm^3). Unless otherwise stated, the data correspond to NpT Monte Carlo simulations of this work.

| TIP3P		TIP4P		TIP5P		SPC		TIP4P/Ice	
150	1.0209	232.45	1.0022	260	0.9777	180	0.9960	260	0.9712
160	1.0300	245	1.0076	270	0.9835	190.5	0.9915	272.2	0.9854
170	1.0378	255	1.0080	273[a]	0.9850	205	1.0018	280	0.9919
180	1.0365	265	1.0064	275[b]	0.9878	215	1.0081	290	0.9930
200	1.0360	275	1.0027	280	0.9887	230	1.0070	298.15	0.9933
230	1.0316	275[b]	1.0053	290	0.9893	250	1.0049	310	0.9922
275	1.0062	285	0.9998	300	0.9826	275[b]	0.9933	325	0.9888
275[b]	1.0052	298.15	0.9941	300[b]	0.9826	275	0.9927	340	0.9845
		300[b]	0.9935	310	0.9785			360	0.9766
		310	0.9851	325	0.9654			380	0.9641
		325	0.9752	325[b]	0.9641				
		325[b]	0.9765						
		340	0.9630						

[a]From Ref. 55.
[b]From Ref. 59.

bration of density is much faster. Completely misleading conclusions about the TMD can be obtained from short runs. Secondly, the way in which long-range electrostatic forces are dealt with is important. Several possibilities are available: simple truncation using the O–O distance as the relevant parameter, Ewald sums, or the reaction field. Ewald sums and reaction fields provide quite similar results for the density of water at a certain temperature and pressure. However, densities obtained by a simple truncation differ from those obtained from these other two methods. For a certain potential model differences between the densities obtained from Ewald summation and simple truncation are about 2% for temperatures below the TMD, of about 1% for temperatures above the TMD, and smaller than 1% for temperatures well above the TMD. These differences in densities also affect somewhat the location of the TMD temperature. Therefore when comparing the TMD temperature T_{TMD} with the melting temperature T_m it is important that long-range electrostatic forces are treated in the same way. For this reason the numerical implementation of the simulations performed in this work are completely identical to that used in our previous work to determine melting temperatures (except the fact that longer runs are required to determine the TMD precisely). In our opinion, to compare melting points and TMD obtained with different implementation of electrostatic forces can lead to wrong conclusions. It is important that both properties are treated in the same way to establish solid conclusions.

III. RESULTS

In Table I simulation results of this work for TIP3P, TIP4P, TIP5P, and SPC are presented. All of them correspond to the isobar $p=1$ bar. For all these models results from other authors have been included. In particular, we have considered the results of Paschek[59] and Lisal et al.[55] Good agreement with their previously reported values of the densities was found. Notice that we compare only with authors that use Ewald sums to deal with the long-range electrostatic forces. For the SPC/E we shall use the recent simulation results of Bryk and Haymet[24] obtained using Ewald sums. Horn et al.[10] has recently proposed a new version of TIP4P which has been denoted as TIP4P/Ew. For this model we shall use the simulation results reported by Horn et al.[10] since they were also obtained using Ewald sums. We have recently proposed a modified version of the TIP4P model (with small changes in the potential parameters with respect to the original parameters of the potential) able to reproduce the experimental melting temperature of ice I_h and to describe qualitatively the phase diagram of water.[53] This model was denoted as TIP4P/Ice. In order to locate the TMD for this model we have performed simulations along the isobar $p=1$ bar. Results are also presented in Table I. The statistical uncertainty of our reported densities is of 0.002 g/cm^3 for high temperatures (20° higher than the TMD), 0.003 g/cm^3 for temperatures close to the TMD, and 0.004 g/cm^3 for temperatures lower than the TMD. Statistical uncertainty increases dramatically from 20° above to 20° below the TMD. The compressibility of real water increases dramatically at low temperatures, so large fluctuations in density are expected at low temperatures.

The results from Table I were fitted to polynomials (depending on the case we use either a third- or fourth-degree polynomial). Using these fits we located the TMD and the value of the density at the maximum. In Fig. 1(a) the results of Table I along with those of the SPC/E model[24] and those of the TIP4P/Ew model[10] are presented. Experimental densities (open circles) along the isobar $p=1$ bar are also included.[60] As can be seen, all of the models considered in this work, SPC, SPC/E, TIP3P, TIP4P, TIP5P, TIP4P/Ew, and TIP4P/Ice, present a maximum in density as a function of temperature. For the models SPC/E, TIP4P, TIP5P, and TIP4P/Ew the presence of a maximum in the density was reported previously by other authors.[9,22–25] For the TIP3P and SPC the existence of this maximum has not been reported before[25] and in the literature one may often read that no TMD exists for these two models. The results of Fig. 1(a)
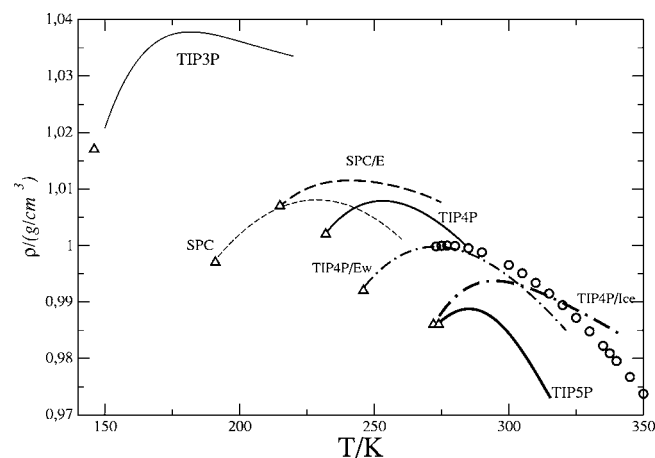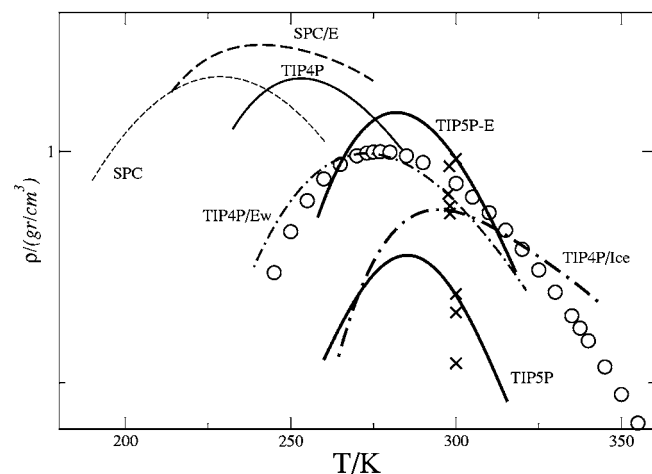
FIG. 1. Density vs temperature along the isobar $p=1$ bar for several models of water as obtained in the Monte Carlo simulations of this work. Results from SPC/E were taken from Bryk and Haymet (Ref. 24) whereas those of the TIP4P/Ew were taken from the work of Horn *et al.* (Ref. 10). Long-range electrostatic forces were implemented with Ewald sums in all the cases. The results of the simulations were fitted to a polynomial expression. Experiment: open circles. Thin solid line: TIP3P; thick solid line: TIP4P; very thick solid line: TIP5P. Thin dashed line: SPC; thick dashed line: SPC/E; thin dashed-dotted line: TIP4P/Ew; thick dashed-dotted line: TIP4P/Ice. (a) For each water potential a symbol (triangle) has been placed at the temperature of the melting point of ice I_h of the model. (b) Symbols (x) have been introduced with the densities of the models at a temperature of either 298.15 or 300 K. From top to bottom the symbols (x) correspond to TIP5P-E, SPC/E, TIP4P/Ew, TIP4P, TIP4P/Ice, TIP5P, TIP3P, and SPC, respectively. The results of the TIP5P-E model as reported by Rick (Ref. 56) have also been included and are represented by a thick solid line.

show that the maximum indeed exists for TIP3P and SPC although at temperatures much lower than in experiment (maybe for this reason the TMD was not found before). The TIP4P/Ice, although derived for solid phases of water, also exhibits a TMD. In summary all models of water considered in this work present a TMD. It is reasonable to expect that any relatively sensible model of water should exhibit a TMD. Another issue is whether the location of the TMD is close or not to the experimental value. In general the TMD of common models of water is below the experimental value, the departures ranging from 90 K for TIP3P to 50 K for SPC, 40 K for SPC/E, and 20 K for TIP4P. The only models that

provide a TMD close to the experimental value are TIP4P/Ew and TIP5P. This is not by chance. These models were designed to reproduce the TMD of real water. The TIP4P/Ew yields a TMD 4 K below the experimental value and the TIP5P yields a TMD 8 K above the experimental value. A comment is needed with respect to the results of the TIP5P model. In the original paper of Mahoney and Jorgensen,[9] where the potential was proposed, it was shown that this potential reproduces the experimental value of the TMD and also that it yields good liquid densities. This appears to be in conflict with the results of Fig. 1(a) where it is shown that the densities of the TIP5P are somewhat low and that the TMD appears 8 K above the experimental value. The origin of the discrepancy is the methodology used to deal with the long-range forces, spherical truncation (Mahoney and Jorgensen) versus Ewald sums (this work). In fact, Lisal *et al.*[55] located the TMD of the TIP5P model when using Ewald sums at 284 K, in good agreement with the results of this work. Notice that we also obtained good agreement with the results of Paschek for the TIP5P model that were obtained using Ewald sums. This illustrates that different treatment for the long-range forces may have an effect of about 8° in the exact location of the TMD of a certain model. It also affects the densities: when Ewald sums are used densities tend to be lower than when spherical truncation is used. Of course it is possible to change the parameters of the TIP5P model slightly to recover good agreement with experiment when Ewald sums are used to deal with long-range forces.[56] This is the origin of the TIP5P-E model proposed recently by Rick.[56] Results for the TIP5P-E model have been included in Fig. 1(b). The performance of TIP4P is reasonable (considering that the location of the TMD was not used in the development of its parameters), being 20 K below the experimental value. The TIP4P/Ice yields a TMD 18 K above the experimental value. The fact that the TMD was not used in the parametrizations of water potential models of the 20th century was due to the fact that the calculation of this property was too expensive from a computational point of view. It is not a surprise that TIP5P and TIP4P/Ew both proposed in the last five years were derived to reproduce the experimental value of the TMD for real water. For this reason we anticipate increasing interest in the reproduction of the TMD when designing water models.

In Fig. 1(b) the density of water obtained at either 298.15 or 300 K for all these water models has been included. SPC/E, TIP4P, TIP4P/Ew, TIP4P/Ice, and TIP5P-E yield a good estimate of the density of liquid water at room temperature. The densities of SPC, TIP3P, and TIP5P at room temperature and pressure are too low when they are used along with Ewald sums (the parameters of these models were proposed to be used with spherical truncation). Apparently some models are more affected than others by the use of Ewald sums, so that SPC/E and TIP4P still provide good estimates of the density of liquid water at room temperature and pressure whereas SPC, TIP3P, and TIP5P are strongly affected and yield too low densities.

Let us now analyze a different issue. Liquids having a TMD also freeze into a low-density solid. Low-density solids and TMD appear for systems where tetrahedral order is

TABLE II. Melting temperature of ice I_h, T_m, and density of the liquid water at the melting point ρ_m at p =1 bar. Temperature of maximum density T_{TMD} and density at the maximum ρ_{TMD} along the isobar p=1 bar. Results are presented for the SPC/E, SPC, TIP3P, TIP4P, TIP4P/Ew, TIP4P/Ice, TIP5P, and TIP5P-E models of water. The difference between T_m and T_{TMD} is presented in the last column. Results for TIP3P, TIP4P, TIP5P, SPC, and TIP4P/Ice are from this work. For the TIP5P-E, SPC/E, and TIP4P/Ew models the TMD was located using the simulation results from the work of Rick (Ref. 56), Bryk and Haymet (Ref. 24), and Horn *et al.* (Ref. 10), respectively. The melting point of I_h for the TIP5P-E model was obtained in this work using the methodology described elsewhere (Ref. 52). Experimental results for water, heavy water, and tritium oxide are presented in the first three lines.

Model	T_m (K)	ρ_m (g/cm³)	T_{TMD} (K)	ρ_{TMD} (g/cm³)	ΔT (K)
H_2O	273.15	0.999 83	277.13	0.999 97	3.98
D_2O	276.97		284.33		7.36
T_2O	277.64		286.55		8.91
SPC/E	215	1.007	241	1.012	26
SPC	191	0.991	228	1.008	37
TIP3P	146	1.017	182	1.038	36
TIP4P	232	1.002	253	1.008	21
TIP4P/EW	246	0.992	273	1.000	27
TIP4P/ICE	272	0.986	295	0.994	23
TIP5P	274	0.987	285	0.989	11
TIP5P-E	271.3	1.002	282	1.004	10.7

important[61] both in the liquid and in the solid (as is the case of water, carbon and silica SiO_2). The proximity of the melting line of a low-density solid to the TMD and the fact that these two features always appear together suggest that both features must indeed be interconnected and indeed that appears to be the case for molecules where tetrahedral coordination is favored.[16,61] Let us now discuss the relative location of the melting temperature of ice I_h with respect to the TMD for these water models. In Table II the melting temperature of ice I_h as determined by us recently[52] and the location of the TMD of this work are presented. As can be seen, for all these water models of water the temperature of maximum density is higher than the melting temperature. In this respect all these models mimic qualitatively the behavior of real water. However, the difference between the melting temperature and the TMD depends on the particular model, ranging from about 10 K for TIP5P models (TIP5P and TIP5P-E) to about 25 K for TIP4P models (TIP4P, TIP4P/Ew, and TIP4P/Ice), to about 26 K for the SPC/E, and to about 36 K for the TIP3P. It appears that the difference between the TMD and the melting temperature is sensitive to the type of geometry of the model. We should recognize that the uncertainty in the difference between the melting temperature T_m and that of the maximum density T_{TMD} is relatively large (of about 10 K). This is due to the fact that both T_m and T_{TMD} present an estimated uncertainty of about 5 K each. In any case, since for all models the T_{TMD} is at least 10 K above that of the T_m of ice I_h, it can be stated safely that for water models the T_{TMD} appears at a temperature above the melting point of the low-density solid. On the other hand the results of Table II suggest an indirect way of estimating the melting temperature of ice I_h for a certain potential model of water (the recipe is evaluate the TMD and subtract 25 K from this number). Notice, however, that the melting temperature of ice I_h at room temperature is not necessarily the melting temperature of the model. In fact, ice II was found to be more stable thermodynamically[52] than ice I_h at normal pressure for the

SPC, SPC/E, TIP3P, and TIP5P models (although for all the models we found ice I_h to be a mechanically stable phase[62]). Only in the case of TIP4P, TIP4P/Ew, and TIP4P/Ice models was ice I_h thermodynamically stable at normal melting. How does this point affect the conclusions of Table II with respect to the difference between the TMD and the real melting point of the model? They are somewhat affected, although the magnitude depends on the particular model. For models having ice II as the stable phase at normal pressure, ice I_h appears as a stable phase at sufficiently negative pressures. Therefore a triple point liquid-ice I_h-ice II exists at negative pressures for SPC, SPC/E, TIP3P, and TIP5P. From this triple point and moving to positive pressures one finds the melting line of ice II with positive slope in the p-T plot and the metastable melting line of ice I_h with negative slope in the p-T plot. The magnitude of the difference between the melting temperature of ice I_h and ice II at normal pressure depends basically on how negative is the pressure at the liquid-ice I_h-ice II triple point. For TIP5P we found that the melting T of ice I_h was 274 K whereas that of ice II was 282 K. According to this for TIP5P model the melting temperature of ice II practically coincides with the TMD temperature. For SPC/E the normal melting point of ice II is only 1 K above that of ice I_h. We should remember that ice II is also a tetrahedral solid where each water molecule forms hydrogen bonds with the four nearest neighbors (although now forming a distorted tetrahedron). Ice II can be also be considered a low-density solid since its density is about 2/3 of that of the high-density ices of water (i.e., ice VII or ice VIII). Finally it should be pointed out that ice II can also become less dense than liquid water (as ice I_h does) by simply increasing the pressure, since it has been shown recently that the melting curve of ice II exhibit reentrant behavior.[46,52] In summary the fact that ice II is the stable solid at melting for TIP3P, SPC, SPC/E, and TIP5P does not contradict the idea of the importance of tetrahedral coordination for those water models since ice II is also a tetrahedral solid. Tetrahedral coordi-
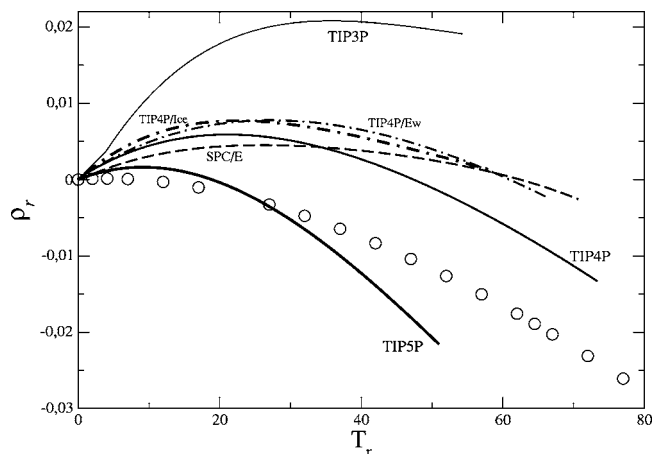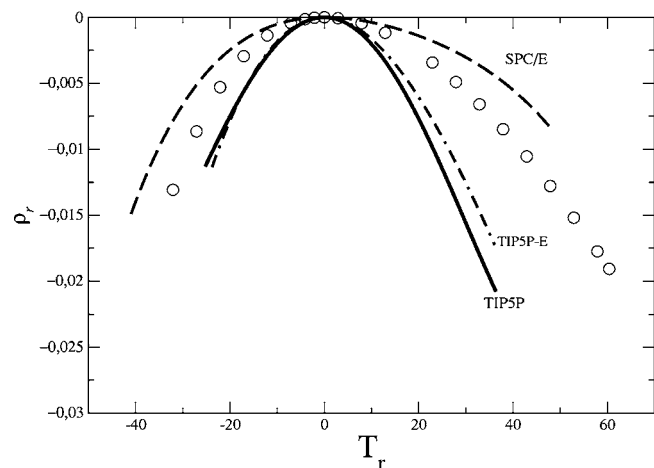
FIG. 2. Relative density ρ_r (g/cm^3) vs relative temperature T_r (K) along the isobar $p=1$ bar for several models of water. The relative density is defined as $\rho_r = \rho - \rho_m$, where ρ_m is the density of the liquid at the normal melting temperature of ice I_h for the model. The relative temperature is defined as $T_r = T - T_m$, where T_m is the normal melting temperature of ice I_h for the model. The symbols are the same as in Fig. 1.

nation is still important for those models where ice I_h is not thermodynamically stable at normal pressure.

In Fig. 2 the densities of water along the $p=1$ bar isobar are plotted as a function of the temperature, taking the temperatures of the melting point of ice I_h for the model as the origin. The density of the liquid at the melting temperature has been chosen as the origin for densities. It can be seen that in this representation none of the models provide a satisfactory description of real water. The TIP3P has a TMD too far from the melting temperature. For TIP5P the TMD is located not too far from the melting temperature (as it should be for real water where the difference in temperatures is of only 4°). However, the densities of the TIP5P model decay too rapidly after the TMD point. For this reason it is likely that the TIP5P will not be a satisfactory model for water at high temperatures. It is not surprising that its prediction of the critical temperature is much lower than the experimental value.[55,63] The behavior of the TIP4P and SPC/E is rather similar. Its main defect is that the location of the TMD is too far from the melting point. However, the density predictions of these two models seem to be parallel to that of real water. Notice also that SPC/E, TIP4P, TIP4P/Ew and TIP4P/Ice present similar behavior when plotted with respect to the properties of water at the melting point. The natural question emerging from Fig. 2 is the following: what is wrong with all the potential models of water (with the exception of TIP5P) which predict a too large a difference between the TMD and the melting temperature? The question deserves further work but we anticipate that two factors may be relevant. First, quantum effects have not been included in our models. The melting temperature and TMD temperature of H$_2$O, D$_2$O, and T$_2$O increase with the molecular weight (see Table II). More importantly the difference between these two temperatures also increases with the molecular weight and takes the values 4, 7.4, and 8.9 for H$_2$O, D$_2$O, and T$_2$O, respectively. As the molecular weight increases quantum effects are less important and water behaves more as a classical fluid. Therefore one may suspect that for "classical" water the difference

between the melting temperature and the TMD would be of about 10 K.[5,21] Taking into account that we are using classical simulations one should expect a difference of 10 K between T_m and T_{TMD}. We frequently found more than 20 K so something else may be missing. The second feature not included in the models is the existence of polarizability in real water. It is likely that the effective dipole moment of the molecule of water in the liquid state does not change much with temperature (in the proximities of the TMD). However, one would expect a somewhat larger (with respect to the liquid) effective dipole for the molecule of water in the solid phase. That has been predicted recently by using a polarizable water model.[31,64] A larger effective dipole moment for the solid phase when compared to that of the liquid will probably move the melting point to higher temperatures when compared to a nonpolarizable model thus reducing the difference between the melting temperature and the TMD. In our view, the persistence in the difference of about 25 K between the TMD and the melting temperature is due to the limitations of our treatment of water (not including quantum effects and neglecting polarizability) and cannot be solved by a minor change of the potential parameters. The comparison of the behavior of the TIP4P/Ew and TIP4P/Ice models is illustrative in this respect. When the model reproduces the experimental TMD (TIP4P/Ew) it yields a too low melting temperature (i.e., 245 K) 28° below the experimental value. When the model reproduces the experimental melting point (TIP4P/Ice) then the TMD occurs at 18° above the experimental value. The message is it is not possible to fit both (T_m and TMD) simultaneously with a nonpolarizable TIP4P-like model. The difference between melting temperature and TMD is of about 25°, no matter how you fit the parameters. The nice feature about this difference of 25 K is that when a more sophisticated treatment is included (i.e., quantum effects and polarizability) it is likely that the TMD is going to be much closer to the melting temperature. This is an interesting issue that probably requires further work.

A property of interest for water is the coefficient of thermal expansion α. This property is negative for temperatures below the TMD, zero at the TMD, and positive at temperatures above the TMD. Sometimes the quality of a potential model is determined by comparing the value of α from experiment to that of simulation. By having a look again to Fig. 1 it is clear what can be expected. For models with a TMD much below the experimental value the value of α will be much larger than the experimental one. The experimental value of α at room temperature and pressure is 26×10^{-5} K^{-1}. The SPC model yields[25,26] 106×10^{-5} K^{-1}. For TIP3P one finds[25] 144×10^{-5} and 92×10^{-5} K^{-1} in another estimate.[26] The agreement is better for TIP4P and TIP4P/Ice due to the fact that their TMDs are closer to the experimental value. Since the TMD of TIP4P is below the experimental value, one would expect that α will be overestimated.[25] For TIP4P/Ice since the TMD is above the experimental value, one would expect α will be underestimated. In fact, for TIP4P α was[25,26] of 44×10^{-5} K^{-1} whereas for TIP4P/Ice the value of α was 9×10^{-5} K^{-1} so that the experimental value (26×10^{-5} K^{-1}) is just between both results. For TIP5P Mahoney and Jorgensen[9] and

(a)
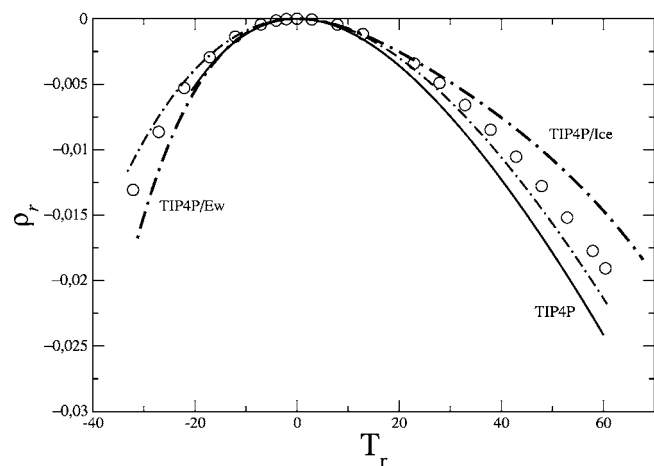
(b)

FIG. 3. Relative density ρ_r (g/cm^3) vs relative temperature T_r (K) along the isobar $p=1$ bar for several models of water. The relative density is defined as $\rho_r=\rho-\rho_{TMD}$, where ρ_{TMD} is the density at the temperature of maximum density. The relative temperature defined as $T_r=T-T_{TMD}$, where T_{TMD} is the temperature at the temperature of maximum density. Open circles: experimental results. (a) Results for SPC/E, TIP5P, and TIP5P-E models. (b) Results for TIP4P, TIP4P/Ew, and TIP4P/Ice.

Jorgensen and Tirado-Rives[26] reported 63×10^{-5} K^{-1}. The best agreement is that of TIP4P/Ew with a value of 32×10^{-5} K^{-1}. Another interesting issue is how quickly α changes with temperature in the proximities of the TMD where α is zero. This is related to the changes in curvature of the isobar in the proximities of the TMD point. In Fig. 3 the densities of the different water models are presented for the isobar $p=1$ bar. The origin of coordinates (both for temperatures and densities) is the TMD of each model (i.e., we define a relative density as $\rho_r=\rho-\rho_{TMD}$ and a relative temperature as $T_r=T-T_{TMD}$). Our intention is to see how quickly changes the density in the proximities of the TMD point. In Fig. 3(a) results are presented for SPC/E, TIP5P, and TIP5P-E. As can be seen the density change of the SPC/E model in the proximities of the TMD is too small, whereas that of TIP5P and TIP5P-E is too big so that the density decreases too quickly as a function of temperature. In Fig. 3(b) results are presented for TIP4P, TIP4P/Ew, and TIP4P/Ice. These models represent better the density change in the proximities of the TMD.
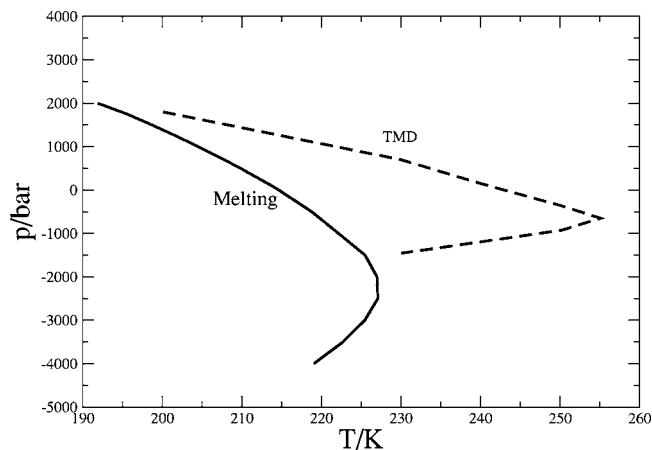

FIG. 4. Melting temperatures of ice I_h at different pressures for the SPC/E model as obtained in this work from Gibbs-Duhem simulations (solid line). Temperature of maximum density for SPC/E model as a function of pressure as determined by Harrington *et al.* (Ref. 22) (dashed line).

Let us finish by discussing the behavior of the TMD with pressure. Recently Harrington *et al.*[22] have determined the location of the TMD for the SPC/E not only for the isobar $p=1$ bar, but for other pressures as well. In Fig. 4 the behavior obtained by these authors is shown. An interesting feature observed by these authors is the change of curvature of the TMD line at negative pressures. This change of curvature makes the crossing of the TMD line unlikely with the spinodal line of the vapor-liquid equilibria. The melting point of ice I_h for the SPC/E model has been obtained previously by us as $T=215$ K. It is then possible to use Gibbs-Duhem integration[65] to obtain the ice I_h-water coexistence line for this model at high, low, or even negative pressures. Details of the Gibbs-Duhem simulations are similar to those described elsewhere.[52] In Fig. 4 the TMD and the melting temperature is presented at different pressures for the SPC/E model. It can be seen that the melting temperatures do also exhibit reentrant behavior. The origin of this reentrant behavior in the melting line is the higher compressibility of the liquid with respect to the solid phase as has been discussed elsewhere.[46,52] By looking at Fig. 4 the feeling of a connection or relationship between the TMD line and the melting curve of a low-density solid is strengthened. Notice that the reentrant behavior of both the TMD and the liquid-ice I_h coexistence curve is not a particular behavior of the SPC/E model. It has also been found in the TIP4P model[28,46] demonstrating that is a general feature of water models (and likely of real water).

IV. CONCLUSIONS

All models of water, SPC, SPC/E, TIP3P, TIP4P, TIP5P, TIP4P/Ew, and TIP4P/Ice, considered in this work exhibited a maximum in the density along the $p=1$ bar isobar. For SPC, SPC/E, TIP3P, and TIP4P the TMD occurs at temperatures below the experimental value. This indicates that models of water fitted to liquid state properties tend to yield a too low TMD. TIP4P/Ew and TIP5P provide a TMD much closer to the experimental result. The new model of ice TIP4P/Ice which reproduces the melting point of water

yields a TMD 18° higher than the experimental value. The location of the TMD of the model helps to clarify the magnitude (too high, i.e., low TMD, or too low, i.e., high TMD) of the values of the coefficient of thermal expansion α of the model at room temperature and pressure.

A comparison has also been made between the melting temperature of ice I_h for the potential model and the TMD of the same model. For all the models considered the TMD is higher than this of the melting point of ice I_h for the model. The difference range from 11 K for TIP5P and TIP5P-E to about 37 K for SPC. A rough estimate of the melting temperature of a model can be obtained from the simple rule, $T_{\mathrm{TMD}} - 25$ K although the error of this rudimentary procedure may be of about 15 K. It is striking that for all models considered here the difference between the melting temperature and the TMD is in the range of 10–40 K, taking into account that for real water this difference is only of 4°. Quantum effects and the lack of polarizability may be at the origin of this discrepancy.

The curvature of the density curve in the proximities of the TMD has also been considered. It was found that SPC/E and TIP5P give too small and too great density change, respectively, in their proximities. The curvature of the models based on the TIP4P geometry seems to be in better agreement with experiment. It has long been thought that the presence of a TMD and that of a low-density solid are somewhat connected. We can just testify from this work that this is indeed the case not only for real water, but also for our "models of water." In fact, it is shown here that for the SPC/E model both the TMD and the melting curve present reentrant behavior.

ACKNOWLEDGMENTS

[1] P. Ball, *Life's Matrix. A biography of Water* (University of California Press, Berkeley, 2001).
[2] J. P. Poirier, Nature (London) **299**, 683 (1982).
[3] J. A. Barker and R. O. Watts, Chem. Phys. Lett. **3**, 144 (1969).
[4] A. Rahman and F. H. Stillinger, J. Chem. Phys. **55**, 3336 (1971).
[5] B. Guillot, J. Mol. Liq. **101**, 219 (2002).
[6] H. J. C. Berendsen, J. P. M. Postma, W. F. van Gunsteren, and J. Hermans, in *Intermolecular Forces*, edited by B. Pullman (Reidel, Dordrecht, 1982), p. 331.
[7] H. J. C. Berendsen, J. R. Grigera, and T. P. Straatsma, J. Phys. Chem. **91**, 6269 (1987).
[8] W. L. Jorgensen, J. Chandrasekhar, J. D. Madura, R. W. Impey, and M. L. Klein, J. Chem. Phys. **79**, 926 (1983).
[9] M. W. Mahoney and W. L. Jorgensen, J. Chem. Phys. **112**, 8910 (2000).
[10] 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).
[11] M. Chaplin, http://www.lsbu.ac.uk/water/ (2005).
[12] R. A. Fine and F. J. Millero, J. Chem. Phys. **63**, 89 (1975).
[13] P. G. Debenedetti, J. Phys.: Condens. Matter **15**, R1669 (2003).
[14] F. Franks, *Water a Matrix of Life* (Royal Society of Chemistry, Cambridge, 2000).
[15] J. R. Errington and P. G. Debenedetti, Nature (London) **409**, 318 (2001).
[16] P. G. Debenedetti and H. E. Stanley, Phys. Today **56**(6), 40 (2003).
[17] F. Saija, A. M. Saitta, and P. V. Giaquinta, J. Chem. Phys. **119**, 3587 (2003).
[18] P. H. Poole, F. Sciortino, U. Essmann, and H. E. Stanley, Nature (London) **360**, 324 (1992).
[19] A. K. Soper, Chem. Phys. **258**, 121 (2000).
[20] T. Head-Gordon and G. Hura, Chem. Rev. (Washington, D.C.) **102**, 2651 (2002).
[21] F. H. Stillinger and A. Rahman, J. Chem. Phys. **60**, 1545 (1974).
[22] S. Harrington, P. H. Poole, F. Sciortino, and H. E. Stanley, J. Chem. Phys. **107**, 7443 (1997).
[23] L. A. Báez and P. Clancy, J. Chem. Phys. **101**, 9837 (1994).
[24] T. Bryk and A. Haymet, Mol. Simul. **30**, 131 (2004).
[25] W. L. Jorgensen and C. Jenson, J. Comput. Chem. **19**, 1179 (1998).
[26] W. L. Jorgensen and J. Tirado-Rives, Proc. Natl. Acad. Sci. U.S.A. **102**, 6665 (2005).
[27] J. R. Griguera, J. Chem. Phys. **114**, 8064 (2001).
[28] P. H. Poole, F. Sciortino, U. Essmann, and H. E. Stanley, Phys. Rev. E **48**, 3799 (1993).
[29] I. M. Svishchev, P. G. Kusalik, J. Wang, and R. J. Boyd, J. Chem. Phys. **105**, 4742 (1996).
[30] B. Guillot and Y. Guissani, J. Chem. Phys. **108**, 10162 (1998).
[31] S. W. Rick, J. Chem. Phys. **114**, 2276 (2001).
[32] S. R. Billeter, P. M. King, and W. F. van Gunsteren, J. Chem. Phys. **100**, 6692 (1994).
[33] B. Guillot and Y. Guissani, J. Chem. Phys. **114**, 6720 (2001).
[34] K. Bagchi, S. Balasubramanian, and M. L. Klein, J. Chem. Phys. **107**, 8561 (1997).
[35] P. Jedlovszky and R. Vallauri, Mol. Phys. **97**, 1157 (1999).
[36] A. Wallqvist and P. O. Astrand, J. Chem. Phys. **102**, 6559 (1995).
[37] O. A. Karim and A. D. J. Haymet, J. Chem. Phys. **89**, 6889 (1988).
[38] O. A. Karim, P. A. Kay, and A. D. J. Haymet, J. Chem. Phys. **92**, 4634 (1990).
[39] S. C. Gay, E. J. Smith, and A. D. J. Haymet, J. Chem. Phys. **116**, 8876 (2002).
[40] L. A. Báez and P. Clancy, J. Chem. Phys. **103**, 9744 (1995).
[41] B. W. Arbuckle and P. Clancy, J. Chem. Phys. **116**, 5090 (2002).
[42] G. T. Gao, X. C. Zeng, and H. Tanaka, J. Chem. Phys. **112**, 8534 (2000).
[43] Y. Koyama, H. Tanaka, G. Gao, and X. C. Zeng, J. Chem. Phys. **121**, 7926 (2004).
[44] M. J. Vlot, J. Huinink, and J. P. van der Eerden, J. Chem. Phys. **110**, 55 (1999).
[45] H. Nada and J. P. J. M. van der Eerden, J. Chem. Phys. **118**, 7401 (2003).
[46] E. Sanz, C. Vega, J. L. F. Abascal, and L. G. MacDowell, Phys. Rev. Lett. **92**, 255701 (2004).
[47] E. Sanz, C. Vega, J. L. F. Abascal, and L. G. MacDowell, J. Chem. Phys. **121**, 1165 (2004).
[48] L. G. MacDowell, E. Sanz, C. Vega, and L. F. Abascal, J. Chem. Phys. **121**, 10145 (2004).
[49] C. McBride, C. Vega, E. Sanz, and J. L. F. Abascal, J. Chem. Phys. **121**, 11907 (2004).
[50] C. McBride, C. Vega, E. Sanz, L. G. MacDowell, and J. L. F. Abascal, Mol. Phys. **103**, 1 (2005).
[51] C. Vega, C. McBride, E. Sanz, and J. L. Abascal, Phys. Chem. Chem. Phys. **7**, 1450 (2005).
[52] C. Vega, E. Sanz, and J. L. F. Abascal, J. Chem. Phys. **122**, 114507 (2005).
[53] J. L. F. Abascal, E. Sanz, R. G. Fernandez, and C. Vega, J. Chem. Phys. **122**, 234511 (2005).
[54] D. van der Spoel, P. J. van Maaren, and H. J. C. Berendsen, J. Chem. Phys. **108**, 10220 (1998).
[55] M. Lísal, J. Kolafa, and I. Nezbeda, J. Chem. Phys. **117**, 8892 (2002).
[56] S. W. Rick, J. Chem. Phys. **120**, 6085 (2004).
[57] D. J. Price and C. L. Brooks, J. Chem. Phys. **121**, 10096 (2004).
[58] H. Yu and W. F. van Gunsteren, J. Chem. Phys. **121**, 9549 (2004).
[59] D. Paschek, J. Chem. Phys. **120**, 6674 (2004).
[60] A. Saul and W. Wagner, J. Phys. Chem. Ref. Data **18**, 1537 (1989).
[61] J. L. Finney, Philos. Trans. R. Soc. London, Ser. B **359**, 1145 (2004).
[62] F. Sciortino, U. Essmann, H. E. Stanley, M. Hemmati, J. Shao, G. H. Wolf, and C. A. Angell, J. Chem. Phys. **52**, 6484 (1995).
[63] M. Lisal, I. Nezbeda, and W. R. Smith, J. Phys. Chem. B **108**, 7412 (2004).
[64] H. Saint-Martin, B. Hess, and H. J. C. Berendsen, J. Chem. Phys. **120**, 11133 (2004).
[65] D. A. Kofke, J. Chem. Phys. **98**, 4149 (1993).