

## Note: Equation of state and compressibility of supercooled water: Simulations and experiment

J. L. F. Abascal<sup>(a)</sup> and C. Vega

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

(Received 21 January 2011; accepted 12 April 2011; published online 10 May 2011)

[doi:10.1063/1.3585676]

The properties of liquid water at low temperatures changes in a completely different way to that exhibited by most of other liquids for similar conditions.<sup>1</sup> In the late seventies, Angell and co-workers presented strong evidence that the compressibility along isobars (from room pressure up to 1500 bar) seems to diverge at low temperatures.<sup>2,3</sup> An explanation of this special behaviour is needed. Divergence of response functions bring to mind the idea of criticality. The existence of two amorphous phases of water<sup>4,5</sup> seems to suggest the existence of two different liquids above the glass transition. In 1992 Poole *et al.*,<sup>6</sup> using computer simulations of the ST2 model of water,<sup>7</sup> found a liquid-liquid transition occurring in supercooled water at moderate pressures which has been further confirmed recently for this model by Liu *et al.*<sup>8</sup> According to the liquid-liquid hypothesis, the apparent divergence of several response functions of supercooled water can be explained by the fact that supercooled water is approaching a Widom line (which can be considered to be an extension of the coexistence curve).<sup>9-15</sup> Only experimental measurements can firmly establish the existence of a second critical point in the supercooled region of water. Unfortunately, in real experiments water freezes before reaching the critical temperature. Computer simulations could be useful in assessing the conditions where the liquid-liquid equilibria may occur because the accessible window of time is enough to sample the properties of the (metastable) liquid, but not to develop nucleation seeds. The problem is that simulations use approximate models to describe water interactions and for this reason their predictions may not be accurate. This is probably the case of the ST2 model of water. Other more elaborated water models also predict a second critical point.<sup>9,16-19</sup> However, the predictions for supercooled water properties have not usually been compared directly to experimental results so it is not completely clear to what extent they should be trusted.

TIP4P/2005<sup>20</sup> is a recently proposed water model which has shown an excellent overall performance in reproducing water properties.<sup>21</sup> Its ability in accounting for the “anomalous” water properties,<sup>22</sup> for the densities of the ices,<sup>20</sup> and for the solid-solid transitions in the region where the second critical point is expected, prompted us to use the model to investigate the supercooled region. Recently, we have reported the results for the Widom line of the TIP4P/2005 model<sup>23</sup> and determined the critical point to be located at 1350 bar and

193 K. A few days after the acceptance of the above mentioned paper, Mishima reported experimental measurements of the density and compressibility of supercooled water<sup>24</sup> reaching temperatures as low as 200 K. These experiments provide, for the first time, the possibility of checking the performance of TIP4P/2005 in the immediate vicinity of the critical point. The purpose of this note is to compare the results obtained by this model for the density and compressibility of supercooled water to experimental results, in order to assess the validity of the predictions of TIP4P/2005 for the Widom line and the liquid-liquid transition.

In Fig. 1, the simulation results for the density are compared to the experimental data.<sup>24-27</sup> The simulation results at low and intermediate temperatures have been taken from Refs. 22 and 23. In order to show the results in a wider context, additional simulations have been done to calculate the density at high temperatures, using the same computational methodology as in Ref. 22. Overall the performance of the model is quite good (and even excellent in the region 1000 to 1500 bar where the model predicts the critical point). The results for the 400 and 1000 bar isobars are in excellent agreement with the experimental data along the whole range of measured temperatures. The same is true for the isobars at higher pressures with the exception of the region of low temperatures (below 240 K). The results at 1500 bar may be affected by the vicinity of the critical point (the pressure is only 150 bar above the critical pressure for TIP4P/2005) where reliable results are hard to obtain. We have no explanation for the discrepancies at 2000 and 3000 bar (we have monitored these runs and we found no signs of vitrification or crystallization).

In Fig. 2, a comparison is made between experimental and simulation results (TIP4P/2005) for the isothermal compressibility at 400, 1000, and 1500 bar. At the higher temperatures investigated, the simulation results are coincident with the experimental measurements for the three isobars considered. The results in the deeply supercooled region are quite satisfactory but far from perfect: very good at 1000 and 1500 bar and acceptable at 400 bar. The results for the 1000 bar and 1500 isobars are particularly important since these pressures bracket the critical pressure for the TIP4P/2005 model. At these pressures, both the densities and the compressibilities are in excellent agreement with the experimental values. This indicates that the model is realistic and accurate

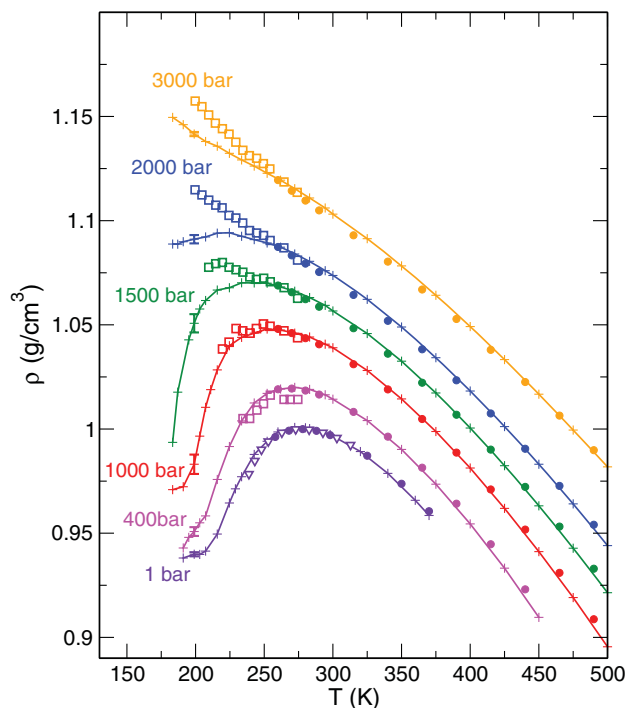


FIG. 1. Equation of state of the TIP4P/2005 water model. The computer simulation results are plotted with plus signs (lines are a guide to the eye). The uncertainty of most of the calculations is smaller than the size of the symbols so it has not been depicted in general (it becomes slightly significant only in the vicinity of the critical point, see the error bars for the results at 199 K). Experimental results were taken from the work of Mishima<sup>24</sup> (open squares), from the 58-coefficient equation of state of Saul and Wagner<sup>27</sup> (filled circles), and (at ambient pressure) from the measurements of Hare and Sorensen<sup>25,26</sup> (open triangles).

enough to have predictive value (both qualitative and quantitative) in the supercooled region. It is then expected that the Widom line and the liquid-liquid critical point obtained with the model (reported in Ref. 23) does indeed represent a close approximation to the behaviour of real water.

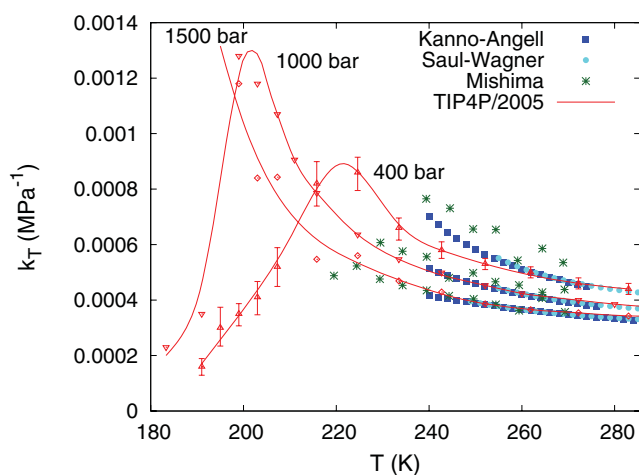


FIG. 2. Isothermal compressibilities for the TIP4P/2005 model (open symbols) compared to experimental results<sup>3,24,27</sup> in the supercooled region of water. Lines are spline fits of the simulation data.

The maximum in compressibility (coincident with the sudden drop in density) can be somewhat influenced by finite size effects. It can also be claimed that nuclear quantum effects are increasingly important as the temperature decreases. Recent investigations<sup>28</sup> show that this is certainly true for the heat capacity but it is not so clear for the density. In summary, the excellent agreement with experiment of the simulation results yielded by TIP4P/2005 for densities and compressibilities, especially in the region 1000-1500 bar, together with the calculations of the Widom line and the liquid-liquid critical point for the same model presented in our previous work,<sup>23</sup> strongly supports the existence of a critical point for real water in the supercooled region.

This work has been funded by grants FIS2010/16159 of the MEC and P2009/ESP-1691 of CAM, and 910570 of UCM.

<sup>a)</sup> Author to whom correspondence should be addressed. Electronic mail: abascal@quim.ucm.es.

<sup>1</sup> P. G. Debenedetti, *J. Phys. Condens. Matter* **15**, R1669 (2003).

<sup>2</sup> R. J. Speedy and C. A. Angell, *J. Chem. Phys.* **65**, 851 (1976).

<sup>3</sup> H. Kanno and C. A. Angell, *J. Chem. Phys.* **70**, 4008 (1979).

<sup>4</sup> O. Mishima, L. D. Calvert, and E. Whalley, *Nature (London)* **314**, 76 (1985).

<sup>5</sup> O. Mishima and H. E. Stanley, *Nature (London)* **396**, 329 (1998).

<sup>6</sup> P. H. Poole, F. Sciortino, U. Essmann, and H. E. Stanley, *Nature (London)* **360**, 324 (1992).

<sup>7</sup> F. H. Stillinger and A. Rahman, *J. Chem. Phys.* **60**, 1545 (1974).

<sup>8</sup> Y. Liu, A. Z. Panagiotopoulos, and P. G. Debenedetti, *J. Chem. Phys.* **131**, 104508 (2009).

<sup>9</sup> F. Sciortino, P. H. Poole, U. Essmann, and H. E. Stanley, *Phys. Rev. E* **55**, 727 (1997).

<sup>10</sup> L. M. Xu, P. Kumar, S. V. Buldyrev, S. H. Chen, P. H. Poole, F. Sciortino, and H. E. Stanley, *Proc. Nat. Acad. Sci. USA* **102**, 16558 (2005).

<sup>11</sup> P. Kumar, Z. Yan, L. Xu, M. G. Mazza, S. V. Buldyrev, S. H. Chen, S. Sastry, and H. E. Stanley, *Phys. Rev. Lett.* **97**, 177802 (2006).

<sup>12</sup> D. A. Fuentevilla and M. A. Anisimov, *Phys. Rev. Lett.* **97**, 195702 (2006).

<sup>13</sup> F. Mallamace, C. Corsaro, M. Broccio, C. Branca, N. Gonzalez-Segredo, J. Spooren, S. H. Chen, and H. E. Stanley, *Proc. Nat. Acad. Sci. USA* **105**, 12725 (2008).

<sup>14</sup> D. Liu, Y. Zhang, Y. Liu, J. Wu, C.-C. Chen, C.-Y. Mou, and S.-H. Chen, *J. Phys. Chem. B* **112**, 4309 (2008).

<sup>15</sup> F. Mallamace, C. Branca, M. Broccio, C. Corsaro, N. Gonzalez-Segredo, J. Spooren, H. E. Stanley, and S. H. Chen, *Eur. Phys. J. Spec. Top.* **161**, 19 (2008).

<sup>16</sup> D. Paschek, A. Rueppert, and A. Geiger, *ChemPhysChem* **9**, 2737 (2008).

<sup>17</sup> S. Harrington, P. H. Poole, F. Sciortino, and H. E. Stanley, *J. Chem. Phys.* **107**, 7443 (1997).

<sup>18</sup> D. Paschek, *Phys. Rev. Lett.* **94**, 217802 (2005).

<sup>19</sup> D. Corradini, M. Rovere, and P. Gallo, *J. Chem. Phys.* **132**, 134508 (2010).

<sup>20</sup> J. L. F. Abascal and C. Vega, *J. Chem. Phys.* **123**, 234505 (2005).

<sup>21</sup> C. Vega, J. L. F. Abascal, M. M. Conde, and J. L. Aragonés, *Faraday Discuss.* **141**, 251 (2009).

<sup>22</sup> H. L. Pi, J. L. Aragonés, C. Vega, E. G. Noya, J. L. F. Abascal, M. A. Gonzalez, and C. McBride, *Mol. Phys.* **107**, 365 (2009).

<sup>23</sup> J. L. F. Abascal and C. Vega, *J. Chem. Phys.* **133**, 234502 (2010).

<sup>24</sup> O. Mishima, *J. Chem. Phys.* **133**, 144503 (2010).

<sup>25</sup> D. E. Hare and C. M. Sorensen, *J. Chem. Phys.* **84**, 5085 (1986).

<sup>26</sup> D. E. Hare and C. M. Sorensen, *J. Chem. Phys.* **87**, 4840 (1987).

<sup>27</sup> A. Saul and W. Wagner, *J. Phys. Chem. Ref. Data* **18**, 1537 (1989).

<sup>28</sup> C. Vega, M. M. Conde, C. McBride, J. L. F. Abascal, E. G. Noya, R. Ramirez, and L. M. Sese, *J. Chem. Phys.* **132**, 046101 (2010).