Supplemental materials for "A comprehensive scenario of the thermodynamic anomalies of water using the TIP4P/2005 model"

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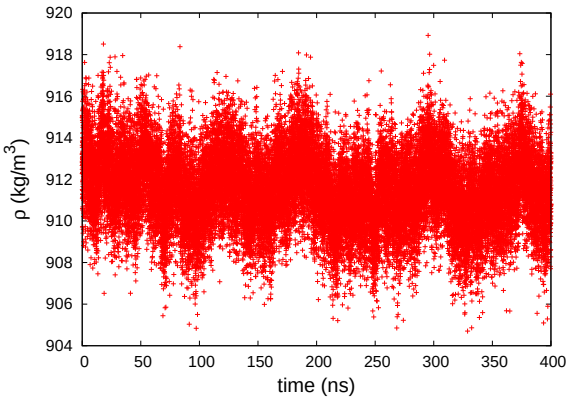
A. Calculation of the uncertainty

The uncertainty has been calculated using a method proposed by Hess[1]. The trajectory is divided in n_{block} blocks of length t_{block} and the average of the density for each block is calculated. The uncertainty of the total trajectory is then calculated as the standard deviation of the values of the n_{block} averages. Notice that these uncertainties are dependent of the number of blocks (or the block length). If t_{block} is very small, consecutive blocks are strongly correlated and the standard deviation does not represent the actual uncertainty of the total trajectory. As the block length increases, the correlation between blocks decreases so the uncertainty tends to an asymptotic value. However, for very large block length (or, more specifically, when n_{block} is low), the number of points to calculate the uncertainty is very reduced so the standard deviation shows a large statistical noise. In fact, well known statiscal considerations indicate that n_{block} should not be less than about 20.

FIG. 1: Densities along a 400 ns trajectory for the state point at T=200 K, p=-125 MPa.



The procedure of Ref. 1 incorporates an important additional element, namely the calculation of the correlation between block averages and its fit to a double exponential. In this way, the discrete nature of the correlation between blocks is smoothed by the fit and the calculated uncertainties (eventually) lead to an asymptotic curve (for long enough trajectories). In summary, the procedure of Hess not only provides a reasonable evaluation of the uncertainty but also sheds light on the convergence of the trajectory. An example of the application of the method is presented in Figs. 2 and 3.

FIG. 2: Uncertainties for the system of Fig. 1. Symbols are the standard deviations of the averages calculated in blocks of length t_{block}. The line is the standard deviation evaluated using a double exponential fit for the correlation between blocks.

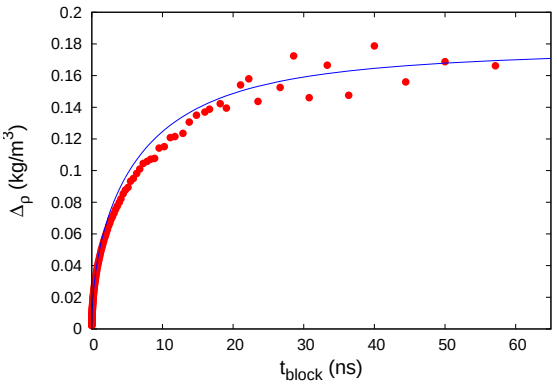
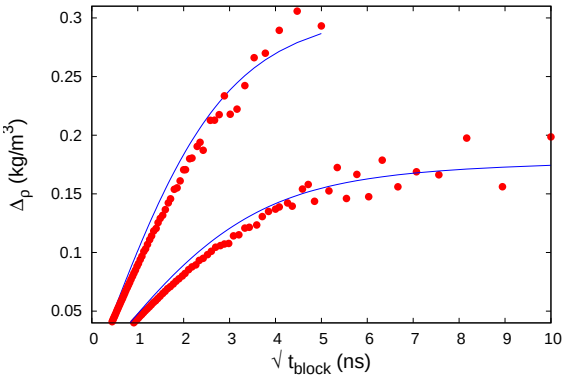


FIG. 3: Block analysis of the uncertainties for the system of Fig. 1 as a function of the square root of the block length. The data correspond to the results for the full 400 ns trajectory (bottom) and for the first 100 ns (top). Notice that the number of blocks corresponding to the larger block length is only 4 in both cases. The analysis clearly indicates that a 100 ns trajectory is not long enough to obtain convergence.



B. Numerical values for the density at selected isobars

Table I presents the numerical values of the simulation results for the density of the TIP4P/2005 model along the isobars shown in Fig. 1 of the main paper.

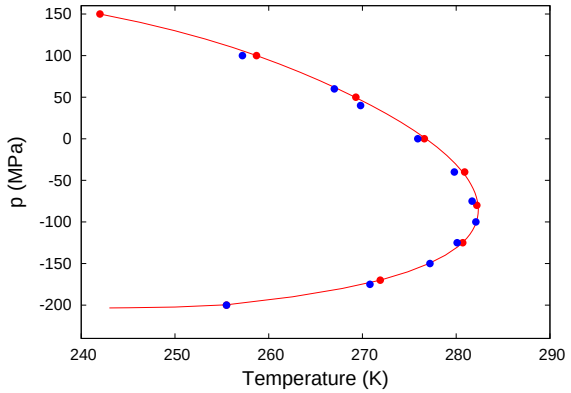
TABLE I: Densities of the TIP4P/2005 model along isobars

Temperature (K)	Pressure (MPa)	Density (kg/m^3)	Pressure (MPa)	Density (kg/m^3)	Pressure (MPa)	Density (kg/m^3)
195	0.1	939.3	-40	930.1	-80	922.9
200	0.1	938.4	-40	929.0	-80	921.7
205	0.1	939.6	-40	930.4	-80	920.7
210	0.1	945.4	-40	932.0	-80	921.9
220	0.1	957.5	-40	939.5	-80	925.7
230	0.1	972.85	-40	950.1	-80	932.0
240	0.1	984.77	-40	961.1	-80	940.35
247	0.1	990.68	-40	967.4	-80	-
260	0.1	997.24	-40	975.58	-80	953.99
270	0.1	999.38	-40	978.63	-80	957.48
280	0.1	999.66	-40	979.71	-80	958.89
290	0.1	998.48	-40	979.04	-80	958.39
300	0.1	996.19	-40	977.06	-80	956.43
310	0.1	992.95	-40	973.83	-80	953.13
320	0.1	988.77	-40	969.64	-80	948.62
340	0.1	978.36	-40	958.71	-80	-
360	0.1	965.52	-40	944.84	-80	921.07

C. Finite size effects on the TMD

Fig. 4 shows a comparison of the TMD line calculated using 500 (data taken from Ref. 2) and 4000 (this work) water molecules. The differences are quite small but systematic. Since the calculations were obtained using slightly different simulation parameters and also different version of GROMACS, it is very difficult to know whether the small departures are a consequence of the differences in the system size or in the simulation details.

FIG. 4: Locus of the maximum density temperatures for systems made of 500 (blue) and 4000 water molecules (red).



[1] B. Hess, J. Chem. Phys. **116**, 209 (2002).

[2] G. Pallares, M. A. Gonzalez, J. L. F. Abascal, C. Valeriani, and F. Caupin, Phys. Chem. Chem. Phys. **18**, 5896 (2016).