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Published Version Information

Citation: Chen, F., & Smith, P.E. (2007). Simulated surface tensions of common water models. *The journal of chemical physics*, 126(22), 3.

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Digital Object Identifier (DOI): doi: 10.1063/1.2745718

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Simulated surface tensions of common water models

Feng Chen and Paul E. Smith^{a)}

Department of Chemistry, Kansas State University, 111 Willard Hall, Manhattan, Kansas 66506-3701

(Received 27 March 2007; accepted 8 May 2007; published online 12 June 2007)

Initial simulated values of the surface tension for the SPC/E water model have indicated excellent agreement with experiment. More recently, differing values have been obtained which are significantly lower than previous estimates. Here, we attempt to explain the differences between the previous studies and show that a variety of simulation conditions can affect the final surface tension values. Consistent values for the surface tensions of six common fixed charge water models (TIP3P, SPC, SPC/E, TIP4P, TIP5P, and TIP6P) are then determined for four temperatures between 275 and 350 K. The SPC/E and TIP6P models provide the best agreement with experiment. © 2007 American Institute of Physics. [DOI: 10.1063/1.2745718]

Surface tension is an important property of water which has significant implications for the behavior of water at a variety of interfaces. The ability of computer simulations to reproduce this interfacial water behavior depends on the quality of the water model. Hence, several studies have been performed to determine the surface tension of different water models. Initially, the simulated surface tension values varied quite widely,¹⁻⁴ presumably due to the different accuracies of the various water models and the slow convergence properties of the computed surface tension.⁵ More recently, consistent values of the surface tension of the SPC/E water model⁶ have appeared which indicate excellent agreement with experiment.⁷⁻⁹ This is somewhat surprising as most water models are developed to reproduce bulk water properties and one would therefore expect some errors for interfacial systems. Here, we present evidence that several of the previous simulated values of the surface tension of SPC/E water have overestimated, for a variety of reasons, the true value by a significant degree (15%).

Three studies of the surface tension of SPC/E water have been presented that appear to be in good agreement with both the experimental data and each other. Alejandre *et al.*, Shi *et al.*, and Lu and Wei determined values of 66 mN/m (328 K),⁷ 72 mN/m (302 K),⁸ and 70 mN/m (300 K),⁹ which compare well to the experimental values of 67.1, 71.3, and 71.6 mN/m,¹⁰ respectively. Several of the studies also emphasized the need to include long range dispersion interactions in determining the pressure tensor and to include additional k vectors in the reciprocal space calculation for rectangular systems.^{7,8} More recently, lower values have been observed by Wemhoff and Carey,¹¹ although a reason for the disagreement with earlier values was not provided. In addition, Ismail *et al.* have quoted a significantly lower value of 55.4 mN/m for SPC/E water at 300 K.⁵ Our own studies using the SPC/E water model have also consistently underestimated the surface tension in comparison to both the experimental data and previous studies. Hence, our aim here is to explain the reasons for some of the different values ap-

pearing in the literature, and thereby determine a consistent value for the surface tension of the SPC/E water model. Having obtained consistent values for the surface tension of SPC/E water at 300 K, we then determined the surface tensions of six common fixed charge water models (TIP3P,¹² SPC,¹³ SPC/E,⁶ TIP4P,¹² TIP5P,¹⁴ and TIP6P¹⁵) at four different temperatures of 275, 300, 325, and 350 K. The surface tensions of the SPC, TIP5P, and TIP6P models have not been determined previously as a function of temperature, while the results for the SPC/E model are found to be different from current literature values.

The overall simulation approach is outlined in detail elsewhere.^{7,16} All simulations were performed with the GRO-MACS program v3.2.1 in single precision.^{17,18} The system involved a slab of 512 water molecules in a constant volume box of $1.97 \times 1.97 \times 10.0$ nm³ coupled to a temperature bath using a Berendsen thermostat.¹⁹ Each system was equilibrated for 1 ns and then simulated for an additional 3–5 ns during which the initial surface tension values (γ_o) were determined from the diagonal elements of the pressure tensor according to the relationship, $\gamma_o = \frac{1}{2}L_z[P_{zz} - \frac{1}{2}(P_{xx} + P_{yy})]$, where L_z is the box length in the z direction and $P_{\alpha\alpha}$ is the $\alpha\alpha$ component of the pressure tensor.¹⁶ Electrostatic energies were determined using the particle mesh Ewald (PME) approach²⁰ with a convergence parameter of 3.1 nm^{-1} , a real space LJ and Coulomb cutoff of 0.98 nm, a grid resolution of 0.12 nm, and tin-foil boundary conditions.²¹ The time step was 2 fs and SETTLE was used to constrain the water geometry.²² The long range dispersion correction (γ_d) was included in the calculated values,²³ giving a final surface tension of $\gamma = \gamma_o + \gamma_d$. The dispersion correction term varied slightly between water models. The average correction was $\gamma_d = 4.4$ mN/m and displayed a small decrease with increasing T .

Before determining the surface tensions of the different models as a function of temperature, it is necessary to investigate the effects of various numerical approximations made during the current and previous simulations. To do so we will focus on the SPC/E model at 300 K and quote all surface tension values before the long range dispersion correction (γ_o) and after at least 5 ns of simulation time. The PME

^{a)} Author to whom correspondence should be addressed. Tel.: 785-532-5109; Fax: 785-532-6666; Electronic mail: pesmith@ksu.edu

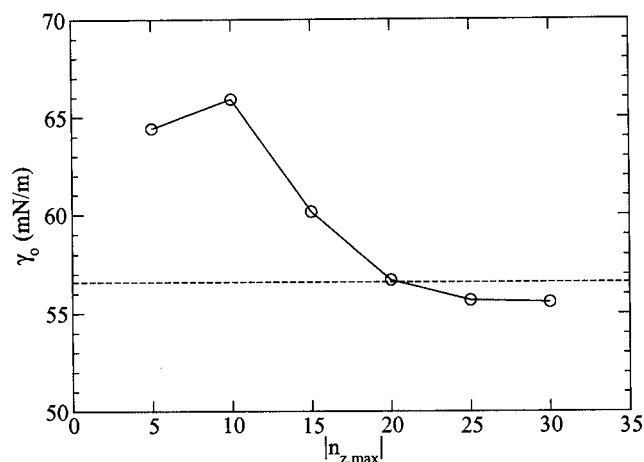


FIG. 1. The simulated surface tension (γ_0) for SPC/E water at 300 K as a function of the maximum number of lattice vectors in the z direction. The dashed line is the PME result of 56.7 mN/m. The data refer to a system of 512 water molecules in a box $1.97 \times 1.97 \times 10.0 \text{ nm}^3$ using $|n_{x,\max}| = |n_{y,\max}| = 5$ and no long range dispersion correction. The real space contribution (electrostatic plus Lennard-Jones) is 52.3 mN/m.

result for γ_0 is 56.7 mN/m. Estimated standard deviations for the current simulations were 1–2 mN/m, but fluctuations as large as 8 mN/m were observed between 1 ns subaverages. The same results were obtained for the SPC/E model using the double precision version of GROMACS.

Alejandre *et al.* provided a thorough analysis of surface tension calculations from computer simulations using Ewald sums and emphasized the need to include additional lattice vectors in the reciprocal space sum to account for the increased box dimensions in the extended (formally nonperiodic) z direction.⁷ In particular, it is important to maintain a fixed ratio of the maximum number of lattice vectors to box length ($|n_{\alpha,\max}|/L_{\alpha}$) in all three directions, especially at high temperatures. However, the systems simulated here have used the PME approach. This solves the reciprocal space sum using three-dimensional (3D) fast Fourier transform routines and interpolation using a 3D grid. Our calculations were insensitive to the grid resolution (between 0.08 and 0.16 nm) as long as the same grid resolution was maintained in each direction.

In an effort to establish a consistent surface tension for SPC/E water, we have reinvestigated the effect of using different numbers of lattice vectors (n_x, n_y, n_z) for the reciprocal space sum by determining the molecular virial, with the electrostatic contribution given by Eq. (A10) from Ref. 7, using 50 000 configurations spanning 5 ns obtained from the PME based simulations. In all calculations $|n_{x,\max}| = |n_{y,\max}| = 5$, while $|n_{z,\max}|$ was varied from 5 to 30. This is the same approach as presented by Alejandre *et al.*,⁷ but performed at a different temperature and expanded to include averaging over multiple configurations. We note that the effect of increasing the number of lattice vectors had a negligible effect on the system energy. The resulting surface tensions are displayed in Fig. 1. It is clear from Fig. 1 that one requires values of $|n_{z,\max}| \geq 25$ in order to obtain reliable surface tension values even at 300 K. Furthermore, the limiting value now agrees with the atomic virial based PME results from the GROMACS program within the statistical error. The differ-

ence in values can be traced to the contribution of P_{zz} which decreased as the number of lattice vectors in the z direction was increased. Unfortunately, although Alejandre *et al.* recognized this issue and increased the number of lattice vectors in the z direction accordingly,⁷ they only included a relatively limited number of additional lattice vectors ($|n_{z,\max}| = 10$) in their calculations at low temperatures. The effect of using a limited number of lattice vectors is to overestimate the surface tension. This issue has also been raised by Ismail *et al.* using an argument based on the mesh size used in the particle-particle particle-mesh (PPPM) approach.⁵ The recent study of Wemhoff and Carey maintained the appropriate ratio of lattice vectors.¹¹ They observed lower values of the surface tension for SPC/E water, which is in agreement with the present study.

A second approximation which can affect the simulated surface tension values involves the use of the PPPM method²⁴ for determining the electrostatic interactions during the simulation, followed by the use of the Ewald based virial expression to obtain the electrostatic contribution to the components of the pressure tensor.⁸ This approach is often adopted as the calculation of the pressure using PPPM electrostatics is nontrivial and computationally inefficient.²⁵ We performed an equivalent simulation with the PPPM approach using a $40 \times 40 \times 200$ mesh. Analysis of the resulting trajectory using the Ewald virial equation provided a surface tension of 65.3 mN/m. This is significantly higher than the PME based result of 56.7 mN/m. Hence, either the PME or PPPM methods produce different results, and/or one has to be consistent when determining the pressure tensor. Evidence for the former comes from the fact that the bulk liquid densities obtained from the two simulations are somewhat different. We find a liquid phase density of 0.987 g/cm^3 for the PME approach compared to a value of 1.017 g/cm^3 for PPPM. Evidence for the latter can be found in the recent study of Ismail *et al.* where their PPPM results for several water models (TIP3P, TIP4P) are in good agreement with our PME results (see below).⁵

In many simulations it is common to use SHAKE²⁶ to constrain the water molecule geometry. However, the SHAKE algorithm involves an iterative procedure to satisfy the constraint equations to within a predetermined tolerance. Our simulations used SETTLE,²² an analytical version of SHAKE developed for simple water models, which solves the constraint equations exactly. Simulations performed using SHAKE and a relative tolerance of either 10^{-4} or 10^{-5} resulted in surface tensions of 61 and 59 mN/m, respectively, after 5 ns of simulation. Only after a further 5 ns of simulation did the average surface tension decrease to a result consistent with the value obtained using SETTLE. Hence, to obtain precise values using SHAKE it appears that one requires significantly longer simulations than have been used previously. This probably reflects the large contribution of the constraint forces to the virial, which can only be approximated by the usual implementation of SHAKE, and therefore provides an additional source of noise. The same conclusion was obtained after analysis of the corresponding trajectory using the molecular based virial.

The use of 3D Ewald sums for slab geometries has been investigated by several authors and found to incorrectly reproduce the characteristics of the nonperiodic dimension even when using a relatively large vacuum region.²⁷ A simple correction for this problem has been suggested by Yeh and Berkowitz,²⁷ and involves the addition of a potential energy term proportional to the square of the dipole moment in the z direction (M_z). To our knowledge, the effect of this correction on the surface tension values of water models has not been studied. While the average value of M_z^2 will be zero for our system, fluctuations between the instantaneous dipole moments could lead to changes in the surface tension. A simulation performed using the above correction results in an initial surface tension of 56.3 mN/m. This suggests that the error arising from the use of a 3D Ewald summation with tinfoil boundary conditions for slab geometries does not significantly affect the simulated surface tension values of pure water.

In summary, conflicting values of the surface tension of SPC/E water have been observed most of which can be traced to a variety of numerical issues. Previous studies have either used too few lattice vectors in the z direction,^{7,9} or combined the PPPM and PME methodologies,⁸ or used SHAKE with a relatively short simulation time.^{7-9,11} Consequently, our final value of 61.3 mN/m for the total surface tension of the SPC/E model at 300 K is lower than most previous estimates.⁷⁻⁹ It is, however, still higher than the value of 55.4 mN/m recently determined by Ismail *et al.* using the PPPM approach.⁵ Interestingly, their corresponding values for the TIP3P and TIP4P models are in excellent agreement with the results obtained here (see below). It is currently unclear why the data differ for just the SPC/E model. Our new value for the SPC/E model at 300 K is also in good agreement with a recently quoted value of 62 mN/m.²⁸ Finally, we also examined the possibility of system size effects by simulating a larger system containing 4340 waters in a box with dimensions of $4 \times 4 \times 12$ nm³. The value for the surface tension was 62.1 mN/m and in very good agreement with the smaller system size result. Therefore, system size effects seem to be negligible.⁷

In the present study consistent surface tension values were obtained for the PME based electrostatic energy, the SETTLE algorithm for constraints, and long 2–5 ns simulations. Using this approach the calculated surface tensions of six different water models at four different temperatures were determined and are presented in Table I. The SPC/E and TIP6P models provide the best agreement with experiment at all temperatures. In addition, it is satisfying that our surface tension value for TIP4P at 300 K is in agreement with the limiting value obtained by Zakharov *et al.* for water droplets,²⁹ which was determined using rigid water molecules and the standard Coulomb potential with no truncation or periodicity effects. The revised value of the surface tension of SPC/E water, while displaying the best agreement with experiment of the simple water models, still underestimates the experimental values by 15%. In our opinion, this is to be expected as the SPC/E model was (i) developed for bulk water properties,⁶ (ii) is nonpolarizable,³⁰ and (iii) overestimates the diffusion constant of water thereby suggesting

TABLE I. Simulated surface tensions (γ in mN/m) of various water models as a function of temperature. Experimental data were taken from Ref. 10 and can be represented by the equation $\gamma(T) = 94.74 + 1.87 \times 10^{-3}T - 2.63 \times 10^{-4}T^2$ between 273 and 373 K. Typical estimated errors in the simulated values were 1–2 mN/m.

Model	275 K	300 K	325 K	350 K
TIP3P	54.0	49.5	44.5	41.7
SPC	59.7	53.4	49.0	45.5
SPC/E	64.5	61.3	58.0	52.7
TIP4P	61.0	54.7	50.8	46.7
TIP5P	57.1	52.3	46.1	42.4
TIP6P	64.8	61.8	55.4	52.8
Expt.	75.4	71.6	67.6	63.2

insufficient hydrogen bonding even in bulk solution.³¹ Nevertheless, these computationally efficient water models are consistently used in simulations of interfacial systems, and it is therefore important to know the appropriate surface tension values.

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