

Correction to

“Molecular Modeling and Simulation of
Vapor-Liquid Equilibria of Ethylene Oxide,
Ethylene Glycol, and Water as Well as their
Binary Mixtures”

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Original manuscript:

Yow-Lin Huang, Thorsten Merker, Manfred Heilig, Hans Hasse, and Jadran Vrabec:

“Molecular Modeling and Simulation of Vapor-Liquid Equilibria of Ethylene Oxide, Ethylene
Glycol, and Water as Well as their Binary Mixtures”

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While preparing a recently published article by some of the authors of this correction,¹ we noticed that the parameters of the water model presented in the original paper by Huang et al.² were misprinted. Those misprints were carried over to a paper by Köster et al.³ The misprinted parameters are the two lengths in the water model: the OH bond length, denoted as h_1 , and the distance between the negative point charge and the center of mass, denoted as h_2 . First, the two values were interchanged, i.e. the value that should have been given for h_1 was given as h_2 , and vice versa. Second, the numeric value of the parameter h_1 was misprinted. It is important to note that the simulations in both the works of Huang et al.² and Köster et al.³ were carried out with the correct parameters, i.e. *not* the ones given in the tables in Refs.^{2,3}

A correction of the parameters for the water model is provided in Table 1.

Table 1: Correct model parameters for the water model by Huang et al.²

$h_1/\text{Å}$	$h_2/\text{Å}$	α/deg	$\sigma_{\text{O}}/\text{Å}$	$(\varepsilon_{\text{O}}/k_{\text{B}})/\text{K}$	q_{O}/e	q_{H}/e
1.1549	0.20482	104.52	3.11831	208.080	-0.83910	+0.41955

Moreover, we realized that the vapor-liquid equilibrium (VLE) data for water given by Huang et al.² are inaccurate, most likely due to insufficient sampling. This issue was already addressed briefly in the aforementioned recent paper by some of the authors of this correction.¹ To investigate this further, we computed more VLE data for the water model of Huang et al. with the Grand Equilibrium method⁴ with the molecular simulation program *ms2*.⁵ First, the chemical potential of the liquid was sampled in a Monte Carlo (MC) simulation in the NpT ensemble with 1372 particles and a cutoff radius of 15 Å. The system was equilibrated for 25,000 MC loops in the NVT ensemble and 50,000 MC loops in the NpT ensemble before the production run. Two methods were used for the determination of the chemical potential of the liquid: Widom’s test particle insertion and thermodynamic integration (TI). The former method only yields reliable results for temperatures higher than about 400 K, where the liquid density is not too high. For the simulations using Widom’s test particle in-

servation, the production runs lasted 500,000 MC loops, and 4,000 test particles were inserted every MC loop. For the simulations using thermodynamic integration, the production runs lasted 1,600,000 MC loops. For both sets of results for the liquid phase, simulations of the vapor phase were then carried out in the pseudo- μVT ensemble, aiming at an average of 500 particles and using a cutoff radius of 20 Å. The system was equilibrated for 10,000 MC loops in the NVT ensemble and 25,000 MC loops in the pseudo- μVT ensemble before sampling for 200,000 MC loops in the pseudo- μVT ensemble. In all simulations, long-range electrostatics were treated by the reaction field method and the usual LJ tail corrections were applied.

A comparison of the VLE results by Huang et al.,² by Kulkarni et al.,¹ and those of the present work is shown in Figures 1 to 4. There, the simulation results (sim) are shown as relative deviations from the IAPWS-95 equation of state (EOS) for water^{6,7}

$$\delta z = \frac{z^{\text{sim}} - z^{\text{EOS}}}{z^{\text{EOS}}}, \quad (1)$$

where z is either of the VLE properties (vapor pressure, saturated vapor density, saturated liquid density, or enthalpy of vaporization). Figures 1 to 4 confirm the accuracy of the data of Kulkarni et al.,¹ which should be favored over those given in the original paper by Huang et al.²

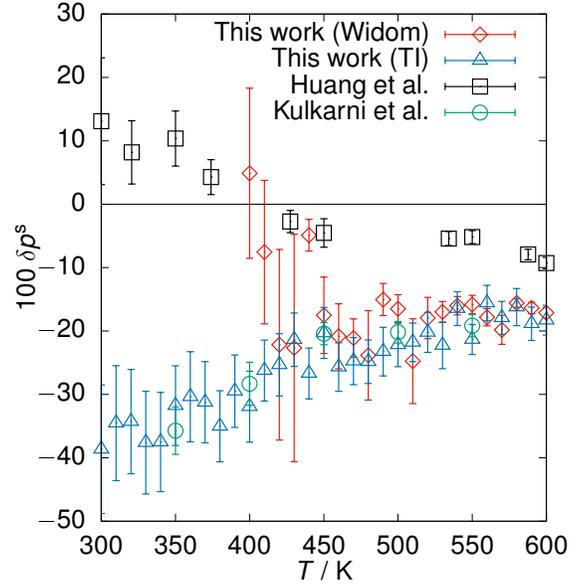


Figure 1: Comparison of different sets of simulation data for the vapor pressure of the Huang et al. water model. Error bars indicate the statistical uncertainties of the simulation results.

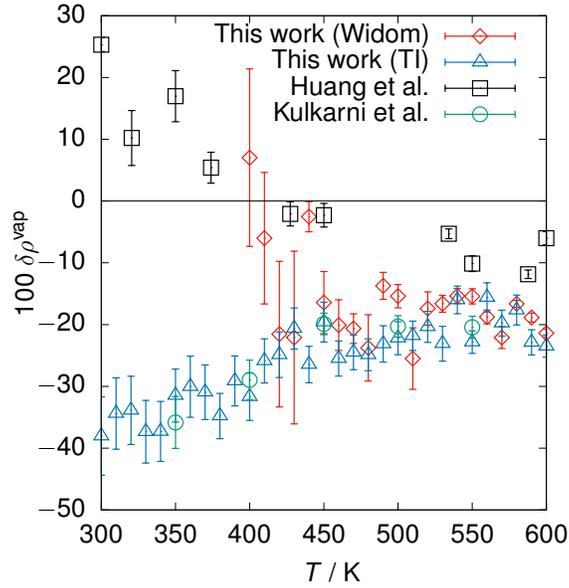


Figure 2: Comparison of different sets of simulation data for the saturated vapor density of the Huang et al. water model. Error bars indicate the statistical uncertainties of the simulation results.

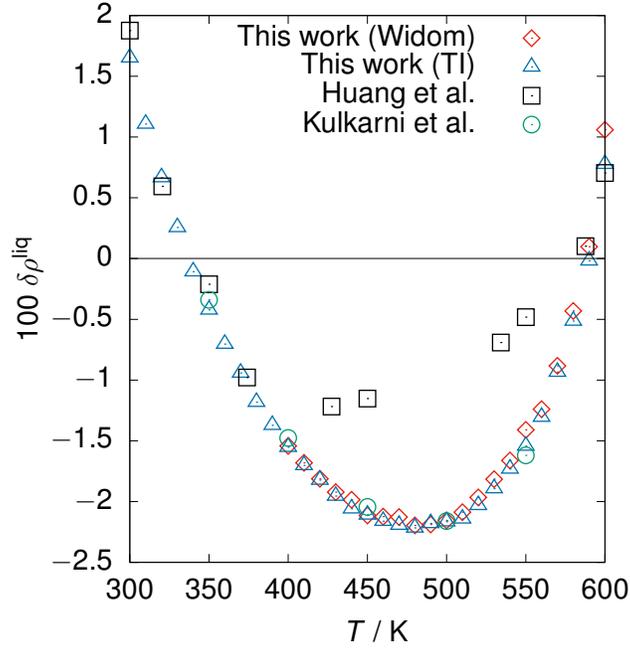


Figure 3: Comparison of different sets of simulation data for saturated liquid density of the Huang et al. water model. Statistical uncertainties are within symbol size.

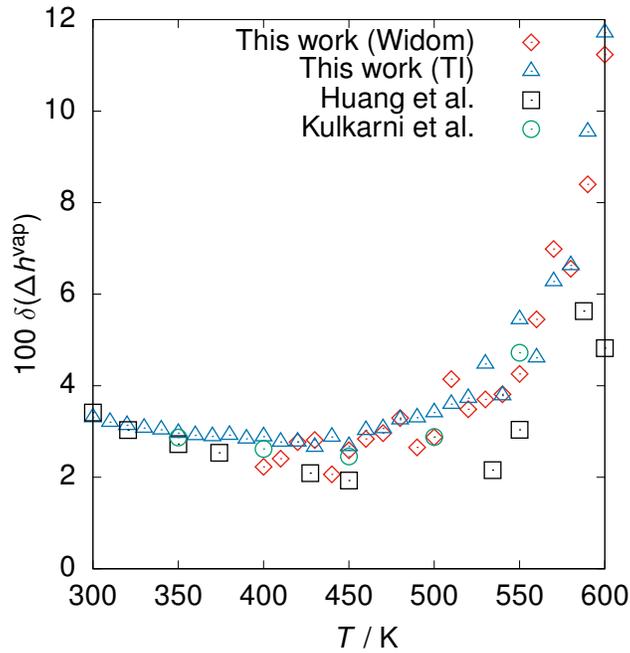


Figure 4: Comparison of different sets of simulation data for enthalpy of vaporization of the Huang et al. water model. Statistical uncertainties are within symbol size.

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