To the Editor:

This letter corrects an error in an article by Shi and Maginn[1] where it was reported that an ammonia force field proposed by Eckl and coworkers[3] does not match experimental data to a high degree. Shi and Maginn used a fully flexible model for ammonia, while Eckl and coworkers used a rigid model. Moreover, the Lennard-Jones potential truncation scheme used by Shi and Maginn differed from that used by Eckl and coworkers. We show here that these differences can have a surprisingly large effect on the computed vapor–liquid equilibria and account for the differences between the simulated and experimental coexistence properties originally described by Shi and Maginn. When the calculations were repeated using exactly the same simulation parameters Eckl and coworkers used, the agreement between our simulations, the published simulation results of Eckl and coworkers and experimental vapor–liquid coexistence data was excellent.

In a recent article by Shi and Maginn[1], we conducted a molecular simulation study of ammonia absorption in the ionic liquid 1-ethyl-3-methylimidazolium bis(triuoromethylsulfonyl)imide. Ammonia was modeled using a force field developed by Gao, Xia and George,[2] which we refer to as the GXG model. After the work was completed, we became aware of an ammonia force field developed by Eckl, Vrabec and Hasse,[3] referred to here as the EVH model. The EVH model was shown by these authors to give much better agreement with experimental vapor–liquid equilibrium data than the GXG model. We performed a cursory test of the EVH model by carrying out a single state point vapor–liquid equilibrium simulation at 347.5 K using the EVH model, and reported that "the difference between the simulated and experimental coexistence liquid and vapor densities was 4.9%, and 39%, while the difference between the simulated and experimental vapor pressure was 32%. Thus, we do not find that the Eckl model is significantly better than the Gao model, so for this reason we only focused on the Gao model".

At the time we were unclear as to why our results would differ from experiment by so much when the results reported in the article by Eckl et al. showed excellent agreement with the experiment. We speculated that it could be due to differences in the way in which electrostatic interactions were treated. In particular, a reaction field method was used to treat electrostatics in the work of Eckl et al., while our calculations utilized a standard Ewald sum procedure.

We were recently contacted by Prof. Vrabec who showed us results of vapor–liquid coexistence calculations performed using the EVH model with a number of different software packages that utilize the Ewald method. The results were virtually indistinguishable from their original simulation results, and disagreed with the results reported by Shi and Maginn.[1] We, therefore, concluded that the difference could not be due to the methods for treating electrostatics. We subsequently carried out a detailed investigation of the possible source of the discrepancy. This letter reports our findings.

After confirming the exact set of simulation parameters that were used in developing the EVH model, including the Lennard-Jones cutoff distance and the method for treating long-range corrections, Gibbs ensemble simulations were carried out using our locally developed code (Cassandra) and a widely-used open source code (Towhee).[4] In these calculations, 500 ammonia molecules were simulated in the *NVT* Gibbs ensemble with roughly equal sized vapor and liquid boxes having edge lengths of 30 Å. A total of 50,000 cycles were used, with one cycle equal to 500 Monte Carlo moves. The suite of Monte Carlo moves consisted of 29.5% translations, 60% rotations, 0.5% volume moves, and 10% particle box swaps. The Ewald summation technique was also used for electrostatic interactions, with αL equal to 5.6 and K_{max} set to 5.0. A Lennard-Jones cutoff of 10 Å and real space electrostatic cutoff of half the box length was used. Standard tail corrections were used beyond the Lennard-Jones cutoff. We will refer to this set of simulations as the "base case".

Table 1 shows the results of four independent Gibbs ensemble simulations at 347.5 K. The second and third rows of Table 1 show that the equilibrium properties calculated with Cassandra are statistically equivalent to those obtained with Towhee for the base case. This suggests that the two codes give equivalent results, and since it is generally accepted that Towhee gives correct results, we assume that Cassandra does as well. (Note that we have benchmarked Cassandra against Towhee and other Monte Carlo codes for other systems, so we do not believe there are errors in the code itself). Since the Cassandra calculations agree with those of Towhee, only Cassandra was used in subsequent calculations. Table 1 also shows that the simulations are within 1% of the experimental values[5] (found in row 1). Note that simulation values in each row correspond to the average of four independent simulations with the uncertainty taken as the standard deviation. This suggests that at this state point and with this set of simulation parameters, the EVH model does in fact reproduce experimental data well, in contrast to the claims made by Shi and Maginn.[1]

Having established that there are no errors in the software and that the EVH model does in fact yield good results when compared to experiment, we investigated the possible sources of the difference observed by Shi and Maginn. We have learned that in addition to the Ewald/reaction field difference, there are two other differences in the way in which the original EVH calculations were performed and those of Shi and Maginn: (1) The EVH model utilizes a completely rigid ammonia model while Shi and Maginn used a fully flexible potential, with harmonic stretching and bending parameters taken from *ab initio* calculations; and (2) the EVH model was developed using a cutoff with long-range corrections for the Lennard-Jones potential, while Shi and Maginn used a "CHARMM-like" switching function to truncate the Lennard-Jones potential. These two factors were tested to see if they could be the source of the differences, as described as follows.

We performed simulations with flexible bond angles using the same angle bending parameter as the study of Shi and Maginn with the results displayed in row 4 and listed as "flexible angle". The suite of Monte Carlo moves consisted of 19.5% translations, 50% rotations, 20% internal reorientation, 0.5% volume moves, and 10% particle box swaps. The cutoffs and Ewald parameters are the same as in the base case. The results demonstrate that a flexible bond angle has a statistically significant effect of the bulk coexistence properties of this model, presumably because the conformations in the liquid and vapor phases differ from those of the rigid model, thereby altering slightly the intermolecular interactions. Specifically, a flexible bond angle results in an increase in the liquid density by 6.4%, a decrease in the vapor density by 24.1%, and a decrease in the vapor pressure by 17.2%. These differences are of the same order of magnitude as those found by Shi and Maginn, and suggest that model flexibility has a surprisingly large effect on coexistence properties. This finding that angle flexibility affects coexistence properties is consistent with a recent study by Engin and coworkers.[6]

Next, we performed simulations using a cut potential with a CHARMM-like switching function of the following form-

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Table 1. Equilibrium Coexistence Data for Ammonia

	ρ_l	ρ_v	p_{sat}
Experiment	30.42	1.73	3.66
Cassandra – base case	30.34 (4)	1.74 (4)	3.69 (12)
Towhee – base case	30.33 (4)	1.76 (2)	3.71 (3)
Flexible angle	32.29 (16)	1.32 (11)	3.03 (19)
Cut switch	29.26 (19)	2.13 (12)	4.34 (21)
Rcut 10 Å	32.68 (29)	1.07 (9)	2.45 (15)

ρ_l, ρ_v, p_{sat} Correspond to Liquid and Vapor Density in (mol/L) and Saturated Vapor Pressure in (MPa). Uncertainties in the last digit(s) are given in parenthesis.

$$V_{switch,LJ}(r_{ij}) = \begin{cases} V_{LJ}(r_{ij}) & r_{ij} < r_{on} \\ V_{LJ}(r_{ij}) \times \frac{(r_{on}^2 - r^2)^2 (r_{off}^2 + 2r^2 - 3r_{on}^2)}{(r_{off}^2 - r_{on}^2)^3} & r_{on} \le r_{ij} \le r_{off} \\ 0 & r_{ij} > r_{off} \end{cases} \qquad (1)$$

where r_{on} and r_{off} serve as the range for which the Lennard-Jones interaction is smoothly forced to zero. This switching function was used by Shi and Maginn, and is used widely in molecular dynamics simulations to avoid a discontinuity in the force calculation. Since the potential goes smoothly to zero, *no additional long-range corrections were added to the potential* by Shi and Maginn, although some authors do add an additional correction when using such a truncation scheme. Row 5 of Table 1 labeled "cut switch" corresponds to simulations using the above potential with r_{on} and r_{off} set to 10 and 11 Å, respectively. These are the same parameters used in the study of Shi and Maginn. Coexistence properties are found to shift significantly with this truncation procedure, with differences of 3.8 and 23% for the liquid and vapor densities, respectively, and 19% for the vapor pressure as compared to experiment. Once again, these differences are of the same order of magnitude as those originally reported by Shi and Maginn.

These results indicate that both model flexibility and the type of potential truncation scheme used can have a large effect on computed coexistence properties. We conclude that it was the failure to use exactly the same model parameters as Eckl et al. that resulted in the reported differences between the computed coexistence properties and experimental values. If a rigid model along with the same cutoff method is used (as in the base case simulations), our results are consistent with those of Eckl et al. Thus, our original statement that the EVH model is not demonstrably superior to the GXG model is incorrect.

While carrying out this study, we also examined the effect the choice of the real-space cutoff of the electrostatic potential energy has on coexistence properties. Row 6 of Table 1 labeled "rcut 10 Å" displays coexistence values calculated using an electrostatic cutoff equal to the Lennard-Jones cutoff of 10 Å. The Ewald sum parameters used were αL 5.6 and K_{max} 5.0. It is clear that the use of a shorter distance real space electrostatic cutoff increases the liquid coexistence density by 7.7%, decreases the vapor coexistence density by 39%, and reduces the vapor pressure by 34% relative to the base case. While this is not the reason for the discrepancy between the work of Shi and Maginn and Eckl et al., since an electrostatic cutoff of half the box length was used in the former case, the results show that it is important to use a sufficiently long real space cutoff for electrostatics.

In summary, the statement in the original article by Shi and Maginn[1] that the EVH ammonia model is no better at modeling vapor–liquid coexistence behavior than the GXG model is incorrect. This error occurred due to the use of a different Lennard-Jones cutoff procedure than that which was used when developing the EVH model as well as the use of a flexible model for ammonia rather than a rigid model. The results presented here show that these simulation details, often thought of as being minor, can have a profound impact on computed phase behavior. These results are perhaps not too surprising, but point out how essential it is to clearly state all the details of a simulation and to carefully follow these procedures if one is attempting to reproduce a set of data.

Acknowledgments

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