# Pairwise Alternatives to Ewald Summation for Calculating Long-Range Electrostatics in Ionic Liquids

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ⓢ *Supporting Information*

ABSTRACT: Room temperature ionic liquid calculations require extensive sampling due to the large degree of localized structuring in the liquid phase relative to conventional solutions. Consequently, a large amount of computer time is required for the convergence of solvent properties, much of which is spent evaluating long-range electrostatics via Ewald summations. The damped Coulomb potential and cutoff-neutralized method of Wolf et al. (*J. Chem. Phys.* **1999**, *110*, 8254) provides the framework for an accurate, linear-scaling alternative to Ewald in the ionic liquid simulations. The method has been the subject of multiple modifications for improved accuracy, including the damped Coulombic potential of Zahn et al. (*J. Phys. Chem. B* **2002**, *106*, 10725), the damped shifted force method of Fennell and Gezelter (*J. Chem. Phys.* **2006**, *124*, 234104), and the shifted force gradient of Kale and Herzfeld (*J. Chem. Theory Comput.* **2011**, *7*, 3620). These pairwise electrostatic interaction alternatives along with the CHARMM shifted force potential and a new method proposed herein, the shifted force third derivative (SF3), have been examined on 59 unique ionic liquid combinations of 1-alkyl-3-methylimidazolium [RMIM] (R = M (methyl), E (ethyl), B (butyl), H (hexyl), and O (octyl)) and N-alkylpyridinium [RPyr] cations, along with Cl^-, PF_6^-, BF_4^-, NO_3^-, $AlCl_4^-$, $Al_2Cl_7^-$, and TfO^- anions. Monte Carlo simulations utilizing our custom OPLS-AA ionic liquid force field and employing the pairwise alternatives with multiple cutoff distances and electrostatic damping values are compared to the energetics from full Ewald sums.
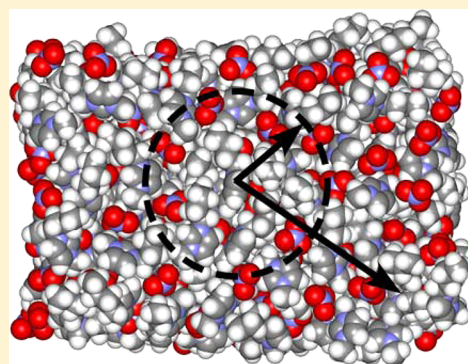
INTRODUCTION

The computational cost of Monte Carlo (MC) and molecular dynamics (MD) methods can present a major obstacle for exhaustive simulations containing thousands or millions of atoms. Periodic boundary conditions minimize the number of atoms required to simulate a bulk environment but also introduce the challenge of evaluating potentials beyond the minimum-image convention. A simple spherical cutoff that only computes nonbonded interactions within a specified distance can improve the efficiency. However, the potential for error is particularly large in the electrostatics portion, as the charge potentials generally decay to zero more slowly with increasing distance than the Lennard-Jones function.[1]

Ewald (or lattice) summation techniques can provide an accurate electrostatic treatment by using a cutoff distance for the quickly decaying short-ranged real-space summation and by performing a second long-ranged reciprocal-space summation.[2,3] As the number of particles, N, increase, a simple Ewald implementation can increase the simulation effort as $O(N^2)$. Optimization of the reciprocal-space summation with Fourier-based approaches, e.g., particle–particle particle-mesh (P3M)[4] and particle-mesh Ewald (PME),[5] has enabled the Ewald sums to scale as low as $O(N \log(N))$.[3,5,6]

Alternatively, truncation artifacts could be reduced by the use of a *shifted potential* scheme that provides a continuous shifting of the potential at all distances such that the value of the potential (or the value and first derivative for a *shifted force potential*) becomes zero at the cutoff distance.[7] For example, the CHARMM program[8] implements an efficient shifted force potential (eq 1),[9] where R_C is the cutoff distance, r_{ij} is the distance between particles, and q_i and q_j are the fixed atomic charges. Recent protein folding MD simulations over long time scales, e.g., up to 125 μs, have shown the CHARMM-SF method to be reasonably effective at treating long-range electrostatics interactions at cutoffs greater than 9 Å.[10]

$$V_{CHARM}^{SF}(r_{ij}) = \begin{cases} \dfrac{q_i q_j}{r_{ij}}\left[1 - \left(\dfrac{r_{ij}}{R_C}\right)^2\right]^2, & r_{ij} \leq R_C \\ \\ 0, & r_{ij} > R_C \end{cases} \quad (1)$$

Of particular interest is the application of pairwise electrostatic interaction methods to the simulation of room temperature ionic liquids. Ionic liquids are a unique class of solvents, defined as a material containing only ionic species. They can be fluid at temperatures as low as 204 K, have low viscosities and vapor pressures and excellent thermal and chemical stabilities, are recyclable, and tolerate impurities such as water.[11] Ion components can be fine-tuned through different functional

groups to enhance the degree of localized structuring in the liquid phase, which distinguishes ionic liquids from molecular solvents and solutions containing dissociated ions. Consequently, a large amount of computer time is required for the convergence of solvent properties due to the extensive sampling required and the costly evaluation of Ewald summations. Some pairwise electrostatic alternatives to Ewald have been applied to individual room temperature ionic liquid simulations. For example, Shi and Maginn employed the *damped shifted force* (DSF) method of Fennell and Gezelter[12] on the ionic liquid 1-*n*-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [HMIM][Tf$_2$N] with good reproducibility of the Ewald electrostatics by using a cutoff value of 12 Å and adjusting the damping parameter to 0.2022 Å^{-1}.[13] Subsequent ionic liquid studies have implemented the Wolf et al. method[14] or used Shi and Maginn's recommendation for a small number of imidazolium-based ionic liquids.[15]

In this work, 59 unique ionic liquid combinations of 1-alkyl-3-methylimidazolium [RMIM], where R = M (methyl), E (ethyl), B (butyl), H (hexyl), and O (octyl), and N-alkylpyridinium [RPyr] cations (Scheme 1), along with Cl$^-$,

Scheme 1. Ionic Liquid Forming Cations [R = M (methyl), E (ethyl), B (butyl), H (hexyl), and O (octyl)]

[RMIM]   [RPyr]
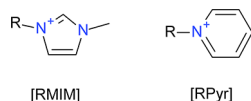
PF$_6^-$, BF$_4^-$, NO$_3^-$, AlCl$_4^-$, Al$_2$Cl$_7^-$, and TfO$^-$ anions have been tested at 25 °C using the *shifted potential* (SP) and *damped shifted potential* (DSP) methods of Wolf et al.,[14] the *shifted force*

(SF) method of Levitt et al.,[16] the DSF method of Fennell and Gezelter,[12] the *shifted force gradient* (SFG) method of Kale and Herzfeld,[17] the *damped Coulomb potential* (DC) method of Zahn et al.,[18] the CHARMM-SF method,[9] and our proposed *shifted force 3rd derivative* (SF3) method. The full Ewald sums energies are used as the benchmark to gauge the accuracy of each method. Multiple cutoffs, i.e., 9, 12, and 15 Å, and damping values (α = 0.1, 0.2, and 0.3 Å^{-1}) were examined, resulting in over 5000 molten salt/pairwise interaction combinations tested. This extensive study provides evidence that simple pairwise electrostatic interaction alternatives to Ewald for computing electrostatics can be an efficient and accurate method for use in the simulation of room temperature ionic liquids. Specific recommendations are given on the basis of the findings.

■ THEORY

As an early alternative to the more costly Ewald schemes, a general shifting scheme was first proposed by Brooks et al.[7] and implemented by Levitt et al. to treat electrostatics in biological simulations.[16] The method modifies the interactions energy by subtracting it from a truncated Taylor series of the original energy (eq 2), where $V(r_{ij})$ and $V(R_C)$ are the original potentials and equal to $1/r_{ij}$ and $1/R_C$, respectively; $dV(R_C)/dr$ is its derivative with respect to r_{ij} evaluated at the cutoff distance R_C, and r_{ij} is the distance between particles. Levitt et al. tested the n = 1 and 2 cases and concluded that the former provided a better electrostatic description in weak to mildly ionic biological environments, e.g., proteins and nucleic acids in water, and had little effect on hydrogen bonding. The n = 1 case is called here the *shifted force* (SF) method and given as eq 3.

$$V_{n\text{-shifted}}(r_{ij}) = \begin{cases} V(r_{ij}) - V(R_C) - \displaystyle\sum_{m=1}^{n} \frac{1}{m!}(r_{ij} - R_C)^m \frac{d^m V(R_C)}{dr^m}, & r_{ij} \le R_C \\ 0, & r_{ij} > R_C \end{cases}$$

(2)

$$V_{SF}(r_{ij}) = \begin{cases} q_i q_j \left[\dfrac{1}{r_{ij}} - \dfrac{1}{R_C} + \left(\dfrac{1}{R_C^2} \right)(r_{ij} - R_C) \right], & r_{ij} \le R_C \\ 0, & r_{ij} > R_C \end{cases}$$

(3)

Wolf et al. proposed a similar technique to Levitt et al. where simulations of Coulombic systems were truncated spherically with a pairwise $1/r_{ij}$ summation.[14] In their method, the electrostatic interaction is effectively short-ranged in the condensed phase, and charge neutrality is enforced within the cutoff radius. Image charges are subtracted out through placement on the cutoff sphere. Their method is called the *shifted potential* (SP) and is specified by eq 4. A distance-dependent damping function given by the complementary error function (erfc) from the Ewald sums was subsequently included to aid in the convergence of the calculated Madelung energies to yield the *damped shifted potential* (DSP) method (eq 5), where α is the damping parameter with units of Å^{-1}. The Wolf technique has proven successful in several condensed-phase MD simulations.[19,20] However, the use of the erfc is time-

consuming, and methods have been proposed that reduce the amount of times the erfc calculation is required.[21]

$$V_{SP}(r_{ij}) = \begin{cases} q_i q_j \left(\dfrac{1}{r_{ij}} - \dfrac{1}{R_C} \right), & r_{ij} \le R_C \\ 0, & r_{ij} > R_C \end{cases}$$

(4)

$$V_{DSP}(r_{ij}) = \begin{cases} q_i q_j \left(\dfrac{\text{erfc}(\alpha r_{ij})}{r_{ij}} - \dfrac{\text{erfc}(\alpha R_C)}{R_C} \right), & r_{ij} \le R_C \\ 0, & r_{ij} > R_C \end{cases}$$

(5)

Truncating the interactions yields a discontinuity in the potential that corresponds to an infinite force acting between atoms that cross the discontinuity. Many MD algorithms neglect this force due to poor treatment in the soft potentials. Consequently, error is manifested by the poor energy conservation in the simulation.[22] Zahn et al. revised Wolf's damping method to achieve energy conservation in MD simulations of TIP3P and SPC water models.[18] The proposed *damped Coulomb potential* (DC) method (eq 6) was found to

yield considerable improvement in dielectric properties and in static properties, including potential energy, particle density, and radial distribution functions. The method was originally intended for molecular liquids consisting of neutral molecules without internal Coulombic interaction; however, larger cutoff radii or a modification to the self-term has been speculated to

satisfy ionic systems. Fennell and Gezelter further revised Zahn et al.'s DC method with two differences: (a) the $V(R_C)$ term has been added to reduce any potential discontinuity as particles cross R_C, and (b) the sign of the derivative portion is changed.[12] Their method is called the *damped shifted force* (DSF) and is given by eq 7.

$$V_{DC}(r_{ij}) = \begin{cases} q_i q_j \left[\dfrac{\text{erfc}(\alpha r_{ij})}{r_{ij}} - \left(\dfrac{\text{erfc}(\alpha R_C)}{R_C^2} + \dfrac{2\alpha}{\pi^{1/2}} \dfrac{\exp(-\alpha^2 R_C^2)}{R_C} \right)(r_{ij} - R_C) \right], & r_{ij} \leq R_C \\ 0, & r_{ij} > R_C \end{cases}$$

$$(6)$$

$$V_{DSF}(r_{ij}) = \begin{cases} q_i q_j \left[\dfrac{\text{erfc}(\alpha r_{ij})}{r_{ij}} - \dfrac{\text{erfc}(\alpha R_C)}{R_C} + \left(\dfrac{\text{erfc}(\alpha R_C)}{R_C^2} + \dfrac{2\alpha}{\pi^{1/2}} \dfrac{\exp(-\alpha^2 R_C^2)}{R_C} \right)(r_{ij} - R_C) \right], & r_{ij} \leq R_C \\ 0, & r_{ij} > R_C \end{cases}$$

$$(7)$$

If the damping parameter α equals zero, then the DSP (eq 5) reduces to the undamped SP prescription of Wolf et al. (eq 4) and the DSF (eq 7) reverts to the undamped SF method (eq 3) derived from the $n = 1$ case in the Levitt et al. study. Extensive examination of the DSF, DSP, SF, and SP methods has been reported by Fennell and Gezelter on liquid and solid water, on crystal NaCl and high temperature (7000 K) molten NaCl melt, and on weak and strong NaCl solutions. They determined the undamped SF and moderately damped DSP methods to be ideal alternatives in the calculation of energetic and dynamic characteristics of the systems when compared to particle-mesh Ewald.[12] Hansen et al. independently verified the accuracy of the SF method with a reported speedup factor of 2−3 relative to the Wolf et al. method for bulk molten salt and the SPC/FW water model.[19]

Some problems have been reported for the SF method, however, including structural artifacts in ionic liquids with charges of large magnitude, i.e., $ThCl_4$ at 1000 K.[17] To address the issue, Kale and Herzfeld extended the potential by taking the second derivative of the potential with respect to distance and called the method the *shifted force gradient* (SFG).[17] The method is derived from the Levitt et al. method (eq 2), where $n = 2$ in this case and yields eq 8. Kale and Herzfeld reported that in cases of extreme ionicity in water, the greater potential softening of the $n = 2$ correction provided a reliable liquid structure in the NVT ensemble. In this work, the Levitt et al. equation is further expanded to the $n = 3$ case and is called the *shifted force 3rd derivative* (SF3) method (eq 9).

$$V_{SFG} = \begin{cases} q_i q_j \left[\dfrac{1}{r_{ij}} - \dfrac{1}{R_C} + (r_{ij} - R_C)\left(\dfrac{1}{R_C^2} \right) - (r_{ij} - R_C)^2 \left(\dfrac{1}{R_C^3} \right) \right], & r_{ij} \leq R_C \\ 0, & r_{ij} > R_C \end{cases}$$

$$(8)$$

$$V_{SF3} = \begin{cases} q_i q_j \left[\dfrac{1}{r_{ij}} - \dfrac{1}{R_C} + (r_{ij} - R_C)\left(\dfrac{1}{R_C^2} \right) - (r_{ij} - R_C)^2 \left(\dfrac{1}{R_C^3} \right) + (r_{ij} - R_C)^3 \left(\dfrac{1}{R_C^4} \right) \right], & r_{ij} \leq R_C \\ 0, & r_{ij} > R_C \end{cases}$$

$$(9)$$

■ COMPUTATIONAL METHODS

Metropolis Monte Carlo (MC) simulations were performed beginning with fully equilibrated ionic liquid boxes from our recent OPLS-AA force field parametrization effort.[23] Periodic boundary conditions have been applied to the boxes containing 190 ion pairs. All cations were fully flexible; i.e., all bond stretching, angle bending, and torsional motions were sampled. Anions were simulated as rigid molecules. The use of rigid

anions in OPLS-AA has been shown to provide an accurate representation of ionic liquid physical properties, including use as a reaction medium for computed QM/MM Diels−Alder[24] and Kemp elimination[23] reaction studies. Solvent−solvent intermolecular cutoff distances of 9, 12, and 15 Å were employed uniformly across all methods using the tail carbon atom of each side chain (methyl and alkyl), a midpoint carbon on the alkyl chain, and the ring carbon between both nitrogens for imidazolium. Center atoms, e.g., B in BF_4^- and P in PF_6^-,
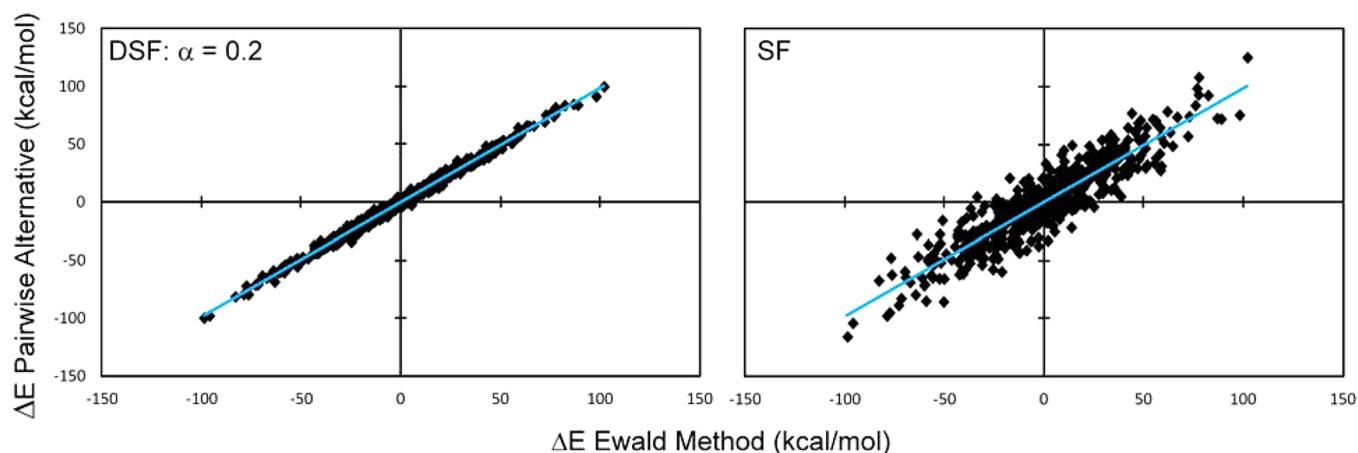
Figure 1. Least squares regressions of the configurational energy differences for the [EPyr][BF$_4$] system using a 15 Å cutoff distance.

Table 1. Statistical Analysis of the Quality of the Configurational Energy Differences for a Given Electrostatic Method Applied Across All Ionic Liquid Simulations Compared to the Reference Ewald Sum[a]

cutoff	9 Å		12 Å		15 Å		15 Å (smoothed)[b]	
method[c]	slope	R^2	slope	R^2	slope	R^2	slope	R^2
SF	1.003	0.156	0.973	0.264	0.988	0.507	1.008	0.689
0.1 DSF	1.006	0.166	0.982	0.378	0.994	0.794	1.002	0.894
0.2 DSF	0.992	0.680	0.982	0.975	0.980	0.982	0.980	0.981
0.3 DSF	0.955	0.928	0.947	0.938	0.945	0.937	0.944	0.933
SP	1.004	0.084	1.032	0.083	1.016	0.141	0.971	0.239
0.1 DSP	1.006	0.213	1.006	0.502	1.000	0.878	0.995	0.930
0.2 DSP	0.992	0.882	0.982	0.978	0.980	0.982	0.980	0.981
0.3 DSP	0.955	0.928	0.947	0.938	0.945	0.937	0.944	0.933
SFG	0.970	0.258	0.995	0.535	0.989	0.801	0.977	0.883
SF3	0.954	0.313	0.949	0.652	0.971	0.888	0.976	0.936
0.1 DC	1.006	0.085	1.048	0.196	1.003	0.578	0.987	0.693
0.2 DC	0.992	0.631	0.983	0.975	0.980	0.982	0.980	0.981
0.3 DC	0.955	0.927	0.947	0.938	0.945	0.937	0.944	0.933
CHARMM-SF	1.108	0.012	0.855	0.014	0.971	0.044	1.102	0.096
pure cutoff	0.725	0.005	1.162	0.009	0.958	0.007	0.979	0.007

[a]Results closest to 1.0 indicate ΔE values identical to those of Ewald. The correlation is indicated by the slope and the correlation coefficient by R^2 in the regression. [b]Quadratic feathering was applied to the final 0.5 Å of the cutoff sphere. [c]α values of 0.1, 0.2, and 0.3 Å^{-1} used for the DSF, DSP, and DC methods.
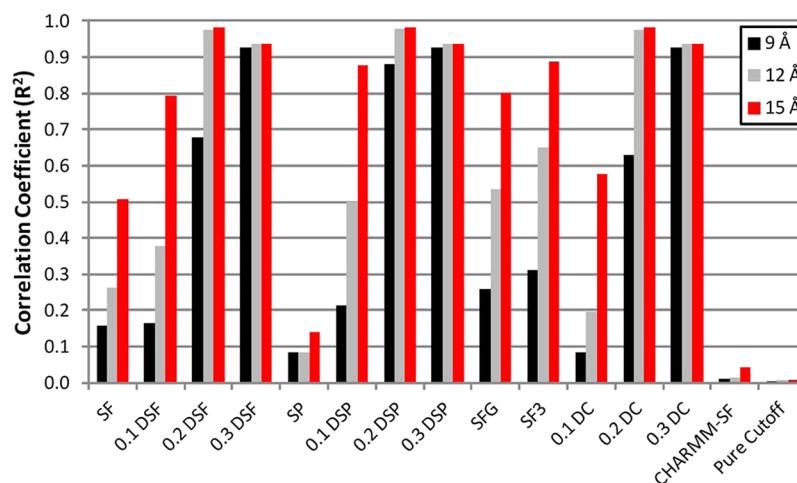

Figure 2. Graphical representation of the correlation coefficient (R^2) of the configurational energy differences for a given electrostatic method applied across all ionic liquid simulations at three cutoff distances—9, 12, and 15 Å. Correlation coefficients closest to 1.0 indicate ΔE values most similar to the reference Ewald sum.
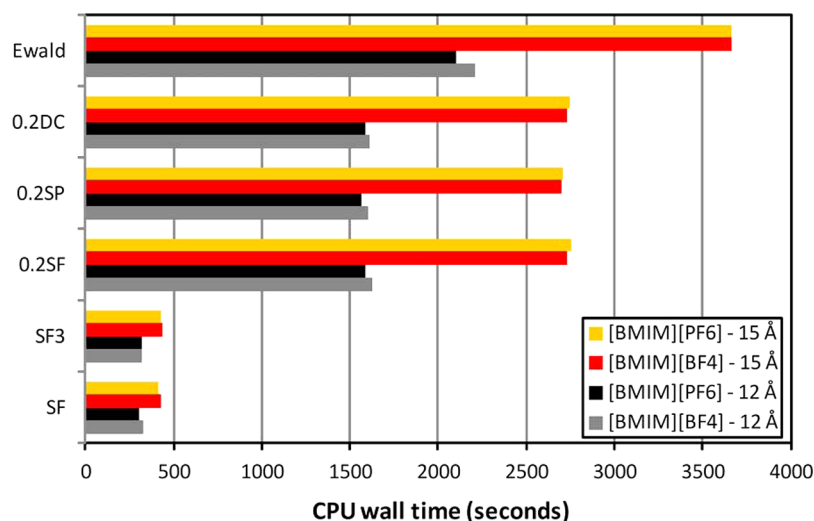
Figure 3. Timings for ionic liquid simulations relative to the full Ewald sums.

were used for the anions. If any distance is within the cutoff, the entire solvent−solvent interaction was included. Adjustments to the allowed ranges for rotations, translations, and dihedral angle movements led to overall acceptance rates of about 30% for new configurations. The ranges for bond stretching and angle bending were set automatically by the BOSS program on the basis of force constants and temperature. All MC calculations were run on a Linux cluster located at Auburn University and carried out using a custom version of BOSS.[25]

■ RESULTS AND DISCUSSION

Each condensed phase ionic liquid system was simulated at 25 °C using an NVT ensemble for 20 million MC configurations, saving individual coordinates every 40 000 MC steps, resulting in 500 configurations. The SP and DSP methods of Wolf et al.,[14] the SF method of Levitt et al.,[16] the DSF method of Fennell and Gezelter,[12] the SFG method of Kale and Herzfeld,[17] the DC method of Zahn et al.,[18] the CHARMM-SF method,[9] and our proposed SF3 method were evaluated through comparison of the energy differences (ΔE) between two conformations as computed by the pairwise alternatives relative to the ΔE derived by the full Ewald sums—analogous to the approach of Fennell and Gezelter.[12] A linear squares regression of the energy gap data was carried out, and results closest to 1.0 for both the correlation (slope) and correlation coefficient (R^2) indicate ΔE values identical to those of Ewald. Figure 1 gives a sample correlation plot for the [EPyr][BF$_4$] ionic liquid system when using DSF ($\alpha = 0.2$ Å^{-1}) and the undamped SF methods. Exhaustive detail for every ionic liquid/pairwise alternative/cutoff combination is provided in the Supporting Information.

From Table 1 (Figure 2 provides a graphical representation of the data) it can be seen that the DSF, DSP, and DC methods employing a damping constant value of 0.2 Å^{-1} and a cutoff distance of 15 Å provided the best energetic agreement with Ewald simulations. The DSP method did provide a negligibly better correlation coefficient at a cutoff distance of 12 Å and offered a slightly improved algorithm speed (discussed later) compared to DC or DSF. However, any one of the methods can be used interchangeably for the ionic liquid simulations with little difference in accuracy at a 15 Å cutoff. The ideal electrostatic damping value of 0.2 Å^{-1} is consistent with

previous benchmarking efforts for water and salt solutions. For example, Zahn et al. recommended a combination of a damping constant of 0.2 Å^{-1} and a cutoff distance of 9 Å from SPC and TIP3P simulations when using their DC method.[18] Fennell and Gezelter also reported the damping constant of 0.2 Å^{-1} to be the best value for the DSP method in Monte Carlo simulations of large chemical systems.[12] While the SF3 method did not perform at the same level of accuracy as the more costly damped methods, it can become a viable alternative for specific ionic liquid combinations. For instance, the [MPyr]-based ionic liquids produced an average slope and correlation coefficient of 0.981 and 0.986, respectively, for all anions using SF3 compared to 0.987 and 0.992 for the DSP method damped by a value of 0.2 Å^{-1} (see the Supporting Information). Specific cation and anion combinations and additional smoothing of the final 0.5 Å before the cutoff further improved the differences between the SF3 and DSP methods (see below).

The overall agreement between the pairwise alternatives and Ewald sums was generally poorer for ionic liquids containing hexyl and octyl substituents. Not surprisingly, removing the results for the hexyl and octyl based ionic liquids from Table 1 improves the average correlation with Ewald sums. For example, the DSP method ($\alpha = 0.2$ Å) improves its average slope and R^2 values to 0.985 and 0.990, respectively, at 15 Å as compared to the 0.980 and 0.982 values from Table 1. The SF3 method also improves considerably to 0.977 and 0.956 without the octyl or hexyl containing [RMIM] and [RPyr] cations relative to the 0.971 and 0.888 values reported in Table 1. Increasing the cutoff distance could potentially improve the energetic agreement for the longer alkyl-chain compounds. Detailed tables comparing the differences can be found in the Supporting Information.

Additional Smoothing. In OPLS-AA simulations, quadratic feathering of the electrostatic interactions to zero over the last 0.5 Å before the cutoff is typically applied to soften the energy discontinuity.[26] Whereas this option in the BOSS program[25] was not applied to the pairwise alternatives reported in Figure 2, it was investigated and reported for 15 Å in Table 1. The additional smoothing effect on the average correlation (slope) and correlation coefficient (R^2) values across all ionic liquid simulations and cutoff distances are given in the Supporting Information. For the methods with the most favorable agreement with full Ewald sums, i.e., DSF, DSP, and

DC all damped by a value of 0.2 Å^{-1}, the feathering did not improve the results. However, for the undamped SF, SP, SFG, and SF3 methods, the agreements with Ewald were all enhanced when applying the additional smoothing. For example, smoothing the SF3 method considerably improved the average slope and R^2 values to 0.976 and 0.936, respectively, compared to the previous values of 0.971 and 0.888 (Table 1) without the quadratic feathering. Many specific combinations of ionic liquids were particularly accurate using SF3 with additional smoothing. For instance, SF3 with a 15 Å cutoff distance on [MMIM][BF$_4$] gave slope and R^2 values of 0.984 and 0.989, respectively, [EPyr][NO$_3$] had values of 0.984 and 0.988, and [MPyr][TFO] produced values of 0.987 and 0.991.

Timings. Part of the motivation in utilizing pairwise alternatives to Ewald sums was to improve the efficiency of the ionic liquid simulations. Therefore, a basic effort has been made to measure differences in algorithm speed on the same computer: a Dell Optiplex GX760 featuring an Intel Core2Quad processor clocked at 2.83 GHz with 2 GB of RAM. A comparison was carried out for two ionic liquids, [BMIM][PF$_6$] and [BMIM][BF$_4$], between the damped pairwise alternatives DC, DSP, and DSF (where α = 0.2 Å^{-1}), and the undamped SF3 and SF methods. All pairwise interaction models used 12 and 15 Å cutoff distances to evaluate the 500 configurations. Figure 3 shows the absolute CPU time utilized in seconds for each technique. Relative timings find that the damped methods required ca. 72 to 75% of the total Ewald sums time at each specific cutoff value. The undamped SF3 and SF systems utilized ca. 15 and 12% for the 12 and 15 Å cutoff distances, respectively (see Supporting Information). The modest gain in simulation speed for the damped pairwise alternatives that employ the erfc function is consistent with the reported time-consuming nature of the erfc function.[21] The undamped SF3 and SF do provide a significant improvement in the calculation time relative to both full Ewald sums and the damped methods, but ultimately at a cost of reduced accuracy (Table 1).

CONCLUSIONS

Monte Carlo simulations of 59 unique room temperature ionic liquid combinations of [RMIM] and [RPyr] cations (where R = M (methyl), E (ethyl), B (butyl), H (hexyl), and O (octyl)) and Cl$^-$, PF$_6^-$, BF$_4^-$, NO$_3^-$, AlCl$_4^-$, Al$_2$Cl$_7^-$, and TfO$^-$ anions have been carried out using multiple pairwise electrostatic interaction alternatives (i.e., SF, DSF, SFG, SF3, SP, DSP, DC, and CHARMM-SF) to Ewald sums. The DSP, DSF, or DC methods provided the best energetic agreement with Ewald when combined with an electrostatic damping value of 0.2 Å^{-1} and a cutoff distance of 15 Å. The results are consistent with the recommendation by Zahn et al. of an ideal damping constant of 0.2 Å^{-1} and a cutoff of 9 Å from SPC and TIP3P simulations when using their DC method.[18] Fennell and Gezelter also reported α = 0.2 Å^{-1} to be the best value for the DSP method in Monte Carlo simulations of liquid and solid water and NaCl solutions.[12] Identical agreement with the full Ewald sums energies, i.e., correlation (slope) and correlation coefficient (R^2) values of 1.0, could potentially be achieved by fine-tuning the damping constant toward specific ionic liquid combinations. For example, Shi and Maginn reported good reproducibility of the Ewald electrostatics for the [HMIM]-[Tf$_2$N] ionic liquid by using the DSF method with an α value of 0.2022 Å^{-1}.[13]

Timings of the individual algorithms found that the damped pairwise methods, i.e., DSP, DSF, and DC, delivered a modest 1.3 to 1.4-fold improvement in calculation speed relative to Ewald simulations. The results are consistent with the reported time-consuming nature of the erfc function used to damp the electrostatics.[21] The undamped methods, e.g., SF and SF3, provided a more significant 8 to 9-fold speed-up; however, the accuracy was generally reduced. Nevertheless, the SF3 method can be a viable alternative to the more costly damped methods for specific ionic liquid combinations, as the ΔE differences computed for the methyl and ethyl substituted [RMIM] and [RPyr] systems rivaled that of the damped methods. In addition, quadratic feathering of the electrostatic interactions to zero over the last 0.5 Å before the cutoff improved the overall agreement for the undamped methods across all ionic liquids relative to the full lattice summation energies. Our extensive study provides evidence that simple pairwise interaction alternatives to Ewald can be an efficient and accurate method for computing electrostatic energies in the simulation of diverse room temperature ionic liquids.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Correlation and correlation coefficients tables and plots for all ionic liquid/pairwise interaction/cutoff combinations, a list of abbreviations for the ionic liquids, and computational timings. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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