

Optimization of the Ewald method for calculating Coulomb interactions in molecular simulations.

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Practical implementations of the Ewald method used to compute Coulomb interactions in molecular dynamics simulations are hampered by the requirement to truncate its reciprocal space series. It is shown that this can be mitigated by representing the contributions from the neglected reciprocal lattice vector terms as a simple modification of the real space expression in which the real and reciprocal space series have slightly different charge spreading parameters. This procedure, called the α' method, enables significantly fewer reciprocal lattice vectors to be taken than is currently typical for Ewald, with negligible additional computational cost, which is validated on model systems representing different classes of charged system, a CsI crystal and melt, water and a room temperature ionic liquid. A procedure for computing accurate energies and forces based on a periodic sampling of an additional number of reciprocal lattice vectors is also proposed and validated by the simulations. The convergence characteristics of expressions for the pressure based on the forces and the potential energy are compared, which is a useful assessment of the accuracy of the simulations in reproducing the Coulomb interaction. The techniques developed in this work can reduce significantly the total computer simulation times for medium sized charged systems, by factors of up to *ca.* 5 for those in the classes studied here.

I. INTRODUCTION

The Ewald method has been used for over fifty years to compute Coulomb interactions in molecular simulations, [45] and is routinely included in many molecular simulation packages. Its inclusion in molecular simulation is expensive and it does not scale well with system size. The weighting parameter in the equations is chosen so that the real space series decays rapidly enough to apply the nearest image convention with minimal truncation error. The reciprocal space series (REC) is as a result relatively slow to converge and has to be truncated before it has converged sufficiently. The problem gets more severe with increasing system size, which has prompted the development of particle mesh treatments of the REC. [63] It is not surprising that so-called truncation methods, which do not have a reciprocal space component, and can treat the Coulomb interactions in the same way as the short-range van der Waals terms have gained in popularity. [53–57] The disadvantage of truncation methods is there is no established way of quantifying the deviation from the true Coulomb interaction. In contrast, the Ewald method involves two series expansions which are separately more amenable to such analysis.

This work proposes new equations to correct for the neglected reciprocal lattice vectors, cast in terms of adjustments of the real space series and the self-energy terms, with the consequence that fewer reciprocal lattice vectors need to be used. In addition, it is shown that significantly improved values of the Coulomb energy and forces can be obtained by adding a correction term based on the periodic evaluation of a larger number of reciprocal lattice vectors. The accurate calculation of the Coulomb interaction component of the pressure is also discussed.

The improved Ewald variant theory is derived in Sec. II. In Sec. III details of simulation methodology and implementation are given. Sec IV presents the results of MD simulations carried out to test the extent to which these new equations improve the computational efficiency of the Ewald method. Calculations on a wide variety of different types of charged system were carried out as part of this exercise. A summary of the conclusions for this work is given in Sec. V.

II. THEORY

This section is concerned with the ways of deriving generalized Ewald formulas for arbitrary charge spreading function. A focus is on mitigating the effects of truncating the REC series, with the usual Ewald formulas which employ a Gaussian charge spreading function, although the treatment is perfectly general and can be applied to other charge spreading functions.

A. The Ewald method and ways to derive the formulas

The Ewald expressions for the electrostatic potential energy, v_i , of point charge i in a lattice of point charges may be written in the general form,

$$\begin{aligned} v_i &= v_{real,i} + v_{rec,i} + v_{self,i}, \\ v_{real,i} &= q_i \sum_{\mathbf{n}=0}^{N'} \sum_{j=1}^N \frac{q_j v_r(|\mathbf{r}_{ij} + \mathbf{n}|, \alpha)}{|\mathbf{r}_{ij} + \mathbf{n}|}, \\ v_{rec,i} &= \frac{q_i 4\pi}{L^3} \sum_{\mathbf{k}} \sum_{j=1}^N \frac{q_j \cos(\mathbf{h} \cdot \mathbf{r}_{ij})}{h^2} \phi(h, \alpha), \\ v_{self,i} &= -q_i^2 V_s(\alpha) \end{aligned} \quad (1)$$

where the specific form of $v_r, \phi(h, \alpha)$ and $V_s(\alpha)$ depends on the choice of implicit charge spreading function. [33]

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The function $\phi(h, \alpha)$ is dimensionless. The standard Ewald method (GEW) uses a Gaussian charge spreading function. The total electrostatic contribution to the system potential energy, U_c , is,

$$U_c = \frac{1}{2} \sum_{i=1}^N v_i. \quad (2)$$

Equation (1) and all subsequent equations are for a periodic array surrounded by a perfect conductor.

To convert to real units the terms in Eq. (1) need to be multiplied by $[4\pi\epsilon_0]^{-1}$, where ϵ_0 is the permittivity of free space. A cubic cell of sidelength, L , is assumed here but the treatment is readily generalizable to other crystal classes. [41] The cell has a total charge of zero and consists of N charges. The separation vector between charges i and j is, $\mathbf{r}_{ij} \equiv \mathbf{r}_i - \mathbf{r}_j$, where $\mathbf{r}_l$ is the location of charge l . The principle is that the original summation slowly converging series in real space is replaced by two more rapidly converging series, one in real space and the other reciprocal space. The real space term, $v_{real,i}$, in Eq. (1) involves a sum of the interactions from within that cell and its periodic images. The real space lattice vector is $\mathbf{n} = (\mathbf{i}_x, \mathbf{i}_y, \mathbf{i}_z)L$ where $\mathbf{i}_\kappa = [0, \pm 1, \pm 2, \dots] \mathbf{i}_{\kappa,0}$ are multiples of the unit vector $\mathbf{i}_{\kappa,0}$ in the κ -direction. The l on the j -summation in the real space term indicates the omission of the $j = i$ term when $\mathbf{n} = \mathbf{0}$. The reciprocal space term, $v_{rec,i}$ involves a sum over reciprocal lattice vectors, $\mathbf{h} = 2\pi(\mathbf{i}_x, \mathbf{i}_y, \mathbf{i}_z)/L$ where the l in Eq. (1) signifies the omission of the $\mathbf{h} = \mathbf{0}$ element term. The last term in Eq. (1) is the self-energy, $v_{self,i}$. The self-energy term typically makes up a significant percentage of the total Coulomb energy.

The adjustable parameter, α , in Eq. (1) controls the relative contribution from the real and reciprocal series to the total energy (the latter increases with α). This adjustable parameter is often expressed in dimensionless form through the parameter, $\kappa = \alpha L$.

There are various ways of deriving the analytic forms of v_r , ϕ and V_s , which will be considered below.

Ewald derivation via charge spreading functions, CSF

The ‘traditional’ way of deriving these three functions is to link them separately to an artificial function which describes the spherically symmetric spreading out of the charges, or ‘charge spreading function’ (CSF), $\sigma(u, \alpha)$, where u is the distance from the center of the charge. The original Ewald formula employs a Gaussian CSF, which is referred to as ‘GEW’ here. The application of Eq. (1) for arbitrary CSF is called an Ewald Variant (EV). In Ref. 33 the CSF, $\sigma(u, \alpha)$ was defined in terms of a more basic function, $f(u, \alpha)$ and a normalization constant, A .

$$\sigma(u, \alpha) = Af(u, \alpha), \quad A^{-1} = 4\pi \int_0^\infty u^2 f(u, \alpha) du, \quad (3)$$

where the volume integral of σ is equal to unity. **The motivation to use the substitution $\sigma(u, \alpha) \equiv Af(u, \alpha)$ is that for some of the series in Ref. 33, a $f(u, \alpha)$ can be defined where $f(u \rightarrow 0, \alpha) = 1$, which facilitates comparisons between the extent of charge diffuseness of the various series.**

The real space summation quantity Eq. (1) is,

$$v_r = \frac{1}{r} - \frac{4\pi A}{r} \int_0^\infty u^2 f(u, \alpha) du, \\ - 4\pi A \int_0^\infty u f(u, \alpha) du, \quad (4)$$

as discussed in Ref. 33.

The Fourier space lattice quantity is,

$$\phi(h, \alpha) = 4\pi A h^{-1} \int_0^\infty u f(u, \alpha) \sin(hr) du, \quad (5)$$

and the self-energy term V_s is,

$$V_s = 4\pi A \int_0^\infty u f(u, \eta) du. \quad (6)$$

Nine analytic forms of the CSF were considered in Ref. 33, four of which are of finite extent and go to zero at $r = \alpha^{-1}$. CSF of this type were widely used from the 1950s onwards for a few decades by transforming the entirety of the original real space r^{-1} Coulomb lattice summation into its reciprocal space representation. [34, 51, 52] The range of the CSF was chosen so they do not overlap in the lattice, which means the EV term $v_{real,i} = 0$, although there is still a self-energy contribution. The series 4 case in Ref. 33 is potentially useful in a modern context as the potential and its first four derivatives are zero at the real space cutoff which should in principal confer excellent anti-drift behavior in a simulation. [17]

Other analytic forms for the CSF have been employed in EV more recently, including a gaussian times a power of r , [39] and a truncated gaussian. [40] Hünenberger, [36] considered the convergence characteristics of CSF with algebraic form and of finite extent.

It is probably fair to state that all the obvious charge spreading functions which are analytically soluble for v_r , ϕ and V_s in Eq. (1) have been considered. There is another route to these three functions which do not rely on choosing a $\sigma(u, \alpha)$ in advance, and expand the range of possible EV formulas.

Ewald derivation without charge spreading functions

The real space series pair term potential, $v_r(r, \alpha)$, can be written in terms of the original Coulomb potential and an ancillary function, $G(r, \alpha)$ which improves the convergence rate of the real space summation (*e.g.*, for GEW this is $G(r, \alpha) = \text{erf}(\alpha r)/r$). Argyriou and Howard derived expressions for the electrostatic potential, cast entirely as reciprocal space summation. [35] Equations (15) and (16) in that work lead to,

$$v_r(r) = r^{-1} - G(r, \alpha), \\ G(r, \alpha) = \frac{1}{2\pi^2} \int \frac{1}{h^2} \phi(h, \alpha) e^{-i\mathbf{h}\cdot\mathbf{r}} d^3\mathbf{h}, \\ = \frac{2}{\pi} \int_0^\infty \phi(h, \alpha) \frac{\sin(hr)}{hr} dh, \quad (7)$$

from Eq. (15) in Ref. 35. The function, $G(r, \alpha)$, can therefore be obtained from a choice for $\phi(h, \alpha)$. From Eq. (16) in Ref. 35,

$$V_s(\alpha) = \lim_{r \rightarrow 0} G(r, \alpha) = \frac{2}{\pi} \int_0^\infty \phi(h, \alpha) dh, \quad (8)$$

from Eq. (7) (see also Ref. 44). Combined use of Eqs. (7) and (8) enables the terms in Eq. (1) to be obtained solely from an input analytic form for $\phi(h, \alpha)$.

The implicit CSF can be obtained from Eq. (8) in Ref. 38,

$$\begin{aligned}\sigma(u, \eta) &= \frac{1}{(2\pi)^3} \int \phi(h, \eta) e^{-\mathbf{h} \cdot \mathbf{r}} d^3 \mathbf{h}, \\ &= \frac{1}{2\pi^2} \frac{1}{u} \int_0^\infty h \phi(h, \eta) \sin(hr) dh, \quad (9)\end{aligned}$$

which, importantly, is not required in obtaining the electrostatic potential. Therefore from a proposed analytic form for $\phi(k, \alpha)$, Eqs. (7) and (8) give the necessary formulas to generate an Ewald-like expression.

Another route is to start from a choice for the analytic form of $G(r, \alpha)$ as the only required input function. The self-energy may be obtained from Eq. (8), and ϕ , by inversion of Eq. (7),

$$\frac{\phi(h, \alpha)}{h} = \int_0^\infty r G(r, \alpha) \sin(hr) dr, \quad (10)$$

and

$$V_s(\alpha) = \lim_{r \rightarrow 0} G(r, \alpha) \quad (11)$$

The advantage of the two routes in Eqs. (7)-(11) is that the analytic form of $\sigma(r, \alpha)$ is not needed in advance, and in fact is not needed at all. A plausible analytic form for either $\phi(h, \alpha)$ or $G(r, \alpha)$, respectively, which can be a more straightforward exercise may lead to an EV series whose underlying CSF is not an obvious one to use via the CSF starting point route. For example, if $v_r(r, \alpha) = \exp(-r\alpha)/r$,

$$\begin{aligned}G(r) &= \frac{1 - \exp(-r\alpha)}{r}, \quad \phi(h, \alpha) = \frac{1}{[h/\alpha]^2 + 1}, \\ V_s &= \alpha, \quad \sigma(u, \alpha) = \alpha^2 \frac{\exp(-u\alpha)}{4\pi u}, \quad (12)\end{aligned}$$

where $\sigma(u, \alpha)$ was obtained using Eq. (9), which diverges at the origin. This is not a problem as $\sigma(u, \alpha)$ is only needed when multiplied by u or u^2 in an integral, *e.g.*, see Eq. (5)). The terms in Eq. (12) substituted in Eq. (1) is referred to as Series 10 in this work (Series 1-9 are given in Ref. 33). **It is not appropriate to use the $\sigma(u, \alpha) \equiv Af(u, \alpha)$ identity here because the CSF has a singularity at the origin, and therefore a $f(u, \alpha)$ cannot be defined which is unity in the zero u limit.**

Extension of truncation methods to Ewald

In recent years truncation methods have become popular as ways of including Coulomb interactions in molecular simulations. [53–57] The potential and force are truncated at a specified pair separation, r_c and they are treated just as the short-range van der Waals terms. One way of quantifying the deviations in this approach from the true Coulomb interaction is to take the truncated potential term to be v_r in the Ewald method. Then as the Ewald formulas gives the exact Coulomb energy, the difference or errors in simply truncating will reside in the reciprocal space term (ϕ) and possibly the self-energy term of Ewald. For all charge interactions where $r > r_c$ the error is given entirely by the reciprocal space term in the Ewald formulas.

In the following derivations it is convenient to replace α^{-1} by r_c , the potential truncation distance. Consider the following CSF,

$$f(u, r_c) = \delta(r - r_c), \quad A = \frac{1}{4\pi r_c^2} \quad (13)$$

where δ is the Dirac delta function. The function, $f(u, r_c)$ substituted in Eq. (4) for v_r and Eq. (6) for V_s gives,

$$\begin{aligned}v_r(r) &= \frac{1}{r} - \frac{1}{r_c} \quad r < r_c, \\ &= 0 \quad r > r_c, \quad V_s = \frac{1}{r_c}.\end{aligned} \quad (14)$$

Introducing Eq. (13) in Eq. (5) gives,

$$\phi(h, r_c) = \frac{\sin hr_c}{hr_c}, \quad (15)$$

the sinc function. The terms in Eq. (14) constitute the Shifted Coulomb pair potential and correction term presented in Eqs. (3.10) and (3.11) in Ref. 54. Therefore the reciprocal lattice series employing the definition of ϕ given in Eq. (15) is the exact expression for the error in the shifted Coulomb pair potential truncation scheme of Wolf *et al.* [54] Equations (13)-(15) are referred to here as EV Series 11.

The truncated and shifted force (SF) type of potential is more widely used in simulations as the potential and its first derivative are zero at the truncation distance, see Eq. (3.17) in Ref. 54, and it is also discussed in Refs. 25, 55, and 57. The SF, pair force, f_{SF} is

$$f_{SF} = -\frac{dv_r(r)}{dr} \Big|_r = \frac{1}{r^2} - \frac{1}{r_c^2} \quad (16)$$

and the associated potential shifted to be zero at $r = r_c$ through the constant of integration is,

$$\begin{aligned}v_r(r) &= \frac{1}{r} - G(r), \\ G(r) &= \frac{2}{r_c} - \frac{r}{r_c^2}\end{aligned} \quad (17)$$

Equation (10) is used to derive ϕ directly from $G(r)$. Using formulas 17.17.2 and 17.17.3 from Ref. 68,

$$\begin{aligned}\phi(h, r_c) &= \frac{1}{(r_c h)^2} (2 - 2\cos(r_c h) - (r_c h)^2 \cos(r_c h)), \\ V_s &= \frac{2}{r_c}.\end{aligned} \quad (18)$$

The charge distribution (and hence V_s from Eq. (6)) is obtained in this case using the Poisson equation, $\nabla^2 \phi(r) = -4\pi\sigma(r)$, where $\phi(r)$ is the Coulomb potential. As the CSF charge distribution is spherically symmetric the Laplacian in spherical coordinates leads to,

$$\begin{aligned}\frac{\partial^2 [rG(r, \alpha)]}{\partial r^2} &= -4\pi r \sigma(r, \alpha), \\ \sigma(r, \alpha) &= \frac{1}{2\pi r r_c^2} \quad r < r_c\end{aligned} \quad (19)$$

for this Series, which has a singularity at the origin as does the $\sigma(r, \alpha)$ of Series 10. Equations (16)-(19) are denoted by EV Series 12 here. Series 11 and 12 have quite different charge distributions. Series 12 does not converge for any value of r_c because of the last term of $\phi(h, r_c)$ in Eq. (18). It was discussed by Argyriou and Howard, [35] that $\phi(h, r_c)$ must decay more rapidly than h^{-1} for the summations to converge. This condition is not met in Eq. (18). For Series 11 the $\phi(h, r_c)$ is a sinc function which apparently decays exactly as h^{-1} but as it is modulated by a sin function its integral, the Si function does converge (to $\pi/2$ for large arguments). Nevertheless, Series 10 and 11 are extremely slow to converge. The rate of convergence can be improved by increasing the value of r_c (to an impractical degree for molecular simulation). It is probably fair to state that Series 10-12 cannot practicably be included in molecular simulation, even just for the purpose of quantifying the errors in the shifted potential and force potentials. A better route to achieve this task would be to generate the system using GEw and calculating the shifted force which does not affect the dynamics as an ancillary operation. The errors in these truncated real space methods can be determined by subtraction with the GEw quantity values therefore.

Equations (16)-(18) are denoted by EV Series 12 here.

B. Truncation of the reciprocal space series at $h = h_c$

For computational efficiency in simulation, the REC series needs to be terminated at a finite reciprocal lattice vector where the contributions from the neglected terms are not negligible, which leads to errors and deviations from the exact Coulomb interaction in the computed electrostatic terms. Routes to reduce the magnitude of these errors by additional correction expressions are proposed and tested here.

Correction in reciprocal space

It is computationally efficient to truncate the real space series at $r = r_c \leq L/2$, *i.e.*, the usual nearest image restriction used for a short range potential such as for the Lennard-Jones interaction. This imposes a lower bound on the value of α and a limit in the rate of convergence of REC. The reciprocal space series vectors are conveniently expressed in integer form, $\mathbf{k} = \mathbf{h}L/2\pi = (\mathbf{i}_x, \mathbf{i}_y, \mathbf{i}_z)$. An upper limit has to be applied to the number of $\mathbf{k}$ vectors considered, such that $|\mathbf{k}| = k \leq k_c$, where $\mathbf{i}_x^2 + \mathbf{i}_y^2 + \mathbf{i}_z^2 \leq k_c^2$, and $h_c = 2\pi k_c/L$ is specified. Note that as k_c^2 is always an integer, then k_c can only take certain discrete values.

An approximate (always positive) expression for the missing h -vector terms is, [42, 46, 49]

$$v_{rec,i}(h > h_c) \simeq q_i^2 \frac{4\alpha^2}{\pi N h_c} \exp\left(-\left(\frac{h_c}{2\alpha}\right)\right), \quad (20)$$

for N charges in the cell. This is derived by replacing the REC summation for $h > h_c$ by an integral. The main assumption in the derivation of Eq. (20) is that the charges are randomly distributed in space so that after averaging the only non-zero terms remaining involve a charge interacting

with its periodic replicas (the ‘diagonal’ approximation). The value of h_c where this formula is appropriate is *ca.* $h_c > 2\pi\alpha$. [49] These approximations inevitably cause a mismatch between the exact reciprocal space series and the correction term at $h = h_c$, whose accuracy is difficult to quantify. The charge-charge correlations found in ionic liquids are not included in Eq. (20). In order to incorporate the effects of charge-charge correlation in correcting for the REC truncation, an alternative strategy is required.

Correction in real space

An alternative route to account for the missing $h > h_c$ terms which does not have the deficiencies of Eq. (20) is proposed here. The effect of truncating REC is to cause a deviation from Coulomb’s law in the modelled system. The real space series, v_r and the self-energy, V_s formulas need to be replaced by v'_r and the self-energy, V'_s , which take this into account. The consequence of this is that the screening constant in the self and real space terms should be h_c -dependent. The formulas derived below have not been used in simulation previously as far as we are aware. When they are made the new expressions are denoted with the superscript, ‘ $'$ ’. Maggs proposed a correction which was also based on the expression of the REC truncation (partly) in real space, although the final expressions and detailed approach are quite different to those derived here. [50]

Starting from Eq. (7) one can formally include h_c in the Ewald construction as follows,

$$\begin{aligned} v_r(r, \alpha) &= r^{-1} - G(r, \alpha), \\ v'_r(r, \alpha) &= r^{-1} - G'(r, \alpha), \\ G'(r, \alpha) &= \frac{2}{\pi} \int_0^{h_c} \phi(h, \alpha) \frac{\sin(hr)}{hr} dh, \\ \delta G'(r, \alpha) &= \frac{2}{\pi} \int_{h_c}^{\infty} \phi(h, \alpha) \frac{\sin(hr)}{hr} dh. \\ v'_r(r, \alpha) &= v_r(r, \alpha) + \delta G'(r, \alpha) \end{aligned} \quad (21)$$

The truncation of the Fourier series at h_c is the same as adding a discontinuous weight function to this series, which is responsible for the additional real space term, $\delta G'$, in Eq. (21). This new term decays with r in a damped oscillatory manner, which is a general feature of real space functions derived from truncated summations in reciprocal space. Templeton also derived an expression for the $k \leq k_c$ error in a purely reciprocal space formulation of the electrostatic energy of a crystal, [34] in real space. This was expressed in part in terms of the damped oscillatory sinc function (*i.e.*, $\text{sinc}(x) = \sin(x)/x$). There is no simple analytic expression for $\delta G'(r, \alpha)$.

Figure 1 for the GEw case shows that the oscillations in $\delta G'(r, \alpha)$ have a periodicity length, $l \simeq L/k_c$ and the function decays slowly with r in an algebraically damped oscillatory way. This poses a problem for simulation as the real space terms are usually truncated at $r_c \leq L/2$. Clearly a real space series term which extends over several periodic cells is not practicable in molecular simulation. A compromise solution is required for efficient simulation which includes a realistic representation of $\delta G'(r, \alpha)$ at short distance, but also decays

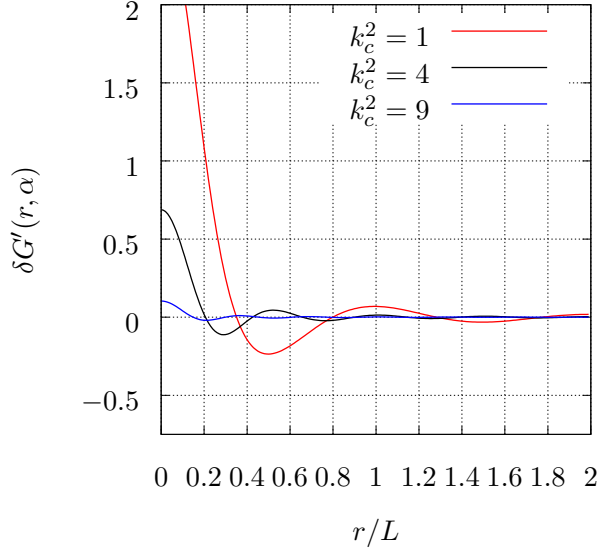


FIG. 1. The h -space truncation function expressed in real space as, $\delta G'(r, \alpha)$, which is formally defined in Eq. (21), where $\alpha = 5.556/L$ and L is the sidelength of the repeat cell. The GEw method which uses a Gaussian charge distribution is considered. The function was obtained from its definition in Eq. (21) by Simpsons rule numerical integration.

rapidly enough with distance to be truncated at reasonable values of r_c with minimal energy and force discontinuities at this distance.

It is convenient to consider first the h_c -dependent self-energy. It follows from Eq. (8), that

$$\begin{aligned} V_s(h_c) &\equiv V'_s = \frac{2}{\pi} \int_0^{h_c} \phi(h, \alpha) dh, \\ &= V_s - \frac{2}{\pi} \int_{h_c}^{\infty} \phi(h, \alpha) dh \\ &= V_s - \delta G'(0, \alpha). \end{aligned} \quad (22)$$

The Ewald self-energy, V_s , is just $V_s(h_c \rightarrow \infty)$. As the integral on the right hand side of the equation on Eq. (22) is greater than zero, $V_s(h_c) < V_s$. The self-energy is subtracted from the other Ewald formula terms, as indicated in Eq. (1). For GEw,

$$\begin{aligned} V_s(h_c) &= \frac{2}{\sqrt{\pi}} \alpha \operatorname{erf}\left(\frac{h_c}{2\alpha}\right) = V_s \operatorname{erf}\left(\frac{h_c}{2\alpha}\right), \\ \alpha' &= \alpha \operatorname{erf}\left(\frac{h_c}{2\alpha}\right), \\ V_s(h_c) &\equiv V'_s = \frac{2}{\sqrt{\pi}} \alpha', \end{aligned} \quad (23)$$

from Eq. (22). The parameter $\alpha' \leq \alpha$ and approaches α in the large h_c limit. Equation (22) and Eq. (23) for GEw are the correct formulas for the self-energy in molecular simulation for finite h_c . For GEw, Eq. (23) indicates that, $G'(0, \alpha) = G(0, \alpha')$, and it is tempting to extend this as an approximate representation of $\delta G'(r, \alpha)$ for finite r .

The approximation, $G'(r, \alpha) \simeq G(r, \alpha')$ cannot be exact for all r as $G(r, \alpha')$ does not exhibit oscillations and it is always positive. Nevertheless, if $G(r, \alpha')$ is in reasonable agreement

with $G'(r, \alpha)$ for small r , its inclusion in the computations should improve the accuracy of the Ewald energy. In its favor, the implementation of $G(r, \alpha')$ would take into account charge correlations of the system being modelled, unlike Eq. (20). Any inaccuracies at large r may be reduced by mutual cancellation of their effects arising from different changes in this distance region.

From this point onwards the GEw with a Gaussian charge distribution will be considered exclusively. The real space contribution to the electrostatic energy for GEw involves $\operatorname{erfc}(\alpha r)/r$, and therefore from Eq. (21),

$$\delta G'(r, \alpha) \simeq \frac{(\operatorname{erf}(r\alpha) - \operatorname{erf}(r\alpha'))}{r} \equiv \delta G'_d(r, \alpha). \quad (24)$$

The value of α' decreases as h_c decreases which may lead to physically significant energy and force discontinuities at the truncation distance. Consequently some fine-tuning of α and the truncation distance in real space would be required to obtain optimum accuracy for a given system size if this route were to be adopted.

An extensive analysis of possible analytic forms for $G'(r, \alpha)$ based on Taylor expansions of the second term in Eq. (24) was made. An expansion of the α' term in powers of $\alpha' - \alpha$ was involved, which leads to additional terms in the real space summation, but they did not obviously perform better than the simple approximation, $G'(r, \alpha) = G(r, \alpha')$ adopted in this study.

Using $\delta G'_d(r, \alpha)$, and following on from Eqs. (23) and (24), the α' modified Ewald formulas are,

$$\begin{aligned} v'_i &= v'_{real,i} + v'_{rec,i} + v'_{self,i}, \\ v'_{r,i} &= q_i \sum_{\mathbf{n}=0}^{N'} \sum_{j=1}^{N'} q_j \left[\frac{\operatorname{erfc}(|\mathbf{r}_{ij} + \mathbf{n}|, \alpha')}{|\mathbf{r}_{ij} + \mathbf{n}|} \right], \\ v'_{rec,i} &= \frac{q_i 4\pi}{L^3} \sum_{\mathbf{h}>0}^{h_c} \sum_{j=1}^N \frac{q_j \cos(\mathbf{h} \cdot \mathbf{r}_{ij})}{h^2} \exp(-(\alpha h)^2/4), \\ v'_{self,i} &= -q_i^2 \frac{2\alpha'}{\sqrt{\pi}}, \quad \alpha' = \alpha \operatorname{erf}\left(\frac{h_c}{2\alpha}\right). \end{aligned} \quad (25)$$

Equation (25) is a readily implemented simple correction to the usual GEe formulas, and only requires the replacement of α by α' in the real space and self-energy terms of Eq. (1). Note that the original α parameter is used in the reciprocal space summation term. The forces are obtained as usual by taking the spatial derivatives of the terms in Eq. (25). One way of looking at Eq. (25) is that some of the energy from the self-energy of GEw is 'transferred' into the real space term. The α' method is illustrated schematically in Fig. 2. Also Eq. (25) represents a sliding-scale from standard GEw (high k_c where $\alpha' \rightarrow \alpha$) down to pure $1/r$ pair potentials (as $k_c \rightarrow 0$). The small modifications to standard GEw given in Eq. (25) partially account for the missing terms in the (truncated) reciprocal space series.

Table I compares the GEw and α' values for the Coulomb potential energy of a charge in a periodically repeated neutral cell containing two charges, as a function of the truncation parameter, k_c for two different locations of the second charge (the first is at the origin of the coordinate system). This is

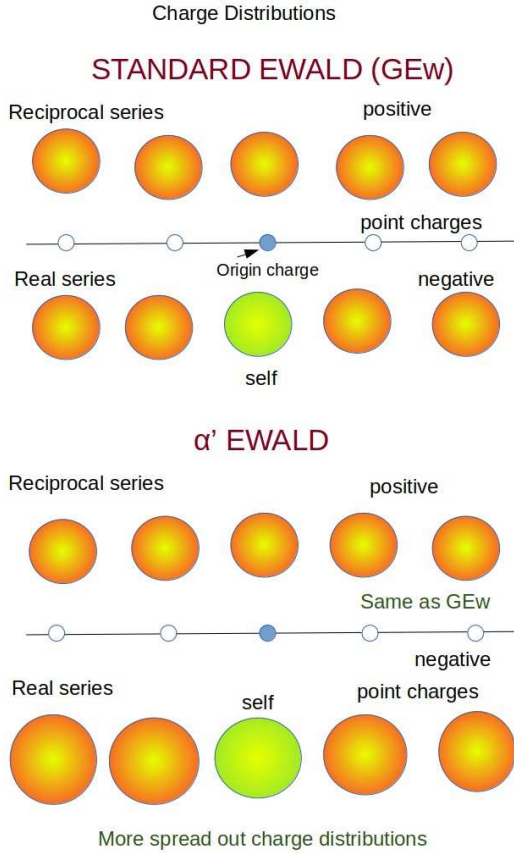


FIG. 2. A schematic diagram illustrating the difference between the standard Ewald method (GEw) and the α' variant where the charge distributions associated with the real space series and the self-energy are more spread out

the same analysis strategy as was used in Ref. 33. The formulas in Eq. (25) are used. The x -component of the force on the first charge, F_x , is also given. It may be seen that the use of $V_s(k_c)$ and v'_r noticeably improves the convergence of the total energy. In fact $k_c = 1$ can be used with very good accuracy for these relative charge separations. The number of k -vectors associated with k_c^2 equal to 1, 4, 9, 16 and 25 are 6, 33, 123, 257 and 515, respectively. This table suggests that a considerable saving in computer time could be achieved by adopting the h_c -corrected terms in the modified Ewald formula of Eq. (25). Table I also shows that data set, *a*, where the charges are close together has better relative convergence as k_c is lowered than data set, *b*, where the charges are further apart. Hence the α' method summarized in Eq. (25) is particularly well suited for the model chemical systems considered in this study where the charges relatively close compared to the simulation cell sidelength dominate the behavior. There could be certain exceptional real situations, however, in which the charged ions are weakly screened (*e.g.*, dilute solutions of organic ion pairs in low dielectric constant solvents, or NaCl in the vapor phase). In these cases longer ranged interactions closer to $L/2$, representing dissociated ions and other ions or ion pairs could also be important factors in determin-

TABLE I. The Coulomb potential energy in units of q/L at $(0,0,0)L$, from a cubic lattice containing a positive charge, q at $(0,0,0)L$ and a negative charge, $-q$, at $(x,y,z)L$ within the unit cell (L is the unit cell side length). For the first set of data, *a*, $(x,y,z)=(0.1,0,0)$, and for the second, *b*, $(x,y,z)=(0.25,0,0)$. The GEw method (series 6 in Ref. 33) was used. The reciprocal space summation was carried out for integer lattice vectors $\leq k_c^2$, with $\alpha = 5.556/L$. The real space summation was conducted for $r \leq L/2$. Key: V_0 is potential energy of the origin charge using the original GEw formulas with α . V' is the corresponding energy using α' where the formulas in Eq. (25) are used. $F_{x,0}$ and F'_x are the corresponding forces in the x -direction. α' is calculated using the formula in Eq. (23).

k_c^2	V_0	V'	$F_{x,0}$	F'_x	α'
1 ^{<i>a</i>}	-10.5010	-10.0313	90.9541	99.3873	3.20070
4	-10.2801	-10.1142	95.1652	98.0433	4.94598
9	-10.0751	-10.0482	98.7856	99.2473	5.46426
16	-10.0291	-10.0268	99.4730	99.5122	5.54789
25	-10.0217	-10.0216	99.5650	99.5668	5.55520
36	-10.0213	-10.0213	99.5686	99.5687	5.55555
1 ^{<i>b</i>}	-6.00442	-4.18040	7.34059	14.6453	3.20070
4	-4.91894	-4.35447	13.6043	15.2936	4.94598
9	-4.22804	-4.14047	15.0591	15.2935	5.46426
16	-4.15174	-4.14435	14.7754	14.7948	5.54789
25	-4.14360	-4.14326	14.7523	14.7532	5.55520
36	-4.14324	-4.14323	14.7535	14.7535	5.55555

ing the physical properties of the system. For these cases the α' method may require further optimization.

III. EWALD SIMULATION METHODOLOGY

This section focuses on details of how the GEw and α' simulations are optimally implemented. Some of the methodology is new to the literature, particularly Secs. III-D and E, while other parts are a clarification of known practices.

A. Molecule and Ion Descriptions

Molecular models representing the simple ionic salt caesium iodide (CsI), the polar liquid TIP3P water, and the room temperature ionic liquid (RTIL) 1-*n*-hexyl-3-methylimidazonium chloride, denoted [hmim]Cl, were used in this work, with full details available in Ref. 17. For the CsI model, the Lennard-Jones (LJ) σ parameter for the ions was changed from 3.924Å to 4.035Å in order to fit better the experimental density of 4.51g/cm³ at 298K and 1 atm pressure. The model for [hmim]Cl was also changed from Ref. 17 by scaling all the fixed partial charges by $1/\sqrt{2}$. This procedure exactly halves the forces between the original partial charges, and may be considered to account for dynamical polarization effects in a mean field sense. [18].

The models are all composed of point masses, which carry LJ interaction sites and point charges, though not always both. CsI is made up of simple point ions, while TIP3P water con-

sists of rigid molecules. The RTIL [hmim]Cl ion pair was composed of free Cl^- point ions, while the $[\text{hmim}]^+$ molecular cations were composed of 15 sites each (including 3 explicit hydrogen sites), with 34 constraints, leaving five torsional degrees of freedom per cation. The large number of constraints in the [hmim]Cl model replaced the many harmonic potentials that would otherwise be needed to maintain the molecular geometry with explicit intramolecular degrees of freedom. The constraints-based molecular model is less common than force-field based approaches in the literature, but can be very effective. Using a fast, accurate, and robust implementation of the SHAKE algorithm [19, 20] all constraints were iterated down to machine accuracy (*i.e.*, relative tolerance $< 10^{-14}$) each time step. This ensures time reversal symmetry was formally preserved when using the original Verlet integrator, [21] which just involved positions and forces. In addition, shadow Hamiltonians [17, 19] remained conserved to a high level of accuracy, proving that the equations of motion were being integrated correctly. The MD simulations were carried out in the NVE ensemble, with all forces evaluated every time step. The simulations were carried out using in-house codes written in modern FORTRAN, on readily available commodity CPUs, that employ standard IEEE-754 64 bit arithmetic.

For rigid TIP3P water, intramolecular forces are not considered part of the thermodynamic description of the system. Therefore, all intramolecular Coulomb interactions were removed in the manner of Sec. II-B of Ref. 17 in which any corresponding GEw r-space pair interaction, denoted by $Y(r)$, was replaced by the function $Z(r)$, where

$$Y(r) = \frac{q_i q_j}{r} \text{erfc}(\alpha r), \quad Z(r) = -\frac{q_i q_j}{r} \text{erf}(\alpha r), \quad (26)$$

with r the distance between charges, i and j . This removes the $q_i q_j / r$ intramolecular interactions from the computed system energy. If the α' method is used, rather than GEw, then α' replaces α in Eq. 26. For [hmim]Cl certain intramolecular Coulomb and LJ interactions do remain part of the model. These correspond to any variable distance interactions between sites that are at least four bonds apart. Since the [hmim]Cl model makes use of many constraints, there are no variable 1,2 or 1,3 intramolecular distances between sites, so the corresponding LJ interactions are omitted, while Coulomb interactions are removed in the manner of Eq. 26. Often variable distance 1,4 intramolecular interactions are modelled using a torsion angle potential which implicitly replaces the 1,4 Coulomb and LJ components too. In Ref. 17 such torsion angle potentials were omitted to allow the molecules to have heightened torsional flexibility for demonstration reasons, but the corresponding 1,4 Coulomb and LJ interactions were still removed. In this work the same scheme was used. For variable distance 1,5 or further apart intramolecular interactions, the Coulomb component was included, so partial charges at opposite ends of the $[\text{hmim}]^+$ cation do influence the conformational dynamics.

B. Improving Integration with Smoothing Potentials

It is now well-established[17, 19, 22–24] that the shadow Hamiltonian of an NVE MD simulation cannot be conserved when pair potentials are simply truncated at a finite value of r_c . Discontinuities in the force (and higher derivatives) prevent the equations of motion from being integrated correctly. This is manifested in NVE simulations as a rise in the total system energy with time, a phenomenon known as ‘energy drift’, which left unchecked will lead to increasingly large errors in the system’s dynamics and computed quantities. This is still the case even if a thermostat is used to remove the resulting drift energy, since the underlying equations of motion would still not be integrated properly and the calculated quantities would be in error as a result. Various methods have been developed to mitigate against drift, one of the most common and primary examples being the shifted forces method. [25] In Refs. 17 and 19 it was shown that drift can be almost completely eliminated by using smoothing potentials with the simple functional form

$$S(r) = \sum_{n=0}^{D_0} C_{2n} r^{2n}, \quad (27)$$

where D_0 is the number of potential energy derivatives to be set to zero at r_c . The potential $S(r)$ is added to any simulation pair potential between two sites (such as the LJ or r-space Ewald terms). The coefficients, $C_0, C_2, C_4, \dots$ can be determined in advance to ensure that the energy, force and any higher derivatives up to D_0 are all zero at r_c . As D_0 increases, the equations of motion can be integrated more accurately, though the perturbation to the system caused by $S(r)$ also increases. When $D_0 = 1$ then $S(r)$ behaves in a similar fashion to the shifted forces method, although it actually introduces a smaller system perturbation. However, $D_0 = 1$ is rarely sufficient to maintain conservation of the shadow Hamiltonian during an NVE simulation. If $D_0 = 4$ the energy drift can be reduced by six orders of magnitude, and so be virtually eliminated, and in principle equilibrium NVE simulations could be carried out well into the millisecond regime with no significant change in the average temperature. [17, 19] In this work a value of $D_0 = 2$ was used, which is sufficient to keep even the worst case temperature drift below $0.01\text{K}/\mu\text{s}$, and gives confidence that the equations of motions are integrated accurately.

In simulations with no smoothing treatment, the interactions between sites on two different molecules are often subjected to a molecular cut-off, based on the distance between molecular centres of mass. This is to prevent artefacts caused by unbalanced partial charge interactions between molecular fragments. However, smoothing potentials allow the truncation at r_c to be applied consistently, and individually, to every site-site interaction in the system. So with smoothing, molecular based cut-offs should actually be avoided, as they introduce new artefacts into a simulation, and can change the average pressure. This occurs since at each time step certain site-site interactions with $r < r_c$ will be omitted depending on the relative molecular orientations.

The smoothing potential, $S(r)$, is a perturbation to any modelled system, and will give rise to unphysical contributions to the energy, forces, and pressure. Typically, the smoothing contributions to the energy and pressure have very small standard deviations, and behave effectively as constant uniform backgrounds. Therefore these contributions can be excluded (under appropriate circumstances) when comparing simulation results with experimental data. Also, in a typical MD simulation, most of the smoothing energy and pressure originates from the attractive part LJ pair potentials. In contrast, for the Ewald r -space terms, charge sign differences lead to considerable cancellation of the corresponding smoothing energy and pressure, so these contributions tend to be very small.

C. Pressure Evaluation

The average pressure is defined from the thermodynamic definition $\langle P \rangle = - \langle (\partial H(\mathbf{r}, \mathbf{p}) / \partial V)_T \rangle$, where H is the Hamiltonian, and $\mathbf{r}$ and $\mathbf{p}$ denote the set of atom positions and momenta, respectively. It is important to calculate pressure accurately in simulations that include Coulombic forces, as the separate pressure components (*e.g.*, Coulomb or LJ) can individually be large in magnitude ($> 10^4$ atm) and of different sign, which largely cancel out, to give a much smaller resultant value for $\langle P \rangle$.

In this work, MD simulations were conducted with either point charge ions, or molecular units whose maximum extent was smaller than half the length, L , of the cubic simulation box. This means the concept of a molecular pressure can be applied simply in the context of periodic boundary conditions (PBCs). In an NVE simulation employing PBCs the system is thermodynamically stable provided the ‘integrator’ pressure, P_I , is positive. P_I is the pressure before the addition of any long range correction terms (LRCs) that are not associated with the integration of the equations of motion. If $P_I < 0$ then the system wants to contract, but cannot do so due to PBCs, and so is metastable. LRCs may make the final pressure have a negative value, but they are not related to thermodynamic stability for NVE and NVT ensembles. This will not be the case for NPT dynamics, however, as the LRC to the pressure will affect the thermodynamic state adopted by the system (note the LRC depends on the current volume of the simulation cell).

Pressure from the forces

In this work, all molecular units had sufficient rigidity (via constraints) to make them geometrically invariant, and retain their original size and conformation, on volume differentiation (or isotropic volume scaling) of the simulation cell. Even flexible polyatomic ions fall into this class, if all the bond lengths between adjacent sites are held constant by constraints. Bond angles and torsion angles are always invariant to affine dilation or contraction, and therefore any occurrence of these in the system should make no contribution to the pressure. This leads to a simplification of the expressions for the pressure, and drawing on previous work [41, 64–66] the total pressure, P^{mol} , is conveniently expressed as the sum of the following

contributions

$$\begin{aligned} P^{\text{mol}} &= \frac{1}{3\Omega} \langle P^A + P^B + P^C + P^D \rangle, \\ P^A &= \sum_I M_I \dot{\mathbf{R}}_I^2, \\ P^B &= \sum_I \sum_i \sum_{j>I} \sum_j \frac{dU(r_{Iij})}{dr} r_{Iij}, \\ P^C &= \frac{1}{4\epsilon_0\Omega} \sum_{\mathbf{h}} (1/h^2 - 1/2\alpha^2) \exp(-h^2/4\alpha^2) \\ &\quad \times \left| \sum_I \sum_i q_{Ii} \exp(i\mathbf{h} \cdot \mathbf{r}_{Ii}) \right|^2, \\ P^D &= - \sum_I \sum_i \mathbf{F}_{Ii}^T \cdot \mathbf{d}_{Ii}, \end{aligned} \quad (28)$$

where Ω is the MD cell volume. The first term, P^A , is the kinetic component of the pressure, where $\dot{\mathbf{R}}_I$ and M_I are the center-of-mass (CoM) velocity and mass of molecule, I . In an NVE ensemble, where the total linear momentum is constant, a direct calculation of CoM velocities during a simulation is more accurate than using the expression, $P^A = \rho k_B \langle T \rangle$, at the end of a simulation, where k_B is Boltzmann’s constant and ρ is the molecular number density. In this work the velocities, $\dot{\mathbf{R}}_I$, were computed using a 6th-order central difference formula, as discussed in Refs. 17 and 19. Second order velocities lead to a systematic time step dependent underestimation of the pressure, which can exceed 10 atm for typical TIP3P water simulations carried out with $\delta t = 2\text{fs}$. This error can exceed the statistical error in $\langle P^{\text{mol}} \rangle$ itself.

Any intermolecular site-site pair potentials, $U(r_{Iij})$, where r_{Iij} is the distance between site i on molecule I , and site j on molecule J , contribute to the pressure component, P^B . Note the summation excludes any $J = I$ terms, as there are no intramolecular pair potential contributions to P^B . The pair potential, $U(r_{Iij})$, will be the sum of any LJ, Ewald r -space $Y(r)$, and smoothing $S(r)$ potentials, up to a distance $|r_{Iij}| \leq r_c$. All $dU(r_{Iij})/dr$ terms will decay smoothly to zero at r_c , due to the addition of the $S(r)$ potentials.

The k -space contribution to the pressure, P^C , involves all charges q_{Ii} , and all k -vectors with $0 < k \leq k_c$, where $k = |\mathbf{h}|L/2\pi$ are normalized k -vector magnitudes. As k_c^2 is always an integer, then k_c can only take certain discrete values in P^C . The terms involving α in Eq. (28) are only appropriate for GEw simulations, and alternative expressions for P^C would be needed for different charge spreading functions. The last term on the right hand side of the equation for P^C , is the conjugate square of the structure factor, and the i factor within the exponential denotes $\sqrt{-1}$. Note that the Ewald self-energy terms make no contribution to the pressure.

The last contribution in Eq. (28), P^D , is known as the ‘molecular virial correction’ (MVC), where $\mathbf{d}_{Ii}$ is the vector from the CoM of molecule I to site i , and $\mathbf{F}_{Ii}^T$ is the total force acting on site Ii resulting from all k -space terms, and all intermolecular pair potential terms. Intramolecular pair potential forces, and all constraint forces, are omitted from $\mathbf{F}_{Ii}^T$ (note that such forces sum to zero across a molecular unit). Constraints therefore have an indirect effect on the pressure, just as they do for the total system energy, but it is their presence

that gives rise to the P^D term, see Ref. 65. For point ions, such as Cs^+ or Cl^- , then $\mathbf{d}_{li} = \mathbf{0}$, and consequently, $P^D = 0$.

Coulomb pressure from the energy

It is also possible to calculate the Coulomb contribution to the pressure, by a different route, which we call the ‘energy method’ (EM) expression. The virial of a system of free point charges is proportional to the negative of their total Coulomb energy, U_C (calculated from Eq. (1)), from which it follows that, $P_{\text{em}} = U_C/3\Omega$. However, systems that contain intramolecular Coulomb interactions (as opposed to simple free ions) often need careful treatment when using the EM method. Intramolecular energy terms can remain invariant with respect to volume differentiation of the simulation cell, due to the presence of constraints, and hence will not contribute to the EM pressure. These considerations lead to the following formula for the EM pressure,

$$\begin{aligned} P_{\text{em}} &= \frac{1}{3\Omega} \langle U_C + U_Z + P^E \rangle, \\ U_Z &= \sum_I \sum_i \sum_{j>i} Z(r_{Iij}) - Y(r_{Iij}), \\ P^E &= - \sum_I \sum_i \mathbf{F}_{li}^C \cdot \mathbf{d}_{li}. \end{aligned} \quad (29)$$

The term, U_Z , accounts for the situation in which a model molecule has a certain number of non-excluded intramolecular Coulomb interactions (which is the case for $[\text{hmim}]^+$ cations, but not for TIP3P water). While such interactions contribute to U_C , in the normal way, the presence of constraints means their volume derivative is actually zero. Therefore since from Eq. (26), $Z(r) - Y(r) = -q_i q_j / r$, the U_Z term subtracts such energy terms out from U_C to ensure the energy-based pressure calculation is correct.

The presence of constraints also means that P_{em} needs the MVC term, P^E in Eq. (29). Here $\mathbf{F}_{li}^C$ is the total Coulomb force on site li resulting from all k-space and intermolecular Ewald r-space terms. In addition, every intramolecular Coulomb interaction contributes to $\mathbf{F}_{li}^C$ using forces based on $Z(r)$, and not $Y(r)$ (even if these interactions normally contribute $Y(r)$ forces into the MD integrator).

For point ions, $U_Z = 0$, and since $\mathbf{d} = \mathbf{0}$, then the expression, $P_{\text{em}} = U_C/3\Omega$, is obtained, as expected. For TIP3P water, each molecule has all three intramolecular Coulomb interactions (two O-H and one H-H) excluded from the model thermodynamics. There are no included intramolecular interactions, and therefore, $U_Z = 0$. The contribution to P^E from the three $Z(r)$ intramolecular Ewald terms is a constant throughout a simulation, as expected for a fully rigid species. A typical value of P^E in this work, for TIP3P water, is $\approx -2300 \pm 10^{-12}$ atm. The extremely small standard deviation is an indication of how well the constraints are maintained *i.e.*, to < 1 part in 10^{14} .

For $[\text{hmim}]^+$ cations, 11 out of 15 sites carry a partial charge, giving rise to 55 intramolecular Coulomb interactions per cation. Of these, 41 are excluded from the model thermodynamics (just like the three for TIP3P water) but 14 remain, and these contribute fully to the system Coulomb energy, U_C . However constraints mean their volume derivative is zero, so U_Z for a $[\text{hmim}]^+$ cation is composed of 14 terms of the form

$Z(r) - Y(r)$. For P^E , all 55 intramolecular Coulomb interactions make a contribution to $\mathbf{F}_{li}^C$ via the $Z(r)$ pair potential terms. Since the cation is flexible, and some partial charges can move relative to each other, P^E varies every time step, with a standard deviation of ≈ 1 atm.

The total system pressure can be evaluated using Eq. (28) alone, or the non-Coulomb parts can be found from appropriate terms of Eq. (28), with the Coulomb contribution being provided by Eq. (29). Either method will yield an identical average pressure, $\langle P \rangle$, in the limit of large r_c and k_c , although their instantaneous pressure fluctuations will be different. If we define P_C^{mol} as the Coulomb contribution to P^{mol} , then with increasing r_c and k_c , the expression P_{em} will converge faster than P_C^{mol} , and so can save computational resources. Also the EM route might be considered a more accurate way of finding the Coulomb pressure, given fixed r_c and k_c . However, any approximation in the calculation of U_C will cause P_{em} to deviate from the true simulation Coulomb pressure (which can always be found using Eq. (28)). Also P_{em} is only valid for simulations that use a formally correct method (such as the Ewald summation) to reproduce the long ranged Coulomb $1/r$ interaction. More approximate methods (*e.g.*, reaction field, Wolf Potentials, shifted force potentials [29]) including the new α' method of Eq. (25) should not use the P_{em} definition of pressure as the fundamental Coulomb relation $P_{\text{em}} = U_C/3\Omega$ is no longer valid. The quantity

$$\Delta_P = P_C^{\text{mol}} - P_{\text{em}}, \quad (30)$$

is therefore a key measure of the accuracy of the implementation of the long range $1/r$ Coulomb interactions within a simulation. If Δ_P is statistically different from zero, then a deviation away from the $1/r$ law is certainly present.

For LJ interactions, standard LRCs are applied beyond r_c to correct the pressure.[45] The repulsive part of such LRCs should not be omitted, as with a relatively short r_c this contribution can exceed the statistical error in $\langle P \rangle$. Simple LRCs are inaccurate for crystalline systems, as $g(r)$ does not tend to 1 until very large r , particularly at low temperature. A possible solution is to use the Ewald method for LJ interactions too, for systems where $g(r)$ is not ≈ 1 beyond r_c , [67] but this has not been pursued in this work. The $S(r)$ smoothing potentials (see Eq. (27)) have no LRCs, since they are only defined for $r \leq r_c$.

D. Estimating the r_c and k_c truncation errors

GEW summations would ideally use very large values for r_c and k_c , to ensure accurate calculation of the Coulomb energy, forces and pressure. However, in practice, both r_c and k_c have more modest values to keep CPU times down. Therefore it is important to know the effects introduced by the r_c and k_c truncation. The Kolafa & Perram (KP) force error estimates [42] have been used for several decades for this purpose. However, the approximations inherent in KP estimates means they are inaccurate for crystalline systems, and simulations that employ particularly small k_c values. Since a major aspect of this work is to show that simulations can be performed using lower

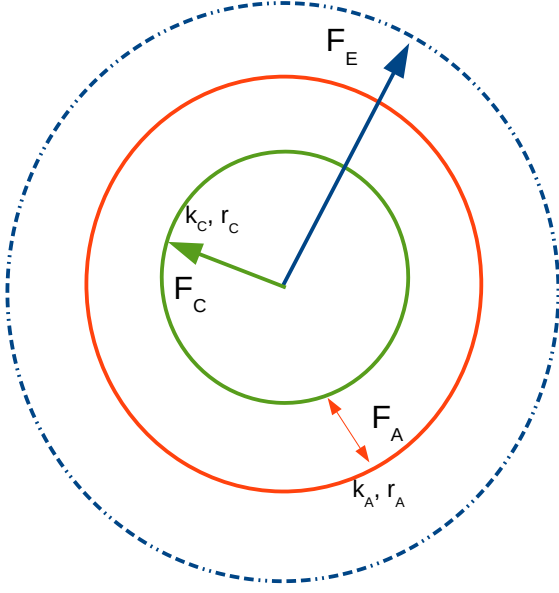


FIG. 3. Schematic drawing of the ‘extended shell’ (ES) method (see Sec. III-D). Every time step, Ewald forces are evaluated using $r < r_c$ and $k \leq k_c$, and used in the MD integrator. Every *ca.* 25 time steps, the energy, pressure, and other quantities are also determined using r_c and k_c . To estimate the effects of the r_c, k_c truncation, every *ca.* 100 time steps, the energy, pressure, and forces, $\mathbf{F}_A$, are also determined in the (‘extended’) region $r_c < r < r_A$ and $k_c < k \leq k_A$. These are known as ‘ES corrections’. The values of r_A, k_A are chosen so that contributions from beyond are of no statistical significance.

k_c than was hitherto thought possible, it is important to have more reliable estimates of the energy, force, and pressure perturbations associated with truncated r_c and k_c .

Figure 3 shows a schematic diagram of an ‘extended shell’ (ES) scheme which allows the effects of r_c and k_c truncation to be quantified accurately with little extra CPU cost. In this procedure, the simulation is conducted with the default values of the r_c and k_c truncations, but at well-separated time steps the additional energy using a larger truncation in real and reciprocal space is calculated. The contributions from the shells bounded by $r_A - r_c$ and $k_A - k_c$ do not affect the dynamics, but play a similar role to the ‘long-range corrections’ employed in Lennard-Jones simulations, for example. The ES corrections are averaged over the simulation, and then combined with the average energies from $r \leq r_c$ and $1 \leq k \leq k_c$, to provide a more accurate final value for the Coulomb energy and pressure. ES forces are not included in the MD integrator, but they can be used to determine the perturbations from the true force arising from the r_c and k_c truncation, this being more accurate than the KP error estimates. For an α' simulation (*i.e.*, one based on Eq. (25)) the k-space component of the ES corrections is taken to be zero, as the α' method implicitly accounts for the truncation at k_c , but r -space ES corrections are still valid. Suitable values of r_A and k_A , for a particular simulation, can be determined by requiring the sum of ‘missed out’ ES corrections beyond r_A and k_A (the outermost ring in Fig. 3) to have magnitudes below the standard errors in the mean for the simulation’s Coulomb energy, total force, and total pressure.

These statistical errors are denoted $\sigma_{\langle U_C \rangle}$, $\sigma_{\langle F \rangle}$, and $\sigma_{\langle P \rangle}$, respectively. The magnitude of ‘missed out’ r -space and k -space ES corrections can be found, as a function of r_A and k_A , by using histogram techniques within short simulations of $\approx 10^4$ time steps. For the simulations in this work, r_A and k_A were set so that any ‘missed out’ ES corrections were a factor of 10 below the production run values of $\sigma_{\langle U_C \rangle}$, $\sigma_{\langle F \rangle}$, and $\sigma_{\langle P \rangle}$, so it was certain that nothing of statistical significance was omitted. Since for α' simulations, k -space ES corrections are not required, only the value of r_A need be determined, but for consistency, r_A was set to $L/2$ for all α' simulations in this work.

The optimal frequency for calculating the ES extended distance and reciprocal lattice vector corrections can be determined from the statistical inefficiencies of the saved ES data sets. For the CsI melt this equates to *ca.* every 400 time steps, but for all production simulations in this work, a frequency of once every 100 time steps was used. The evaluation of ES corrections typically increases the total simulation CPU time by only a few percent, but yielded considerably more accurate values for the computed energy and pressure. In Ref. 17 the magnitude of the k -space force errors was evaluated using a rudimentary version of the ES method, which has been developed more fully in this work.

E. Ewald Force Perturbations

Since the forces acting on particles are of primary importance in MD, it is desirable to know the extent to which the ideal Coulomb forces are perturbed by the r_c and k_c truncations, and by the addition of any smoothing potentials used to conserve the shadow-Hamiltonian. The truncation perturbation forces within an Ewald MD simulation can be defined as follows

$$\begin{aligned} \mathbf{F}_E &= \mathbf{F}_C + \mathbf{F}_a \\ \mathbf{F}_E &= \text{forces within a perfect Ewald calculation } (r_c, k_c \rightarrow \infty) \\ \mathbf{F}_C &= \text{forces when } r \leq r_c, k \leq k_c \\ \mathbf{F}_a &= \text{additional forces due to } r_c < r \leq \infty, k_c < k \leq \infty. \end{aligned} \quad (31)$$

The Coulomb related forces incorporated within the MD integrator are,

$$\mathbf{F}_I = \mathbf{F}_C + \mathbf{F}_S, \quad (32)$$

where $\mathbf{F}_S$ represents any applied Ewald r -space smoothing force (see Sec. III-B). From Eq. (31) this gives

$$\mathbf{F}_I = \mathbf{F}_E - \mathbf{F}_a + \mathbf{F}_S, \quad (33)$$

from which the total perturbation force $\mathbf{F}_P$ (the difference between integrator forces and exact Ewald forces) can be defined as

$$\begin{aligned} \mathbf{F}_P &= \mathbf{F}_I - \mathbf{F}_E, \\ &= \mathbf{F}_S - \mathbf{F}_a. \end{aligned} \quad (34)$$

In an MD code, $\mathbf{F}_C$ and $\mathbf{F}_S$ are calculated exactly, and a very good estimate of $\mathbf{F}_a$ comes from the forces $\mathbf{F}_A$ calculated by

the ES method (Sec. III-D and Fig. 3), in which r_A and k_A replace ∞ in the last line of Eq. (31). The root mean square (rms) magnitude of $\mathbf{F}_P$,

$$F_P^{\text{rms}} = \left\langle \left(\frac{1}{N} \sum_{i=1}^N (\mathbf{F}_P^i)^2 \right)^{1/2} \right\rangle, \quad (35)$$

gives a measure of the force perturbation, where $\langle \dots \rangle$ denotes an average over simulation configurations, and $\mathbf{F}_P^i$ is the perturbation force acting on site i . The quantity F_P^{rms} can be normalized by the corresponding rms of the total force acting on sites, F_T^{rms} , composed from all contributions within the system, including any LJ and constraint forces. Thus the quantity

$$\Delta_F = F_P^{\text{rms}} / F_T^{\text{rms}}, \quad (36)$$

can be treated as a measure of the simulation accuracy. This analysis of the Ewald perturbation forces is only possible because actual vector estimates for $\mathbf{F}_A$ can be calculated using the ES method. It cannot be performed with KP (or similar) force error estimates, as they only yield a single scalar number.

IV. RESULTS AND DISCUSSION

Microcanonical ensemble (NVE) molecular dynamics simulations were performed to demonstrate the methodology of Secs II and III, using the basic MD simulation parameters given in Table II. The r_c values used were relatively short, moving more of the Coulomb calculation into k-space. This reduced the r-space computational effort as the average number of r-space force interactions evaluated per site per time step, $N(r_c)$ scales approximately as ρr_c^3 .

Table III presents the Ewald parameters for four classes of simulation involving different phases and types of chemical system, which are denoted by :1 to :4. The :1 class are accurate GEw simulations in which α and k_c were tuned so all the ES corrections were equal or below the corresponding statistical errors. The :1 calculations therefore give essentially exact results for their lengths. If longer simulations were conducted the statistical errors would fall, and consequently α and k_c would need to be larger. The :2 computations are GEw simulations with lower α and k_c values. The :3 GEw simulations had very low α and k_c values. The :4 cases are α' simulations where $k_c^2 = 6$, which is an exceptionally low value. The κ' values for :4 runs are very close to 7 in Table III.

Table III summarizes the performance characteristics of the different model chemical systems, primarily in terms of the nominal number of k-vectors required to calculate the k-space forces within the MD integrator, $N(k_c)$, and the corresponding number for the ES corrections, $N(k_A)$. However, in practice the k-vector based computations can be reduced, and these values are denoted by $N^{\text{opt}}(k_c)$ and $N^{\text{opt}}(k_A)$, respectively. This is because a typical MD code will exclude half of all k-vectors, as the contributions from $\mathbf{k}$ and $-\mathbf{k}$ are identical, hence the remaining forces are doubled. Only half the actual

number of k-vectors need to be considered explicitly. Further optimization is possible since when a cartesian component β of a k-vector is zero then $\exp(ik_\beta r_\beta) = 1$ and the computation of that element is faster. For example, for the case $\mathbf{k} = (1, 0, 0)$ the force can be calculated three times faster than for $\mathbf{k} = (1, 1, 1)$. Therefore, $N^{\text{opt}}(k_c)$ and $N^{\text{opt}}(k_A)$ are measures of the computational effort required.

The proportion of such zero components rises as k_c falls, reaching 25% when $k_c^2 = 6$. Thus $N^{\text{opt}}(k_c)$ is always less than $N(k_c)/2$ in Table III. The effective computational effort needed to calculate the ES corrections is minor, as they are only evaluated once every 100 time steps. Consequently, $N^{\text{opt}}(k_A)$ is always much smaller than $N(k_A)$.

The CsI crystal simulations were performed at 295 K. For the TIP3P water and CsI melt systems, the respective temperatures were 323 K and 1230 K, these being midway between experimental melting and boiling points. Calculations of 10^6 time steps were sufficient to obtain good statistics for the CsI and water systems. For the [hmim]Cl system, the temperature was set at 373 K, this being the upper limit of what might be considered to be a ‘room temperature’ ionic liquid. A higher temperature was chosen to enhance the rate of exploration of the phase space, which gave a [hmim]⁺ cation diffusion coefficient of $3.5 \times 10^{-6} \text{ cm}^2/\text{s}$. Simulations of 4×10^6 time steps (12.8 nanoseconds) were needed to produce rapid convergence of statistical errors, estimated using the block averaging technique. For all simulations, the data were saved every 25 time steps, with ES corrections only being calculated every 100 time steps.

Calculated quantities from benchmarking simulations are given in Tables IV to VII for the different chemical systems. The energies, forces and pressures are given in model LJ reduced units per site, which are the same units as those used in Figs 4 to 8. By comparing the quantity averages from the simulations through the series, :1 to :4, the trends introduced by lowering α and k_c can be quantified, as well as the effect of switching from GEw to α' simulations at very low k_c .

The uncorrected Coulomb energy, U_C and its statistical error were calculated. The corresponding ES correction Coulomb energy is denoted by U_C^{ES} . For all the :1 simulations, the value of U_C^{ES} was equal to or less than the statistical error in U_C , which confirms that the :1 class of simulation gave essentially exact GEw properties.

Figure 4(a) presents the Coulomb potential energy component, U_C , as a function of k_c for the model CsI crystal. The ES corrections greatly improve the accuracy for low k_c GEw, bringing them very close to the exact U_C value. This is also the case for α' simulations, where the limiting U_C is recovered at $k_c^2 = 6$. Such good results might be expected for the ordered environment of a crystal. In the CsI melt, shown in Fig. 4(b), both the low k_c GEw simulation, and the α' simulation at $k_c^2 = 13$ give excellent agreement with the exact result. For the molecular TIP3P water and [hmim]Cl systems, the deviation of U_C away from exact values is much less than for CsI as k_c is reduced, and the size of U_C^{ES} corrections are also much smaller. This is not surprising as Coulomb interactions in point ion systems are typically larger than those between partial charges on molecular sites. An accurate estimate of

TABLE II. NVE simulation parameters used in the simulations of the four system types. N is the total number of sites, δt the time step, ρ the density, and L the box length. The r-space cut-off is r_c , while $N(r_c)$ is the average number of r-space force interactions evaluated per site per time step. $P_{\text{LJ-LRC}}$ is the Lennard-Jones (LJ) long range pressure correction (see Sec. III-C). Values of $\delta t, \rho, L, r_c$, and $P_{\text{LJ-LRC}}$ are given in model LJ reduced units. For the systems used in this work we chose one of the LJ interactions to represent the unit of energy and length. In the case of CsI and TIP3P there is only one LJ interaction, but for the RTIL there are several, and the N-N interaction was chosen. For CsI the LJ σ was 4.035 Å and ϵ/k_B was 257.4 K. The corresponding numbers for the model water molecule were, 3.1506 Å and 76.58 K. For [hmim]Cl these number are 3.25 Å and 85.548 K. The energy and pressures herein were given in these basic units, specific to each system. P_{atm} is the pressure conversion factor from model LJ reduced units to atm.

System	N	δt	$\delta t/\text{fs}$	ρ	$\rho/(\text{g}/\text{cm}^3)$	L	r_c	$r_c/\text{\AA}$	$N(r_c)$	$P_{\text{LJ-LRC}}$	P_{atm}
CsI _C (crystal)	1024	0.0032	10.18	1.391	4.567	9.029	2.646	10.7	56.0	-1.747	533.9
CsI _M (melt)	1024	0.0022	7.00	0.877	2.880	10.530	3.08	12.4	53.3	-0.441	533.9
TIP3P water	1536	0.005044	2.00	3.02682	0.965	7.976	2.5	7.9	97.7	-1.089	338.1
[hmim]Cl	2048	0.002396	3.20	1.565	0.959	10.938	3.2	10.4	103.4	-1.347	339.6

TABLE III. Ewald related parameters used in the simulations. The splitting parameter is α and $\kappa = \alpha L$, where L is the simulation cell length from Table II. Corresponding values are given for α' simulations. The k-space cut-off is k_c (where k_c^2 is an integer) and $N(k_c)$ is the corresponding number of k-vectors. The extended shell (ES) cut-offs are k_A and r_A , while $N(k_A)$ is the number of additional k-vectors considered. $\langle T \rangle$ is the average simulation temperature in Kelvin. The α, α' and r_A parameters are given in model LJ reduced units.

Run	α	κ	α'	κ'	k_c^2	$N(k_c)$	$N^{\text{opt}}(k_c)$	k_A^2	$N(k_A)$	$N^{\text{opt}}(k_A)$	r_A	$\langle T \rangle / \text{K}$
CsI _C :1	1.274	11.503	-	-	113	5040	2342	192	6034	29.0	$r_c + 0.34$	295.15(3)
CsI _C :2	1.002	9.047	-	-	53	1646	735	82	1472	6.9	$r_c + 0.96$	295.09(3)
CsI _C :3	0.816	7.368	-	-	20	388	160	64	1720	8.0	$r_c + 1.78$	295.09(3)
CsI _C :4	1.000	9.029	0.772	6.970	6	80	30	-	-	-	$L/2$	294.98(3)
CsI _M :1	0.984	10.362	-	-	98	4066	1881	125	1820	8.6	$r_c + 0.30$	1229.8(2)
CsI _M :2	0.898	9.456	-	-	69	2468	1124	105	2084	9.9	$r_c + 0.58$	1230.2(2)
CsI _M :3	0.695	7.318	-	-	18	340	140	69	2128	9.8	$r_c + 1.60$	1229.7(2)
CsI _M :4	0.850	8.951	0.660	6.945	6	80	30	-	-	-	$L/2$	1229.3(2)
TIP3P:1	1.231	9.819	-	-	93	3790	1749	129	2396	11.4	$r_c + 0.30$	322.89(5)
TIP3P:2	1.127	8.989	-	-	62	2102	955	106	2522	11.9	$r_c + 0.56$	322.83(5)
TIP3P:3	0.911	7.266	-	-	21	436	184	61	1570	7.2	$r_c + 1.24$	322.88(5)
TIP3P:4	1.100	8.774	0.864	6.889	6	80	30	-	-	-	$L/2$	322.81(5)
[hmim]Cl:1	0.895	9.790	-	-	69	2468	1124	93	1322	6.2	$r_c + 0.18$	373.1(2)
[hmim]Cl:2	0.864	9.450	-	-	59	1934	875	88	1496	7.0	$r_c + 0.30$	372.5(2)
[hmim]Cl:3	0.680	7.438	-	-	25	514	217	54	1228	5.7	$r_c + 1.22$	372.9(2)
[hmim]Cl:4	0.850	9.297	0.644	7.049	6	80	30	-	-	-	$L/2$	372.5(2)

the total potential energy (including LJ terms) in the limit of infinite r_c, k_c is

$$U_{\text{final}} = U_C + U_C^{\text{ES}} + U_{\text{LJ}} + U_{\text{LJ-LRC}}, \quad (37)$$

where $U_{\text{LJ-LRC}}$ is the Lennard-Jones long range correction. Unphysical smoothing energy terms are excluded from Eq. (37), since these tend to zero for infinite r_c . The values of U_{final} in Tables IV to VII do not vary significantly from :1 to :4, showing that even very low k_c simulations can give accurate energies.

In Tables IV to VII, F_T^{rms} is the total rms force magnitude from all integrator contributions (*i.e.*, Coulomb, LJ, constraints and smoothing). The statistical error for this whole system quantity is also given. F_C^{rms} is the Coulomb rms force magnitude alone. Note that the ES correction forces are not included, as these are not used to integrate the equations of motion. The quantity Δ_F is related to the size of Ewald perturbation forces, see Eq. (36). The k-space and r-space Kolafa-Perram force error estimates are denoted F_k^{KP} and F_r^{KP} while

the corresponding, and much more accurate, ES force corrections are denoted by F_k^{ES} and F_r^{ES} . For some simulations, the KP errors are over an order of magnitude too large (*e.g.*, see run TIP3P:3 in Table VI) and are therefore not suitable for optimizing such simulations.

Figure 5 shows the k_c dependence of the Coulomb component of the force F_C^{rms} and the total force, F_T^{rms} , which includes all system contributions (*i.e.*, Coulomb, LJ, constraints, and smoothing). Fig. 5(a) is for TIP3P water and Fig. 5(b) is for [hmim]Cl. It is notable how little variation there is in F_T^{rms} and F_C^{rms} with k_c , particularly for TIP3P water. For [hmim]Cl it is the very low k_c and α' cases that show closest agreement with the limiting values. TIP3P water is unique among the systems in this work in having $F_C^{\text{rms}} > F_T^{\text{rms}}$, which is due to the large number of closely spaced H and O sites on different molecules. This gives rise to large Coulombic forces, which are mitigated by the LJ and constraint force components.

The integrator pressure, P_I in Tables IV to VII, is P^{mol} (Eq. (28)) before any long range corrections are included, and

TABLE IV. Calculated thermodynamic quantities from CsI crystal simulations carried out at 295 K. The first column of data is the ‘exact’ result and the last column is for the α' method. See Sec. IV for the definitions of the quantities in this table.

Simulation	CsI _c :1	CsI _c :2	CsI _c :3	CsI _c :4
U_C	-145.0601(6)	-145.2125(6)	-145.4504(6)	-145.6827(6)
$U_C + U_C^{\text{ES}}$	-145.0595	-145.0583	-145.0561	-145.0633
$\sigma_{S_C}/\sigma_{U_C}$	0.000068	0.0043	0.051	0.088
U_{Final}	-147.5696	-147.5700	-147.5560	-147.5587
F_T^{rms}	80.52(1)	80.52(1)	80.32(1)	80.13(1)
F_C^{rms}	37.19	37.17	37.08	36.88
$\log_{10}(\Delta_F)$	-3.78	-3.00	-2.00	-2.04
$F_k^{\text{KP}}/F_k^{\text{ES}}$	4.5	3.7	12.0	-
$F_r^{\text{KP}}/F_r^{\text{ES}}$	3.0	4.5	6.6	7.1
P_l	3.994(3)	4.737(3)	3.458(3)	3.139(3)
P_{Final}	-0.070	-0.080	-0.005	0.073
P_{em}	-67.260	-67.330	-67.441	-67.548
$P_{\text{em}}^{\text{ES},k}$	0.000	0.055	0.003	-
$P_{\text{em}}^{\text{ES},r}$	0.000	0.016	0.179	0.287
P_C^{mol}	-67.261	-66.720	-69.018	-69.761
$P_C^{\text{mol,ES},k}$	-0.002	-0.795	-0.044	-
$P_C^{\text{mol,ES},r}$	0.004	0.256	1.804	2.552
ΔP	0.000	0.000	0.000	0.052
k-space speed up	1	3.2	14	78

is positive in all cases (indicating thermodynamic stability). The statistical error for this whole system quantity is also given. The estimate of the pressure in the limit of infinite r_c and k_c is

$$P_{\text{Final}} = P^{\text{mol}} + P_C^{\text{mol,ES}} + P_{\text{LJ-LRC}} - P_S, \quad (38)$$

where $P_C^{\text{mol,ES}}$ is the ES Coulomb pressure correction, P_S is the unphysical contribution to the pressure due to the smoothing forces, and $P_{\text{LJ-LRC}}$ is the long-range correction to the Lennard-Jones pressure. The :4 α' simulations have slightly higher pressures than the GEw cases. Breakdowns of the Coulomb pressure contributions for CsI (crystal), CsI (melt), water, and the RTIL are given in Tables IV to VII, respectively, for both the faster converging P_{em} ‘energy method’ (see Eq. (29)), and the slower to converge but formally correct, P^{mol} method. The corresponding k-space and r-space ES corrections are also given in the tables. For all the (‘exact’) :1 simulations, the ES corrections for P_{em} are zero within statistical error, indicating that the P_{em} pressure had converged fully. Slightly higher α, k_c values would be needed for the ES corrections to P^{mol} to be essentially zero.

Figure 6 presents the average simulation pressure calculated for the same CsI simulations as for Fig. 4. Figure 6(a) shows the pressure for the CsI crystal, and Fig. 6(b) is for the CsI melt as a function of k_c . The figure shows how P_l and P_{Final} vary with k_c in both cases. For the crystal, the figure indicates that the values of P_{Final} for $k_c \leq 6$ α' are in good agreement with the exact GEw value. In the CsI melt case, the P_{Final} agreement with α' is not so good, but the increase in pressure seen for the α' model is minor in absolute terms by MD standards for such systems. Similar results to the CsI melt were obtained for TIP3P water and [hmim]Cl, which is not surprising as they are also liquids.

Figure 7 shows the important quantity, ΔP , defined in

Eq. (30) for the four chemical systems, which in effect gives a measure of how closely a simulation implements the Coulomb $1/r$ law. It is seen that ΔP remains at zero, within statistical error, for all the GEw simulations of every system. This shows that even very low α and k_c GEw simulations still maintain the formal $1/r$ Coulomb law, and that the large ES corrections for the :3 simulations must be very accurate. For the α' runs, the approximations introduced by Eq. (25) do result in some deviation away from the $1/r$ Coulomb law, but at very low k_c the magnitude of ΔP becomes relatively small. Therefore, in an α' simulation, the Coulomb pressure is slightly less negative, and consequently the charged particles behave as if they were very slightly larger. Within a constant pressure simulation, a very small increase in the cell volume would compensate for this.

The last row in Tables IV to VII is denoted ‘k-space speed up’ and shows the relative k-space CPU saving compared to the ‘exact’ :1 simulations. These are determined from the $N^{\text{opt}}(k_c)$ and $N^{\text{opt}}(k_A)$ values given in Table III. For :3 runs, and particularly for the :4 α' runs, the speed up factors are dramatic, and virtually eliminate the k-space CPU, so the r-space interactions then dominate the simulation CPU time. Since the r-space cut-offs, r_c , were also set to fairly low values in this work, then both :3 and :4 simulations represent very fast charged particle simulations, with little compromise on the accuracy of the resulting forces, energies and pressures.

Constant volume heat capacities obtained from α' simulations never deviate by more than 3% from exact GEw results. Pair correlation functions, $g(r)$, are almost indistinguishable between exact GEw and α' simulations, indicating that the structural differences with the α' simulations are negligible. Correlation and relaxation times for some quantities do decrease slightly in very low k_c α' simulations, and this is expected, as the simulations become more like short r_c pair-

TABLE V. Simulation data from the CsI melt simulations at 1230 K. The first column of data corresponds to the ‘exact’ result and the last column is for the α' method. See Sec. IV for definitions of the quantities.

Simulation	CsI _M :1	CsI _M :2	CsI _M :3	Cs _M I:4
U_C	-132.851(2)	-132.877(2)	-132.777(2)	-132.716(2)
$U_C + U_C^{\text{ES}}$	-132.850	-132.859	-132.851	-132.910
$\sigma_{S_C}/\sigma_{U_C}$	0.00091	0.0026	0.053	0.084
U_{Final}	-131.325	-131.333	-131.299	-131.347
F_T^{rms}	149.34(3)	149.43(3)	149.35(3)	149.27(3)
F_C^{rms}	101.00	100.99	100.85	100.60
$\log_{10}(\Delta_F)$	-3.63	-3.00	-2.00	-2.05
$F_k^{\text{KP}}/F_k^{\text{ES}}$	1.1	0.8	5.3	-
$F_r^{\text{KP}}/F_r^{\text{ES}}$	1.1	1.1	1.3	1.3
P_I	1.079(6)	1.153(6)	1.037(6)	1.073(6)
P_{Final}	0.071	0.079	0.194	0.416
P_{em}	-38.837	-38.844	-38.815	-38.797
$P_{\text{em}}^{\text{ES},k}$	0.001	0.006	0.011	-
$P_{\text{em}}^{\text{ES},r}$	0.000	-0.001	-0.032	-0.057
P_C^{mol}	-38.823	-38.729	-38.344	-38.034
$P_C^{\text{mol,ES},k}$	-0.009	-0.095	-0.100	-
$P_C^{\text{mol,ES},r}$	-0.002	-0.014	-0.392	-0.629
ΔP	0.001	0.001	0.001	0.191
k-space speed up	1	1.7	9.2	63

TABLE VI. Simulation data from the TIP3P water simulations at 323 K. See Sec. IV for definitions of the quantities. The first column of data corresponds to the ‘exact’ results and the last column is for the α' method.

Simulation	TIP3P:1	TIP3P:2	TIP3P:3	TIP3P:4
U_C	-23.260(2)	-23.266(2)	-23.269(2)	-23.264(2)
$U_C + U_C^{\text{ES}}$	-23.258	-23.263	-23.263	-23.267
$\sigma_{S_C}/\sigma_{U_C}$	0.00045	0.0058	0.041	0.071
U_{Final}	-20.314	-20.317	-20.312	-20.319
F_T^{rms}	150.78(3)	150.68(3)	150.65(3)	150.24(3)
F_C^{rms}	482.41	482.50	482.55	482.33
$\log_{10}(\Delta_F)$	-3.64	-3.01	-2.04	-2.03
$F_k^{\text{KP}}/F_k^{\text{ES}}$	1.2	2.5	11.0	-
$F_r^{\text{KP}}/F_r^{\text{ES}}$	1.2	1.3	1.4	1.5
P_I	2.47(1)	2.50(1)	2.57(1)	2.74(1)
P_{Final}	-0.03	-0.03	0.04	0.27
P_{em}	-84.01	-84.01	-84.05	-84.02
$P_{\text{em}}^{\text{ES},k}$	0.00	0.01	0.02	-
$P_{\text{em}}^{\text{ES},r}$	0.00	0.00	-0.01	-0.01
P_C^{mol}	-83.98	-83.97	-83.93	-83.72
$P_C^{\text{mol,ES},k}$	-0.03	-0.05	-0.06	-
$P_C^{\text{mol,ES},r}$	0.00	0.00	-0.03	-0.05
ΔP	0.00	0.00	0.00	0.27
k-space speed up	1	1.8	13	59

potential systems, and have less k-space imposed long range order.

The results above show that accurate simulations can be carried out with very low k_c values. However, for systems with very low α or α' values, the size of perturbation and smoothing forces must be monitored, especially if r_c has been made fairly small too. For the :3 and :4 calculations in Tables IV to VII, the values of α and k_c were tuned so that $\Delta_F \leq 0.01$ (see Eq. (36)) to ensure Ewald perturbation forces never exceeded 1% of the total F_T^{rms} force. In addition, α and k_c were tuned to ensure the standard deviation of the Ewald r-

space smoothing energy is at least a factor of 10 below that for the total Coulomb energy, so $\sigma_{S_C}/\sigma_{U_C} \leq 0.1$. While it is possible to ignore the two criteria suggested above, as was done for the $k_c^2 = 5$ and $k_c^2 = 4$ α' simulations reported in Figs. 4 to 7, it has to be acknowledged that smoothing forces begin to play a significant role in these simulations.

Figure 8(a) shows the instantaneous values of U_C and S_C as a function of time for the [hmim]Cl system. The fluctuations in S_C are seen to be much smaller than those in U_C . This figure indicates the degree to which the Ewald r-space smoothing energy, S_C , can be considered to act like a uniform background

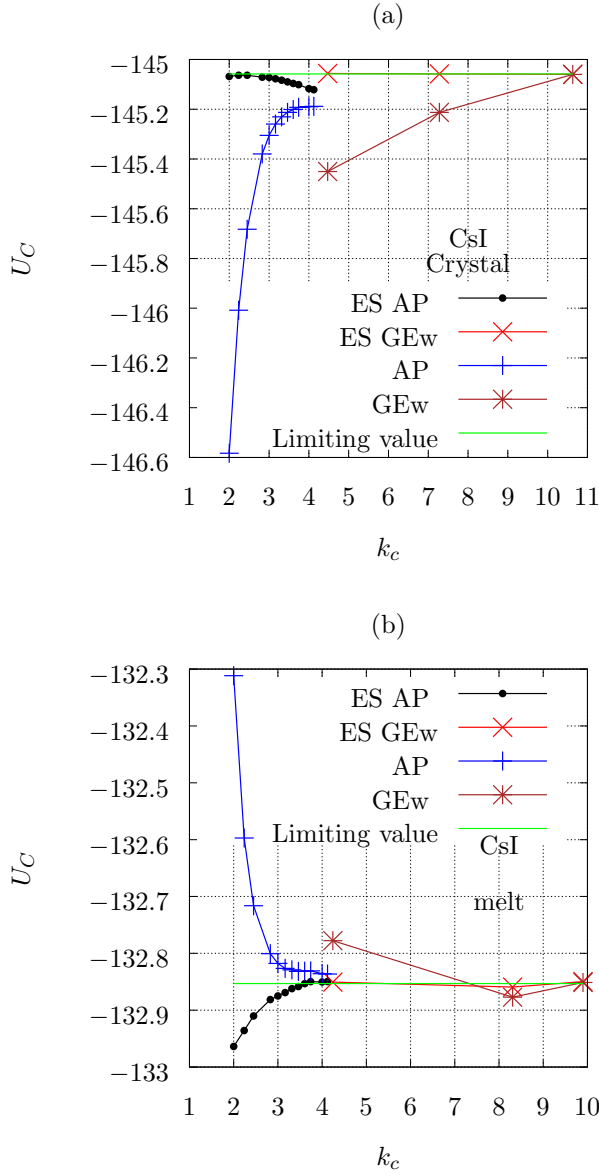


FIG. 4. The k_c dependence of the Coulomb energies, U_C from GEw and from the α' ('AP') simulations, for CsI (a) crystal and (b) melt systems. Data for the extended shell ('ES') are included on the figure. The limiting value is that of the highest k_c GEw simulation, where U_C^{ES} is zero within statistical error. The GEw and $k_c = \sqrt{6}$ points are from data given in Tables IV and V. The α' simulations used the same α values as the :4 cases in Table III.

in relation to the total Coulomb energy U_C . The ratio of the standard deviations, $\sigma_{S_C}/\sigma_{U_C}$, was 0.048 for this simulation, which indicates that the smoothing contribution can be considered to act essentially as a uniform background which only very weakly perturbs the thermodynamic state of the system. Figure 8(b) shows the time dependence of the NVE ensemble nominal Hamiltonian energy, E_0 , compared to the shadow Hamiltonian, E_s . Note the fine resolution on the y-axis. The E_0 is noisy while E_s is extremely flat, with just a few minor outliers. The corresponding drift rate for the [hmim]Cl:4 run was 0.006 K/ μ s, which is extremely small by literature stan-

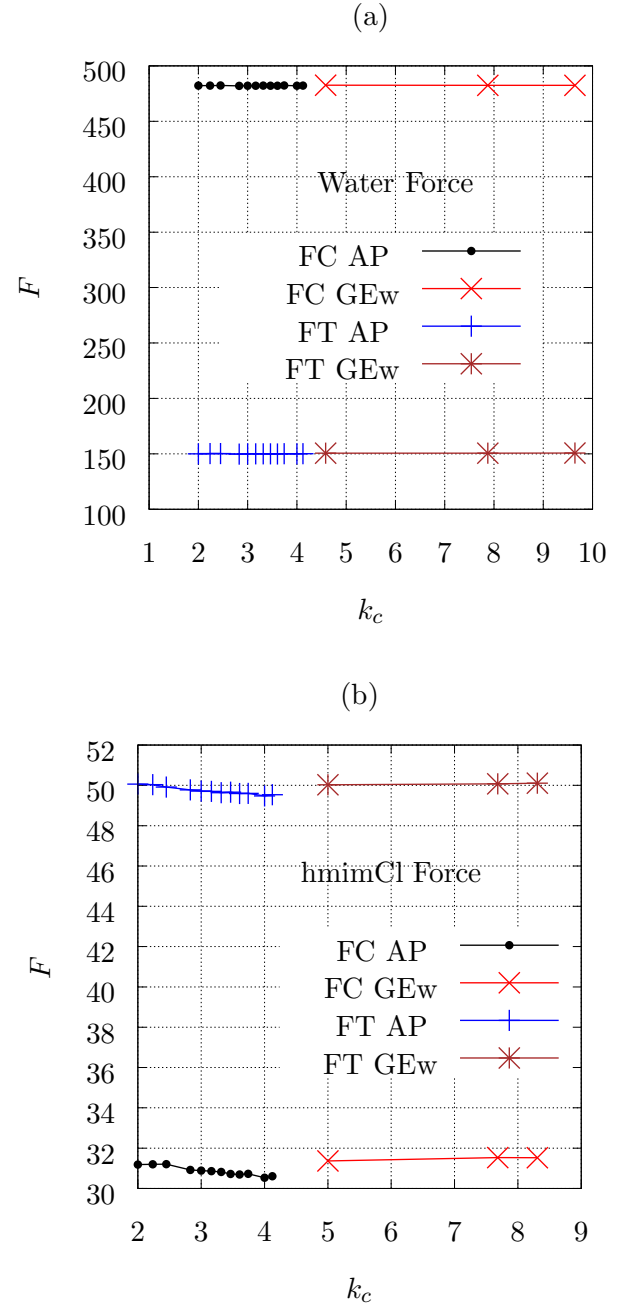


FIG. 5. The k_c dependence of the total ('FT') and Coulomb ('FC') rms integration forces for GEw and α' simulations, for (a) TIP3P water and (b) [hmim]Cl systems. Note that ES correction forces are not included, as these are not used to integrate the equations of motion. The limiting values are those of the highest k_c GEw runs. The GEw and $k_c = \sqrt{6}$ points are from data in Tables VI and VII. The α' ('AP') simulations used the same α values as the :4 runs in Table III.

dards, and implies a 1 millisecond simulation would only produce a temperature rise of 6 K, thus showing the high quality of the MD integration. Without smoothing forces, drift rates above 100 K/ μ s were observed, indicating the underlying integration of the equations of motion was deficient.

For the CsI crystal the speed-up in total simulation time

TABLE VII. Simulation data from the [hmim]Cl simulations at 373 K. The first column of data is the ‘exact’ result and the last column uses the α' method. See Sec. IV for definitions of the quantities.

Simulation	[hmim]Cl:1	[hmim]Cl:2	[hmim]Cl:3	[hmim]Cl:4
U_C	-17.918(2)	-17.917(2)	-17.933(2)	-17.944(2)
$U_C + U_C^{\text{ES}}$	-17.916	-17.915	-17.902	-17.950
$\sigma_{S_C}/\sigma_{U_C}$	0.0015	0.0025	0.030	0.048
U_{Final}	-23.322	-23.321	-23.312	-23.360
F_T^{rms}	50.11(3)	50.08(3)	50.03(2)	49.91(2)
F_C^{rms}	31.53	31.53	31.36	31.20
$\log_{10}(\Delta_F)$	-3.19	-3.00	-2.00	-2.01
$F_k^{\text{KP}}/F_k^{\text{ES}}$	0.8	0.8	0.7	-
$F_r^{\text{KP}}/F_r^{\text{ES}}$	0.7	0.7	0.8	0.8
P_I	3.25(1)	3.24(1)	3.38(1)	3.54(1)
P_{Final}	0.17	0.15	0.12	0.48
P_{em}	-10.23	-10.23	-10.22	-10.24
$P_{\text{em}}^{\text{ES},k}$	0.00	0.00	0.00	-
$P_{\text{em}}^{\text{ES},r}$	0.00	0.00	0.00	0.00
P_C^{mol}	-10.21	-10.21	-10.00	-9.81
$P_C^{\text{mol,ES},k}$	-0.01	-0.02	-0.20	-
$P_C^{\text{mol,ES},r}$	0.00	0.00	-0.02	-0.03
Δ_P	0.00	0.00	0.00	0.40
k-space speed up	1	1.6	7.9	38

for the :2-:4 cases relative to the :1 ‘exact’ reference simulation is 2.2,3.9 and 4.9. For the melt these values are 1.4, 3.1 and 3.7. For TIP3P water, they are 1.4, 2.1 and 2.5, and for [hmim]Cl these numbers are 1.07, 1.36 and 1.43. Therefore for the simple CsI systems the overall speed enhancement from the α' method is notable, by a factor of 4.9 for the crystal but 3.7 for the melt, because the crystal needed significantly more k-vectors for comparable accuracy. For the more complex molecular systems, the overall speed increase is more modest. For TIP3P water, and [hmim]Cl, the number of real space interactions per site is double that for the CsI systems, see $N(r_c)$ in Table II, which means that the fraction of CPU time devoted to the k-space terms is reduced, and there is less scope for α' improvement in this case. The [hmim]Cl system shows little overall speed up, as the constraints also take up a significant amount of CPU time, and can be considered to be part of the r-space CPU. Also note that $N^{\text{opt}}(k_c)$ in Table III is half the value for [hmim]Cl than for the CsI crystal, which means that there is less potential for k-space speed up for this system. Also only 75% of the [hmim]Cl sites are charged, and only 75% are involved in k-space CPU, but 100% of sites are involved in the r-space CPU consumption. It should be noted that as MD systems get larger, the proportion of time spent in k-space force evaluation increases, and so the speed improvement due to the α' method will be more pronounced.

V. CONCLUSIONS

A new and computationally much faster approximation to the exact Ewald (GEW) result has been formulated and demonstrated to provide a significant reduction in the time it takes to compute the reciprocal space series, by reducing the number of k-vectors required. This method is referred to as

the α' method, and is summarized in Eq. (25). This procedure for some of the properties (*e.g.*, the forces and pressure) and chemical systems studied gives the perhaps surprising trend that the exact result is approached as the magnitude of the reciprocal space cut-off vector *decreases*.

An *in situ* extended shell (ES) method for quickly, but accurately, finding long range energy, force and pressure corrections within GEW simulations has been implemented in the simulation codes (these do not affect the dynamics of the system). This enables new classes of GEW and α' simulations to be carried out, with short r_c and very low k_c values. Such charged particle simulations are very fast, and only consume about 3 times the CPU of corresponding LJ particle simulations, with little compromise being introduced to the accuracy of the results.

The tuning of GEW simulation parameters has been improved by using the perturbation forces described by Eq. (36). These are more accurate than Kolafa-Perram estimates, and also take into account any unphysical smoothing forces needed to integrate correctly the equations of motion, and so virtually eliminate simulation drift.

Accurate pressure calculations were a particular focus of this work, and the quantity Δ_P (see Eq. (30)) represents a stringent test of how closely any charged particle simulation obeys Coulomb’s $1/r$ law. It is found that GEW simulations that employ a short r_c and very low k_c do continue to implement accurately the $1/r$ law, provided ES corrections are applied. There is a slight deviation away from the $1/r$ law for α' simulations, which is not a surprise as the method is an approximation to the formally correct GEW method, but the resulting pressure deviations are minor compared to typical values obtained by MD for such systems. Even commonly used polynomial approximations for the $\text{erfc}(x)$ function will cause sufficient deviation from Coulomb’s $1/r$ law to be readily de-

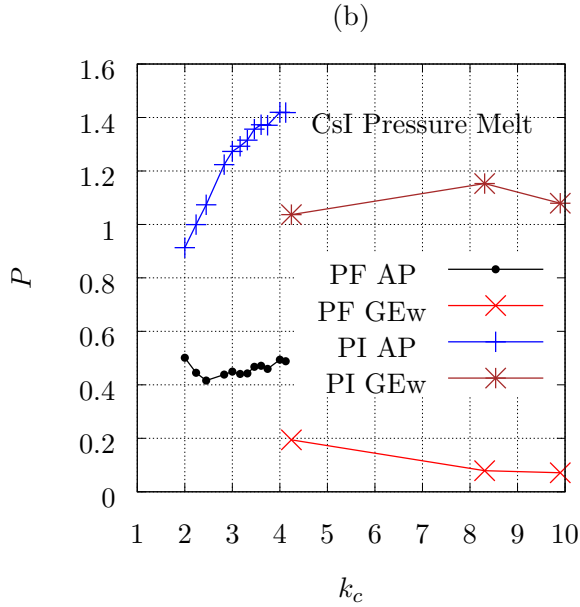
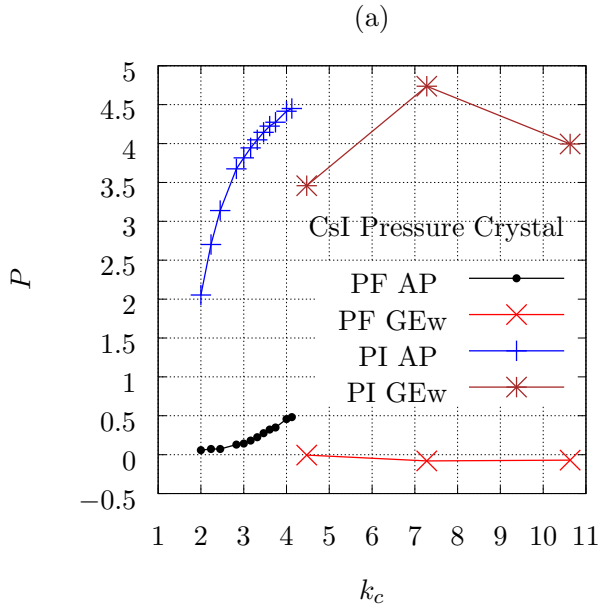


FIG. 6. The k_c dependence of the integrator pressure, P_I , ('PI') and the final pressure ('PF') defined in Eq. (38) for (a) the CsI crystal, and (b) the CsI melt, for GEw and α' ('AP') simulations. The GEw and $k_c = \sqrt{6}$ points are taken from Tables V and VI. The α' simulations used the same α values as the :4 runs in Table III.

tectable by ΔP . Hence a new and more accurate approximation to $\text{erfc}(x)$ was developed as part of this work, see Appendix A and Eq. (A1).

NVE MD simulations were performed on a range of ionic and molecular systems, and all show similar behavior, suggesting that low k_c GEw and α' simulations are suitable for a large variety of problems involving high dielectric constant systems. The level of approximation introduced by the new methods is sufficiently small that coarse grained modelling (where interaction sites represent more than one atomic site)

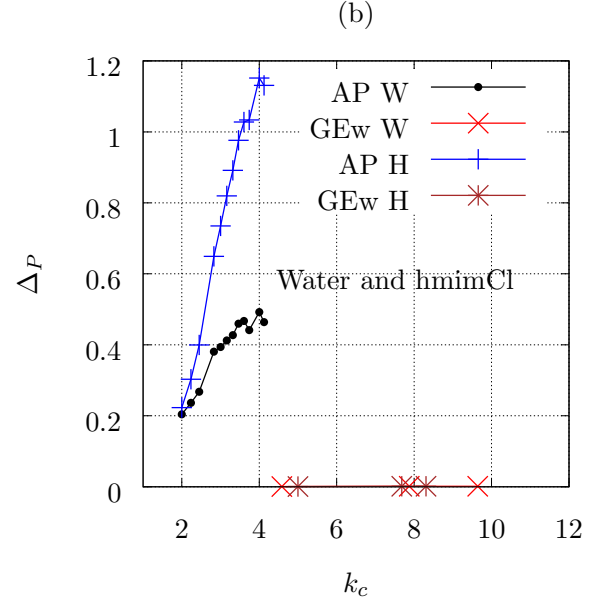
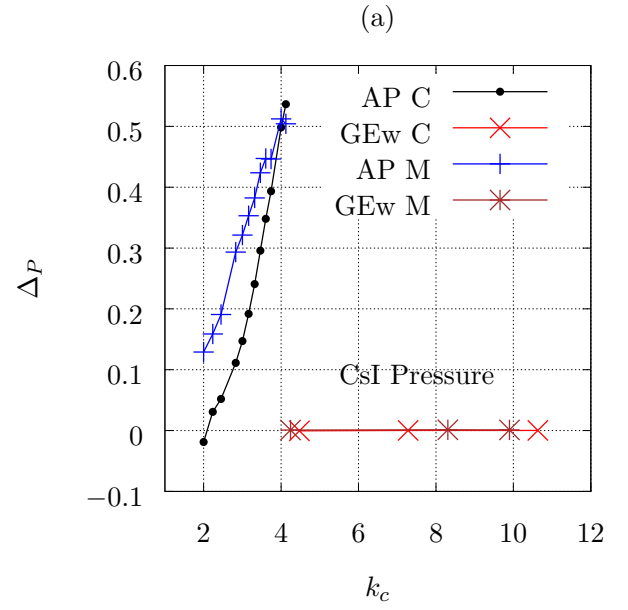


FIG. 7. The k_c dependence of ΔP defined in Eq. (30) for GEw and α' ('AP') simulations for, (a) crystalline ('C') and melt ('M') CsI, and (b) TIP3P water ('W') and [hmim]Cl ('H'). The GEw and $k_c = \sqrt{6}$ points are from data in Tables IV to VII. The α' simulations used the same α values as the :4 runs in Table III.

could be carried out with confidence. In addition, the approximations in the nonCoulombic terms in many potential models are probably a greater factor in governing agreement with experiment than the use of the α' method.

Only minor modifications to an existing standard Ewald code are needed to implement the α' method. The other methodological improvements in this work are fairly simple in concept, and so are not difficult to program in. A sufficiently good implementation of the smoothing forces is required when using the new methods to compensate for the

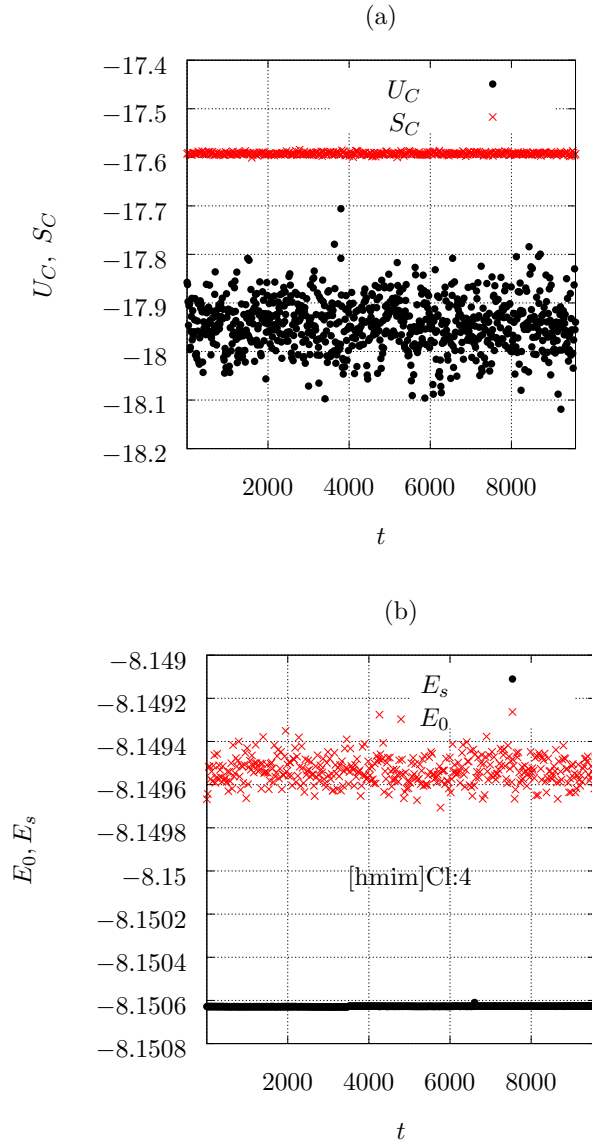


FIG. 8. The time dependence of different energy quantities for the [hmim]Cl:4 system of Table VII. Panel (a) compares the Coulomb energy (U_C) and the unphysical Ewald r-space smoothing energy (S_C). Points for S_C have been shifted down 17.9 units to allow comparison, since $\langle S_C \rangle = +0.30777(6)$. Panel (b) compares the NVE ensemble nominal Hamiltonian energy (E_0) and the shadow-Hamiltonian energy (E_s). For each set of points, the maximum outliers are shown from a data set of 160,000 points.

r-space cut-offs in the potential to achieve accurate integration of the equations of motion. The α' method could also be used in Monte Carlo or Lattice Dynamics calculations, where unphysical smoothing forces are not required. For medium sized systems of up to $\sim 10^4$ sites the new methods enable very fast but reliable charged particle simulations to be performed.

Further work is required to demonstrate the suitability of the α' method for liquid interfacial systems, where accurate modelling of surface tension effects may be of importance. Also, it would be of interest to investigate using this method,

systems with low concentrations of ionic species in a low dielectric constant medium (*e.g.*, dilute solutions of alkylammonium salts in halogenated solvents) where long range charge screening effects are much reduced compared to high ionic strength aqueous solutions, and the high dielectric constant systems considered in this study.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

DATA AVAILABILITY

The data that support the findings of this study and the FORTRAN code can be made available from the first author upon reasonable request.

Appendix A: A new polynomial approximation for $\text{erfc}(x)$

Compiler implementations of the intrinsic Fortran $\text{ERFC}(X)$ or complementary error function are slow to evaluate $\text{erfc}(x)$ to full 64 bit accuracy. A polynomial approximation can be used to obtain a near order of magnitude speed improvement. However, when using published approximations for $\text{erfc}(x)$ designed for 32 bit IEEE-754 accuracy (such as 7.1.28 in Ref. 31) then Δ_P (see Eq. (30)) is not zero within statistical pressure errors, even for accurate high k_c GEW simulations. This implies that these $\text{erfc}(x)$ approximations result in subtle changes in the GEW r-space interactions, which cause them to deviate from the $1/r$ Coulomb law to a degree that is easily detected. As a result, for this work, a new and more accurate polynomial approximation for the complementary error function has been derived by a process of nonlinear least squares fitting to a set of closely separated $\text{ERFC}(X)$ values. The functional form adopted (see Ref. 32 for the series progression) is,

$$\text{erfc}(x) = \left(1 + \sum_{i=1}^9 a_i x^i \right)^{-32}$$

$$\begin{aligned} a_1 &= 0.0352618572545339, \\ a_2 &= 0.0205159036756772, \\ a_3 &= 0.00392157470526262, \\ a_4 &= -0.000277792637346837, \\ a_5 &= 5.15742744370975 \times 10^{-5}, \\ a_6 &= 4.39647743338576 \times 10^{-5}, \end{aligned}$$

$$\begin{aligned} a_7 &= -1.68025752652442 \times 10^{-5}, \\ a_8 &= 3.22287284502991 \times 10^{-6}, \\ a_9 &= -2.45761793518861 \times 10^{-7}, \end{aligned} \quad (\text{A1})$$

for $x \leq 4$. The largest value of x needed for $\text{erfc}(x)$ in the simulations performed in this study was 3.37, which was for the CsI crystal case. Therefore the fit range chosen for the formula in Eq. (A1) was adequate for all the simulations carried out herein.

The maximum deviation from the exact result is almost two orders of magnitude smaller than the fit mentioned above from Ref. 31. Using Eq. (A1) satisfies the $\Delta\rho = 0$ goal well within statistical errors for accurate GEW simulations, which implies the $1/r$ Coulomb law is now being accurately modeled with this reparametrization of the fit to the complementary error function. Derivatives of Eq. (A1), for evaluating forces and smoothing function coefficients, can be determined using a symbolic algebra package.

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