Plain Ewald and PME

Thierry Matthey
matthey@ii.uib.no

June 24, 2005

1 Introduction

1.1 Standard Ewald summation

A general potential energy function U of a system of N particles with an interaction potential $\phi(\vec{x}_{ij} + \vec{n})$ and periodic boundary conditions can be expressed as

$$U = \frac{1}{2} \sum_{\vec{n}}^{\dagger} \sum_{i=1}^{N} \sum_{j=1}^{N} \phi(\vec{x}_{ij} + \vec{n}), \tag{1}$$

where $\sum_{\vec{n}}$ is the sum over all lattice vectors $\vec{n} = (L_x n_x, L_y n_y, L_z n_z)$, $n_{x,y,z} \in \mathbb{N}$ and $L_{x,y,z}$ are the dimensions of the unit MD cell and $\vec{x}_{ij} = \vec{x}_j - \vec{x}_i$. The "daggered" (†) summation indicates the exclusion of all pairs $i = j$ inside the original unit MD cell ($\vec{n} = \vec{0}$). Most molecular force fields provide exclusion schemes to exclude additional pairs, e.g., the so-called *1-3 exclusion* excludes directly connected pairs and pairs with a direct common neighbor. Furthermore, some exclusion schemes may also modify the potential by a factor for certain pairs.

If the potential ϕ satisfies

$$|\phi(\vec{x})| \leq A|\vec{x}|^{-3-\epsilon} \tag{2}$$

for large enough $\vec{x}$ and $A > 0$ and $\epsilon > 0$, then the sum in Eq. (1) is absolute convergent[1].

Inequality (2) is not satisfied by the Coulomb potential $\phi(\vec{x}_{ij}) = cq_i q_j |\vec{x}_{ij}|^{-1}$, such that the infinite lattice sum in Eq. (1) is only conditionally convergent[2]. In case of the Lennard-Jones potential, the sum is absolutely convergent.

The well-known Ewald summation method [6] is in general useful in systems with large, spatial potential differences, where the summation over one unit cell does not converge sufficiently, i.e., the lattice sum is not absolutely convergent. The lattice sum with the Coulomb potential is usually expressed as

$$U^{\text{electrostatic}} = \frac{1}{4\pi\epsilon_0} \frac{1}{2} \sum_{\vec{n}}^{\dagger} \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{q_i q_j}{|\vec{x}_{ij} + \vec{n}|}. \tag{3}$$

To overcome the conditionally and insufficient convergence of Eq. (3), the sum is split into two parts by the following trivial identity

$$\frac{1}{r} = \frac{f(r)}{r} + \frac{1 - f(r)}{r}. \tag{4}$$

[1] The sum converges and does not depend on the order of summation.

[2] The convergence of the sum depends on the order of summation.

The basic idea is to separate the fast variation part for small r and the smooth part for large r. In particular, the first part should decay fast and be negligible beyond some cutoff distance, whereas the second part should be smooth for all r, such that its Fourier transform can be represented by a few terms. Ewald [6] suggested to choose a Gaussian convergence factor $g(s, \vec{n}) = e^{-s|\vec{n}|^2}$ such that the sum becomes (see [3] for a detailed mathematical derivation of the Ewald summation)

$$
\begin{aligned}
U^{\text{electrostatic}} &= \underbrace{\frac{1}{4\pi\epsilon_0}\frac{1}{2}\sum_{\vec{n}}^{\dagger}\sum_{i=1}^{N}\sum_{j=1}^{N} q_i q_j \frac{\operatorname{erfc}(\alpha|\vec{x}_{ij}+\vec{n}|)}{|\vec{x}_{ij}+\vec{n}|}}_{\text{Real-space term}} \\
&+ \underbrace{\frac{1}{\epsilon_0 V}\frac{1}{2}\sum_{\vec{k}\neq 0}\frac{1}{\vec{k}^2}e^{-\frac{\vec{k}^2}{4\alpha^2}}\left[\left|\sum_{i=1}^{N} q_i\cos(\vec{k}\cdot\vec{x}_i)\right|^2 + \left|\sum_{i=1}^{N} q_i\sin(\vec{k}\cdot\vec{x}_i)\right|^2\right]}_{\text{Reciprocal-space term}} \\
&- \underbrace{\frac{1}{4\pi\epsilon_0}\frac{1}{2}\sum_{j=1}^{M}{}^{\dagger^{-1}}\sum_{k=1}^{N_j}\sum_{l=1}^{N_j} q_{j_k} q_{j_l}\frac{\operatorname{erf}(\alpha|\vec{x}_{j_k j_l}|)}{|\vec{x}_{j_k j_l}|}}_{\text{Intra-molecular self energy}} \\
&- \underbrace{\frac{\alpha}{4\pi^{\frac{3}{2}}\epsilon_0}\sum_{i=1}^{N} q_i^2}_{\text{Point self energy}} - \underbrace{\frac{1}{8\epsilon_0 V\alpha^2}\left|\sum_{i=1}^{N} q_i\right|^2}_{\text{Charged system term}} + \underbrace{\left[\frac{1}{6\epsilon_0 V}\left|\sum_{i=1}^{N} q_i\boldsymbol{x}_i\right|^2\right]}_{\text{Surface dipole term}}.
\end{aligned}
\tag{5}
$$

Here, α is the splitting parameter of the real and reciprocal part. For an optimal α the Ewald summation scales as $\mathcal{O}(N^{\frac{3}{2}})$ [6, 7, 16] in Eq. (8). $^{\dagger^{-1}}$ is the "inverse daggered" summation. The intra-molecular self term corrects interactions on the same molecule, which are implicitly included in the reciprocal-space term, but are not required in the exclusion model. Self interactions are canceled out by the self point term. The charged system term is only necessary if the total net charge of the system is non-zero. Note, that some MD systems have an additional surface dipole term to model dipolar systems more accurately [3, 19]. This term is not suited for mobile ions, since it will create discontinuities in the energy and force contributions when ions cross boundaries. The meaning of the symbols is

$\boldsymbol{n}$	lattice vector of periodic cell images
$\boldsymbol{k}$	reciprocal lattice vector of periodic cell images
k	modulus of $\boldsymbol{k}$
i, j	absolute indices of all charged sites
n	index of molecules
κ, λ	indices of sites within a single molecule
N	total number of charged sites
M	total number of molecules
N_j	number of sites on molecule j
q_i, q_j	charge on absolute site i, j
$q_{m\kappa}$	charge on site κ of molecule m
$\boldsymbol{x}_i$	Cartesian co-ordinate of site i
$\boldsymbol{x}_{ij}$	$\boldsymbol{x}_j - \boldsymbol{x}_i$
α	real/reciprocal space partition parameter

The electrostatic force on particle i is given by

$$
\begin{aligned}
F_i^{\text{electrostatic}} &= -\nabla_{\vec{x}_i} U^{\text{electrostatic}} \\
&= \underbrace{\frac{q_i}{4\pi\epsilon_0} \sum_{\vec{n}}^{\dagger} \sum_{j=1}^{N} q_j \left[\frac{\text{erfc}(\alpha|\vec{x}_{ij}+\vec{n}|)}{|\vec{x}_{ij}+\vec{n}|} + \frac{2\alpha}{\sqrt{\pi}} e^{-\alpha^2|\vec{x}_{ij}+\vec{n}|^2} \right] \frac{\vec{x}_{ij}+\vec{n}}{|\vec{x}_{ij}+\vec{n}|^2}}_{\text{Real-space term}} \\
&+ \underbrace{\frac{1}{\epsilon_0 V} \sum_{\vec{k}\neq 0} q_i \frac{\vec{k}}{\vec{k}^2} e^{-\frac{\vec{k}^2}{4\alpha^2}} \left[\sin(k\cdot r_i) \sum_{j=1}^{N} q_j \cos(\vec{k}\cdot\vec{x}_j) - \cos(k\cdot r_i) \sum_{j=1}^{N} q_j \sin(\vec{k}\cdot\vec{x}_j) \right]}_{\text{Reciprocal-space term}} \\
&+ \underbrace{\frac{q_i}{4\pi\epsilon_0} \frac{1}{2} \sum_{j}^{\dagger^{-1}} q_j \left[\frac{2\alpha}{\sqrt{\pi}} e^{-\alpha^2|\vec{x}_{ij}|^2} - \frac{\text{erf}(\alpha|\vec{x}_{ij}|)}{|\vec{x}_{ij}|} \right] \frac{\vec{x}_{ij}}{|\vec{x}_{ij}|^2}}_{\text{Intra-molecular term}} \qquad (6) \\
&+ \underbrace{\left[\frac{q_i}{6\epsilon_0 V} \left(\sum_{j=1}^{N} q_j \boldsymbol{x}_j \right) \right]}_{\text{Surface dipole term}} \qquad (7)
\end{aligned}
$$

Furthermore, the Ewald method can also be used for van der Waals interactions [1, 11] and several other potentials [8, pp. 237-256],[3]. The computational efficiency and accuracy for 2-dimensional periodic boundary conditions in a 3-dimensional system is discussed in [12]. The case with 1-dimensional periodic boundary conditions is addressed in [15]. To some extent, vacuum systems can be treated by imposing periodic boundary conditions. The dimensions of the original unit cell are chosen big enough, such that the contributions between cell images are negligible. In practice, the dimensions of the unit cell are a factor of 100 larger than the minimal bounding box of particles.

The real, reciprocal and correction terms (the last 3 terms of Eq. (5)) can be evaluated independently. This is typically used in combination with MTS to split the force into fast and slow varying parts. Furthermore, the real space term supports not only simple truncation, but also switching functions to modify the potential. The implementation supports parallelism (range computation) for the real, reciprocal and correction terms. It handles MD systems for both vacuum and periodic boundary conditions. Due to the relatively expensive sine and cosine functions, PROTOMOL uses look-up tables and the addition theorem to evaluate $\cos(\vec{k}\cdot\vec{x}_i)$ and $\sin(\vec{k}\cdot\vec{x}_i)$ more efficiently in Eqs. (5) and (6); $\text{erf}(x)$ and $\text{erfc}(x)$ are by default not approximated, since the system platforms provide a well optimized implementation.

Uniform Sheet Correction

The 5th term in Equation 5 is necessary only if the system has a non-zero net electric charge, and is useful in special cases such as framework systems.

In a periodic system the electrostatic energy is finite only if the total electric charge of the MD cell is zero. The reciprocal space sum in Equation 5 for $\boldsymbol{k} = 0$ takes the form

$$
\frac{1}{k^2} e^{-\frac{k^2}{4\alpha^2}} \left| \sum_{i=1}^{N} q_i \right|^2
$$

which is zero in the case of electroneutrality but infinite otherwise. Its omission from the sum in Equation 5 is physically equivalent to adding a uniform jelly of charge which exactly neutralizes the unbalanced point charges. Though the form of the reciprocal space sum is unaffected by the uniform charge jelly the real-space sum is not. The real-space part of the interaction of the jelly with each point charge as well as the self-energy of the jelly itself must be included giving the fifth term in Equation 5.

Surface Dipole Term

The optional final term in Equations 5 and 6 if used performs the calculations under different periodic boundary conditions. It was suggested by De Leeuw, Perram and Smith[] in order to accurately model dipolar systems and is necessary in any calculation of a dielectric constant.

The distinction arises from considerations of how the imaginary set of infinite replicas is constructed from a single copy of the MD box[, pp 156-159]. Consider a near-spherical cluster of MD cells. The "infinite" result for any property is the limit of its "cluster" value as the size of the cluster tends to infinity. However this value is non-unique and depends on the dielectric constant, ϵ_s of the physical medium surrounding the cluster. If this medium is conductive ($\epsilon_s = \infty$) the dipole moment of the cluster is neutralized by image charges, whereas in a vacuum ($\epsilon_s = 1$) it remains. It is trivial to show that in that case the dipole moment per unit volume (or per MD cell) does *not* decrease with the size of the cluster.

The final term in Equation 5 is just the dipole energy, and ought to be used in any calculation of the dielectric constant of a dipolar molecular system. Note that as it represents the dipole at the surface of the cluster the system is no longer truly periodic.

Conversely it *must not* be used if the simulated system contains mobile ions. Consider an ion crossing a periodic boundary and jumping from one side of the MD cell to another. In that case the dipole moment of the MD cell changes discontinuously. Because of the surface dipole term the calculation would model a discontinuous macroscopic change in the dipole moment of the whole system caused by an infinite number of ions jumping an infinite distance. This is manifested in practice by a large and discontinuous change in the energy of the system and on the force on each charge within it.

This situation is completely non-physical but is easily avoided. However the problem may also arise more subtly even when there are no mobile ions if a framework is being simulated. The framework is treated as a set of discrete, but fixed atoms rather than a molecular unit. If the shape of the unit cell is allowed to vary then ions constituting the framework may indeed cross MD cell boundaries causing the aforementioned problems.

Figure 1 shows the maximum relative force error of the Ewald method for different accuracy parameters ϵ compared to the Ewald method with accuracy parameter $\epsilon = 10^{-18}$ (see Eqs. (8-10)) under periodic boundary conditions. There was no significant improvement for smaller ϵ, which is obvious, due to machine precision of order 10^{-16}. The maximum relative error of the Ewald implementation compared against the direct method in vacuum is less than 10^{-15} with an accuracy parameter $\epsilon = 10^{-18}$ and a unit MD cell 10^8 times larger than the minimal bounding box of particles. Figure 2 illustrates the corresponding normalized run-time. Figure 3 shows excellent energy conservation with a maximum relative force error of order 10^{-10}. Moldy [18] was also used for further validation.

Choice of parameters

The accuracy and performance of the Ewald summation is governed by the splitting factor α, the real- and reciprocal-space term cutoffs r_c and k_c, and the accuracy ϵ. The splitting parameter α defines how fast the sums converge and defines the cutoffs r_c and k_c for a given accuracy ϵ. For most applications, r_c is small enough such that $\vec{n} \in \{\vec{0}\}$, which also simplifies the sum for the real-space term. Both the real- and reciprocal-space term converge rapidly, such that only a few terms need to be considered. For the real part

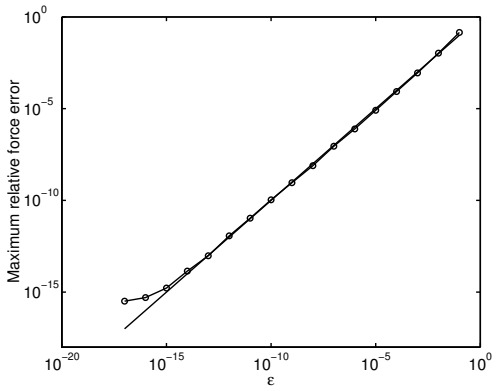

Figure 1: The maximum force error for a given accuracy parameter ϵ.

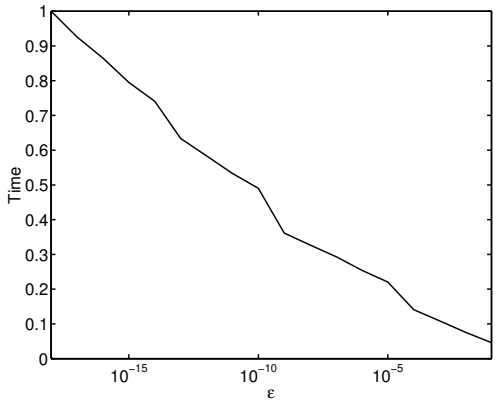

Figure 2: Normalized run-time for a given accuracy parameter ϵ.

only terms satisfying $|\vec{x}_{ij} + \vec{n}| < r_c$ are included, whereas for the reciprocal part only summands with $|\vec{k}| < k_c$ are evaluated.

From Eq. (5) it is obvious that for a given accuracy and a fixed α the required work scales as $\mathcal{O}(N^2)$ for the reciprocal term and as $\mathcal{O}(N)$ for the real term. To achieve an overall work complexity of $\mathcal{O}(N^{\frac{3}{2}})$, α must vary with N

$$\alpha = c\sqrt{\pi}\left(\frac{N}{V^2}\right)^{\frac{1}{6}} \tag{8}$$

$$r_c = \frac{\sqrt{-\ln\epsilon}}{\alpha} \tag{9}$$

$$k_c = 2\alpha\sqrt{-\ln\epsilon}\,. \tag{10}$$

Here, V is the volume and the constant c determines the ratio of execution time of the real and reciprocal term, which may vary from one platform to another. The standard Ewald summation is unsurpassed for very high accuracy. It is relatively easy to implement and the desired accuracy can be increased and controlled up to machine precision without any additional programming effort (see Figure 1). Due to these excellent properties, the Ewald method is often used as reference for the evaluation of other methods with periodic boundary conditions. A more detailed discussion for the optimal choice of α and more accurate error estimates can be found in [4, 7, 14, 17].

1.2 Mesh-based Ewald methods (PME)

The mesh-based Ewald methods approximate the reciprocal-space term of the standard Ewald summation by a discrete convolution on an interpolating grid, using the discrete Fast-Fourier transforms (FFT). By choosing an appropriate splitting parameter α, the computational cost can be reduced from $\mathcal{O}(N^{\frac{3}{2}})$ to $\mathcal{O}(N \log N)$. The accuracy and speed are additionally governed by the mesh size and the interpolation scheme, which makes the choice of optimal parameters more difficult. At present, there exist several implementations based on this idea, but they differ in detail. In [4] three essential methods are compared and summarized: particle-particle-particle-mesh [9] (P^3M), particle-mesh Ewald [2] (PME) and smooth particle-mesh Ewald [5] (SPME).

Unfortunately, the mesh-based Ewald methods are affected by errors when performing interpolation, FFT, and differentiation [17]. However, it would be misleading to infer that these methods sacrifice accuracy

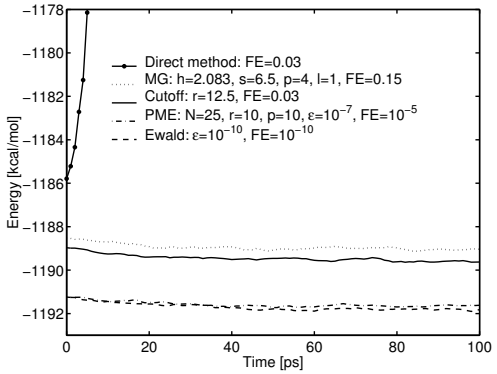

Figure 3: The energy for periodic boundary conditions and step size 1 fs.

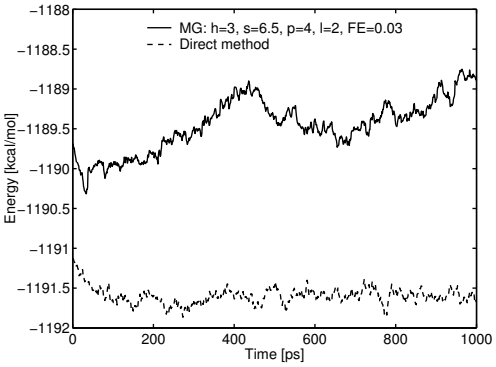

Figure 4: The energy for vacuum and step size 1 fs.

in favor of run-time performance.

For the fast mesh-based Ewald methods, there exists a critical number N^* such that they are faster than the standard Ewald method for $N > N^*$, due to the fact of better scaling. In [13], the computational efficiency and accuracy with 2-dimensional periodic boundary conditions for 3-dimensional systems are discussed.

PROTOMOL supports PME with a generic interpolation scheme interface of arbitrary order. Actually, B-splines and Hermitian interpolation are implemented. The real, reciprocal and correction term can be evaluated separately, as for the standard Ewald implementation. The real term can be modified by a generic switching function. The implementation supports parallelism (range computation) for the real and correction terms. The work of the reciprocal term cannot be distributed in the actual implementation.

The maximum relative error of the PME method compared against the standard Ewald summation is less than $2 \cdot 10^{-14}$. Both methods used an accuracy parameter $\epsilon = 10^{-18}$. The PME was defined with mesh size of 0.1Å, cutoff in real-space part $r_c = 10$, and B-splines of order 12. Figure 3 shows excellent energy conservation with a maximum relative force error of order 10^{-5}. NAMD2 [10] was used to validate the results.

1.3 Parameter Values

Both the real- and reciprocal-space series (the sums over $\boldsymbol{n}$ and $\boldsymbol{k}$) converge fairly rapidly so that only a few terms need be evaluated. We define the *cut-off* distances r_c and k_c so that only terms with $|\boldsymbol{x}_{ij} + \boldsymbol{n}| < r_c$ and $|\boldsymbol{k}| < k_c$ are included. The parameter α determines how rapidly the terms decrease and the values of r_c and k_c needed to achieve a given accuracy.

For a fixed α and accuracy the number of terms in the real-space sum is proportional to the total number of sites, N but the cost of the reciprocal-space sum increases as N^2. An overall scaling of $N^{\frac{3}{2}}$ may be achieved if α varies with N. This is discussed in detail in an excellent article by David Fincham[]. The optimal value of α is

$$\alpha = \sqrt{\pi} \left(\frac{t_R}{t_F} \frac{N}{V^2} \right)^{\frac{1}{6}} \tag{11}$$

where t_R and t_F are the execution times needed to evaluate a single term in the real- and reciprocal-space sums respectively. If we require that the sums converge to an accuracy of $\epsilon = \exp(-p)$ the cutoffs are then given by

$$r_c = \frac{\sqrt{p}}{\alpha} \quad (12)$$

$$k_c = 2\alpha\sqrt{p} \quad (13)$$

A representative value of t_R/t_F specific to PROTOMOL has been established as 5.5. Though this will vary on different processors and for different potentials its value is not critical since it enters the equations as a sixth root.
It must be emphasized that the r_c is used as a cutoff for the short-ranged potentials as well as for the electrostatic part. The value chosen above *does not* take the nature of the non-electrostatic part of the potential into account. It is therefore the responsibility of the user to ensure that r_c is adequate for this part too.

In case of Particle-Mesh Ewald sum, the reciprocal term is computed by a Fourier transform. The cutoff r_c, α and ϵ are chosen such as

$$\frac{\text{erfc}(\alpha r_c)}{r_c} = \epsilon \quad (14)$$

.

2 Input parameters

This sections gives the definition of the plain Ewaldc for PROTOMOL .

2.1 General syntax plain Ewald

PROTOMOL expects the following input plain Ewald:

```
Coulomb -algorithm FullEwald -real -reciprocal -correction
  -alpha     <real=-1>
  -accuracy  <real=1e-05,positive>
  -j         <real=3,positive>     # Vacuum
```

, where =*value* defines the default value, i.e. optional input.
Note that `Coulomb` can be replaced by a new, user defined potential, which is of the form cr^a, where c is a constant and r is the distance between particle pairs. For the Lennard-Jones potential a new template is required due to the sum in the potential definition. '`-j <real=3>`' is only available for vacuum.

2.2 Real space term

The flag `-real` emphasizes the computation of the real space term.

2.3 Reciprocal space term

The flag `-reciprocal` emphasizes the computation of the reciprocal space term.

2.4 Correction space term

The flag `-correction` emphasizes the computation of the resting terms in Eq. 5: point self term, intramolecular self term, charged system term and surface dipole term. Note that the surface dipole term is not considered in the actual implementation.

2.5 Switching function

The switching function is by default an ordinary cutoff. If an other switching function is required, one must register the corresponding prototype in the according factory.

2.6 Accuracy

The optional parameter `-accuracy <real>` defines the accuracy of the splitting. By default PROTOMOL will use an accuracy of $1e-06$.

2.7 Splitting of the sum – alpha

The optional parameter α (`-alpha <real>`) determines how rapidly the terms decrease and the values of cutoff (real space term) r_c and lattice cutoff (reciprocal space term) k_c needed to achieve a given accuracy. α is the so-called splitting parameter of the Ewald summation. $\alpha \in (0, 1)$, where 0^+ and1^- means only real space or reciprocal space term, respectively. By default PROTOMOL will compute depending on the cutoff and for the given accuracy, Eq. 10,14.

2.8 J – expansion factor for vacuum

In order to make PME work with vacuum we add a shell around the actual simulation box (bounding box of all particles) to be able to use PME together with periodic boundary conditions. With a large enough shell we can mimic vacuum. By default PROTOMOL will use a factor of 3, which means it will add 1 simulation boxes in each dimension (see Fig. 5), or in other words expanding the simulation box by a factor 3.

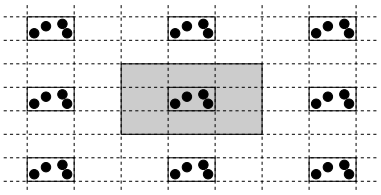

Figure 5: Example of expansion factor of 3 in 2d.

2.9 Compilation

For experimental purpose the Ewald has several conditional compilation flags.

`DEBUG_PME_TIMING`	Printing the different timings
`DEBUG_PME_ENERGIES`	Printing the different energy contributions
`USE_PME_EXACT_SOLUTION`	Using the exact solution of erf() in the real part

2.10 General syntax PME

PROTOMOL expects the following input for PME:

```
Coulomb -algorithm PMEwald -correction -interpolation BSpline
  -gridsize   <uint,positive> <uint,positive> <uint,positive>
  -cutoff     <real,positive>
  -order      <uint=4,positive>
```

```
-accuracy   <real=1e-06,positive>
-alpha      <real=-1>
-j          <real=3>
```

, where =*value* defines the default value, i.e. optional input.
Note that `Coulomb` can be replaced by a new, user defined potential, which is of the form cr^a, where c is a constant and r is the distance between particle pairs. For the Lennard-Jones potential a new template is required due to the sum in the potential definition. '`-j <real=3>`' is only available for vacuum.

2.11 Real space term

The flag `-real` emphasizes the computation of the real space term.

2.12 Reciprocal space term

The flag `-reciprocal` emphasizes the computation of the reciprocal space term.

2.13 Correction space term

The flag `-correction` emphasizes the computation of the resting terms in Eq. 5: point self term, intra-molecular self term, charged system term and surface dipole term. Note that the surface dipole term is not considered in the actual implementation.

2.14 Interpolation

`-interpolation` defines the interpolation scheme between the grids the particle level. For the moment PROTOMOL does only accept b-splines interpolation (`BSpline`). Other interpolations like Hermitian (`Hermite`) did not improve the accuracy.

2.15 Switching function

The switching function is by default an ordinary cutoff. If an other switching function is required, one must register the corresponding prototype in the according factory.

2.16 Gridsize

`-gridsize <uint,positive> <uint,positive> <uint,positive>` defines the grid for the reciprocal space term using FFT. The grid size should be shosen such that

$$n_i = ce_i \left(\frac{N}{V}\right)^{\frac{1}{3}} \tag{15}$$

is satisfied for some c.

2.17 Cutoff

`-cutoff <real>` defines the cutoff of the real space term.

2.18 Order

The optional parameter `-order` defines the interpolation order. The interpolation order must be even, where 4 and 6 stand for a *cubic* and *quintic* interpolation respectively. By default PROTOMOL will use 4th order interpolation.

2.19 Accuracy

The optional parameter `-accuracy <real>` defines the accuracy of the splitting. By default PROTOMOL will use an accuracy of $1e-06$.

2.20 Splitting of the sum – alpha

The optional parameter α (`-alpha <real>`) determines how rapidly the terms decrease and the values of cutoff (real space term) r_c and lattice cutoff (reciprocal space term) k_c needed to achieve a given accuracy. α is the so-called splitting parameter of the Ewald summation. $\alpha \in (0, 1)$, where 0^+ and1^- means only real space or reciprocal space term, respectively. By default PROTOMOL will compute depending on the cutoff and for the given accuracy, Eq. 1014.

2.21 J – expansion factor for vacuum

In order to make PME work with vacuum we add a shell around the actual simulation box (bounding box of all particles) to be able to use PME together with periodic boundary conditions. With a large enough shell we can mimic vacuum. By default PROTOMOL will use a factor of 3, which means it will add 1 simulation boxes in each dimension (see Fig. 5), or in other words expanding the simulation box by a factor 3.

2.22 Compilation

For experimental purpose the Ewald has several conditional compilation flags.

`DEBUG_PME_TIMING`	Printing the different timings
`DEBUG_PME_ENERGIES`	Printing the different energy contributions
`USE_PME_EXACT_SOLUTION`	Using the exact solution of erf() in the real part

References

[1] Z. M. Chen, T. Cagin, and W. A. Goddard. Fast Ewald sums for general van der Waals potentials. *J. Comp. Chem.*, 18:1365–1370, 1997.

[2] T. Darden, D. York, and L. Pedersen. Particle mesh Ewald: An N log(N) method for Ewald sums in large systems. *J. Chem. Phys.*, 98(12):10089–10092, 1993.

[3] S. W. de Leeuw, J. W. Perram, and E. R. Smith. Simulation of electrostatic systems in periodic boundary conditions. *Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences*, 373(1752):27–56, 1980.

[4] M. Deserno and C. Holm. How to mesh up Ewald sums. I. A theoretical and numerical comparison of various particle mesh routines. *J. Chem. Phys.*, 109(18):7678–7693, 1998.

[5] U. Essmann, L. Perera, and M. L. Berkowitz. A smooth particle mesh Ewald method. *J. Chem. Phys.*, 103(19):8577–8593, 1995.

[6] P. Ewald. Die Berechnung optischer und elektrostatischer Gitterpotentiale. *Ann. Phys.*, 64:253–287, 1921.

[7] D. Fincham. Optimisation of the Ewald sum for large systems. *Mol. Sim.*, 13:1–9, 1994.

[8] G. Gao. *Large Scale Molecular Simulations with Application to Polymers and Nano-scale Materials*. PhD thesis, Caltech, 1998.

[9] R. W. Hockney and J. W. Eastwood. *Computer Simulation Using Particles*. McGraw-Hill, New York, 1981.

[10] L. Kalé, R. Skeel, M. Bhandarkar, R. Brunner, A. Gursoy, N. Krawetz, J. Phillips, A. Shinozaki, K. Varadarajan, and K. Schulten. NAMD2: Greater scalability for parallel molecular dynamics. *J. Comput. Phys.*, 151:283–312, 1999.

[11] N. Karawasa and W. A. Goddard. Acceleration of convergence for lattice sums. *J. Phys. Chem.*, 93:7320, 1989.

[12] M. Kawata and M. Mikami. Rapid calculation of two-dimensional Ewald summation. *Chemical Physics Letters*, 340(1-2):157–164, 2001.

[13] M. Kawata and U. Nagashima. Particle mesh Ewald method for three-dimensional systems with two-dimensional periodicity. *Chemical Physics Letters*, 340(1-2):165–172, 2001.

[14] J. Kolafa and J. W. Perram. Cutoff errors in the Ewald summation formulae for point charge systems. *Molecular Simulation*, 9:351–368, 1992.

[15] D. J. Langridge, J. F. Hart, and S. Crampin. Ewald summation technique for one-dimensional charge distributions. *Comput. Phys. Commun.*, 134(1):78–85, 2001.

[16] J. W. Perram, H. G. Petersen, and S. W. de Leeuw. An algorithm for the simulation of condensed matter which grows as the $\frac{3}{2}$ power of the number of particles. *Mol. Phys.*, 65:875–893, 1988.

[17] H. G. Petersen. Accuracy and efficiency of the particle mesh Ewald method. *J. Chem. Phys.*, 103(3668–3679), 1995.

[18] K. Refson. Moldy: A portable molecular dynamics simulation program for serial and parallel computers. *Comput. Phys. Commun.*, 126(3):309–328, 2000.

[19] Z. Wang and C. Holm. Estimate of the cutoff errors in the Ewald summation for dipolar systems. *J. Chem. Phys.*, 115(14):6351–6359, 2001.