Supporting Information

For

Periodic Coulomb Tree Method: An Alternative to Parallel Particle Mesh Ewald

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1 Implementation in DL_POLY Classic

DL_POLY Classic is a parallel molecular dynamics simulation package written in Fortran 90 and uses a replicated data strategy for load balancing. The package comes with an extensive manual.[1] We added PCT (Algorithm 2) to DL_POLY Classic as a module. In order to perform a simulation run, the package reads directives from a file called CONTROL. The subroutine that reads the CONTROL file is called **simdef**. We added additional options to **simdef** to read the CONTROL files for the directives needed to use PCT. Figure 1 is a sample CONTROL file showing the directives for PCT. The key **ltree** causes the package to compute forces with PCT instead of the other choices in the force module. The multipole acceptability criterion is set by **mactheta** and in this work we use $\theta = 0.6$. The maximum number of particles N_0 is read in through the directive **maxparnode** and is set to 500 in this work. The order of the Taylor approximation, p is determined by **torder** which is 0 in Figure 1. We also use $p = 2$ and $p = 4$. Finally, the directive **lattlim** determines the range of periodic images, s. We use $s \in \{1, 2, 3\}$ in this work. The other directives in the CONTROL file are explained in the manual for the package. In addition to **simdef**, DL_POLY Classic does a scan of the CONTROL file using the subroutine **conscan**. We modified **conscan** as well to read the tree directives.

2 Numerical Results

2.1 System 1

We compare PME and PCT results for an NVT ensemble MD simulation of 6912 molecules of SPC water in a $(69.5\text{Å})^3$ box at 307.46 K.[2,3] The charges for the oxygen and hydrogens were set to $-0.730e$ and $0.365e$ respectively with intermolecular Lennard-Jones (LJ) interactions between oxygen atoms only. The potential well depth for the Lennard-Jones interactions was $\xi = 0.16$ kcal/mol and the distance at which there was zero LJ interaction was $\sigma = 3.196\text{Å}$.

```
WATER (20736 ATOMS)

integration velocity verlet
temperature        307.46

ensemble nvt hoover 0.125

timestep           0.0005

steps              100000
equilibration      0

cutoff             8.0
delr width         1.2
rvdw               8.0
shake              1e-8
rdf                1000

print rdf

ltree
mactheta               0.6
maxparnode             500
torder                 0
lattlim                1

print every        1000

traj               1 10 2

stats every        1000
stack              1000

job time           1000000
close time            1000

finish
```

Figure 1: A sample DL_POLY Classic CONTROL file showing additional directives for the periodic Coulomb treecode

We held the O-H bond length at 1.03Å and the distance between the two hydrogens was fixed at 1.682982Å as well. A Nosé-Hoover thermostat was used for equilibration with a relaxation constant of 1.0 ps for PME and 0.125 ps for PCT. Time-stepping was done with the velocity Verlet integrator and bond constraints were maintained by the SHAKE algorithm. [4,5] The cutoff for Lennard-Jones interactions and the real space sum of PME were both set to $r_{\mathrm{cut}} = 8.0$Å. To achieve moderate accuracy for PME, we set the desired error $\epsilon = 10^{-5}$. DL_POLY used r_{cut} and ϵ to determine the convergence parameter $\alpha = 0.036037$Å^{-1} and a minimum grid of size $32 \times 32 \times 32$. A nice overview of the procedure for determining α and the minimum grid size required to achieve an error of ϵ is provided in chapter 6 of the book by W. Smith. [6]

We run production simulations for 100000 times steps each of size 0.5 fs. Radial distribution functions were computed every 1000 steps and the positions, velocities and forces were

stored each tenth step. We averaged the computed structural and dynamical properties over ten different ensembles.

2.1.1 Velocity and Force Autocorrelation Functions - Spectral Analysis

We also performed spectral analysis of the normalized correlation functions. Figure 2 shows the normalized correlation functions and their corresponding Fourier transforms for PME and PCT with $p = 0$ and $s = 1$. We see that the peaks for both methods occur at the same frequency and the spectra are almost indistinguishable.
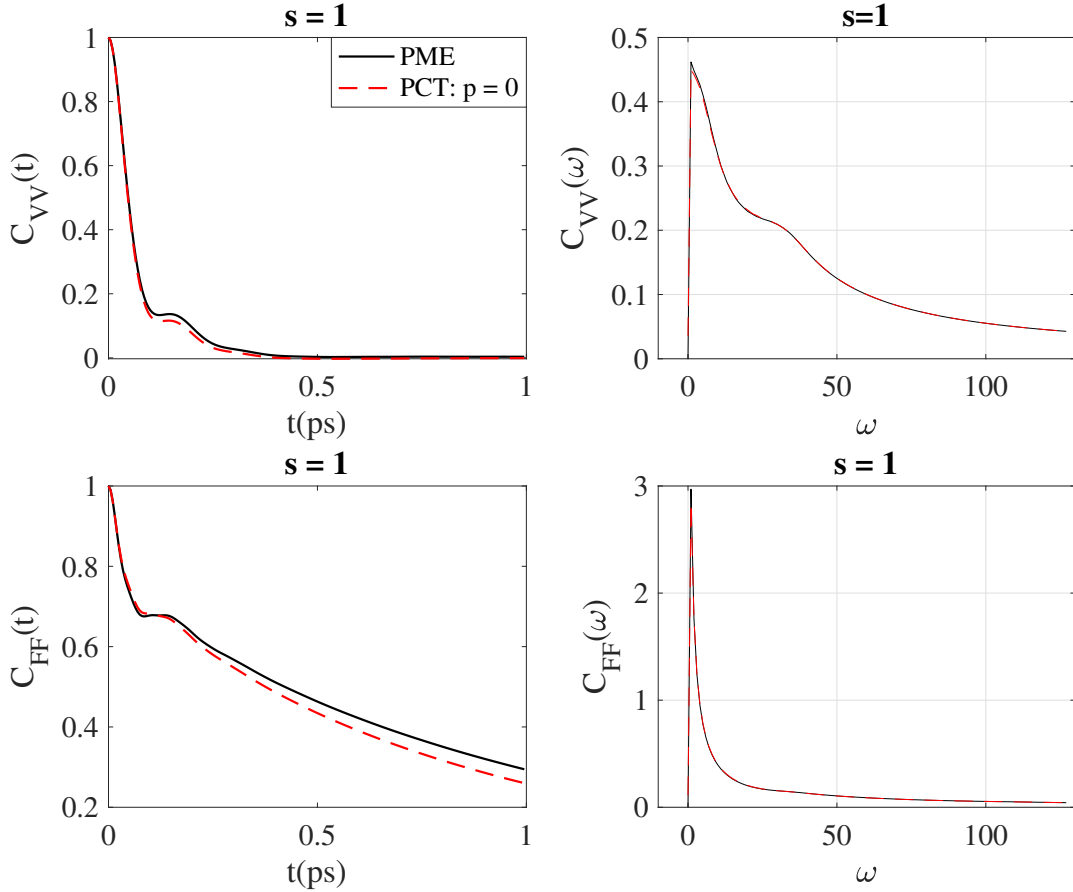

Figure 2: The normalized center of mass autocorrelation function $C(t)$ and their Fourier transforms $C(\omega)$. The top row is velocity and the bottom row is force.

2.2 System 2

Here we compare PCT to PME for an NVT system of Na^+ and Cl^- ions in a solution of 139 SPC water molecules. The specifications for the water molecules are the same as described earlier for the pure water system and the velocity Verlet time integrator was used with the SHAKE algorithm for maintaining constraints with timestep of 1fs. The sodium ion has a plus one charge and the chloride ion has a minus one charge. The short-range interactions were modeled with a Lennard-Jones potential and the parameters are provided in Table 1. The error for PME was set to $\epsilon = 10^{-5}$ with a cutoff of 8Å. For PCT, $N_0 = 100$ and $\theta = 0.6$. For each simulation, the system was equilibrated for 100000 steps and production runs were

Table 1: Parameters for Lennard-Jones Potential for system 2

	Lennard-Jones Parameter	
Atom pair	ξ (kcal/mol)	σ(Å)
O-O	0.16	3.196
O-Na^+	0.14422205	2.773
O-Cl^-	0.12649111	3.823
Na^+-Cl^-	0.11401754	3.4

over 100000 steps as well averaged over 100 ensembles.

2.2.1 Effect of Periodic Images

Figure 3 looks at the effect of different lattice sums on the PCT radial distribution function for order $p = 0$. Again we observe a significant difference in the structure between simulations with and without periodic images. Figure 4 shows the effect of the periodic images on $G_k(r)$. We see a large discrepancy between $s = 0$ and $s \geq 1$ but negligible difference between $s = 1$ and $s \in \{2, 3\}$. This provides further evidence for the sufficiency of using just the nearest neighbor periodic images, i.e. $s = 1$.
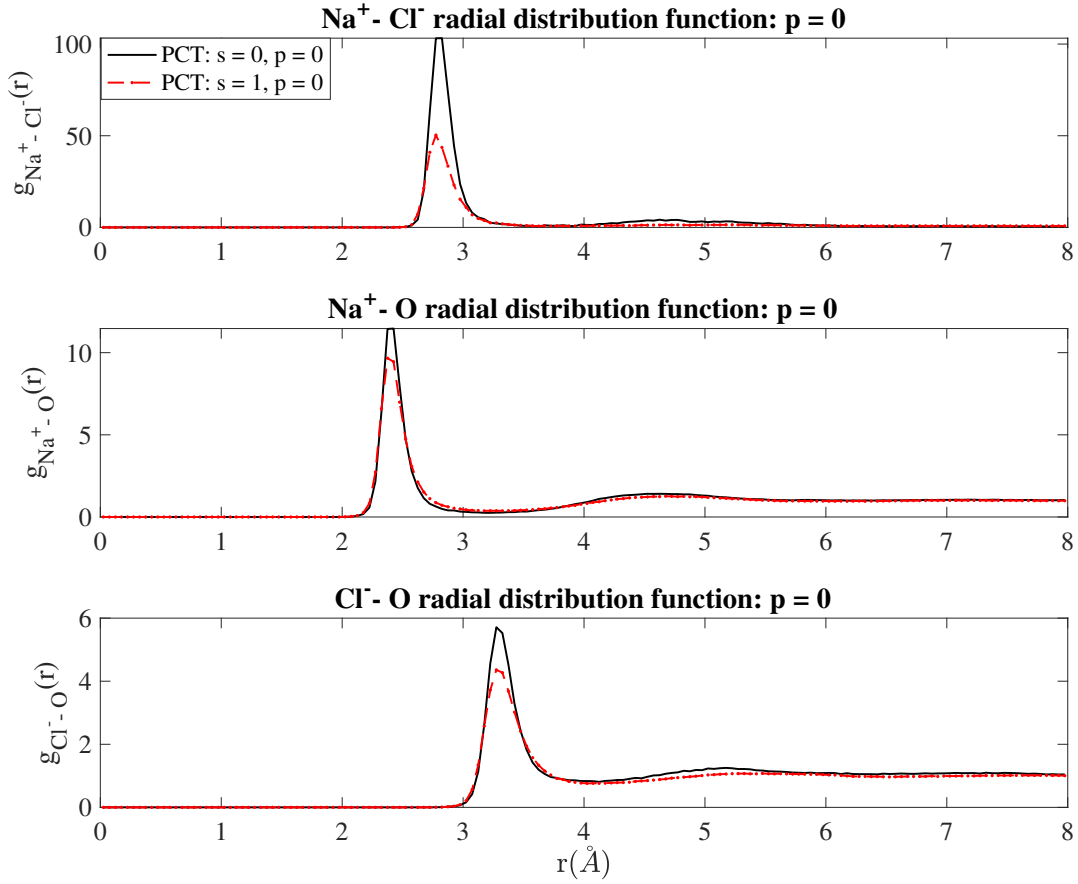
Figure 3: The Na^+-Cl^- (top), Na^+-O (middle) and Cl^--O (bottom) radial distribution functions for $s = 0$ and $s = 1$

2.3 System 3

The third system for comparison is a molecule of valinomycin in 1223 molecules of SPC water. The parameters of the system are described in previous work by several authors.[7–10] The desired error for PME is set to $\epsilon = 10^{-5}$ with a cutoff of 12Å. For PCT, $N_0 = 100$ and $\theta = 0.6$. The simulations were performed with a timestep of 0.5 fs using the velocity Verlet integrator with the SHAKE algorithm to maintain constraints and the NOSQUISH[11] algorithm to handle rotational motion. The system was equilibrated over 100000 steps and production runs were over 100000 steps.
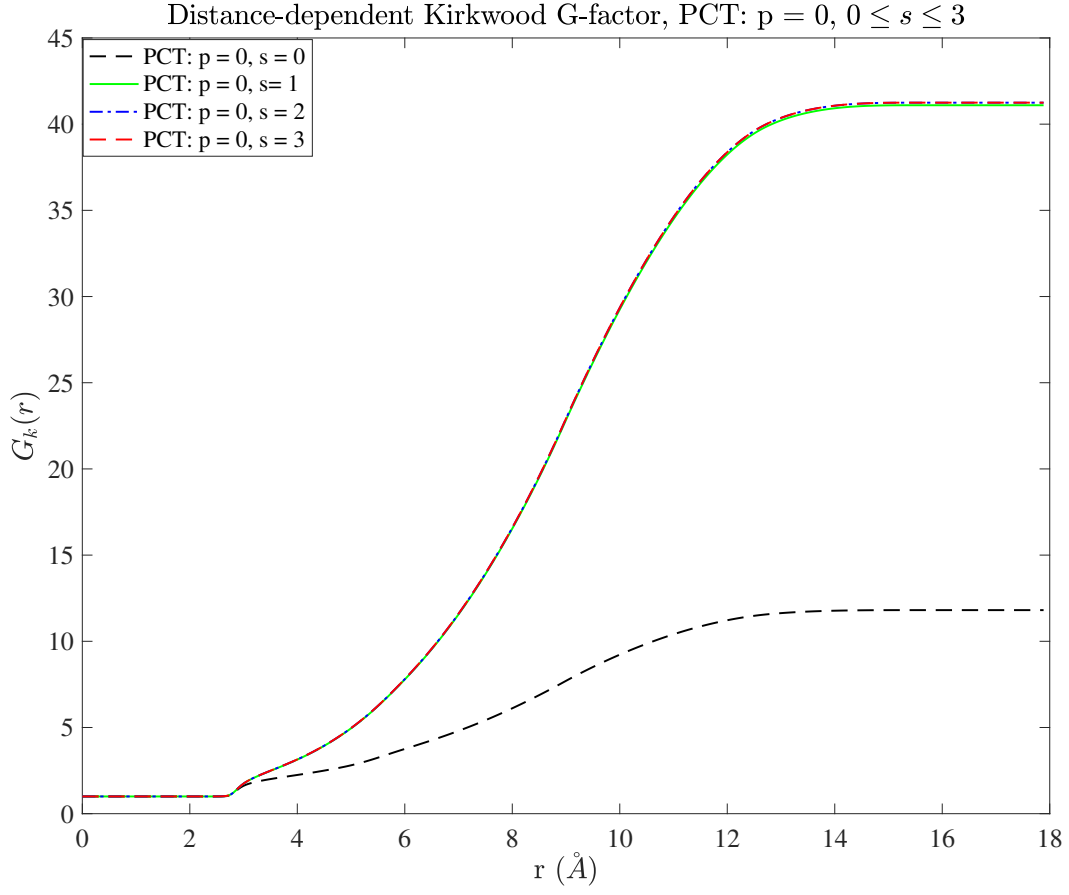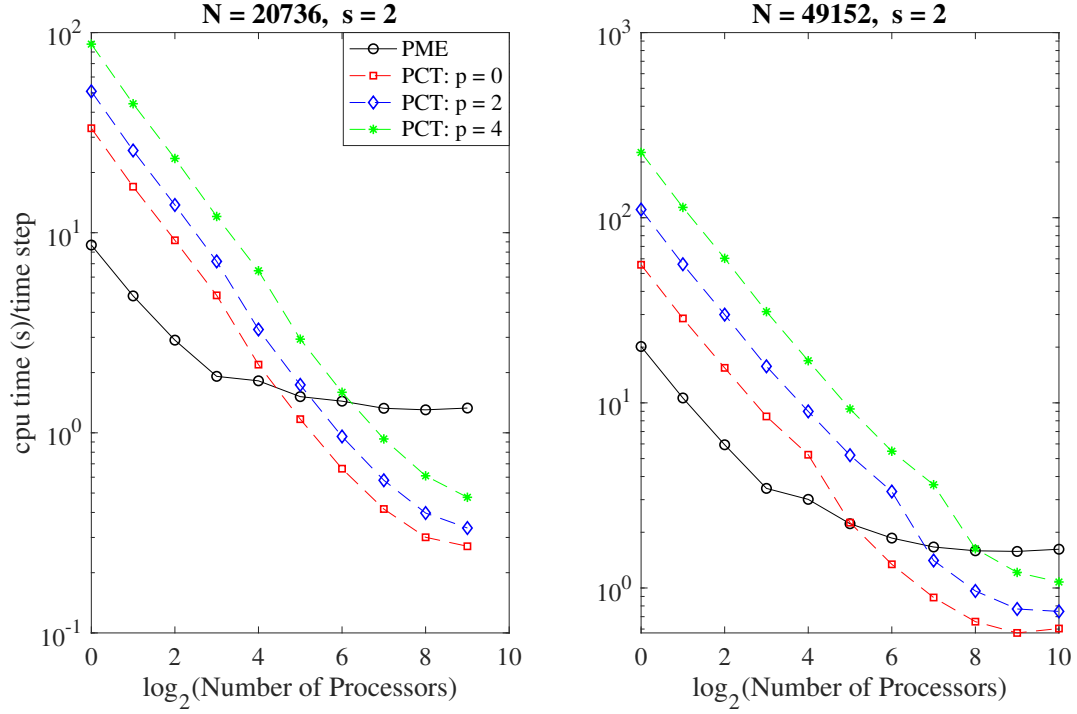
Figure 4: A comparison of $G_k(r)$ for PCT with $p = 0$ and $s \in \{0, 1, 2, 3\}$

2.4 Timing Comparisons for $s = 2$ and $s = 3$ periodic images

Here we provide timing comparisons for $s = 2$ in Figure 5a and $s = 3$ in Figure 5b for $N = 20736$ and $N = 49152$. As expected, PCT is less efficient in these regimes but it still offers some speedup over PME for high processor counts.

(a) Cpu time per time step averaged for different processor counts for PME and PCT with $s = 2$
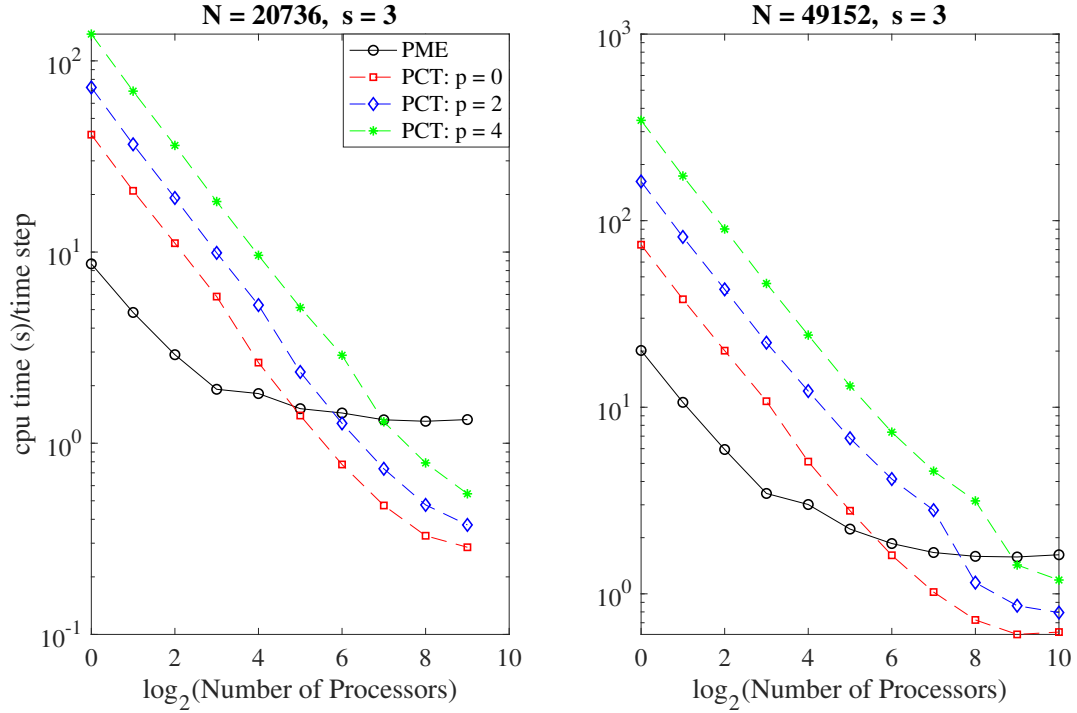
(b) Cpu time per time step for different processor counts for PME and PCT with $s = 3$

Figure 5: Cpu time per time step averaged over 100 MD steps for different processor counts for PME and PCT with (a) $s = 2$, (b) $s = 3$.

References

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