Calculating the Electrostatic Potential Energy Based on the Madelung Constant for B1 Crystal Lattice in LAMMPS with PPPM

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Introduction

This is a series of LAMMPS run that calculates the potential energy from a system that is arranged in a B1 lattice structure. The B1 structure is similar to the crystal structure of NaCl. The simulation box consists of charges arranged in the B1 lattice structure with separation distance r_o of 2.0 σ hence the lattice constant a is 4.0σ.

The objective is to test the accuracy of the PPPM[1] implementation in LAMMPS by comparing the value of the electrostatic potential energy calculated from the analytical Madelung constant from the normalized electrostatic energy that is calculated by LAMMPS with PPPM.

Method

The simulation box consists of 1000 LJ beads arranged in a B1 cubic lattice structure with a separation distance of 2σ. 500 beads are positively charged and the other 500 is negatively charged (See Fig. 1). The charges are arranged alternately such that one cation is adjacent to six anions and vice versa. The forces and velocities are not time integrated because only the potential energy is required. This is achieved by using a "run 0" in the LAMMPS input file. Several "run 0's" are used with varying target accuracy for the "kspace_style pppm" and kspace cutoff in "lj/cut/coul/long". The analytical value of the Madelung constant, M_a is 1.747564594633182[2].

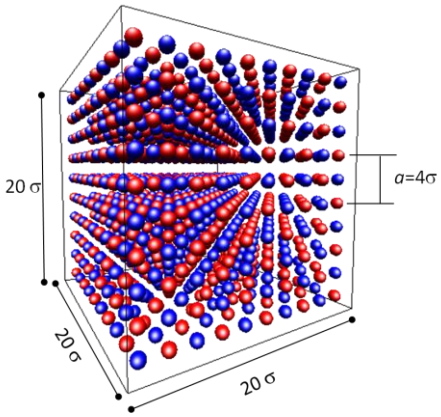

Figure 1. Simulation box showing the B1 lattice structure with alternating placement of cations(red) and anions (blue). The lattice constant a is equal to 4.0σ.

The electrostatic potential energy of a cation at a site r_i is the product of its charge with the potential acting at its site is:

$$E_{el,i_+} = z_i e V_i = \frac{e^2}{4\pi\varepsilon_o r_o} z_i M_{i+}$$

Where M_{i+} is the Madelung constant for the cations. In reduced units:

$$E_{el,i_+} = \frac{q^{*2}}{r_o} z_i M_{i_+} \text{ where } q^* = \frac{e}{\left(4\pi\varepsilon_o \sigma k_B T\right)^{1/2}}$$

For this system $r_o = a/2.0 = 2\sigma$, $z_i = 1.0$ and $q^* = 1.0$. Hence the $E_{el,i}$ is:

$$M_{i_+} = 2E_{el,i_+}$$

A similar method is done to calculate the Madelung constant for the anions and would result in the same value.

$M_{i-} = 2E_{el,i-}$

For an ionic solid, the sum of contributions of cations and anions of a crystal would then be the sum of the partial Madulung constants of cation and anion subarrays[3]. Hence the total Madelung constant is,

$M_a = M_{i+} + M_{i-} = 2E_{el,i+} + 2E_{el,i-} = 4E_{el,i}$ where $E_{el,i}$ would be the normalize potential energy that will be outputted by LAMMPS.

Thus, in order to compare the results of the "run 0" LAMMPS run with the analytical expected value of the electrostatic energy, we should divide the analytical Madelung constant, M_a by 4 ($E_{el,i,analytical} = M_a / 4$). The expected normalized electrostatic potential energy up to 15 decimal places is 0.436891148658295 $k_B T$.

Results and Discussions

Table 1 shows the target accuracy value, the LAMMPS potential energy output from different near field cutoffs, the absolute value of the difference of the between the LAMMPS calculated energy to the electrostatic potential energy calculated from the Madelung constant and the estimated RMS[4] calculated by LAMMPS.

Table 1

Target Accuracy	Cutoff = 6σ			Cutoff = 8σ			Cutoff = 10σ		
	RMS	$E_{el,i}$	Δ*	RMS	$E_{el,i}$	Δ*	RMS	$E_{el,i}$	Δ*
1.00E-01	5.641E-02	0.316353	4.523E-02	4.886E-02	0.35422	8.267E-02	5.082E-02	0.391665	4.523E-02
5.00E-02	3.221E-02	0.373343	1.780E-02	2.323E-02	0.40338	3.351E-02	2.495E-02	0.419089	1.780E-02
1.00E-02	4.414E-03	0.429696	8.856E-04	1.922E-03	0.43504	1.851E-03	2.243E-03	0.436006	8.856E-04
5.00E-03	2.896E-03	0.432315	8.856E-04	1.922E-03	0.43504	1.851E-03	2.243E-03	0.436006	8.856E-04
1.00E-03	5.097E-04	0.436167	1.091E-04	3.311E-04	0.43664	2.507E-04	3.947E-04	0.436782	1.091E-04
5.00E-04	2.254E-04	0.436584	6.252E-05	3.311E-04	0.43664	2.507E-04	2.467E-04	0.436829	6.252E-05
1.00E-04	6.156E-05	0.436812	7.524E-06	5.331E-05	0.436859	3.200E-05	3.966E-05	0.436884	7.524E-06
5.00E-05	3.620E-05	0.436845	5.424E-06	3.315E-05	0.436872	1.880E-05	2.965E-05	0.436886	5.424E-06
1.00E-05	6.240E-06	0.436883	7.487E-07	5.404E-06	0.436889	2.449E-06	4.833E-06	0.43689	7.487E-07
5.00E-06	3.702E-06	0.436887	6.237E-07	4.060E-06	0.436889	1.799E-06	4.033E-06	0.436891	6.237E-07
1.00E-06	7.861E-07	0.43689	1.237E-07	9.035E-07	0.436891	3.487E-07	8.080E-07	0.436891	1.237E-07

* $\Delta = \left| E_{el,i} - \frac{M_{crystal}}{4} \right|$

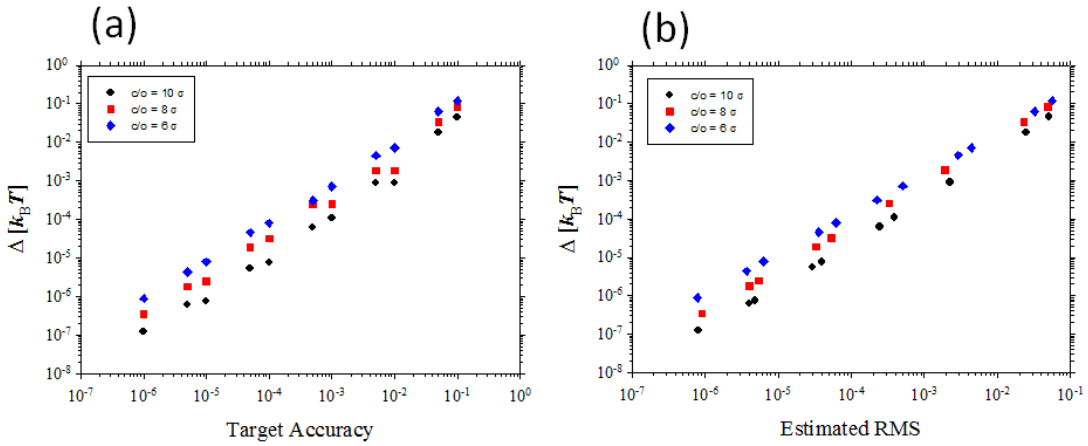

Figure 2. Dependence of Δ to the target accuracy (a) and dependence of Δ to the estimated RMS value (b) for a simulation box with reduced density, $\rho=0.125\sigma^{-3}$ and lattice constant,$a=4\sigma$.

Figure 2 summarizes the results tabulated in Table 1. A similar simulation run is done for a box that is $10\times10\times10\ \sigma^3$. This is to see the effect of density in the PPPM calculation of the electrostatic potential energy. The results for this run are shown in figure 3.

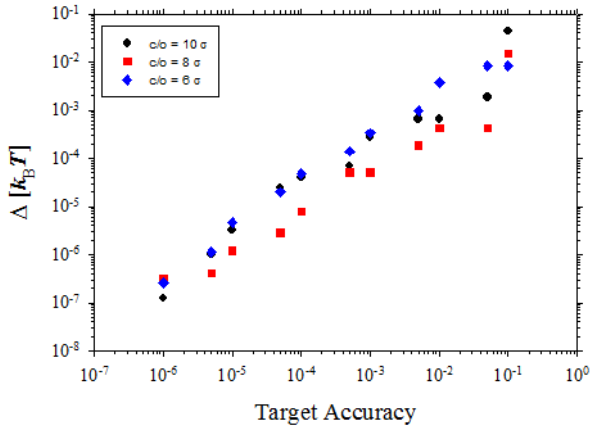

Figure 3. Dependence of Δ to the target accuracy for a simulation box with reduced density, $\rho=1.0\sigma^{-3}$ and lattice constant,$a=2\sigma$.

The implementation of PPPM in LAMMPS can correctly recover the electrostatic potential energy based on the Madelung constant. For a system with a reduced density of $0.125\ \sigma^{-3}$, the near field cutoff of 10σ has the least value of Δ (error) and specifying a target accuracy of $1x10^{-4}$ in the "kspace_style" argument results in an error or Δ in the order of $1x10^{-5}$ for the electrostatic potential energy.

To comment on the probable result for more dense systems, when there are more neighboring particles, this result might reverse and a near field cutoff that is less than 10 σ might get a lower value of Δ. The reason for this is there would be more contribution to the potential energy that is calculated in real space as opposed to the inverse space. For the system with reduced density of $1.0\sigma^{-3}$, the near field cutoff of 8σ has the least value of Δ (error) as shown in figure 3. The user is

advised to check what is the optimal near field cutoff for the desired error in the potential energy calculation for a given system before proceeding to do production runs. For inhomogeneous systems, e.g. interfaces, a test run is strongly advised. Furthermore, specifying very small target accuracy is computationally expensive and the user is advised to find the best value for the near field cutoff with respect to desired accuracy and simulation time.

Conclusions

The implementation of PPPM in LAMMPS can correctly recover the electrostatic potential energy based on the Madelung constant. For a system with a reduced density of $0.125\ \sigma^{-3}$, the near field cutoff of 10σ has the least value of Δ (error) and specifying a target accuracy of $1x10^{-4}$ in the "kspace_style" argument results in an error or Δ in the order of $1x10^{-5}$ for the electrostatic potential energy. For the more dense system, the system with reduced density of $1.0\sigma^{-3}$, the near field cutoff of 8σ has the least value of Δ (error). The user is advised to check what is the optimal near field cutoff with respect to the desired error in the potential energy and the simulation time for a given system before proceeding to do production runs.

References

1. Hockney, R. W.; Eastwood, J. W., *Computer simulation using particles*. Special student ed.; A. Hilger: Bristol [England] ; Philadelphia, 1988; p xxi, 540 p.
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4. Deserno, M.; Holm, C., How to mesh up Ewald sums. II. An accurate error estimate for the particle-particle-particle-mesh algorithm. *Journal of Chemical Physics* **1998,** *109* (18), 7694-7701.