Long Range Potentials and the Ewald Method

Kenneth P. Esler Jr.

UIUC Department of Physics
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Review: Periodic Boundary Conditions

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Why do we use periodic boundary conditions?

- Macroscopic systems $O(10^{23})$ particles.
- We eliminate surfaces from the simulation.
- Allows us to get at bulk properties with few particles.
- Applies to solids, liquids, gases, and plasmas. (Must be careful with solids.)
- Some finite size effects remain, but most can be removed with scaling.
Long Range Potentials

- What makes a potential long range?
  Consider an infinite cubic lattice of particles with charge +1.
What makes a potential long range?
Consider an infinite cubic lattice of particles with charge +1.

Consider the potential on a single charge from all the other charges in the lattice.

$$V(r_i) = \sum_{L \neq 0} \frac{1}{|r_i - L|}$$
Let’s approximate with an integral

\[ V(r_i) \approx \int_0^\infty 4\pi r^2 dr \frac{\rho}{r} \]  

(2)
Long Range Potentials (continued)

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(4)

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Is this result physically correct?
Long Range Potentials (continued)

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\[ V(r_i) \approx \int_0^{\infty} 4\pi r^2 dr \frac{\rho}{r} \]  

(5)

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- Is this result physically correct?
- YES! The potential due an infinite amount of charge is infinite.
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\[ V(r_i) \approx \int_{0}^{\infty} 4\pi r^2 \, dr \frac{\rho}{r} \]  \hspace{1cm} (6)

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• YES! The potential due an infinite amount of charge is infinite.
• What’s the catch? Why do we bother with this problem?
Long Range Potentials (continued)

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(7)

- This diverges!

- Is this result physically correct?

- YES! The potential due an infinite amount of charge is infinite.

- What’s the catch? Why do we bother with this problem?

- Physical systems are *charge neutral*. 
In a neutral system, the + and − charges screen each other, so the energy per cell is finite.

But, we still don’t know how to do the lattice sums:

\[ V_{\text{cell}} = \frac{1}{2} \sum_{i \neq j} \sum_{L} \frac{Z_i Z_j}{|\mathbf{r}_i - \mathbf{r}_j - \mathbf{L}|} \] (8)
What is Long Range?

- A potential is long range if the real-space lattice sum will not (naively) converge.

In $\mathbb{R}^3$, a potential is long range if it decays at a rate $< r^{-3}$.

In $\mathbb{R}^2$, a potential is long range if it decays at a rate $< r^{-2}$.

In practice, we often use the techniques we will discuss for potentials that aren't strictly long range.
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- In practice, we often use the techniques we will discuss for potentials that aren’t strictly long range.
Motivation

Before we begin with some (not so) nasty math, take a step back to see why this is necessary. Most interesting systems contain charges:

- any atomic system at level of nuclei and electrons.
- at the atom level, any system with charged defects.
- any system with dissolved ions (biological system).
- partial charges (in chemistry).
Fourier Transforms

Idea: Take advantage of periodicity using *Fourier Transforms.*

- If $f(r)$ is a continuous periodic function such that
  \[ f(r + L) = f(r), \]  
  where $L = n_x L_x \hat{x} + n_y L_y \hat{y} + n_z L_z \hat{z}$, then we can write
  \[ f(r) = \sum_k e^{i\mathbf{k} \cdot r} f_k, \]  

- Note that the $k$-vectors are *discrete, not continuous.*
Fourier Transforms and Potentials

Idea: If we write the potential energy in \( k \)-space, perhaps our sum will converge... Let’s try!

\[
V = \frac{1}{2} \sum_{i \neq j} \sum_{\mathbf{L}} v(|\mathbf{r}_i - \mathbf{r}_j - \mathbf{L}|) 
\]

\[
= \frac{1}{2} \sum_{i \neq j} \sum_{\mathbf{L}} \sum_{\mathbf{k}} e^{i \mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_j - \mathbf{L})} v_{\mathbf{k}}^{\text{cell}} 
\]

\[
= \frac{1}{2} \sum_{i \neq j} \sum_{\mathbf{k}} e^{i \mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_j)} v_{\mathbf{k}}^{\text{all space}} 
\]

\[
v_{\mathbf{k}}^{\text{cell}} = \frac{1}{\Omega} \int_{\text{cell}} d^3 \mathbf{r} e^{-i \mathbf{k} \cdot \mathbf{r}} v(|\mathbf{r}|) 
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v_{\mathbf{k}}^{\text{all space}} = \frac{1}{\Omega} \int_{\text{all space}} d^3 \mathbf{r} \sum_{\mathbf{L}} e^{-i \mathbf{k} \cdot (\mathbf{r} + \mathbf{L})} v(|\mathbf{r} + \mathbf{L}|) 
\]

\[
= \frac{1}{\Omega} \int_{\text{all space}} d^3 \mathbf{r} e^{-i \mathbf{k} \cdot \mathbf{r}} v(|\mathbf{r}|) 
\]
Did it work?!

- We did succeed in writing down potential in $k$-space.
- But, let’s look at $v_k$ for coulomb potential.

$$v_{k}^{\text{coulomb}} = \frac{4\pi q_1 q_2}{k^2}$$

- Potential is decays slowly in $k$-space too. Summation won’t converge!
- Have I wasted our time?
Origins of convergence problems

Coulomb potential in real space

Coulomb potential in k space
Origins of convergence problems

- Real space convergence problem comes from this tail, which corresponds to the singularity in $k$-space as $k \to 0$. 
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- Real space convergence problem comes from this tail, which corresponds to the singularity in $k$-space as $k \to 0$.
- $k$-space converge problem comes from this tail, which corresponds to origin singularity in real space.
The Ewald Breakup Method: Concept

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![Short range part of coulomb potential](image1.png)

![Long range part of coulomb potential](image2.png)
The Ewald Breakup Method: Concept

Idea: Break the potential into two pieces:

- one short ranged in real space
- one short ranged in $k$-space
In the classical breakup of the coulomb potential, we choose

\[ v_{\text{short}} = \frac{q_1 q_2}{r} \text{erfc}(\kappa r) \]

\[ v_{\text{long}}(r) = \frac{q_1 q_2}{r} \text{erf}(\kappa r) \]

\[ v_{k_{\text{long}}} = \frac{4\pi q_1 q_2}{\Omega k^2} \exp \left( \frac{-k^2}{4\kappa^2} \right) \]

\[ \text{erf}(z) \equiv \frac{2}{\sqrt{\pi}} \int_{0}^{z} e^{-t^2} dt \]

\[ \text{erfc}(z) \equiv 1 - \text{erf}(z) \]
The Ewald Breakup Method: Conventional Breakup

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- Choose \( \kappa \) such that \( v^{\text{short}}(r) \) is negligible at \( r = L/2 \).
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- Choose \( \kappa \) such that \( v^{\text{short}}(r) \) is negligible at \( r = L/2 \).
- Need only one image in real space: *minimum image convention.*
The Ewald Breakup Method: Accuracy

The total potential may be written as

\[ V = C + \sum_{i \neq j} \left\{ v^{\text{short}}(r_{ij}) + \sum_{|\mathbf{k}| < k_c} e^{i\mathbf{k} \cdot (\mathbf{r}_j - \mathbf{r}_i)} v^{\text{long}}_k \right\}, \quad r_{ij} = \min_{\mathbf{L}} |\mathbf{r}_i - \mathbf{r}_j - \mathbf{L}| \]

- In conventional breakup,
  \[ v^{\text{short}} \left( \frac{L}{2} \right) = \frac{2q_1 q_2}{L} \text{erfc} \left( \frac{\kappa L}{2} \right) \neq 0. \]

This gives some error.
- Summation in \( k \)-space is truncated at desired accuracy.
- We adjust parameter \( \kappa \) to minimize total error.
The Ewald Breakup Method: Physical Interpretation

- The Poisson equation is linear, therefore we are free to add charge as long as we subtract it again.
- Ewald breakup can be thought of as adding a neutralizing cloud of charge in real space, then subtracting that same charge cloud in $k$-space.
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Optimized Breakup Method

Is the conventional method the best we can do? No!

- Write
  
  \[ v^{\text{short}}(r) = \sum_n c_n h_n(r) \]  
  or 
  
  \[ v^{\text{long}}(r) = \sum_n c_n h_n(r) \]

- \( h_n \)'s subject to appropriate boundary conditions.
- Choose \( k \)-space cutoff, \( k_c \).
- Write error that comes from neglecting larger \( k \)'s.
- Minimize error w.r.t \( c_n \)'s.
Method and results due to Ceperley and Natoli (1995).
Let’s look at the $k$-space sum.

$$V_k = \frac{1}{2} \sum_{i \neq j} \sum_k e^{ik \cdot (|r_i - r_j|)} v_k$$

$$= \frac{1}{2} \sum_{i, j} \sum_k e^{ik \cdot (|r_i - r_j|)} v_k - \frac{1}{2} \sum_k v_k$$

$$= \frac{1}{2} \sum_k \left[ \sum_i e^{ik \cdot r_i} \right] \left[ \sum_j e^{-ik \cdot r_j} \right] v_k + C$$

- $\rho_k = \rho^*_{-k}$, so we need only compute one of them.
- Computation of all $\rho_k$’s goes as $NM_k$, where $M_k$ is the number of $k$-vectors.
Algorithm for $k$-space sums

Compute $\rho_k$ for all $k$.

for all $k \in k$-vector list do

$V_{\text{long}} := V_{\text{long}} + \rho_k \rho_{-k} v_k$

end for

Changes due to moving a few particles can be computed more quickly.
Computing $\rho_k$

Recall that $k = \frac{2\pi m_1}{L} \hat{x} + \frac{2\pi m_2}{L} \hat{y} + \frac{2\pi m_3}{L} \hat{z}$. Then

$$e^{ik \cdot r} = \left[ e^{\frac{2\pi ir_1}{L}} \right]^{m_1} \left[ e^{\frac{2\pi ir_2}{L}} \right]^{m_2} \left[ e^{\frac{2\pi ir_3}{L}} \right]^{m_3}$$

Complex multiplication is much faster than complex exponentiation. (Need sin’s and cos’s)
Algorithm to quickly compute $\rho_k$

Create list of $k$ & corresponding $(m_1, m_2, m_3)$ indices.
Zero out $\rho_k$

for all $i \in \text{particles}$ do
  for $j \in \{1 \cdots 3\}$ do
    Compute $C_{ij} \equiv e^{ib_j \cdot r_i}$
    for $m \in [-m_{\text{max}} \cdots m_{\text{max}}]$ do
      Compute $[C_{ij}]^m$ and store in array
    end for
  end for
end for

for all $(m_1, m_2, m_3) \in \text{index list}$ do
  Compute $e^{ik \cdot r_i} = [C_{1i}]^{m_1} [C_{2i}]^{m_2} [C_{3i}]^{m_3}$ from array
  Accumulate to $\rho_k$
end for
end for
Computational Complexity

- If we use neighbor tables and optimize $\kappa$, Ewald method has a complexity $\mathcal{O} \left( N^{3/2} \right)$.
- If we do not reoptimize, then we have $\mathcal{O} \left( N^2 \right)$.
- With efficient code, prefactor is small relative to more sophisticated methods.
Alternative Methods

- **Fast Multipole Method**
  - Recursively subdivide space into cells.
  - Find dipole moment of each cell.
  - Use specialized rules to determine how multipole moments for cells depends on cells below them in the hierarchy.
  - $\sim O(N)$ for large systems

- **Particle Cell Method**
  - Perform $k$-space sums on a regular grid using *Fast Fourier Transforms*.
  - Developed by Hockney
  - $O(N \ln(N))$