Long Range Potentials and the Ewald Method

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Review: Periodic Boundary Conditions

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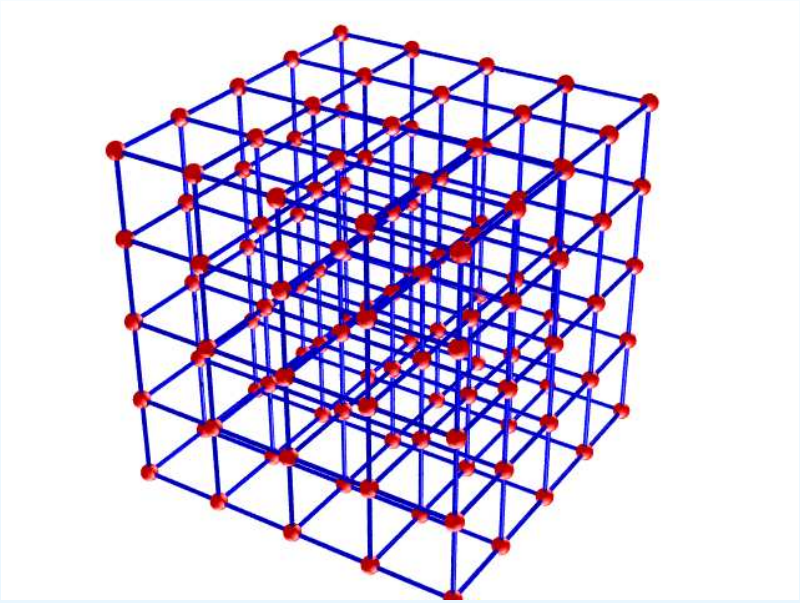
- We eliminate surfaces from the simulation.
- Allows us to get at bulk properties with few particles.
- Applies to solids, liquids, gases, and plasmas.
  (Must be careful with solids.)
- Some finite size effects remain, but most can be removed with scaling.

Long Range Potentials

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



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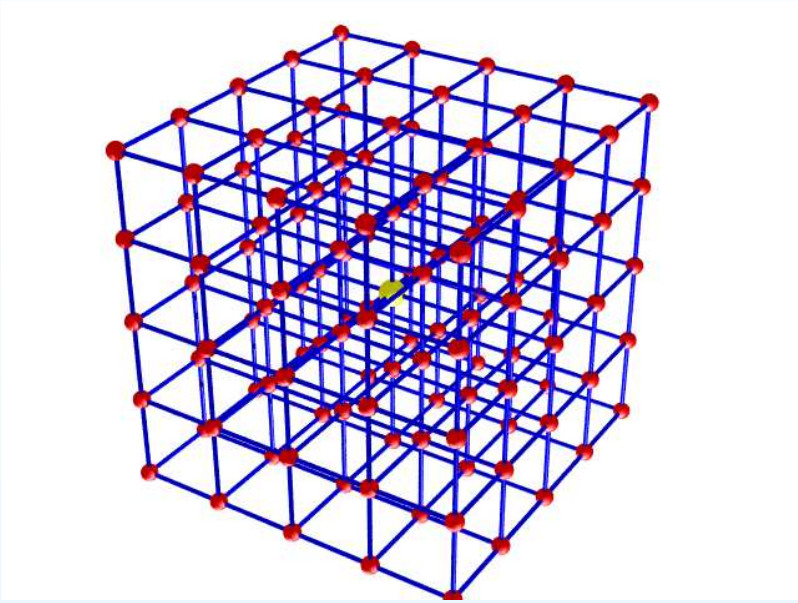

- Consider the potential on a single charge from all the other charges in the lattice.

$$V(\mathbf{r}_i) = \sum_{\mathbf{L}\neq\mathbf{0}} \frac{1}{|\mathbf{r}_i - \mathbf{L}|} \tag{1}$$

Long Range Potentials (continued)

- Let's approximate with an integral

$$V(\mathbf{r}_i) \approx \int_0^\infty 4\pi r^2 \, dr \, \frac{\rho}{r} \tag{2}$$

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Long Range Potentials (continued)

- Let's approximate with an integral

$$V(\mathbf{r}_i) \approx \int_0^\infty 4\pi r^2 \, dr \, \frac{\rho}{r} \tag{4}$$

- This diverges!
- Is this result physically correct?

Long Range Potentials (continued)

- Let's approximate with an integral

$$V(\mathbf{r}_i) \approx \int_0^\infty 4\pi r^2 \, dr \, \frac{\rho}{r} \tag{5}$$

- This diverges!
- Is this result physically correct?
- YES! The potential due an infinite amount of charge is inifinite.

Long Range Potentials (continued)

- Let's approximate with an integral

$$V(\mathbf{r}_i) \approx \int_0^\infty 4\pi r^2 \, dr \, \frac{\rho}{r} \tag{6}$$

- This diverges!
- Is this result physically correct?
- YES! The potential due an infinite amount of charge is inifinite.
- What's the catch? Why do we bother with this problem?

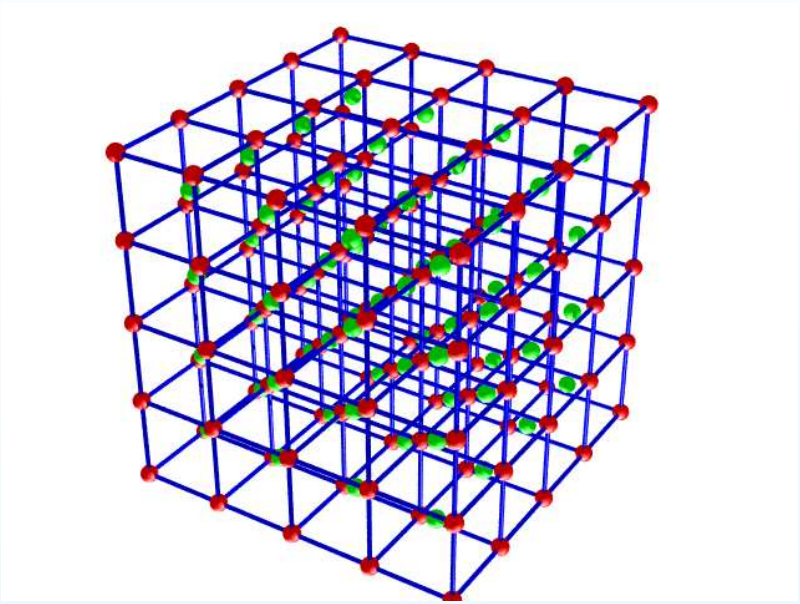
Long Range Potentials (continued)

- Let's approximate with an integral

$$V(\mathbf{r}_i) \approx \int_0^\infty 4\pi r^2 \, dr \, \frac{\rho}{r} \tag{7}$$

- This diverges!
- Is this result physically correct?
- YES! The potential due an infinite amount of charge is inifinite.
- What's the catch? Why do we bother with this problem?
- Physical systems are *charge neutral*.

Neutral Systems



- 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:

$$V_{\text{cell}} = \frac{1}{2} \sum_{i \neq j} \sum_{\mathbf{L}} \frac{Z_i Z_j}{|\mathbf{r}_i - \mathbf{r}_j - \mathbf{L}|} \tag{8}$$

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- A potential is long range if the real-space lattice sum will not (naively) converge.
- In $3D$, a potential is long range if it decays at a rate $< r^{-3}$.
- In $2D$, 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.

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 disolved ions (biological system).
- partial charges (in chemistry).

Fourier Transforms

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

- If $f(\mathbf{r})$ is a continuous periodic function such that

$$f(\mathbf{r}+\mathbf{L}) = f(\mathbf{r}), \tag{9}$$

where $\mathbf{L} = n_x L_x \hat{x} + n_y L_y \hat{y} + n_z L_z \hat{z}$, then we can write

$$f(\mathbf{r}) = \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} f_{\mathbf{k}}, \tag{10}$$

$$\mathbf{k} = m_x \frac{2\pi}{L_x}\hat{x} + m_y \frac{2\pi}{L_y}\hat{y} + m_z \frac{2\pi}{L_z}\hat{z}. \tag{11}$$

$$f_{\mathbf{k}} = \frac{1}{\Omega}\int_{\text{all space}} d^3\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} f(\mathbf{r}) \tag{12}$$

- Note that the k-vectors are *discrete, not continuous*.

Fourier Tranforms and Potentials

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

$$V = \frac{1}{2}\sum_{i\neq j}\sum_{\mathbf{L}} v(|\mathbf{r}_i - \mathbf{r}_j - \mathbf{L}|) \tag{13}$$

$$= \frac{1}{2}\sum_{i\neq j}\sum_{\mathbf{L}}\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot(\mathbf{r}_i-\mathbf{r}_j-\mathbf{L})} v_{\mathbf{k}}^{\text{cell}} \tag{14}$$

$$= \frac{1}{2}\sum_{i\neq j}\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot(\mathbf{r}_i-\mathbf{r}_j)} v_k^{\text{all space}} \tag{15}$$

$$v_{\mathbf{k}}^{\text{cell}} = \frac{1}{\Omega}\int_{\text{cell}} d^3\mathbf{r}\, e^{-i\mathbf{k}\cdot\mathbf{r}} v(|\mathbf{r}|) \tag{16}$$

$$v_{\mathbf{k}}^{\text{all space}} = \frac{1}{\Omega}\int_{\text{cell}} d^3\mathbf{r} \sum_{\mathbf{L}} e^{-i\mathbf{k}\cdot(\mathbf{r}+\mathbf{L})} v(|\mathbf{r}+\mathbf{L}|) \tag{17}$$

$$= \frac{1}{\Omega}\int_{\text{all space}} d^3\mathbf{r}\, e^{-i\mathbf{k}\cdot\mathbf{r}} v(|\mathbf{r}|) \tag{18}$$

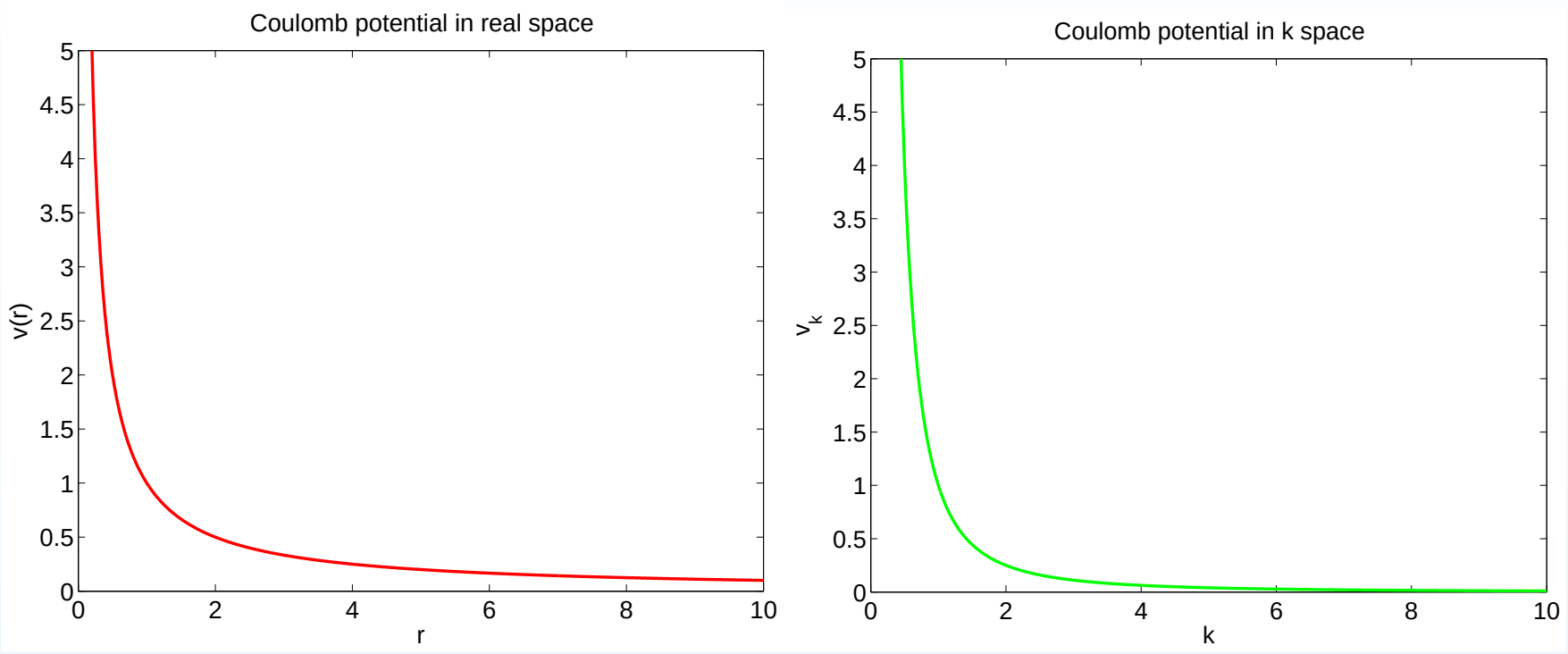
Did it work?!

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

$$v_k^{\text{coulomb}} = \frac{4\pi q_1 q_2}{k^2} \tag{19}$$

- Potential is decays slowly in k-space too. Summation won't converge!
- Have I wasted our time?

Origins of convergence problems



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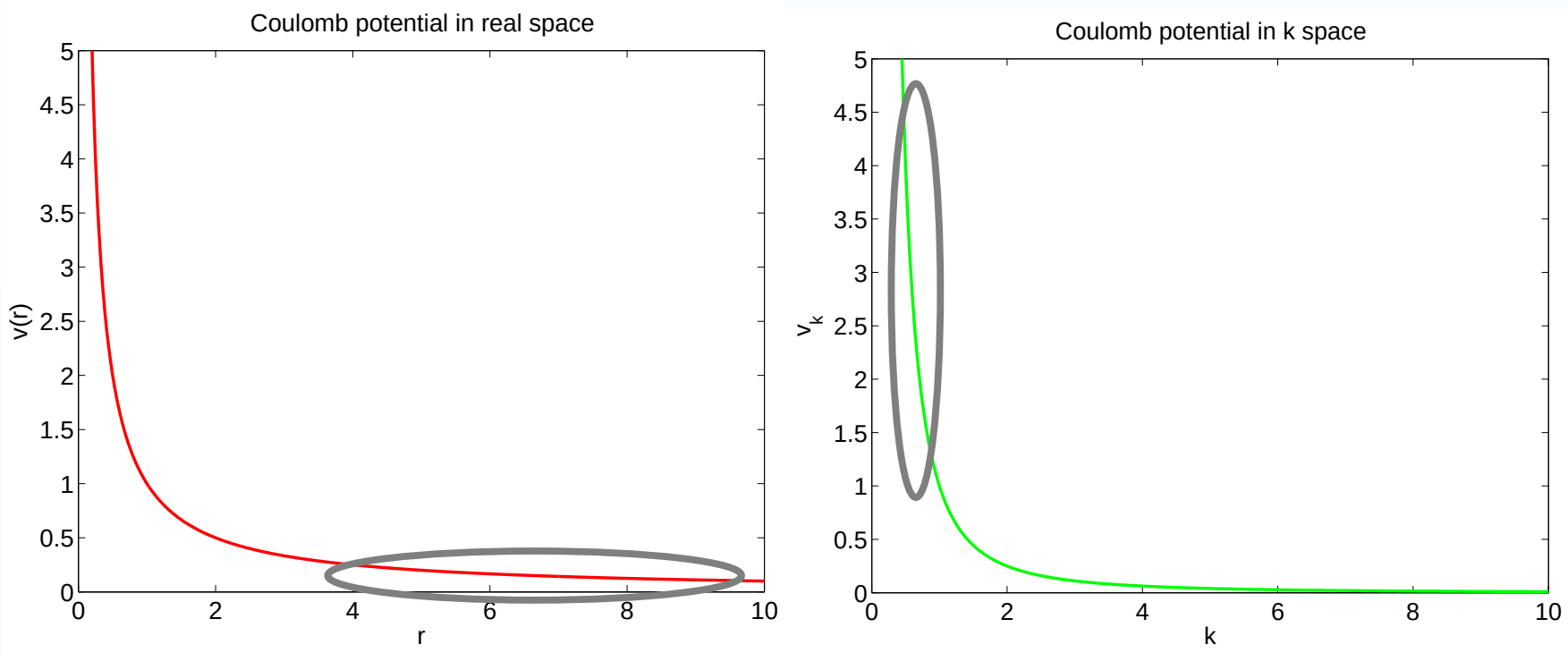

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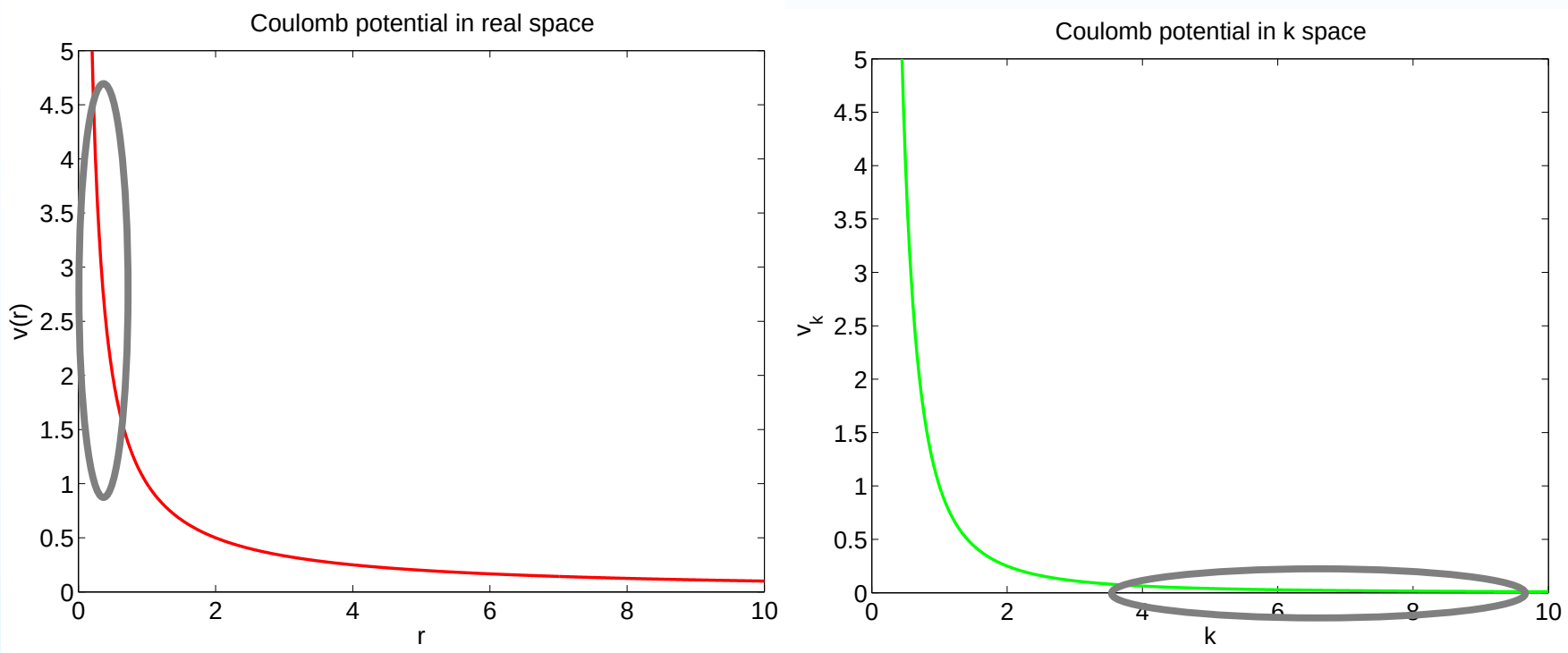

- Real space convergence problem comes from this tail, which corresponds to the singularity in k-space as $k \to 0$.
- k-space converge problem comes from this tail, which corresponds to origin singularity in real space.

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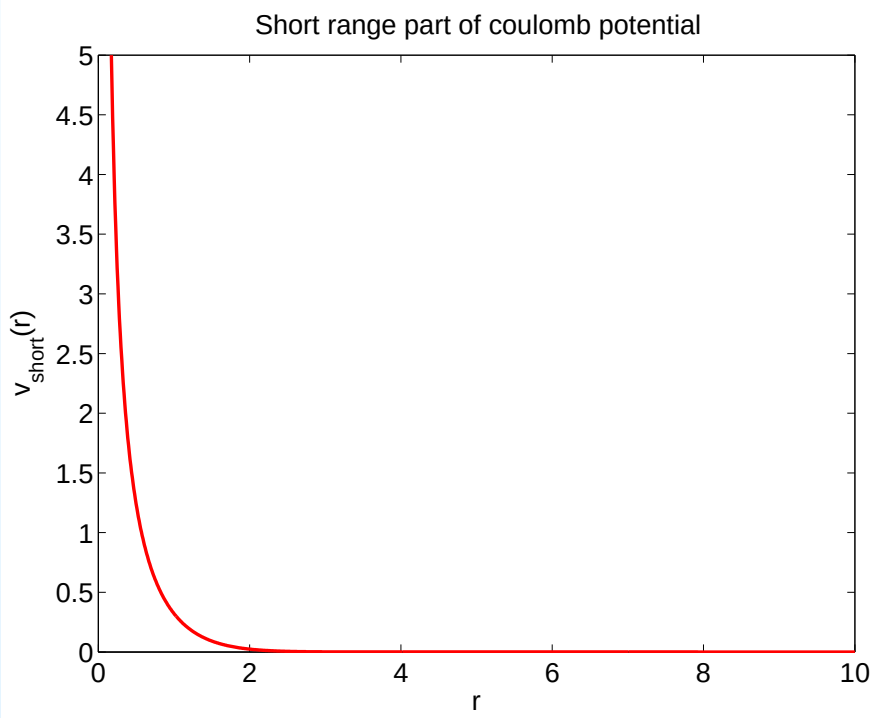

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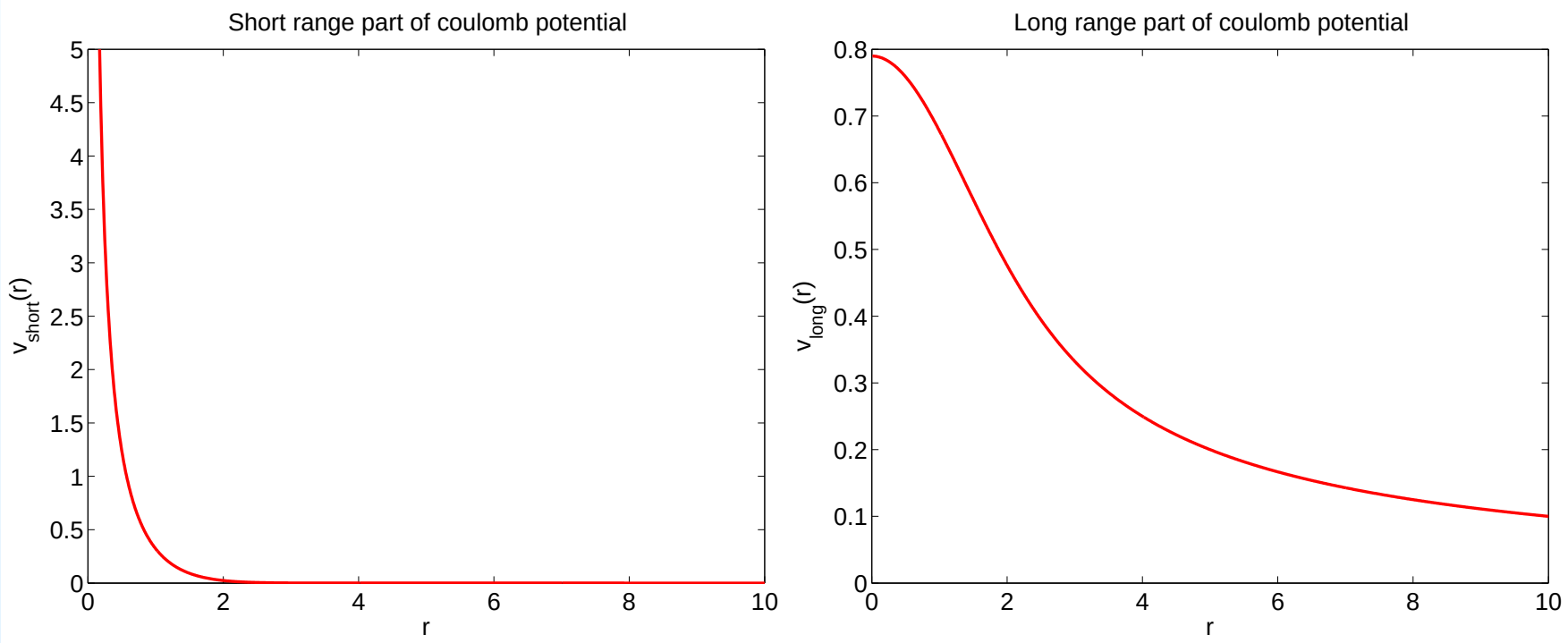

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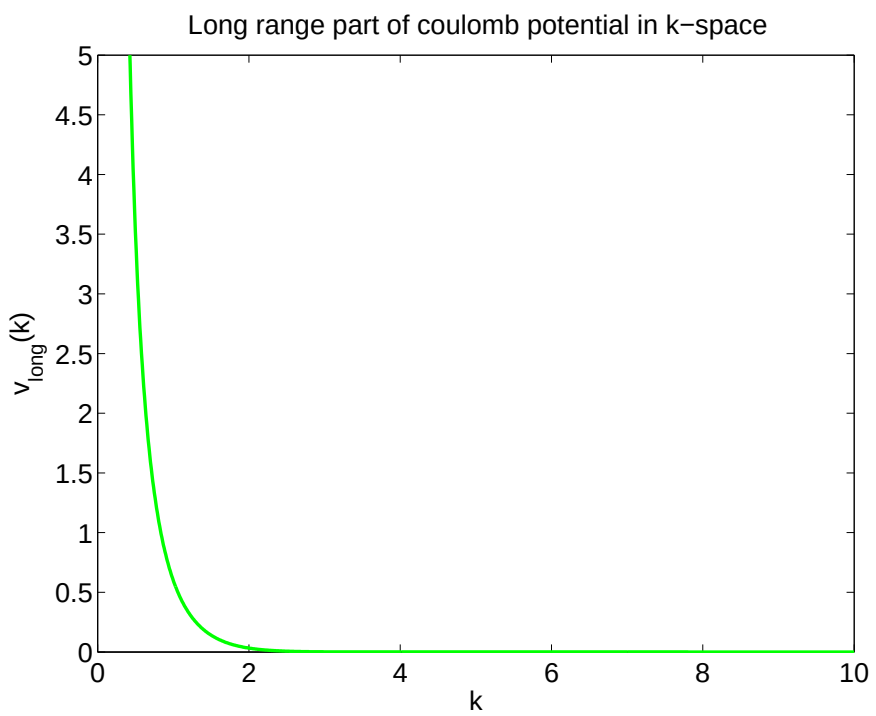

The Ewald Breakup Method: Conventional Breakup

In the classical breakup of the coulomb potential, we choose

$$
\begin{aligned}
v^{\text{short}} &= \frac{q_1 q_2}{r}\operatorname{erfc}(\kappa r) \\
v^{\text{long}}(r) &= \frac{q_1 q_2}{r}\operatorname{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) \\
\operatorname{erf}(z) &\equiv \frac{2}{\sqrt{\pi}}\int_0^z e^{-t^2}\,dt \\
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- Choose κ 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

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

- In conventional breakup,

$$v^{\text{short}}\left(\frac{L}{2}\right) = \frac{2q_1q_2}{L}\text{erfc}\left(\frac{\kappa L}{2}\right) \neq 0.$$

  This gives some error.
- Summation in k-space is truncated at desired accuracy.
- We adjust parameter κ 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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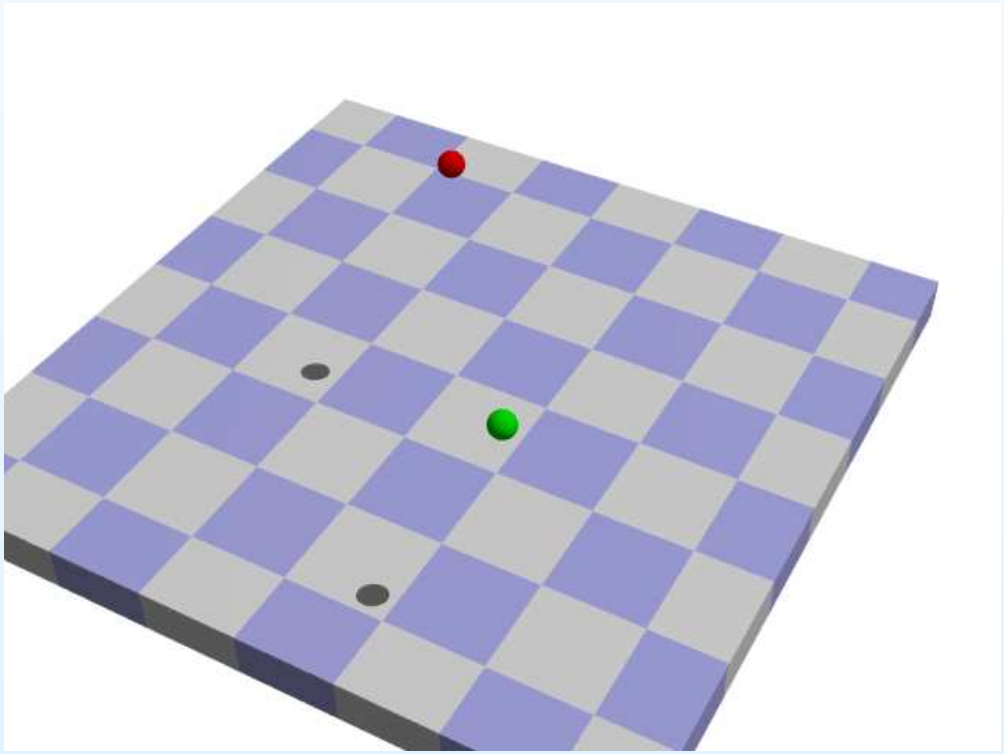

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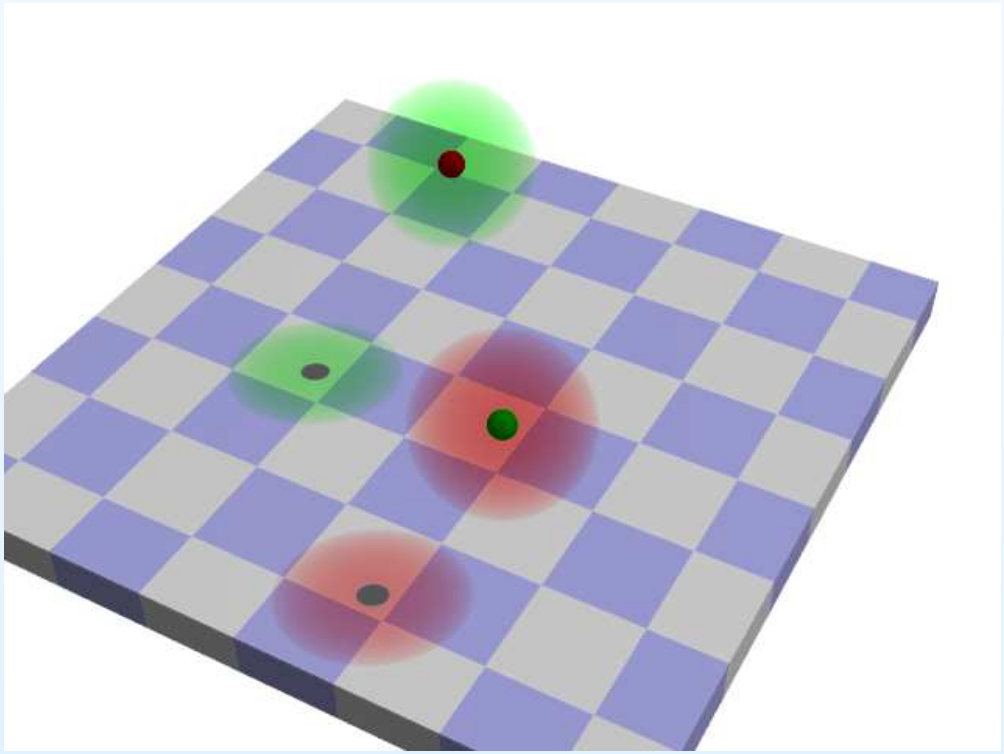

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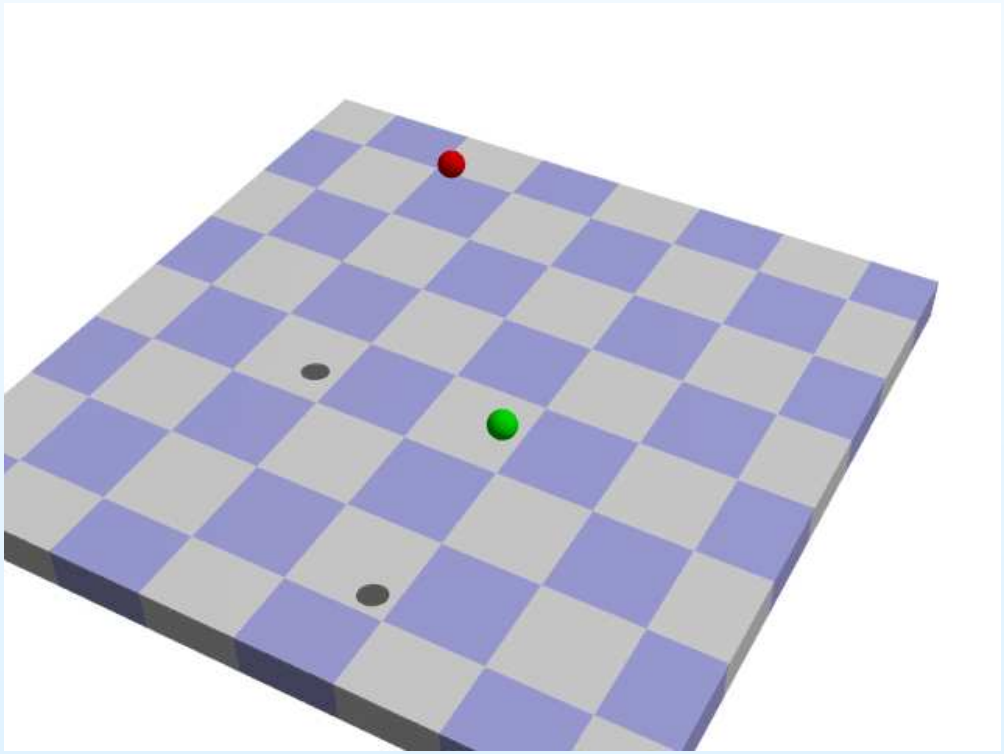


Optimized Breakup Method

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

- Write

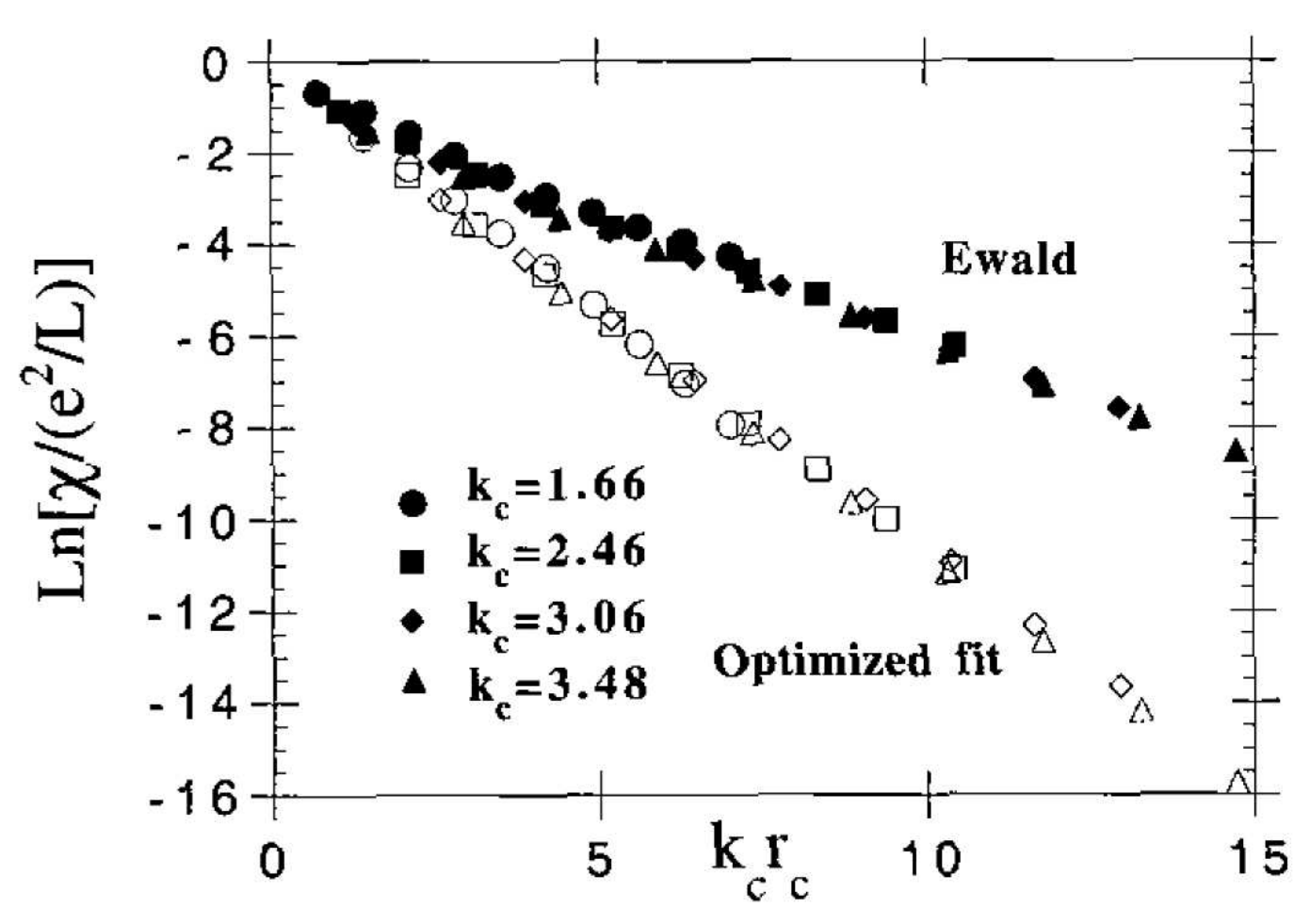
$$v^{\text{short}}(r) = \sum_n c_n h_n(r) \tag{20}$$

or

$$v^{\text{long}}(r) = \sum_n c_n h_n(r) \tag{21}$$

- h_n's subject to appropriate boundary condtions.
- Choose k-space cutoff, k_c.
- Write error that comes from neglecting larger $\mathbf{k}$'s.
- Minimize error w.r.t c_n's.

Optimized Breakup Method Results



Method and results due to Ceperley and Natoli(1995).

Algorithms

Let's look at the k-space sum.

$$V_k = \frac{1}{2}\sum_{i\neq j}\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot(|\mathbf{r}_i-\mathbf{r}_j|)}v_k \tag{22}$$

$$= \frac{1}{2}\sum_{i,j}\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot(|\mathbf{r}_i-\mathbf{r}_j|)}v_k - \underbrace{\frac{1}{2}\sum_{\mathbf{k}} v_k}_{C} \tag{23}$$

$$= \frac{1}{2}\sum_{\mathbf{k}} \underbrace{\left[\sum_i e^{i\mathbf{k}\cdot\mathbf{r}_i}\right]}_{\rho_{\mathbf{k}}} \underbrace{\left[\sum_j e^{-i\mathbf{k}\cdot\mathbf{r}_j}\right]}_{\rho_{-\mathbf{k}}} v_k + C \tag{24}$$

- $\rho_{\mathbf{k}} = \rho^*_{-\mathbf{k}}$, so we need only compute one of them.
- Computation of all ρ_k's goes as NM_k, where M_k is the number of k-vectors.

Algorithm for k-space sums

Compute $\rho_{\mathbf{k}}$ for all $\mathbf{k}$.
for all $\mathbf{k} \in$ k-vector list **do**
$V_{\text{long}} := V_{\text{long}} + \rho_{\mathbf{k}} \rho_{-\mathbf{k}} v_k$
end for

Changes due to moving a few particles can be computed more quickly.

Computing $\rho_{\mathbf{k}}$

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

$$e^{i\mathbf{k}\cdot\mathbf{r}} = \left[e^{\frac{2\pi i r_x}{L}}\right]^{m_1}\left[e^{\frac{2\pi i r_y}{L}}\right]^{m_2}\left[e^{\frac{2\pi i r_z}{L}}\right]^{m_3}$$

Complex multiplication is *much* faster than complex exponentiation. (Need $\sin$'s and $\cos$'s)

Algorithm to quickly compute $\rho_{\mathbf{k}}$

Create list of $\mathbf{k}$ & corresponding (m_1, m_2, m_3) indices.
Zero out $\rho_{\mathbf{k}}$
for all $i \in$ particles **do**
  for $j \in [1 \cdots 3]$ **do**
    Compute $C_j^i \equiv e^{i\mathbf{b}_j \cdot \mathbf{r}_i}$
    for $m \in [-m_{\text{max}} \ldots m_{\text{max}}]$ **do**
      Compute $[C_j^i]^m$ and store in array
    end for
  end for
  for all $(m_1, m_2, m_3) \in$ index list **do**
    Compute $e^{i\mathbf{k}\cdot r_i} = [C_1^i]^{m_1}[C_2^i]^{m_2}[C_3^i]^{m_3}$ from array
    Accumulate to ρ_k
  end for
end for

Computational Complexity

- If we use neighbor tables and optimize κ, Ewald method has a complexity $\mathcal{O}\left(N^{\frac{3}{2}}\right)$.
- 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.
  - $\sim \mathcal{O}(N)$ for large systems
- Particle Cell Method
  - Perform k-space sums on a regular grid using *Fast Fourier Transforms*.
  - Developed by Hockney
  - $\mathcal{O}(N \ln(N))$