Neighbor Tables
Long-Range Potentials

Today we learn how we can handle long range potentials.
- Neighbor tables
- Long-range potential
- Ewald sums

Periodic distances

- **Minimum Image Convention**: take the closest distance
  \[ |r|_M = \min (r + nL) \]

  Potential is **cutoff** so that \( V(r) = 0 \) for \( r > L/2 \) since force needs to be continuous. Remember perturbation theory.

- **Image potential**
  \[ V_I = \Sigma_n v(r_i - r_j + nL) - \text{background (if needed)} \]

  For long-range potential (e.g. Coulomb) need the **Ewald image potential**. You need a back ground and convergence method.
Perturbation theory

• One can restore a cutoff potential by using a \textit{tail correction}:

$$V_{tail} = \frac{P}{2} \int dr \, g(r) \Delta \varphi(r)$$

• To do better one has to find \textit{effect of perturbation on $g(r)$}. E.g. one can use the RHNC equation: integral equation involving the potential and $g(r)$.

• The Stillinger-Lovett condition says that $S(k)$ at low $k$ for a charged system is different than in a neutral system.

\begin{align*}
S(k) &= c \, k^2 \quad \text{for charged system} \\
S(k) &= c \quad \text{for uncharged system}
\end{align*}

Complexity of Force Calculations

• Complexity is the scaling with the number of degrees of particles.

• Number of terms in pair potential is $N(N-1)/2 \approx O(N^2)$

• For short-range potential you can use neighbor tables to reduce it to $O(N)$

  – (Verlet) \textit{neighbor list} for systems that move slowly.
  – \textit{bin sort list} (map system onto a $r_c \times r_c$ mesh and find neighbors from the mesh table, only n.n. cells matter).
  – Or both

If $v(r > r_c) = 0$, force calculations are $O(N)$ with $M$ neighbors.
CLAMPS uses bin-sort method for neighbor tables

- Particles are put into the cells (e.g., linked list).

- To compute the force or potential on a given particle, first one computes the label of its cell. Also the names of the cells within the cutoff radius are identified. The neighbor list is constructed from that and we calculate forces.

- Now the construction of the neighbor list is O(N).

- We need to optimize the number of cells.
  - Too small and one will have to loop over an excessive number of cells to find the few ones that have particles.
  - Too large and many extra particles will be on the neighbor list.
CLAMPS uses the bin-sort method

Example of 848 argon atoms:

optimizing the number of bins

search will be between 1 and 15 divisions in each direction

examine the bin division ndiv(3)=

<table>
<thead>
<tr>
<th>total number of bins</th>
<th>number of neighboring bins</th>
<th>cpu secs/step</th>
<th>potential energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0.13426E+00</td>
<td>-0.14605271E+04</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>0.60312E-01</td>
<td>-0.14648783E+04</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>0.32911E-01</td>
<td>-0.14648783E+04</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>0.60229E-01</td>
<td>-0.14648783E+04</td>
</tr>
</tbody>
</table>

bin scheme used with divisions 5 5 5

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Charged systems

How can we handle charged systems?

- **Treat like short-ranged potential**: cutoff potential at r>L/2.

  Problems:
  - Effect of discontinuity never disappears ((1/r) (r²) gets bigger.
  - Will violate Stillinger-Lovett conditions because Poisson equation is not satisfied.
  - Even a problem with dipolar forces.

- **Image potential solves this**:

  \[ V_I = \sum_n v(r_i-r_j+nL) \]

  - But summation diverges!
    We need to resum: use the Ewald image potential.
  - For one component system, need to add a background to make it neutral.

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1-D Madelung Sum: Prelude to Ewald Sum

\[ \alpha = \sum_{j \neq i} \left( \pm \frac{1}{R_{ij}} \right) \]

The value of \( \alpha \) will depend on whether it is define in terms of the lattice constant \( R \). Start on negative ion, summing (left and right)

\[ \alpha = 2 \ln 2 \]

In 3D the series presents greater difficulty. Series will not converge unless successive terms in the series are arranged so that + and - terms nearly cancel. Powerful methods were developed by Ewald (Ann. Physik 64, 253 (1921), and Evjen (Phys. Rev. 39, 675 (1932) and Frank (Phil. Mag. 41, 1287 (1950)).

Long-Ranged Potentials

- Why make the potential long ranged?
  - Consider a cubic lattice with +1 charges, and its Coulomb potential.

\[ V(r_i) = \sum_{L \neq 0} \frac{1}{|r_i - L|} \approx \int_0^\infty dr \frac{4 \pi r^2 \rho}{r} \]

- Approximate integral diverges!
  - Correct! Non-neutral system with infinite charge has infinite potential.

- Consider a cubic lattice with charge neutrality, i.e. with ±1 charges.

\[ V_{cell} = \frac{1}{2} \sum_{i \neq j} \sum_L \frac{Z_i Z_j}{|r_i - r_j - L|} \]

- Again need convergent lattice sum.
  - Energy is finite in charge neutral cell
What is Long-Ranged Potential?

• A potential is long-ranged if the real-space lattice sum does not (naively) converge.
  - In 3D, a potential is long-ranged if converges at rate \( r^{-3} \).
  - In 2D, a potential is long-ranged if converges at rate \( r^{-2} \).
  - In practice, we often use techniques for potentials that are not strictly long-ranged.

• MOTIVATION for bothersome math: Most interesting systems contain charge:
  - Any atomic system at the level of electrons and nuclei.
  - Any system with charged defects (e.g., Frenkel defects)
  - Any system with dissolved ions (e.g. biological cases)
  - Any system with partial charges (e.g. chemical systems)

Use Fourier Transform: large \( r \)= small \( k \)

If \( f(r) \) is a continuous periodic function such that \( f(r+L) = f(r) \), with \( L_n = n_x L_x x + n_y L_y y + n_z L_z z \), then

\[
f(r) = \sum_k e^{ik\cdot r} f_k \quad ; \quad k = m_x \frac{2\pi}{L_x} \hat{x} + m_y \frac{2\pi}{L_y} \hat{y} + m_z \frac{2\pi}{L_z} \hat{z}
\]

\[
f_k = \frac{1}{\Omega_{all-space}} \int dr \ e^{ik\cdot r} f(r)
\]

With \( f(r) \rightarrow v(r) = e^{\frac{r^2}{2\gamma}} \), \( v_i = \frac{1}{\Omega} \int dr \ e^{ik\cdot r} v(r) = 4\pi e^2 \frac{1}{k^2} \)

Potential decays slowly in k-space also.

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Origin of Convergence Problem

\[ v(r) = \frac{e^2}{r}, \quad \int dr e^{ikr} v(r) = 4\pi e^2/k^2 \]

• r-space convergence issue comes from \( r \to \infty \) (\( k \to 0 \)).
• k-space convergence issue comes from \( k \to \infty \) (\( r \to 0 \)).

Ewald summation method

• Key idea: **Split potential into k-space and real-space parts.**
  We can do since Fourier Transform is linear.

\[ V = \sum_{i<j} \varphi(|r_i - r_j + nL|) \quad V = \sum_{i<j} \rho_i (|\rho_i|^2 - N) \]

\[ \rho_i = \sum e^{ikr}, \quad \varphi(r) = \frac{e^2}{r} \quad \text{and} \quad \varphi_k = \frac{1}{\Omega} \int dr e^{ikr} \varphi(r) = 4\pi e^2/k^2 \]

• SLOW convergence at large \( r \) (in r-space) and slow at small \( k \) (in k-space)
Classic Ewald

- In this conventional break up,

\[ v_{\text{short}}(L/2) = \frac{2q_1q_2}{L} \text{erfc}(\kappa L/2) \neq 0 \text{ which gives some error!} \]

- Summation in k-space is truncated at desired accuracy.
- Adjust \( \kappa \) to minimize total error!

- Physical “trick”: Poisson Eq. is linear so we are free to add and subtract charge that conserves system neutrality, making sure charges screen out long-range part.

\[ \text{Gaussian charge (black) screens pt. charge.} \]
\[ \text{Gaussian charge (red): Ewald sum!} \]

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\[ \text{decays fast at big } r \]
\[ v_{\text{long}}(r) = \frac{q_1q_2}{r} - v_{\text{short}}(r) = \frac{q_1q_2}{r} \text{erf}(\kappa r) \]

\[ \text{decays fast at big } k \]
\[ v_{\text{long}}(k) = \frac{4\pi}{\Omega k^2} e^{-k^2/4\kappa^2} \]

- Choose Ewald parameter \( \kappa \) such that \( v_{\text{short}}(r) = 0 \) at \( r=L/2 \).
- Need only one image in real space: min. image potential.

- Total Potential is then:

\[ V = C + \sum_{i\neq j} \left[ v_{\text{short}}(r_{ij}) + \sum_{|k|<k_c} e^{ik\cdot r_{ij}} v_{\text{long}}(k) \right] \]

\[ r_{ij} = \min_k |r_i - r_j - L| \]

- Extra term for insulators:

\[ V_{\text{dipole}} = \frac{2\pi}{(2\varepsilon + 1)\Omega} \left| \sum_i \mu_i \right|^2 \]

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Ewald: optimizing breakup

- Improve the conventional break up, by
  \[ v_{\text{short}}(r) = \sum_n c_n h_n(r) \quad \text{or} \quad v_{\text{long}}(r) = \sum_n c_n h_n(r) \]

- \( h_n \)'s satisfy B.C.
- Choose k-space cutoff, \( k_c \).
- Write error that comes from neglecting higher k's.
- Minimize error w.r.t. \( c_n \)'s.

Look at k-space: the algorithm

\[
V_k = \frac{1}{2} \sum_{i \neq j} \sum_k e^{ik(r_i - r_j)} \quad v_k = \frac{1}{2} \sum_{i \neq j} \sum_k e^{ik(r_i - r_j)} v_k - \frac{1}{2} \sum_k v_k
\]

\[
= \frac{1}{2} \sum_k \left[ \sum_{i,j} e^{ik r_i} \right] \left[ \sum_{i,j} e^{-ik r_j} \right] v_k + C
\]

- \( \rho_k = \rho^{* -k} \) so only have to compute one of them.
- Computation of \( \rho_k \sim NM_k \) with \( M_k \) the number of k vectors.

Algorithm for computing k-space sums:

\[
\text{for all } k \in \text{k-vector-list do}
V_{\text{long}} := V_{\text{long}} + \rho_k \rho_{-k} v_k
\text{end for all}
\]

Changes due to moving a few particles can be calculated more quickly
Look at k-space: the algorithm

\[ V_k = \frac{1}{2} \sum_k \rho_k \rho_{-k} V_k + C \]

**Algorithm to compute \( \rho_k \)**

- Complex multiply is much faster than complex exponentiation.
  *Use sin's and cos's!*

\[ e^{i k \cdot r} = e^{\frac{2 \pi}{L} r_x} e^{\frac{2 \pi}{L} r_y} e^{\frac{2 \pi}{L} r_z} \]

Algorithm for quickly computing \( \rho_k \):

Create list of \( k \) & corresponding \((m_1,m_2,m_3)\) indices.

Zero out \( \rho_k \) for all \( i \) \( \in \) particles do

for all \( j \) \( \in \) \([1,2,3]\) do

compute \( C_j^i \equiv e^{i \kappa \cdot r_i} \)

for \( m \in \{-m_{\text{max}}, \ldots, m_{\text{max}}\} \) do

Compute \( [C_j^i]^m \) and store in array

end for \((m_1,m_2,m_3)\) \( \in \) index list do

Compute \( e^{i k \cdot r_i} = [C_1^i]^m [C_2^i]^m [C_3^i]^m \) from array

Accumulate to \( \rho_k \)

end for

end for
How to do it

• r-space part same as short-ranged potential \( \mathcal{O}(N^{3/2}) \)

• k-space part:
  1. Compute \( \exp(i k_0 x_i) = (\cos(i k_0 x_i), \sin(i k_0 x_i)) \), \( k_0 = \frac{2\pi}{L} \). \( \mathcal{O}(N) \)
  2. Compute powers \( \exp(i2k_0 x_i) = \exp(ik_0 x_i) \ast \exp(ik_0 x_i) \) etc. \( \mathcal{O}(N^{3/2}) \)
  - Get all values of \( \exp(i k \cdot r_i) \) with just multiplications.
  3. Sum over particles to get \( \rho_k \) all \( k \). \( \mathcal{O}(N^{3/2}) \)
  4. Sum over \( k \) to get the potentials. \( \mathcal{O}(N^{1/2}) \)
  5. Forces can also be done by taking gradients. \( \mathcal{O}(N^{3/2}) \)

• Constant terms to be added. \( \mathcal{O}(1) \)

• Checks: perfect cubic lattice: \( V = -1.4186487/a \).

Complexity of Fast Multipole

• Coulomb potentials with Ewald sums are \( \mathcal{O}(N^{3/2}) \) if you adjust \( \kappa \) and use neighbor tables.

• Fast Multipole Methods are \( \mathcal{O}(N) \) for large \( N \).
  - Divide space into cells recursively
  - Find dipole moment of each cell
  - Find rules for how dipole moments for supercells are related to moments for smaller cells.
  - Effective for large systems for molecular dynamics

• Other related method: Particle cell methods (Hockney)
  - Compute the k-space parts on a grid with FFTs.
  - \( N \ln(N) \)
Problems with Image potential

- Introduces a lattice structure which may not be appropriate.
- Example: a charge layer.

- We assume charge structure continues at large r.
- Actually nearby fluid will be anticorrelated.
- This means such structures will be penalized.

- One should always consider the effects of boundary conditions, particularly when electrostatic forces are around!