

Neighbor Tables Long-Range Potentials

Today we learn how we can handle long range potentials.

- Neighbor tables
- Long-range potential
- Ewald sums

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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*

$$V_I = \sum_n v(r_i - r_j + nL) - \text{background (if needed)}$$

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



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Perturbation theory

- One can restore a cutoff potential by using a *tail correction*

$$V_{tail} = \frac{\rho}{2} \int dr g(r) \Delta\phi(r)$$

- To do better one has to find *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.

$$S(k) = c k^2 \quad \text{for } \textit{charged} \text{ system}$$

$$S(k) = c \quad \text{for } \textit{uncharged} \text{ system}$$

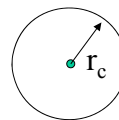
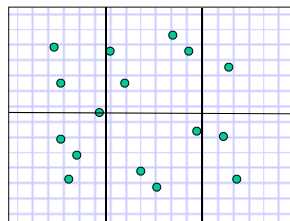
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Complexity of Force Calculations

- Complexity is the scaling with the number of degrees 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) *neighbor list* for systems that move slowly.
 - *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



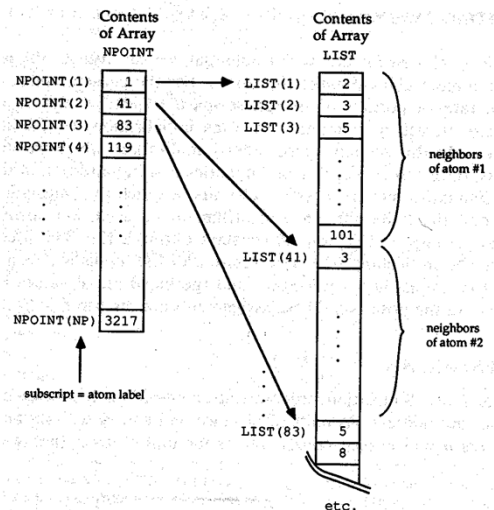
If $v(r > r_c) = 0$, force calculations are $O(N)$ with M neighbors

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 r_c

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CLAMPS uses bin-sort method for neighbor tables



Use *two 1-dimensional arrays* to store a *neighbor list* for each particle during a simulation of a systems with N particles.

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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.

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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)= 1 1 1	
total number of bins 0	number of neighboring bins 0
cpu secs/step 0.13426E+00	potential energy -0.14605271E+04
examine the bin division ndiv(3)= 4 4 4	
total number of bins 64	number of neighboring bins 26
cpu secs/step 0.60312E-01	potential energy -0.14648783E+04
examine the bin division ndiv(3)= 5 5 5	
total number of bins 125	number of neighboring bins 26
cpu secs/step 0.32911E-01	potential energy -0.14648783E+04
examine the bin division ndiv(3)= 6 6 6	
total number of bins 216	number of neighboring bins 80
cpu secs/step 0.60229E-01	potential energy -0.14648783E+04

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 ($1/r$) (r^2) 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



Madelung const. $\frac{\alpha}{R} = \sum_{j \neq i} \frac{(\pm)}{Rp_{ij}} \quad (r_{ij} = Rp_{ij})$

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

$$\alpha = \sum_{j \neq i} \frac{(\pm)}{p_{ij}} = 2 \left[\frac{1}{1} - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \dots \right]$$

Since $\ln(1+x) = \left[x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \dots \right]$

Sum is conditionally convergent

$$\alpha = 2 \ln 2$$

$V_{\text{electrostatic}} \sim \alpha/R$

Structure	α
NaCl	1.747565
CsCl	1.762675
ZnS	1.6381

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)).

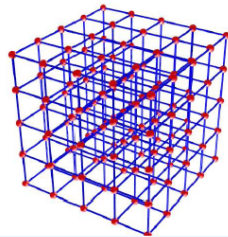
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Long-Ranged Potentials

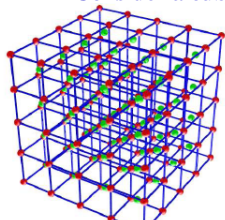
- Why make the potential long ranged?
 - Consider a cubic lattice with +1 charges, and its Coulomb potential.



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

- 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.



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

- Again need convergent lattice sum.
 - Energy is finite in charge neutral cell

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What is Long-Ranged Potential?

- A potential is long-ranged if the real-space lattice sum does not (naively) converge. Look at $v(r)r^k$ finite
 - In 3D, a potential is short ranged if converges at rate $k>3$.
 - In 2D, a potential is short ranged if converges at rate $k>2$.

- 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)

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Use Fourier Transform: large r =small k

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

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

$$f_k = \frac{1}{\Omega} \int_{\text{all-space}} d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} f(\mathbf{r}) \quad \text{k's are discrete!}$$

With $f(r) \rightarrow v(r) = e^2/r$, $v_k = \frac{1}{\Omega} \int d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} v(r) = 4\pi e^2/k^2$

Potential decays slowly in k-space also.

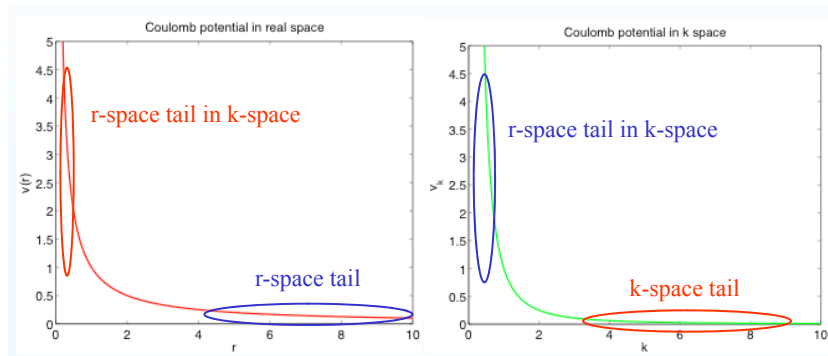
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Origin of Convergence Problem

With $v(r) = e^2/r$, $v_k = \frac{1}{\Omega} \int dr e^{ik \cdot r} v(r) = 4\pi e^2/k^2$



- r-space convergence issue comes from $r \rightarrow \infty$ ($k \rightarrow 0$).
- k-space convergence issue comes from $k \rightarrow \infty$ ($r \rightarrow 0$).

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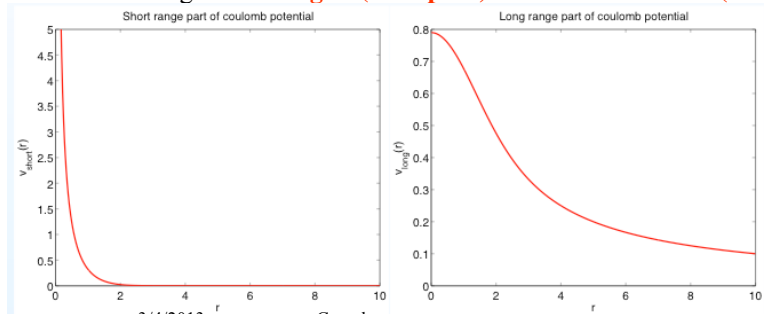
Ewald summation method

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

$V = \sum_{i < j, n} \varphi(r_i - r_j + nL) \quad V = \sum_{i < j, n} \varphi_k(|\rho_k|^2 - N)$

$\rho_k = \sum e^{ik \cdot r}, \quad \varphi(r) = e^2/r \quad \text{and} \quad \varphi_k = \frac{1}{\Omega} \int dr e^{ik \cdot r} \varphi(r) = 4\pi e^2/k^2$

- SLOW convergence **at large r (in r-space) and slow at small k (in k-space)**



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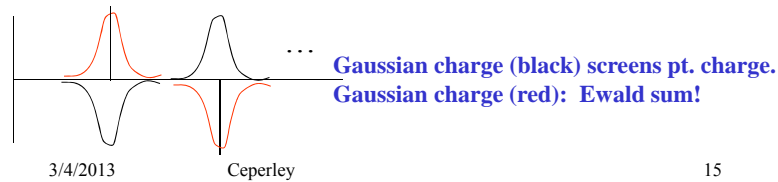
Classic Ewald

- In this conventional break up,

$$v_{short}(L/2) = \frac{2q_1q_2}{L} \operatorname{erfc}(\kappa L/2) \neq 0$$

- Summation in k-space is truncated at desired accuracy.
- Adjust κ 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.*



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Classic Ewald

- Split up via *Gaussian charge distribution* $\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z dt e^{-t^2}$

$$v_{short}(r) = \frac{q_1q_2}{r} \operatorname{erfc}(\kappa r) \quad v_{long}(r) = \frac{q_1q_2}{r} - v_{short}(r) = \frac{q_1q_2}{r} \operatorname{erf}(\kappa r)$$

decays fast at big r $v_k^{long} = \frac{4\pi}{\Omega k^2} e^{-k^2/4\kappa^2}$ *decays fast at big k*

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

- Total Potential is then:

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

- Extra term for insulators: $V_{dipole} = \frac{2\pi}{(2\epsilon + 1)\Omega} \left| \sum_i \mu_i \right|^2$

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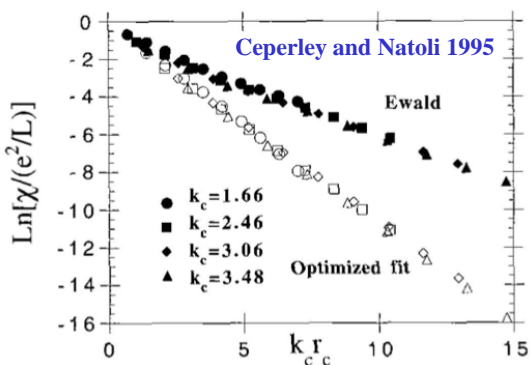
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Ewald: optimizing breakup

- *Improve the conventional break up, by*

$$v_{short}(r) = \sum_n c_n h_n(r) \quad \text{or} \quad v_{long}(r) = \sum_n c_n h_n(r)$$

- 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.**



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Look at k-space: the algorithm

$$\begin{aligned} V_k &= \frac{1}{2} \sum_{i \neq j} \sum_{\mathbf{k}} e^{i\mathbf{k} \cdot |\mathbf{r}_i - \mathbf{r}_j|} v_k = \frac{1}{2} \sum_{i,j} \sum_{\mathbf{k}} e^{i\mathbf{k} \cdot |\mathbf{r}_i - \mathbf{r}_j|} v_k - \frac{1}{2} \sum_{\mathbf{k}} v_k \\ &= \frac{1}{2} \sum_{\mathbf{k}} \left[\sum_{i,j} e^{i\mathbf{k} \cdot \mathbf{r}_i} \right] \left[\sum_{i,j} e^{-i\mathbf{k} \cdot \mathbf{r}_j} \right] v_k + C \end{aligned}$$

- $\rho_{\mathbf{k}} = \rho_{-\mathbf{k}}^*$ so only have to compute one of them.
- Computation of $\rho_{\mathbf{k}} \sim N M_k$ with M_k the number of k vectors.

Algorithm for computing k-space sums:

```

for all k ∈ k-vector-list do
     $V_{long} := V_{long} + \rho_{\mathbf{k}} \rho_{-\mathbf{k}} v_{\mathbf{k}}$ 
end for all
    
```

Changes due to moving a few particles can be calculated more quickly

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Look at k-space: the algorithm

$$V_k = \frac{1}{2} \sum_{\mathbf{k}} \rho_k \rho_{-\mathbf{k}} v_k + C$$

Algorithm to compute ρ_k

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

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

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Look at k-space: the algorithm

Algorithm for quickly computing ρ_k :

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

Zero out ρ_k

for all $i \in$ particles **do**

for all $j \in [1,2,3]$ **do**

 compute $C_j^i \equiv e^{i\mathbf{b}_j \cdot \mathbf{r}_i}$

for $m \in [-m_{\max} \dots m_{\max}]$ **do**

 Compute $[C_j^i]^m$ and store in array

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

 Compute $e^{i\mathbf{k}\cdot\mathbf{r}_i} = [C_1^i]^{m_1} [C_2^i]^{m_2} [C_3^i]^{m_3}$ from array

 Accumulate to ρ_k

end for

end for

- Use neighbor tables and optimize κ , Ewald is $O(N^{3/2})$
- If we do not reoptimize, then $O(N^2)$
- With efficient code, prefactor is small.

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How to do it

- r-space part same as short-ranged potential O(N^{3/2})
- k-space part:
 1. **Compute** $\exp(i\mathbf{k}_0\mathbf{x}_i) = (\cos(k_0x_i), \sin(k_0x_i))$, $k_0 = 2\pi/L \forall i$. O(N)
 2. **Compute powers** $\exp(i2\mathbf{k}_0\mathbf{x}_i) = \exp(i\mathbf{k}_0\mathbf{x}_i) * \exp(i\mathbf{k}_0\mathbf{x}_i)$ etc. O(N^{3/2})
 Get all values of $\exp(i\mathbf{k} \cdot \mathbf{r}_i)$ with just multiplications.
 3. Sum over particles to get $\rho_{\mathbf{k}}$ all \mathbf{k} . O(N^{3/2})
 4. Sum over \mathbf{k} to get the potentials. O(N^{1/2})
 5. Forces can also be done by taking gradients. O(N^{3/2})
- Constant terms to be added. O(1)
- Checks: perfect cubic lattice: $V = -1.4186487/a$.

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CLAMPS use of EWALD sums

Hansen Phys. Rev. A 8, 3096 (1973).

```
TYPE e 128 1. 1.
DENSITY 0.238732414 ! using plasma units
LATTICE
EWALD 3 1.
```

INPUT

OUTPUT

```
ifchrg = 1
nkcut, ckcut, and sqal are 3 0.2320251E+01 0.5945963E+00
ewald sums used.
lattice size in k-space 0.7734169E+00 0.7734169E+00 0.7734169E+00
selfen and sqal -0.6710867E+00 0.5945963E+00
potential summed for abs(k).le. 0.2320251E+01
this comprises 11 shells with 141 vectors
```

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Complexity of Fast Multipole

- Coulomb potentials with Ewald sums are $O(N^{3/2})$ *if you adjust κ* and use neighbor tables.
- *Fast Multipole Methods* are $O(N)$ *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.
 - $N \ln(N)$

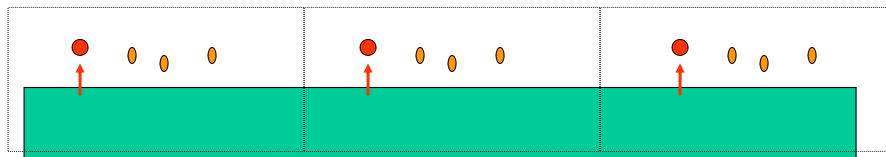
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Problems with Image potential

- 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!

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