Long-Range Potentials

Today we learn how we can handle long range potentials.

- What are they?
- Ewald sums

Ways to treat 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 background and a convergence method.

Perturbation theory

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

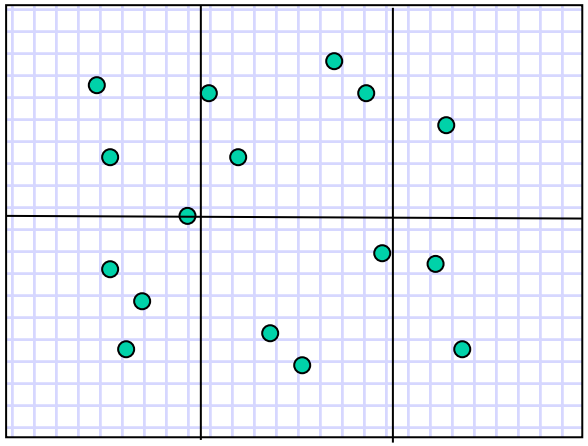
$$V_{tail} = \frac{\rho}{2} \int dr \; g(r) \Delta\varphi(r)$$

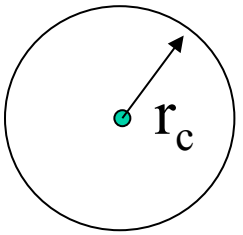
- To do better one has to find *effect of perturbation on g(r),* e.g. one can use an integral equation (such as HNC) involving the potential and g(r).

- The Stillinger-Lovett condition says that S(k) as k→0 for a charged system is different that in a neutral system.
  - $S(k)=c\,k^2$ for *charged* system
  - $S(k)=c>0$ for *uncharged* system

Complexity of Force Calculations

- Complexity is the scaling with the number of particles.
- Number of terms in a pair potential is $N(N-1)/2 \sim O(N^2)$
- 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 x r_c mesh and find neighbors from the mesh table, only n.n. cells matter) is O(N).





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

What is Long-Ranged Potential?

- A potential is long-ranged if the real-space lattice sum does not (naively) converge. Look at v(r) as $r \rightarrow \infty$
  - In 3D, a potential is short-ranged if converges faster than r^{-3}
  - In 2D, a potential is short-ranged if converges faster than r^{-2}

- MOTIVATION: Many interesting systems contain charges:
  - 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)

How can we handle charged systems in PBC?

- 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.
  - One even has a problem with dipolar forces.
  - Cutting off is a BAD idea!
- The "image potential" solves most problems:

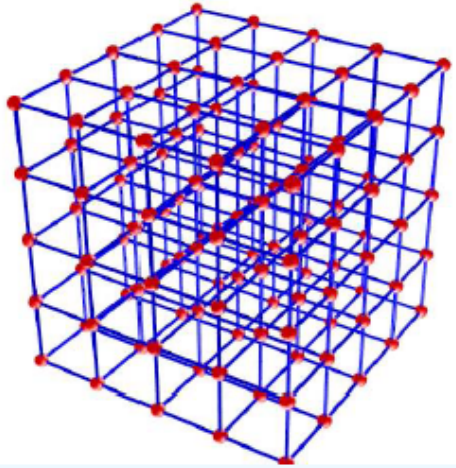
$$V_I = \Sigma_n \, v(r_i - r_j + nL)$$

  - But summation diverges!

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

Long-Ranged Potentials

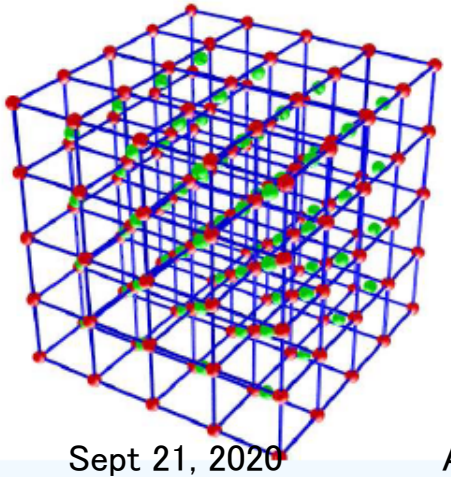
- Why make the potential long ranged?
  - Consider a cubic lattice with +1 charges, and its Coulomb potential.



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

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

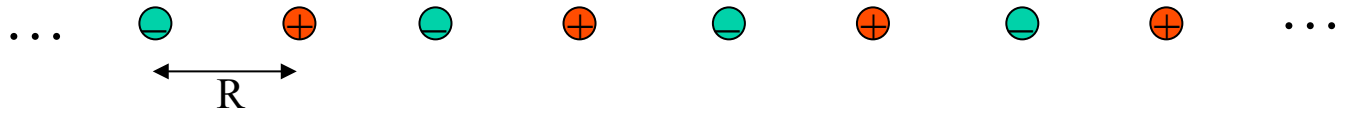
– Consider a cubic lattice with charge neutrality, i.e. with ±1 charges.



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

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

1-D Madelung Sum: Prelude to Ewald Sum



Madelung const. $\dfrac{\alpha}{R} = \sum_{j \neq i} \dfrac{(\pm)}{R p_{ij}} \qquad (r_{ij} = R p_{ij})$

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

Sum is conditionally convergent

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

$\alpha = -2\ln 2$

$V_{electrostatic}$ ~ α/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) .

Use Fourier Transform: large r=small k

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

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

$$f_k = \frac{1}{\Omega}\int_{all-space} d\mathbf{r}\, e^{i\mathbf{k}\bullet\mathbf{r}} f(\mathbf{r})$$

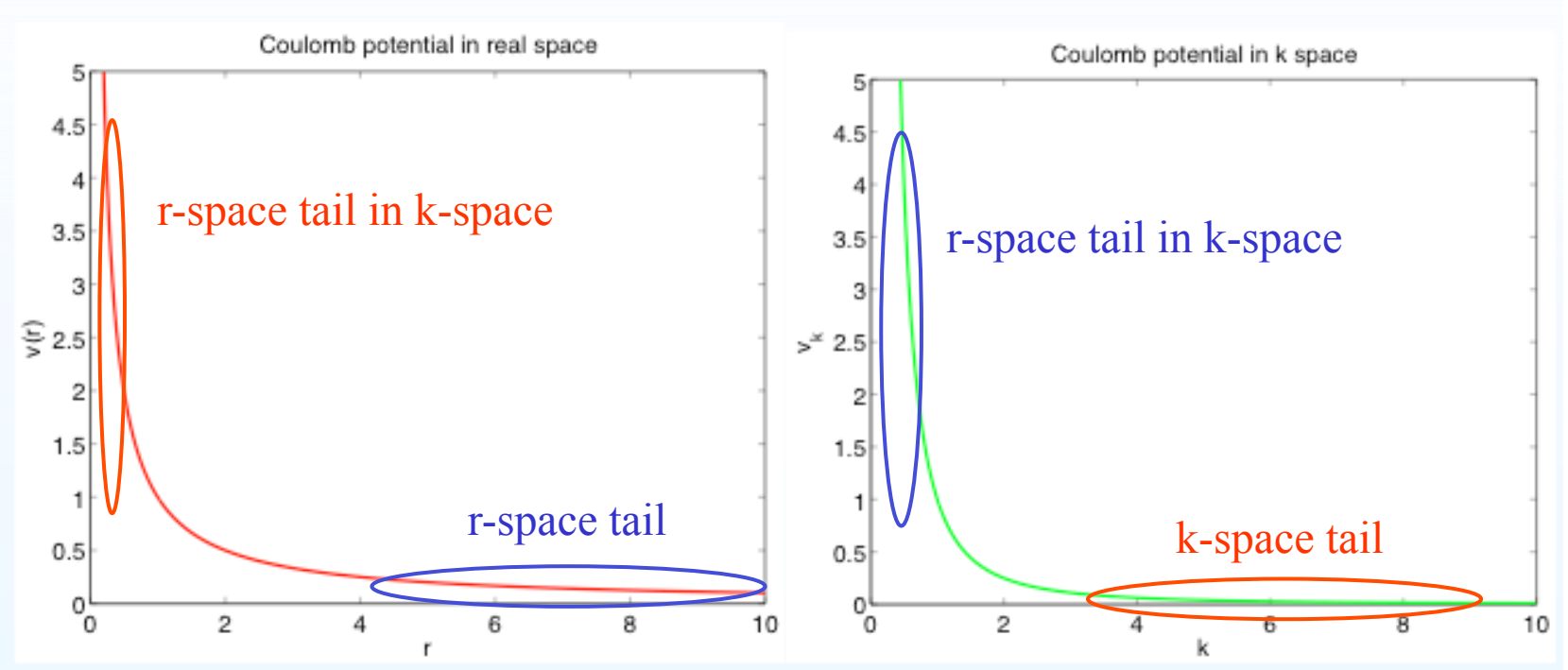
k is discrete!

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

Potential decays slowly in k-space also.

Origin of Convergence Problem

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



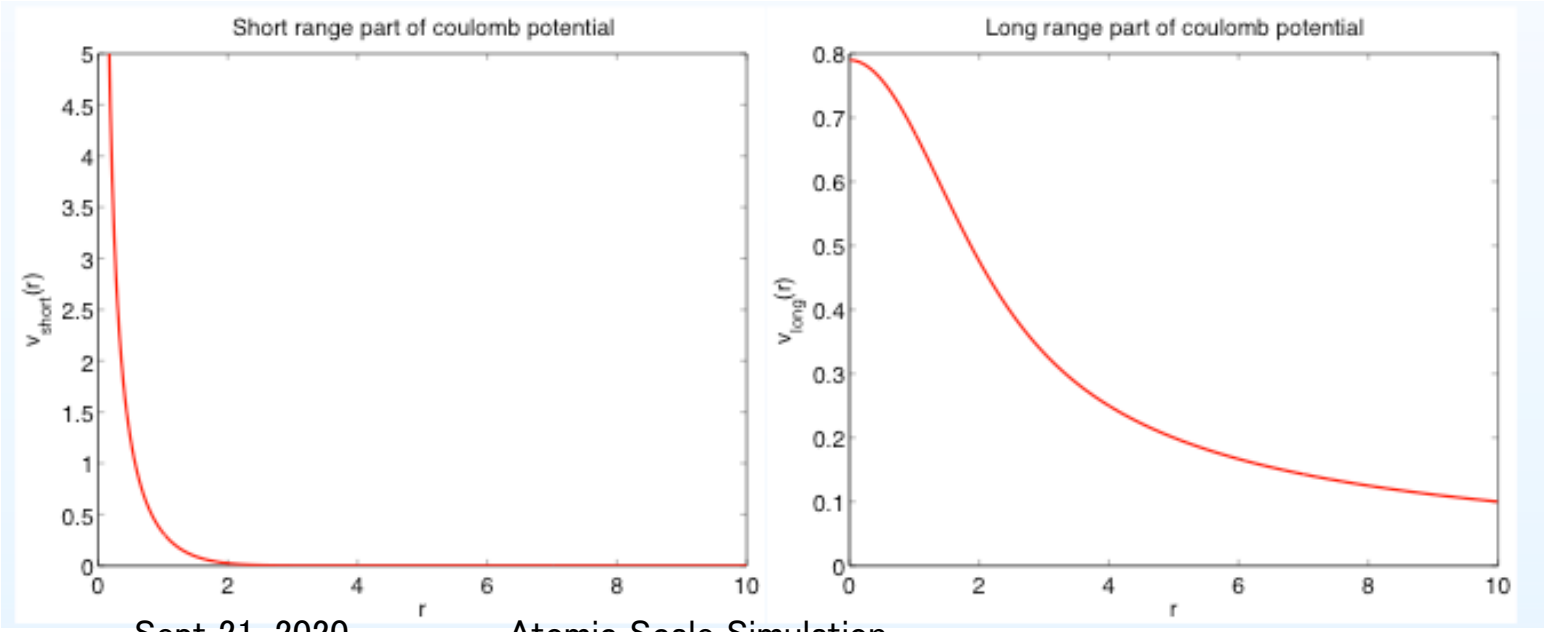
- r-space convergence issue comes from r→∞ (k→0).
- k-space convergence issue comes from k→∞ (r→0).

Ewald summation method

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

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

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



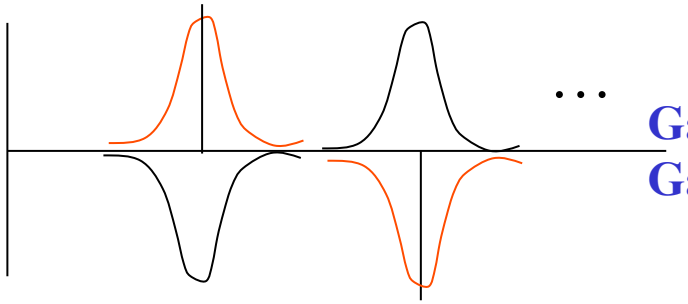
Classic Ewald

In the conventional break up,

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

- Summation in k-space is truncated at desired accuracy.
- Adjust κ to *minimize total error!*

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.



Gaussian charge (black) screens pt. charge.
Gaussian charge (red): Ewald sum!

Classic Ewald (A&T C.5)

- Split up via *Gaussian charge distribution*

$$erf(z) = \frac{2}{\sqrt{\pi}} \int_0^z dt\ e^{-t^2}$$

$$v_{short}(r) = \frac{q_1 q_2}{r} erfc(\kappa r) \qquad v_{long}(r) = \frac{q_1 q_2}{r} - v_{short}(r) = \frac{q_1 q_2}{r} erf(\kappa r)$$

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

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

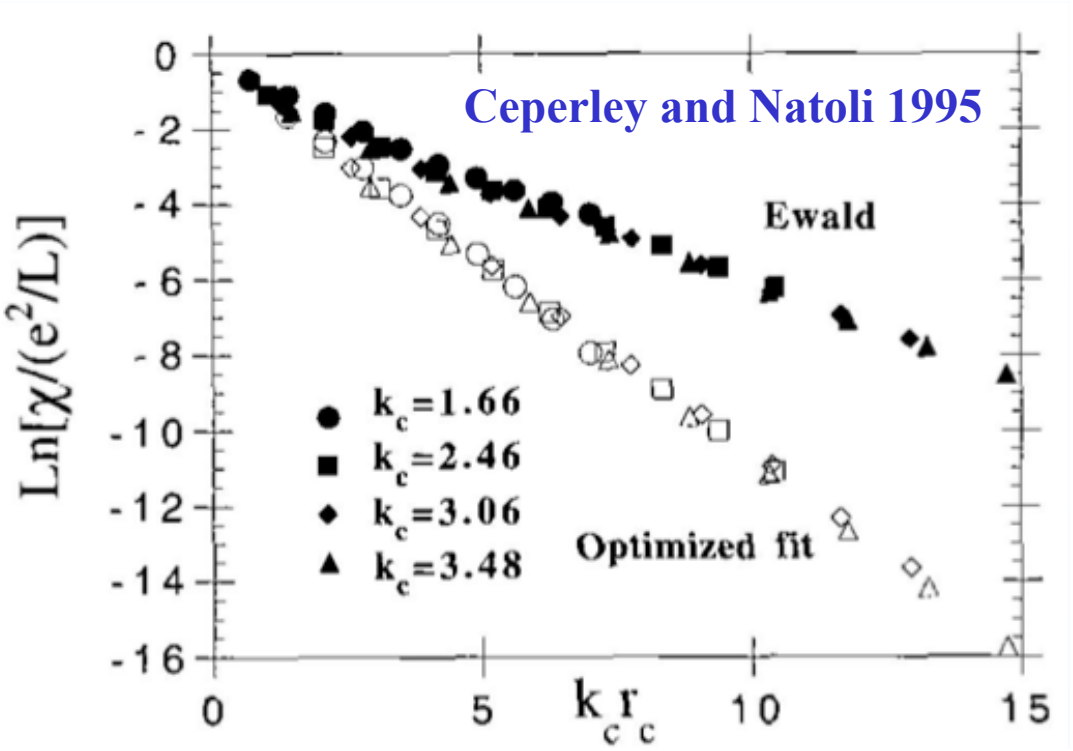
- Extra term for insulators: $V_{dipole} = \frac{2\pi}{(2\varepsilon+1)\Omega} |\sum_i \mu_i|^2$

Ewald: optimizing breakup

- *Improve the conventional break up, by*

$$v_{short}(r) = \sum_n c_n h_n(r) \qquad v_{long}(r) = v(r) - v_{short}(r)$$

- 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

$$V_k = \frac{1}{2}\sum_{i\neq j}\ \sum_{\mathbf{k}} e^{i\mathbf{k}\bullet\left(\mathbf{r}_i-\mathbf{r}_j\right)} v_k = \frac{1}{2}\sum_{i,j}\ \sum_{\mathbf{k}} e^{i\mathbf{k}\bullet\left(\mathbf{r}_i-\mathbf{r}_j\right)} v_k - \frac{N}{2}\sum_{\mathbf{k}}\ v_k$$

$$= \frac{1}{2}\sum_{\mathbf{k}}\ \left[\overbrace{\sum_i e^{i\mathbf{k}\bullet\mathbf{r}_i}}^{\rho_k}\right]\left[\overbrace{\sum_j e^{-i\mathbf{k}\bullet\mathbf{r}_j}}^{\rho_{-k}}\right] v_k + C$$

- $\rho_k = \rho^*_{-k}$ *so we 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:

for all k in k-vector-list **do**

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

end for all

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

Look at k-space: the algorithm

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

Algorithm to compute ρ_k

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

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

Look at k-space: the algorithm

Algorithm for quickly computing ρ_k*:*

Create list of **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 $C_j^i \equiv e^{i\mathbf{b}_j \bullet \mathbf{r}_i}$

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

Compute $\left[C_j^i\right]^m$ *and store in array*

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

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

Accumulate to ρ_k

end for

end for

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

How to do it

- r-space part same as short-ranged potential — $O(N^{3/2})$

- k-space part:
  1. **Compute $\exp(ik_0x_i)$** $=(\cos(ik_0x_i), \sin(ik_0x_i))$, $k_0=2\pi/L$. — $O(N)$
  2. **Compute powers $\exp(i2k_0x_i)$** $= \exp(ik_0x_i)*\exp(ik_0x_i)$ etc. — $O(N^{3/2})$
     Get all values of $\exp(ik \cdot r_i)$ with just multiplications.
  3. Sum over particles to get ρ_k all k. — $O(N^{3/2})$
  4. Sum over 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.

Complexity of Fast Multipole

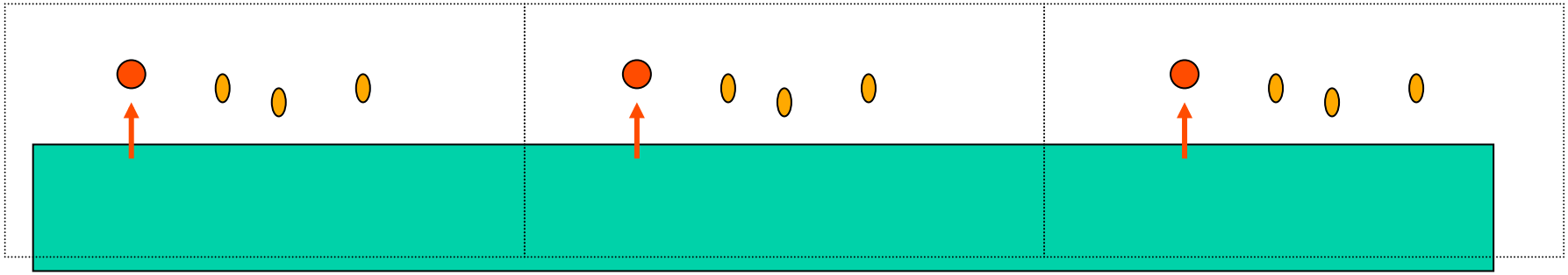
- Coulomb potentials with Ewald sums are $O(N^{3/2})$ *if you adjust* κ and use neighbor tables.

- *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.
  - But requires a **very large system** with all particles moving.

- 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!