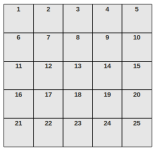
Cell Structures

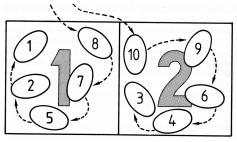
- Divide system into MxMxM cells
- Size of cells l = L/M is bigger than cutoff
- Keep a list of neighboring cells
- Each cell has a list of particles in them

Neigh. 13: 7,8,9,12,14,17,18,19

Cell Structures

- $N_c = N/M^2$ particles in each cell (N/M^3 in 3D)
- In 2D only examine $9NN_c$ pairs
  - not $N(N-1)/2$





Can do half that using 3rd law

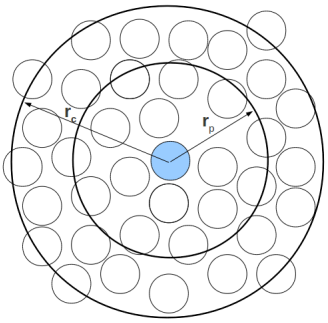
Each cell has its list

Summary (2D)

	Brute Force	Cutoff	Verlet	Cell
Force Pairs	$\frac{N(N-1)}{2}$	$N\rho\frac{\pi r_c^2}{2}$	$N\rho\frac{\pi r_l^2}{2}$	$\frac{9}{2}N\rho l^2$
Distance pairs at every step	$\frac{N(N-1)}{2}$	N^2	$N\rho\frac{\pi r_l^2}{2}$	$\frac{9}{2}N\rho l^2$
Update list			$\frac{N(N-1)}{2}$	N
Storage			$N\rho\frac{\pi r_l^2}{2}$	N

Can combine the use of the Cell method to only update the lists!

Multiple Time Steps



Update at two different time scales, thus get at least two time scales of updates

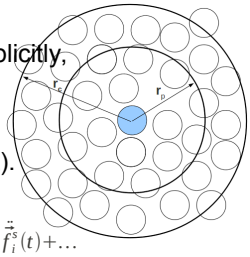
- Further efficiency may come from defining a "primary" and a "secondary" neighborhood within rc
- Within r_p (in *cage*) effect of forces vary rapidly – update every time
- Between r_p and r_c effect of the smaller forces vary less rapidly – update less often

Multiple Time Steps

- Total force on i: $\vec{f}_i = \vec{f}_i^p + \vec{f}_i^s$
- At time t, f_i^p and f_i^s are calculated explicitly, along with $\dot{\vec{f}}_i^s$ and $\ddot{\vec{f}}_i^s$
- For the next τ_m-1 steps, f_i^p is still calculated explicitly (using a sub-list).
- f_i^s are approximated:

$$\vec{f}_i^s(t+\tau\delta t) \approx \vec{f}_i^s(t) + (\tau\delta t)\dot{\vec{f}}_i^s(t) + \frac{1}{2}(\tau\delta t)^2\ddot{\vec{f}}_i^s(t) + \ldots$$

- After τ_m steps, recalculate everything explicitly.
- Two time scales: δt for primary, $\tau_m \delta t$ for secondary.



In a typical LJ, r_p between σ and 1.5σ.

Long-range Forces

- Interactions that fall no faster than r^{-d} (*d*-dimensionality)
  - Charge-charge interaction most notable example with $V(r) \sim r^{-1}$
  - Dipole-dipole interaction between molecules $V(r) \sim r^{-3}$
- Brute force approach of making system bigger will not work since $t \sim N^2 \sim L^6$ (through density)

Long-range Forces

Simple "solutions":

- Spherical truncation at some r_c':
  - Truncation sphere around any atom may have net charge
  - This net charge fluctuates depending on exiting/entering ions
  - Movements of ions across r_c will create artificial effects
  - Artificially charging the sphere only ameliorates the problem
- Minimum image convention:
  - Cuts off at the cube (size L) that is neutral
  - However, equal charges will go to opposing corners

Long-range Forces

Two typical ways to tackle long-range forces:

- Ewald sum (1921) for charged ions
  - Calculates the interaction between an ion and all of its images
  - Cons: overemphasizes periodicity of the PBC
- Reaction field method for dipole-dipole
  - Handle interactions beyond a cutoff by an effective medium
  - Cons: overemphasizes continuum nature of polar fluid and needs estimate of relative permittivity

Ewald Sum

- Technique for summing (efficiently) interaction between an ion an all of its periodic images
- Assume neutral system of N charged particles
- Coulombic energy

$$V_{zz} = \frac{1}{2}\sum_{i=1}^{N} z_i \phi(r_i)$$

n=0 is within the central box

$$\phi(r_i) = \sum_{\mathbf{n}}{}' \sum_{j=1}^{N} z_j \frac{1}{|\mathbf{r}_{ij} + \mathbf{n}|}$$

Prime ' indicates sum over all particles and images except j=i when **n**=0.
Vector **n** = (n_xL, n_yL, n_zL)

Ewald Sum

Not so easy:

- Straight addition of Coulombic terms is conditionally convergent
  - The positive and negative (neutral mix of ions) terms have to be added in a very specific way
  - Each sign (±charge) sum does not converge by itself

Ewald Sum

- A series is *conditionally convergent* if $\sum_{n=1}^{\infty} a_n$

converges but $\sum_{n=1}^{\infty} |a_n|$

diverge.

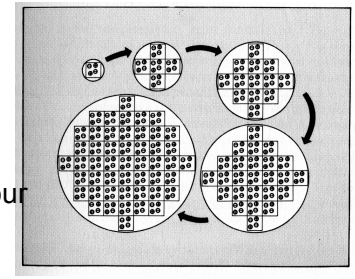
e.g. $1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \cdots$ converges

$1 + \frac{1}{2} + \frac{1}{3} + \frac{1}{4} + \cdots$ diverges even with $a_n \to 0$ for $n \to \infty$

- It also depends on the order of the summation.

Ewald Sum

- Have to add in "layers" to avoid divergence of sum.
- Equivalent to summing by shells
- In 2D first shell is four boxes (**n**=L)
- Keep an eye on the "outside" gray medium.



BTW, the sphere will have a dipolar layer on its surface.

This way of summing avoids divergence, but it is conditionally convergent → with a very slow convergence.

Ewald Sum

- The Ewald sum is a “trick” on how to perform the sum.
- Trick: replace the conditionally convergent sum by two rapidly convergent sums.

$$\frac{1}{r} = \frac{f(r)}{r} + \frac{1-f(r)}{r}$$

- Challenge is to find f(r) to satisfy the condition.

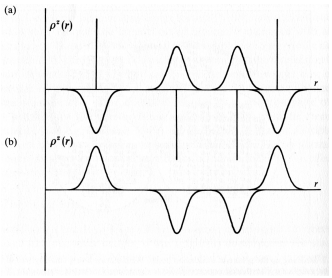
Ewald Sum

- Use sums of Gaussian distributions of the form

$$\rho_i^z(\mathbf{r}) = z_i \alpha^3 exp(-\alpha^2 r^2)/\pi^{3/2}$$

- Trick:
  - Add one sum of Gaussians to screen the net charges of each ion centered at the ion (the f(r)/r)
  - Add the negative (canceling) to preserve the form of the potential (the [(1-f(r)]/ r)

Ewald Sum



- In (a) original charges are deltas, screening distribution are Gaussian (it screens and makes interaction short ranged)
- In (b) take away the one just added by canceling it

Ewald Sum

Method:

- Add the original charges plus screening Gaussians in real space
- Add the canceling Gaussians in reciprocal space using Fourier transforms. Then can transform back to real space.
- Keep an eye on self-energy when summing the canceling Gaussians

Ewald Sum

- The total potential will include:
  - The original charged distribution + the screening (opposite sign) sum in real space
  - The cancelling (short range) distribution in k-space
  - Subtraction of a self-energy term (from the cancelling distribution)
  - A term to take into account the surface. Potential of the boxes surrounded by a conductor (ε=∞) are different from that in vacuum (ε=1). Ewald sum gives V(ε=∞)

$$V(\epsilon=\infty) = V(\epsilon=1) - \frac{2\pi}{3L^3}\left|\sum_i z_i \vec{r}_i\right|^2$$

Ewald Sum

$$V_{zz}(\epsilon_s = 1) = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\left(\sum_{|\mathbf{n}|=0}^{\infty'} z_i z_j \frac{erfc(\alpha|\mathbf{r}_{ij}+\mathbf{n}|)}{|\mathbf{r}_{ij}+\mathbf{n}|}\right.$$

$$\left. + (1/\pi L^3)\sum_{\mathbf{k}\neq 0} z_i z_j (4\pi^2/k^2) exp(-k^2/4\alpha^2) cos(\mathbf{k}\cdot\mathbf{r}_{ij})\right)$$

$$- (\alpha/\pi^{1/2})\sum_{i=1}^{N} z_i^2 + (2\pi/3L^3)\left|\sum_{i=1}^{N} z_i \mathbf{r}_i\right|^2$$

$$erfc(x) = (2/\pi^{1/2}) \times \int_x^{\infty} exp(-t^2)dt$$

In detail

mult. by $\frac{1}{4\pi\epsilon_o}$