

# Methods for Simulating Large Systems

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The size of a system is limited by storage on the computer and by speed of processors & patience of researchers.

There are a few important tricks that most computer simulations use to speed things up:

## 1. Non-bonded cutoffs:

The force<sup>loop</sup> requires  $N^2$  calculations for  $N$  atoms and is usually the rate limiting step.

Bonds, Bends, Torsions  $\leftarrow$  scales with  $N$ , so even though these are mathematically complicated, they aren't the slow part.

To save time, we impose spherical cutoffs:

$$V(r) = \begin{cases} V_{nb}(r) & r < r_c \\ 0 & r \geq r_c \end{cases}$$

This reduces the number of neighbors by  $\frac{4\pi r_c^3}{3L^3}$   $\leftarrow$  spherical cutoff radius (usually  $\sim 9-12 \text{ \AA}$ )  
length of side of the box  $\leftarrow$  (can be  $30-100 \text{ \AA}$ )

$r_c$  should be large enough that it produces only a small perturbation on  $V_{nb}(r)$

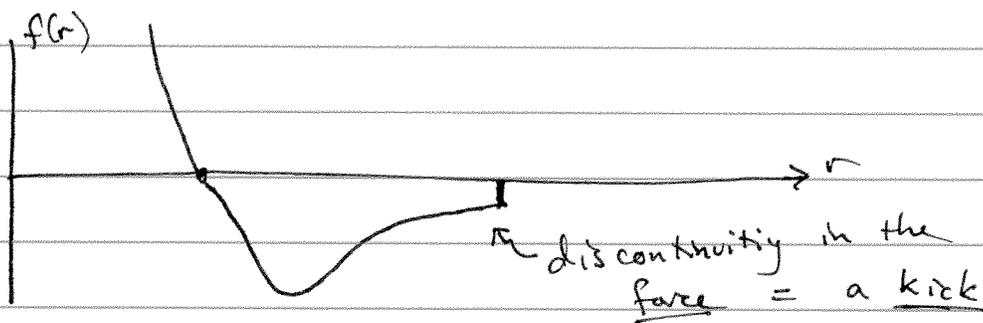
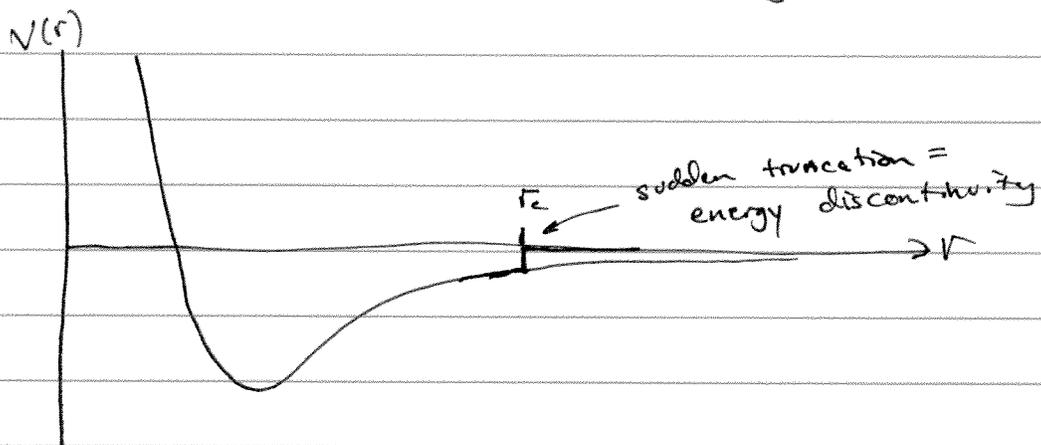
For Lennard-Jones systems, this is usually  $2.5\sigma$  (potential is only 1.6% of the well depth)

Electrostatic contributions can be significant up to 15Å or more!

Some disadvantages & warnings:

1) We need to be relatively sure that the calculated properties for a truncated potential have almost the same properties as the full potential.

2) A sudden cutoff of non-bonded interactions creates discontinuities in the energies & forces.



## Fixing discontinuities

(3)

1) Do nothing 
$$V(r) = \begin{cases} V_{nb}(r) & r \leq r_c \\ 0 & r > r_c \end{cases}$$

Energy is discontinuous @  $r_c$

Force is discontinuous @  $r_c = -\left(\frac{\partial V}{\partial r}\right)$

2) Shifted Potential = Lifting up the potential

$$V(r) = \begin{cases} V_{nb}(r) - V_{nb}(r_c) & r \leq r_c \\ 0 & r > r_c \end{cases}$$

Energy is continuous

Force is discontinuous

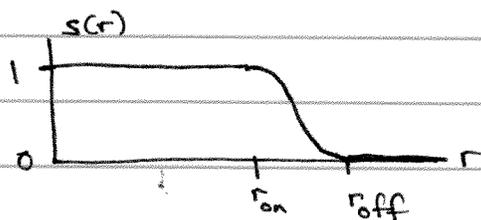
3) Shifted Force

$$V(r) = \begin{cases} V_{nb}(r) - V_{nb}(r_c) - \left(\frac{\partial V_{nb}(r)}{\partial r}\right)_{r=r_c} (r-r_c) & r \leq r_c \\ 0 & r > r_c \end{cases}$$

Energy & forces are continuous @  $r_c$

Forces have been perturbed inside  $r_c$

4) Switching Functions

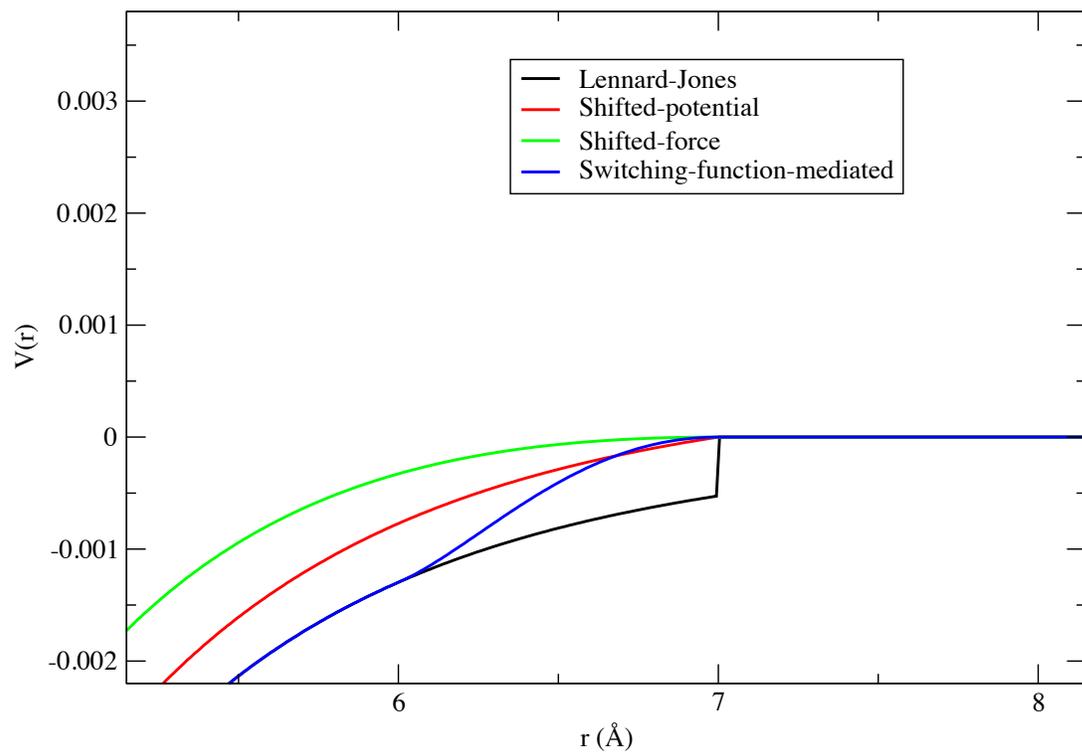
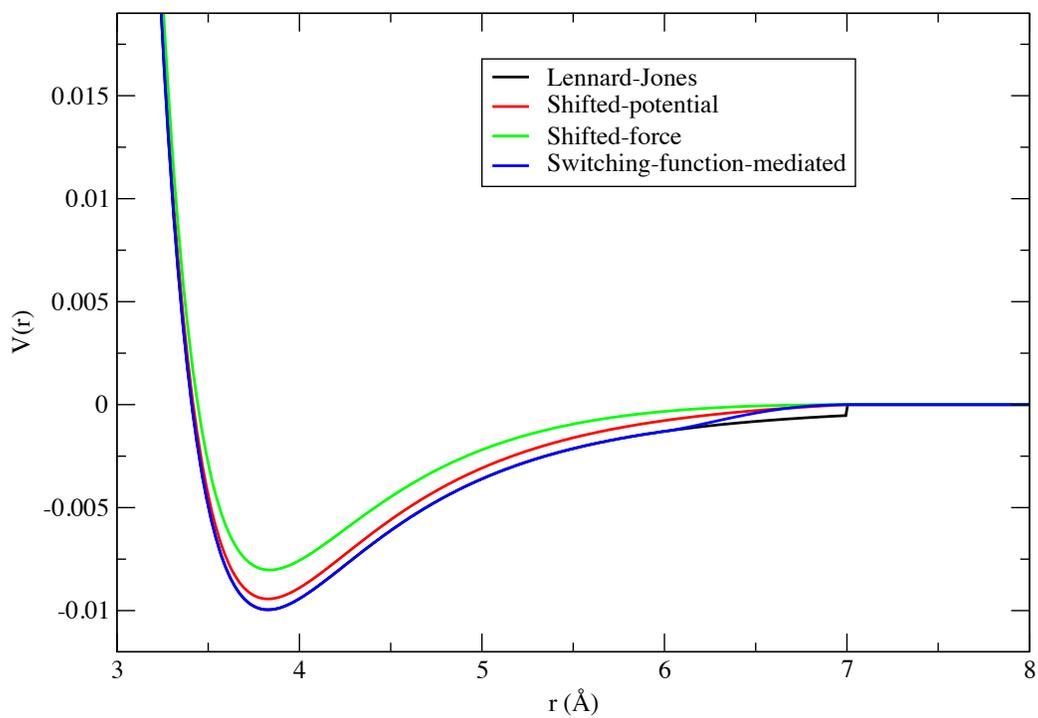


$$s(r) = \begin{cases} 1 & r < r_{on} \\ \frac{(r_{off} - r)^2 (r_{off} + 2r - 3r_{on})}{(r_{off} - r_{on})^3} & r_{on} \leq r < r_{off} \\ 0 & r > r_{off} \end{cases}$$



This is a cubic switching function that smoothly goes from  $1 \rightarrow 0$

## Dealing with potential discontinuities at cutoff distances



To use it:

$$V(r) = \begin{cases} V_{nb}(r) S(r) & r \leq r_c \\ 0 & r > r_c \end{cases}$$



now energies & forces are continuous, but we've added a "shoulder" to the potential close to the cutoff.

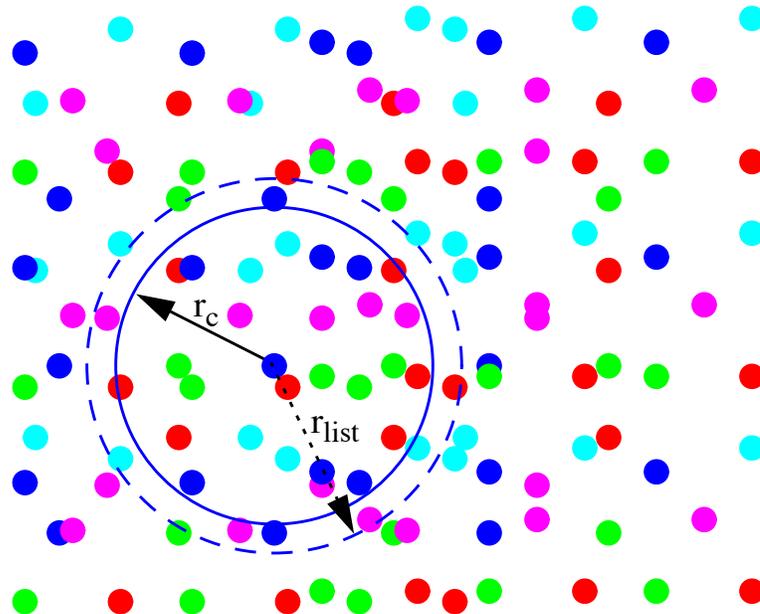
The most common truncation methods are shifted force & switching functions!

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### Neighbor lists

- A buffer region or "skin" is created between  $r_c$  &  $r_{list}$  (typically  $r_{list}$  is 1-2 Å bigger than  $r_c$ )
- We keep a list of neighbors for all atoms within  $r_{list}$  of each other.
- Neighbor lists are not updated every step
- Only those pairs of atoms within each other's neighbor lists are calculated in non-bonded force calculation
- We must update the neighbor list often enough to ensure that no atom from outside the buffer region has made it into  $r_c$

## Neighbor Lists



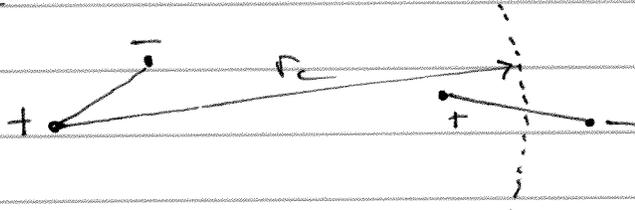
- We need to calculate forces on the blue atom due to all atoms inside the spherical cutoff region (solid circle). This means we have to calculate forces from all atoms that are less than  $r_c$  away from the central blue atom.
- Finding this list of atoms is expensive, so we don't want to have to do it every time step.
- At the beginning of the simulation, we create a "neighbor list," or the list of all atoms inside the  $r_{list}$
- We only have to update the neighbor list when any single atom in the simulation has moved more than  $(r_{list} - r_{cut}) / 2$  from its original position. Why?
- Spherical cutoffs with Neighbor lists are a *huge* algorithmic improvement! They take a calculation that originally had  $N(N-1)/2$  force calculations and reduce it to a calculation with  $n*N$  force calculations ( $n$  is a relatively small number). This improvement is what makes large-scale MD simulations possible!

For example, if any atom moves more than  $\frac{1}{2}$  of the buffer width since previous update, we need to update the lists!

- Buffer widths & velocities determine frequency of updates.

### Charge groups & switching atoms

- vdW truncation is OK @ 8-10 Å
- Electrostatics have  $\frac{1}{r}$  dependence which is long-ranged
- Most molecules are neutral fragments with dipolar interactions:

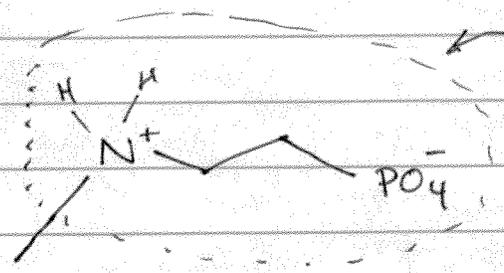


If we truncate electrostatics @  $r_c$ , we go from dipole-dipole ( $\frac{1}{r^3}$ ) to ion-dipole ( $\frac{1}{r^2}$ ) and we'll see big jumps in energy if our cutoffs split neutral groups in half.

Charge-groups: Small group of atoms that have net charge = 0

Switching-atom: one atom in this group is the designated switching atom

Example



this whole assembly could be a charge group

Mathematically:

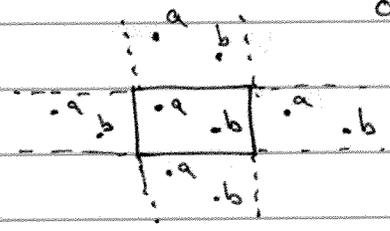
$$V = \sum_a \sum_b S(r_{ab}) \sum_{i \in a} \sum_{j \in b} V_{ij}(r_{ij})$$

↻
switching atoms
↑
members of the charge groups

Periodic Boundaries:

We want to simulate materials in bulk conditions, so we don't want vacuum or walls surrounding our molecules!

A periodic replica is an imaginary copy of our system shifted



in one or more coordinates.

Atom a can interact with the closest copy of atom b, or with many copies of a & b.

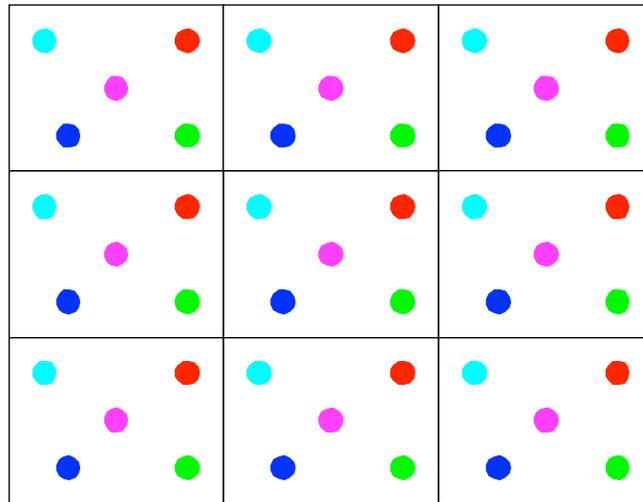
Closest copy: Minimum Image

← more common today!

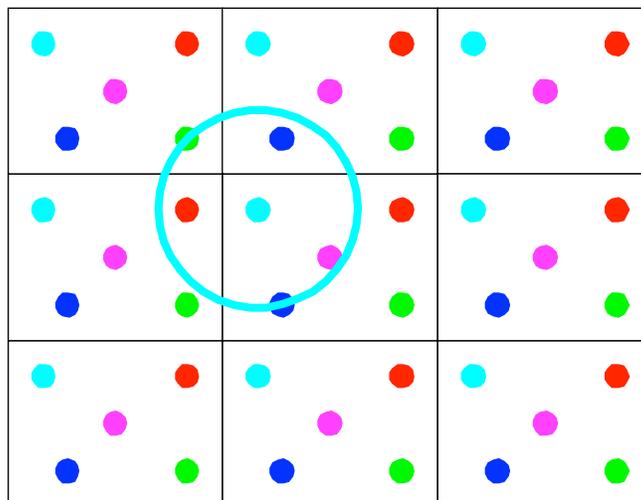
Many copies: Explicit Image

## What keeps the atoms from leaving the box?

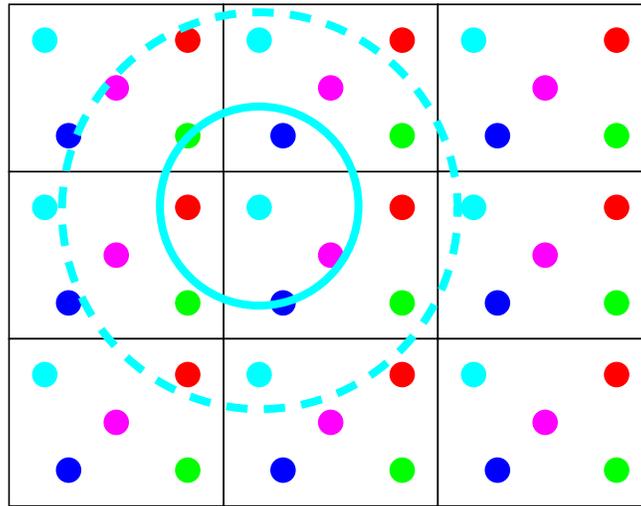
Periodic boundary conditions make the atoms see copies of all of the other atoms on all sides. We replicate the central box to form an infinite 3-dimensional lattice. If an atom leaves the central box, a copy of that atom re-enters on another face.



We only store the positions of the atoms in the central box. We use a cutoff radius and look at the nearest or “minimum” image of all of the other particles:

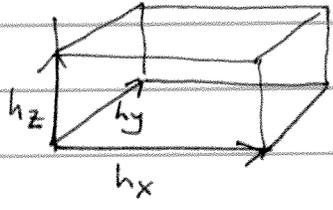


## Minimum vs. Explicit image



- Minimum Image (solid line): molecule interacts only with nearest copies of other molecules from the periodic box.  
 $r_c$  must be smaller than  $L/2$ .  
maximum of  $N(N-1)/2$  terms in the non-bonded potential
- Explicit image (dashed line): molecule interacts with all images of all molecules within the cutoff radius.  
We must create “ghost” molecules if we interact with multiple copies of the the same molecule.  
Ghost molecules shadow their respective particles during the simulation.  
A molecule might interact with a ghost of itself! (only if  $r_c > L$ ).  
The ghosts that interact with a molecule may change during the simulation.  
 $r_c$  may be larger than  $L/2$

Boundaries are cool mathematically:



$\vec{h}_x, \vec{h}_y$  &  $\vec{h}_z$  are vectors along 1 edge of a simulation cell. They don't need to be perpendicular

$$\underline{\underline{H}} = (\vec{h}_x, \vec{h}_y, \vec{h}_z) = \begin{pmatrix} h_{xx} & h_{xy} & h_{xz} \\ h_{yx} & h_{yy} & h_{yz} \\ h_{zx} & h_{zy} & h_{zz} \end{pmatrix}$$



Box or H-matrix describes periodic cell geometry

$\underline{\underline{H}}^{-1}$  is a scaling matrix

Suppose we have atoms  $i$  &  $j$

$$\underline{\underline{d}}_{ij} = \vec{r}_j - \vec{r}_i \quad \leftarrow \text{separation vector}$$

$$\underline{\underline{s}}_{ij} = \underline{\underline{H}}^{-1} \cdot \underline{\underline{d}}_{ij} \quad \leftarrow s_{ij} \text{ is in units of "boxes"}$$

$$\underline{\underline{s}}_{ij}^t = \underline{\underline{s}}_{ij} - \text{arint}(\underline{\underline{s}}_{ij}) \quad \leftarrow \text{truncated portion}$$

$$\underline{\underline{d}}_{ij}^t = \underline{\underline{H}} \cdot \underline{\underline{s}}_{ij}^t = \text{closest image!}$$

## Spherical Boundary conditions

Suppose our system fits nicely inside a sphere:

- Proteins with some explicit water molecules
- Nanoparticles

We can impose a *spherical* boundary which mimics the potential that a solvent or lattice might produce.

- Outer shell (1Å) is a “buffer region”. Molecules in this region obey stochastic (Brownian or Langevin) equations of motion rather than the standard Newtonian equations.
- To prevent evaporation of solvent, we often include an additional shell (4 Å) of frozen solvent molecules outside the buffer region.
- Another way of preventing evaporation is to have an effective boundary potential (a *restraining* potential) that forces a wayward solvent molecule back to the central region.

