Periodic boundary conditions, supercells and slabs

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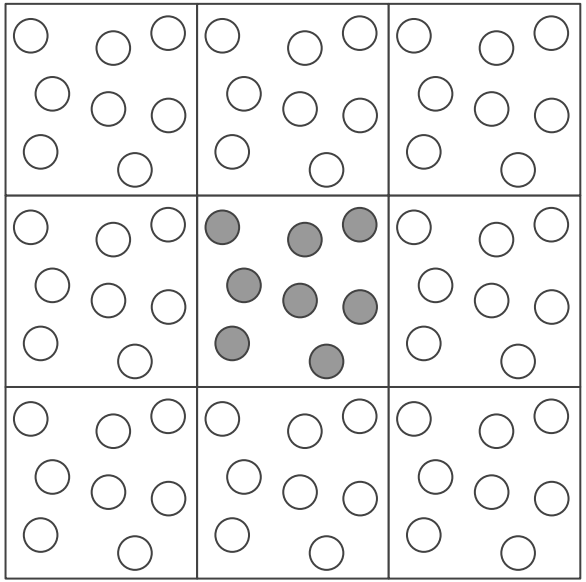
Periodic boundary conditions (PBC)



- A ”real” system might contain $N_A \sim 6 \cdot 10^{23}$ atoms
- Typical simulations can handle at most 1’000’000 atoms
- A small cube of 10x10x10 atoms has about half of the atoms at the surface. → Not a good description of a bulk system.

Periodic boundaries offers a solution:

- Small box with atoms that is repeated in all directions
- There are no surface at all in this system
- The central cell is called the unit cell or simulation cell
- The surrounding cells are often called images

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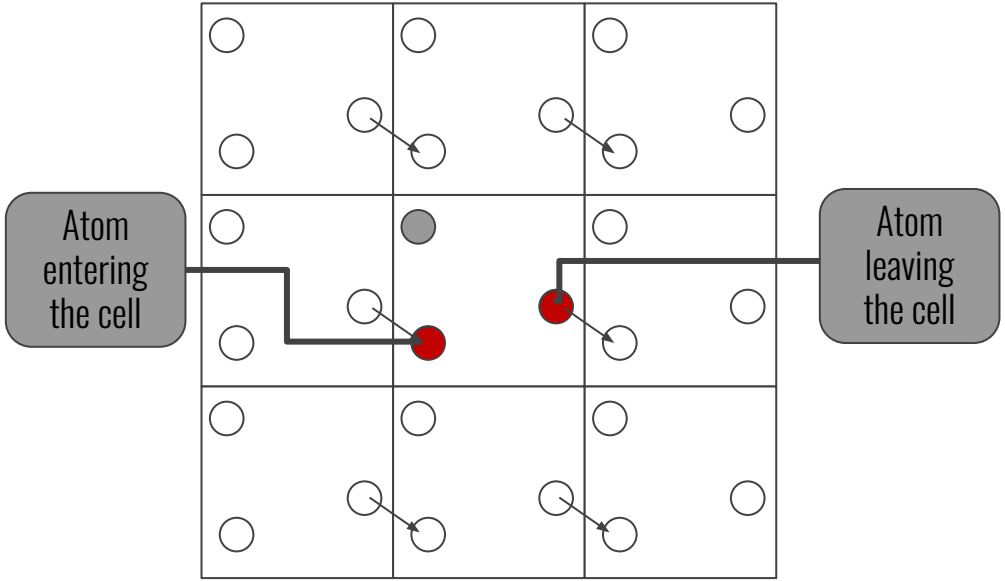
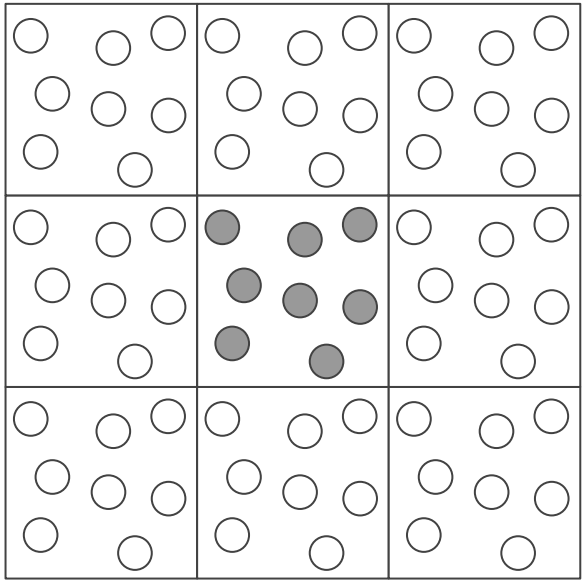
Crossing the border

-When an atom moves across a boundary it is re-inserted on the opposite side of the cell



Interactions in periodic systems

-Dealing with infinity



Under periodic boundary conditions every atoms interacts with an infinite number of surrounding atoms in the replicated images.

There are two main strategies to deal with this problem:

1. Ignore faraway atoms.
   - Ex 1: Truncated potentials
   - Ex 2: Minimum image convention
2. Try to find a closed expression for the infinite series representing all interactions.
   - Ex 1: Tail correction
   - Ex 2: Ewald summation for electrostatics

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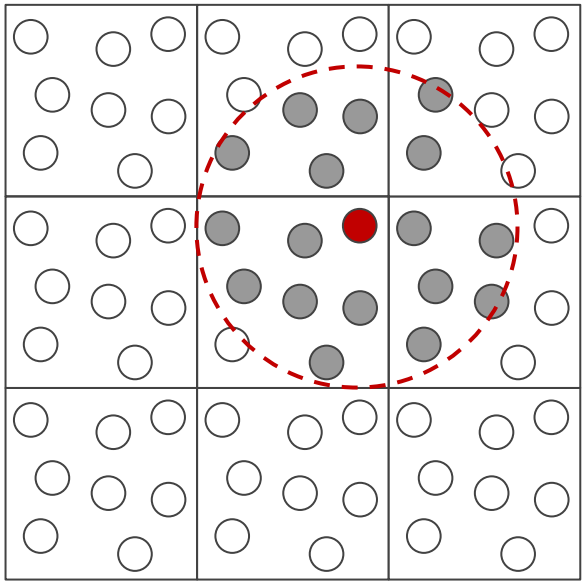
Interactions in periodic systems

Truncation of the potential



When applying a distance cutoff, atoms only interact with nearby atoms. For example, the red atom is only allowed to interact with gray atoms within the dashed circle.

- Under periodic boundary conditions every atoms interact with an infinite number of neighbors.
- One way to mitigate this is to enforce an cutoff distance beyond which atoms are not considered to interact.
- We can now compute the interaction on each atom in the simulation cell.

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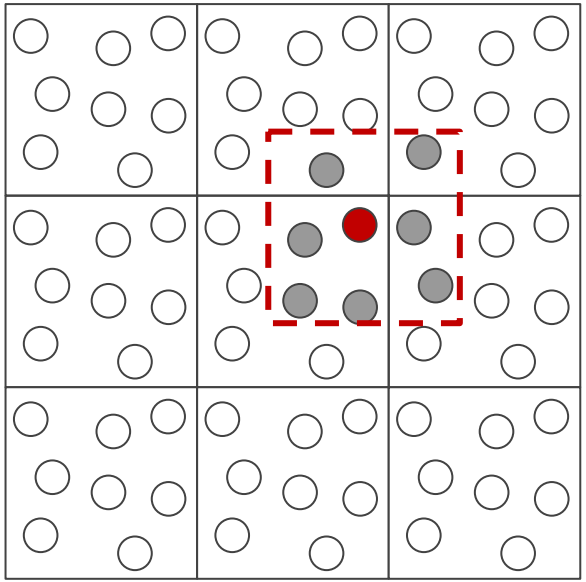
Interactions in periodic systems

-Minimum image convention



The red atom interact once with other atoms in the simulation cell, within the cell or via a closeby copy.

- In the minimum image convention each atom only interact with the closest copy of every other atom in system.
- This means that that each atom of the simulation cell interact exactly once with every other atom of the simulation cell. Either directly within the cell or through an copy in a neighboring image.

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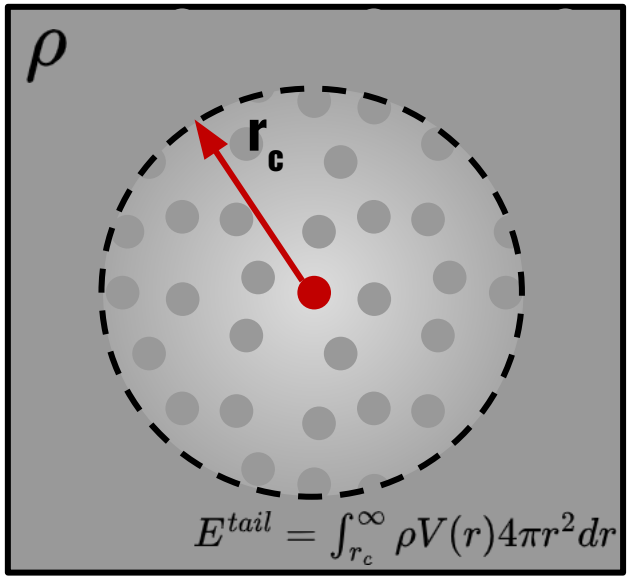
Interactions in periodic systems

-Tail correction



In an amorphous system distant atoms appear as a “blur”. We can therefore replace the direct interaction with distant atoms with an average interaction that depend on the density of the system.

- One way to address the infinite series of the interacting atoms is to use a so-called tail correction.
- The approach is strictly only valid for amorphous system (e.g. liquids and gases) where we can assume that the radial distribution function approach one some finite distance r_c.
- The infinite series in the interaction is replaced with an integral and solved. It only works for simple interaction models V(r) e.g. the Lennard-Jones potential.

$$E^{tail} = \int_{r_c}^{\infty} \rho V(r) 4\pi r^2 dr$$

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Example of a tail correction for the Lennard-Jones potential. Note that the tail correction only works for simple interaction models where the integral can be solved.

$$E^{tail} = \int_{r_c}^{\infty} \rho V(r) 4\pi r^2 dr$$

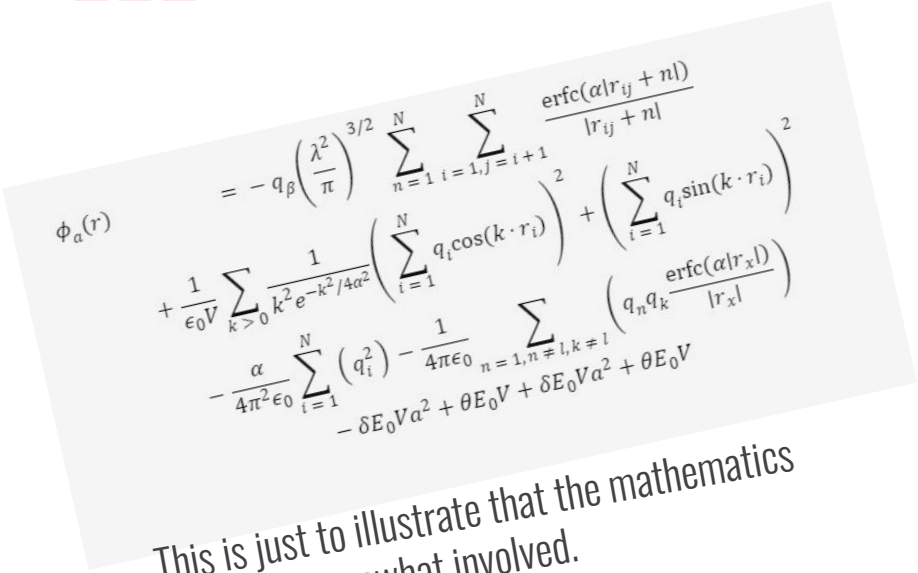
$$V_{\mathrm{LJ}} = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right]$$

Calculus and algebra.
Why not try it yourself!

$$E_{LJ}^{tail} = \rho\varepsilon\sigma^3 \frac{16\pi}{3} \left[\left(\frac{\sigma}{r_c}\right)^{9} - \left(\frac{\sigma}{r_c}\right)^{3} \right]$$

Interactions in periodic systems

-Ewald summation



$$\phi_a(r) = -q_\beta\left(\frac{\lambda^2}{\pi}\right)^{3/2}\sum_{n=1}^{N}\sum_{i=1,j=i+1}^{N}\frac{\operatorname{erfc}(\alpha|r_{ij}+n|)}{|r_{ij}+n|} + \frac{1}{\epsilon_0 V}\sum_{k>0}\frac{1}{k^2 e^{-k^2/4a^2}}\left(\sum_{i=1}^{N}q_i\cos(k\cdot r_i)\right)^2 + \left(\sum_{i=1}^{N}q_i\sin(k\cdot r_i)\right)^2 - \frac{\alpha}{4\pi^2\epsilon_0}\sum_{i=1}^{N}\left(q_i^2\right) - \frac{1}{4\pi\epsilon_0}\sum_{n=1,n\neq l,k\neq l}\left(q_n q_k\frac{\operatorname{erfc}(\alpha|r_x|)}{|r_x|}\right) - \delta E_0 V a^2 + \theta E_0 V + \delta E_0 V a^2 + \theta E_0 V$$

This is just to illustrate that the mathematics behind is somewhat involved.

- Electrostatic interaction decay too slowly for the infinite series to converge (formally they are conditionally convergent).
- Ewald summation baer similarity to the tail correction.
- Electrostatic interaction are partitioned into short and long ranged contribution.
  - Short-ranged: computed in real space
  - Long-ranged: computed in reciprocal space

The detail mathematics and derivation is beyond the scope of this presentation.

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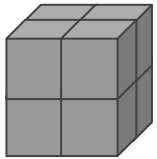
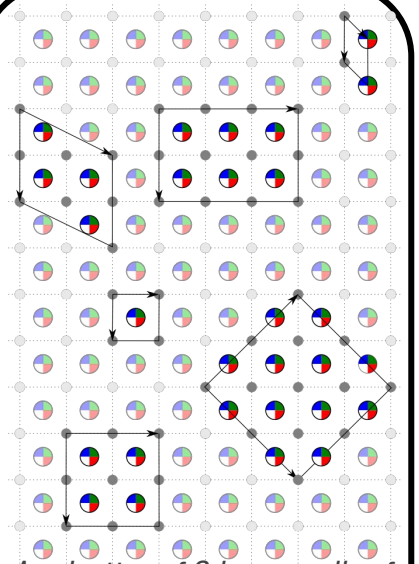
Supercells

Unit cell



(2x2x2) supercell

An example of a supercell built by repeating the unit cell twice in all directions.



A selection of 2d supercells of various shapes.

- In simulations of crystalline materials, the unit cell of the material and our simulation cell must be consistent.
- The simplest approach is to use a so-called ***supercell*** were the simulation cell is built from the unit cell by replicating it a number of times in each direction.
- We use a notation (NxMxL) to describe the replication.
- Supercell with varying shapes can be constructed. However, they must yield the same tiling as the unit cell when replicated.

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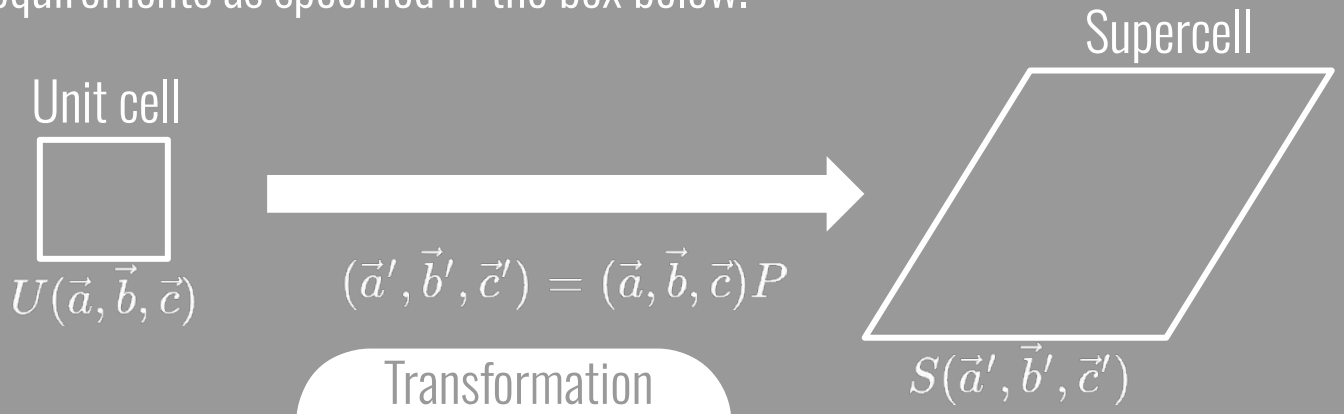
Image to the right is taken from wikipedia.

Supercells can be be constructed using linear algebra. Given a set of cell vectors U we can construct the supercell vectors S by multiplication of a transformation matrix P. P need to fulfill certain requirements as specified in the box below.



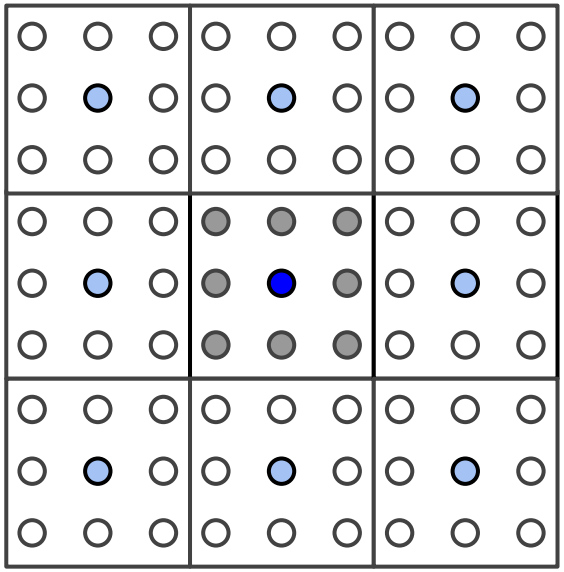
Transformation matrix, P

$$P = [p_{ij}]_{(3\times3)}$$

$$\det(P) > 1$$

$$p_{ij} \in \mathbb{Z}$$

Supercells
-Why?



A point defect in the simulation cell (e.g. a vacancy, substitutional defect, or interstitial) is replicated in all images. To avoid them interacting directly with their images we need a supercell to provide some “padding”.

- When do we need a supercell? Ex:
  - If we like to consider point defects we need to make sure that they do not directly interact with their own images in neighboring cells. (Illustration to the left)
  - When considering vibrations (phonons) since we should make room for the *waves*.
  - In molecular dynamics simulations where atoms can diffusion due to thermal motion.

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The slab model

-Modelling surfaces under periodic boundary conditions

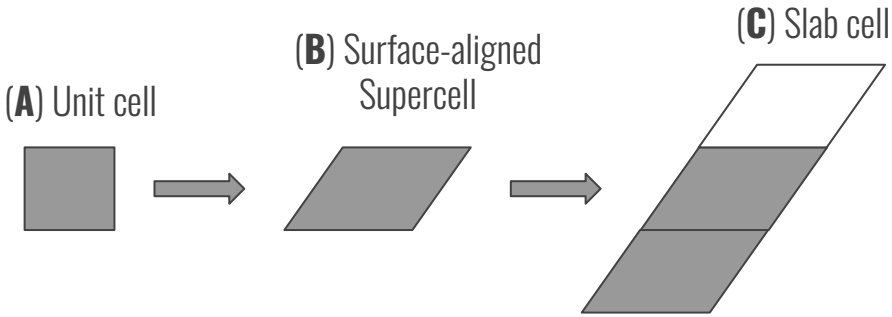

*Illustration showing how a slab cell can be constructed. Starting from the unit cell (**A**) we first construct a supercell (**B**) with one of its cell axis parallel to the surface normal. The supercell (**B**) is then stacked together we some empty boxes to create a slab cell (**C**).*

- We can simulate surfaces under periodic boundary conditions by making construction similar to the supercell approach with some empty cells along the direction of the surface normal.
- The building blocks of the slab cell needs to be prepared in such a way that the surface normal aligns with one of the cell axis. This is a non-trivial task! Fortunately algorithms helping us with task are available in softwares e.g. Atomic Simulation Environment (ASE).

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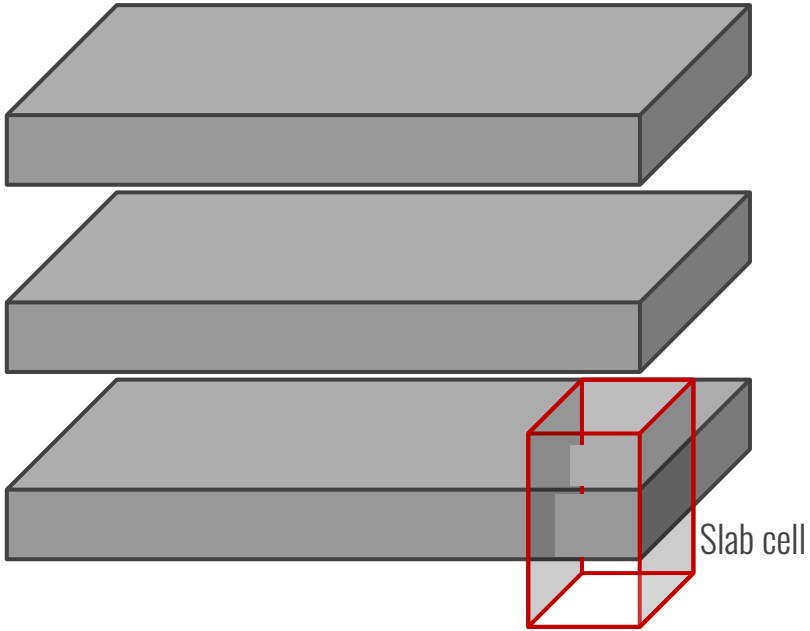
The slab model

-Modelling surfaces under periodic boundary conditions



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Schematic illustration of the resulting slabs from the slab model, with the slab cell indicated in red.

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Summary

- Real systems typically contain to many atoms to handle in electronic and atomistic simulations.
- Periodic boundary condition allow us to treat infinite systems built from a small repeating unit.
- The infinite series occurring in the interaction between atom must be addressed. Ex:
    - Truncating potentials or using the minimum image convention
    - Trying to approximate the series via a tail correction
    - Ewald summation (electrostatic interactions)
- For crystalline solids the repeating unit need to match that of the material. In these cases we make use of supercells which (in the simple case) are built by replication of the unit cell along each of it cell axis.
- Surfaces can be treated under periodic boundary conditions using the so-called slab model.