Simulation of small systems

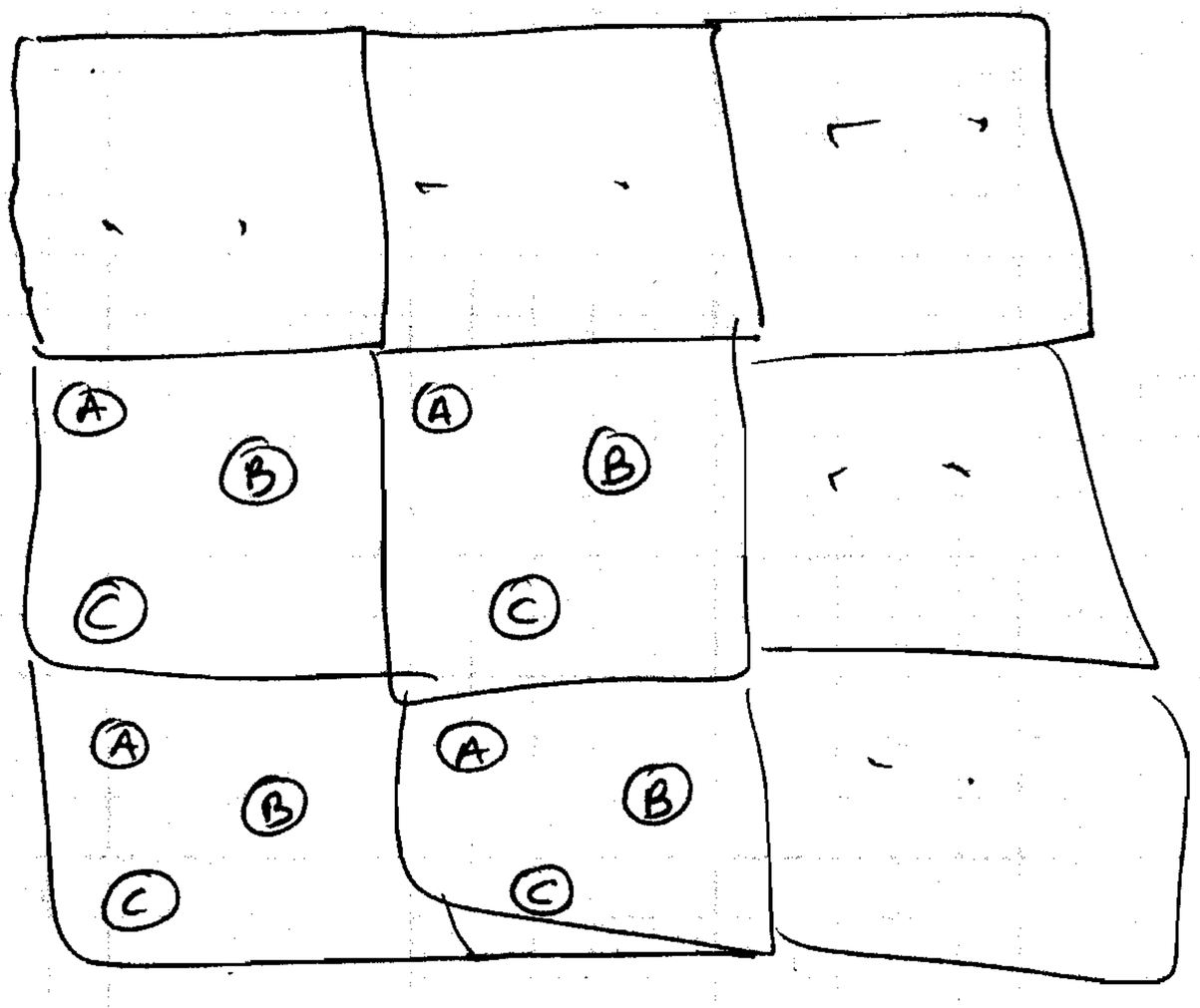
Simulations are usually performed on a small number of molecules, $100 \leq N \leq 10\,000$.

Limitations: memory,
speed of execution
equilibration time for large systems

If we are indeed interested in small systems (e.g. a small drop or crystal in vaccum), things are straightforward. Otherwise, we need to construct an environment that approaches that of a bulk (macroscopic) sample - otherwise most of our system will be on the boundary:

for 1000 molecules, $10 \times 10 \times 10$ cube, most molecules would "feel the wall".

Solution: Periodic Boundary Conditions

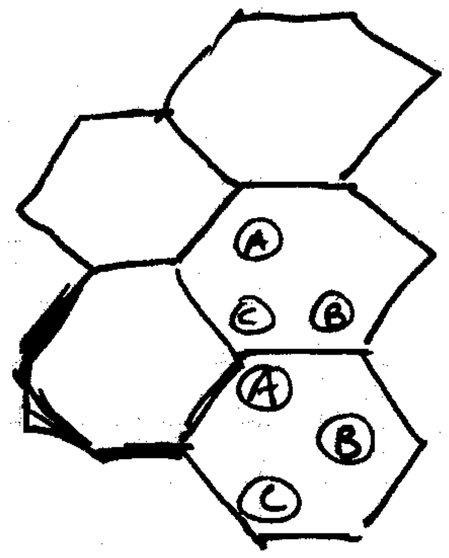


← 2-D, square

(equivalent to 3-D, cubic)

Other possibilities

In 2-D, hexagonal



Any advantages / disadvantages?

+ closer to circle ⇝ interactions of longer range
  Can "fit in the box" – more about this later.

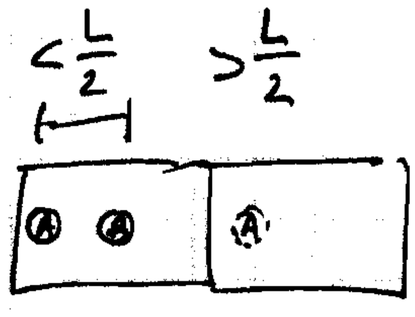
– Complexity in calculating "minimum image distance" between neighbors

In 3-D: various Platonic solids: rhombic dodecahedron, truncated octahedron

<u>The minimum image problem:</u>

We would like to be able to compute forces energies and pressures by summing over a <u>fixed</u> number of particles.

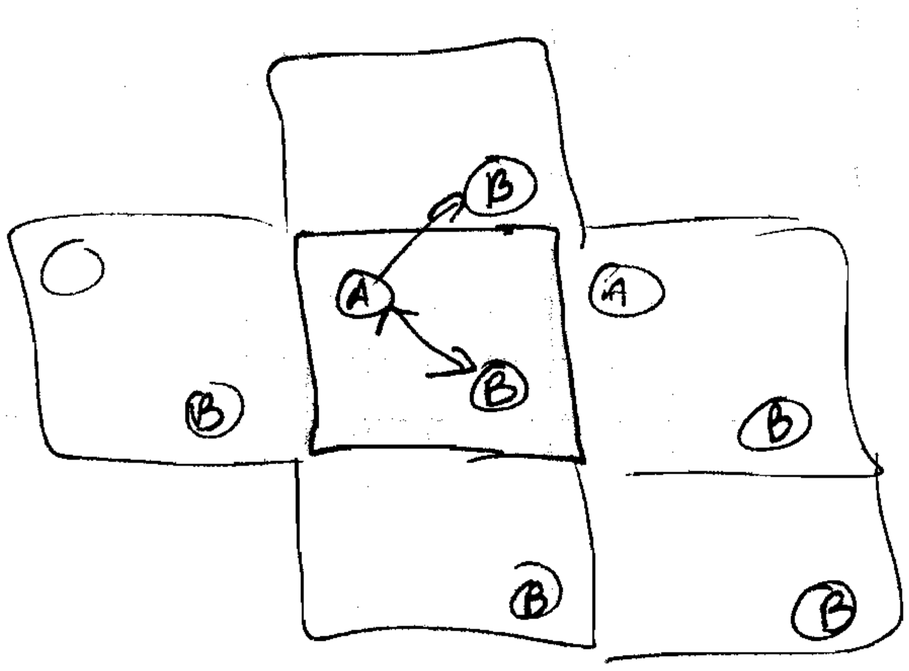
In conventional thinking, this restricts the explicit calculation of forces to particles that are less ~~than~~ apart than ~~~~ a certain minimum distance (L/2 for square of cubic B.C).



As will be explained later, this restriction is not necessary, and a calculation can be performed without a cutoff distance.

Comments on previous material: periodic images of system extend to infinity —
Problem with "range" will become clear as follows:

How do we actually calculate the energy of our infinite periodic system?



Do we take into account <u>all</u> (A)-(B) interactions?
Practically, one wants to include only as many interactions as there are particles in our central box.

<u>Minimum image convention</u>: include only interactions between a particle in the central box and the "minimum image" of any other particle — that is the image of the second particle nearest to the first.

For consistency, then, one typically would "cutoff" the potential at a distance equal to $L/2$ (the minimum possible minimum-image distance) for a cubic or square box.

<u>Spherical BC</u>: Non-euclidian <u>space</u>!