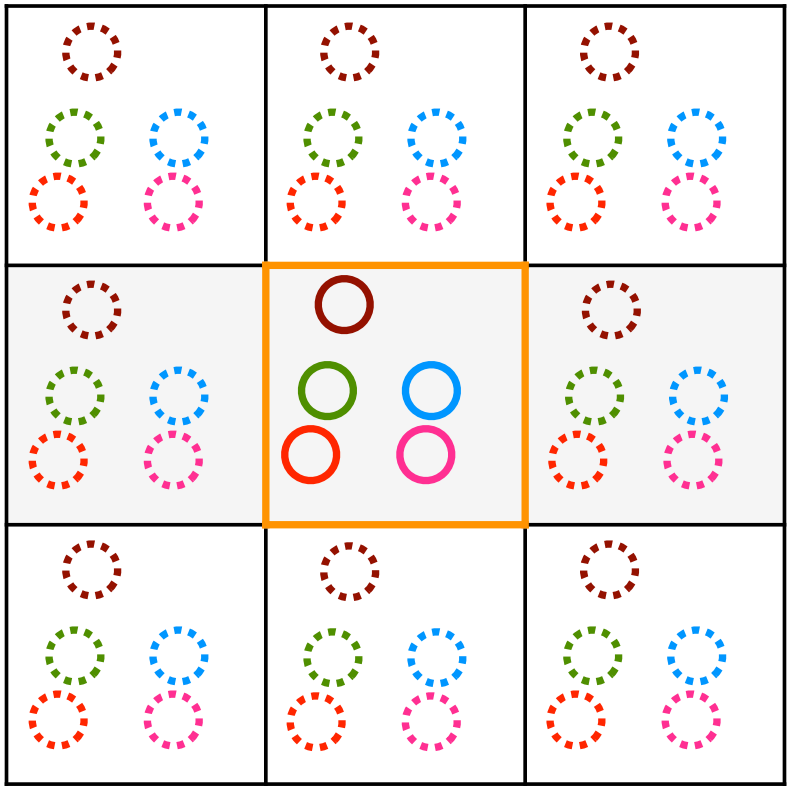
Molecular Modelling and Simulations



Shampa Raghunathan

Recap...

- Analytical forms of various functions to model different types of interactions (bonded and nonbonded) in order to describe a system/molecule–called potential energy functions in classical molecular mechanics

Outline

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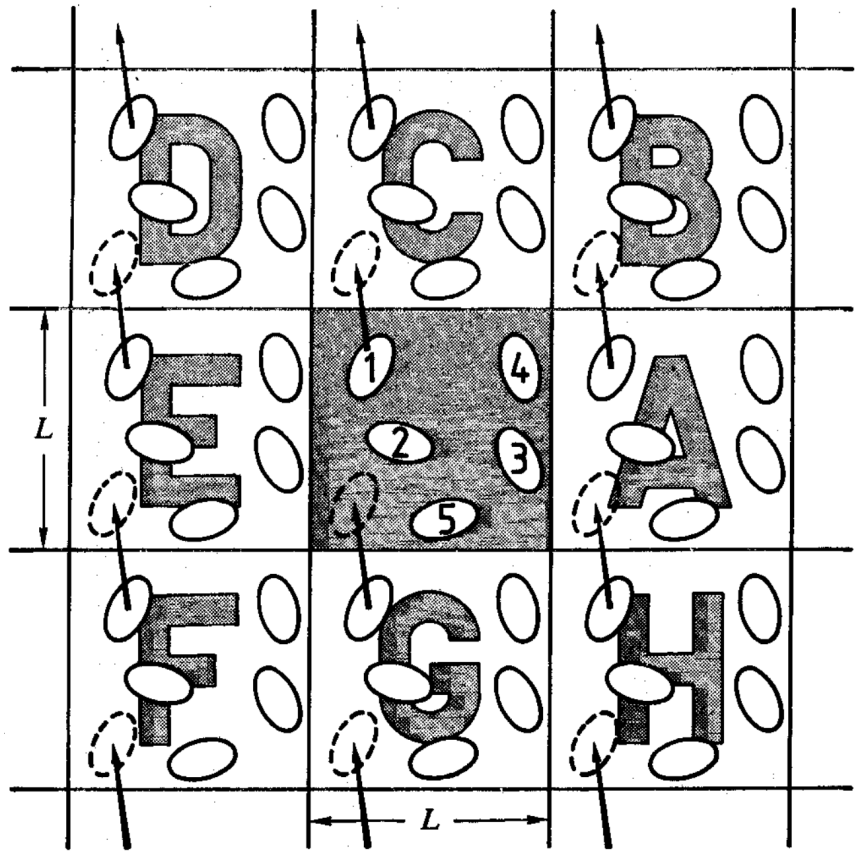
Why periodic boundary conditions (PBCs) during simulations?

- A "real" system (truly macroscopic) contains Avogadro's number of 6.0 x 10^{23} particles per mole
- Computer simulations may contain $\sim 10 \leq N \leq 1000000$ molecules
- In a typical simulation system of a small cube of 10x10x10 molecules has approximately half of the molecules on the surface
- In a cube surrounded by wall, molecules on the surface will experience quite different forces from molecules in the bulk
- The problem of "surface effect" can be overcome by using PBCs

Periodic Boundary Conditions

- Small box replicated in all directions
- A particle that leaves the box on one side is replaced by an image particle that enters from the other side
- There are no walls and no surface particles

- Some systems inherently contain a boundary, e.g., a liquid droplet, or a surface, or an interface

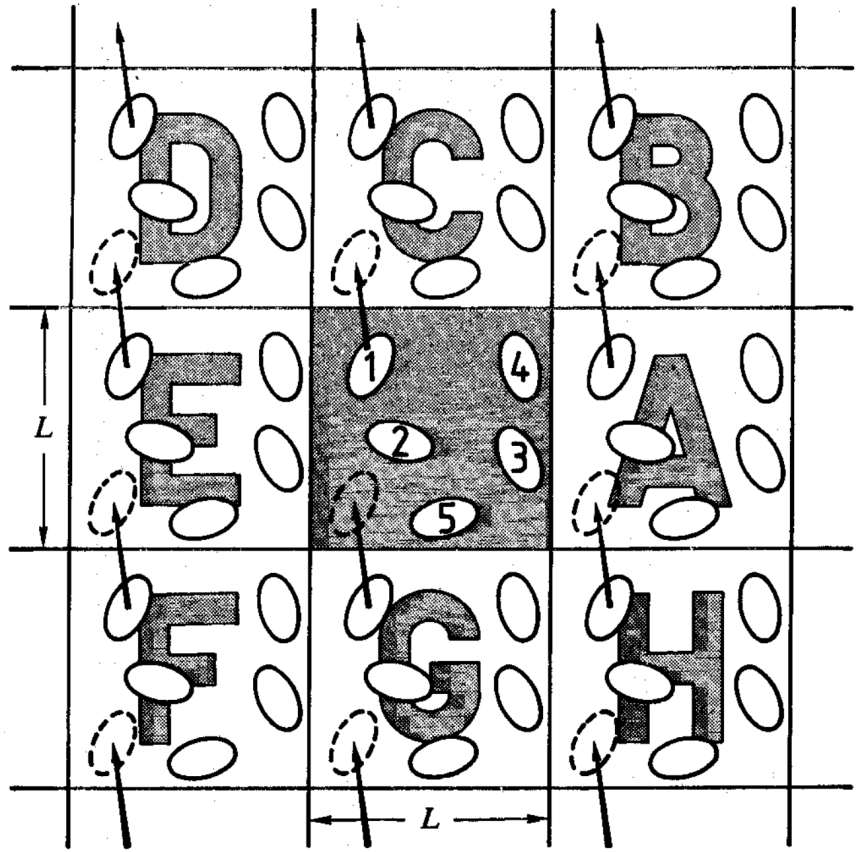


A 2-dimensional periodic system

Allen, M. P., & Tildesley, D. J. (2017). *Computer simulation of liquids*. Oxford university press.

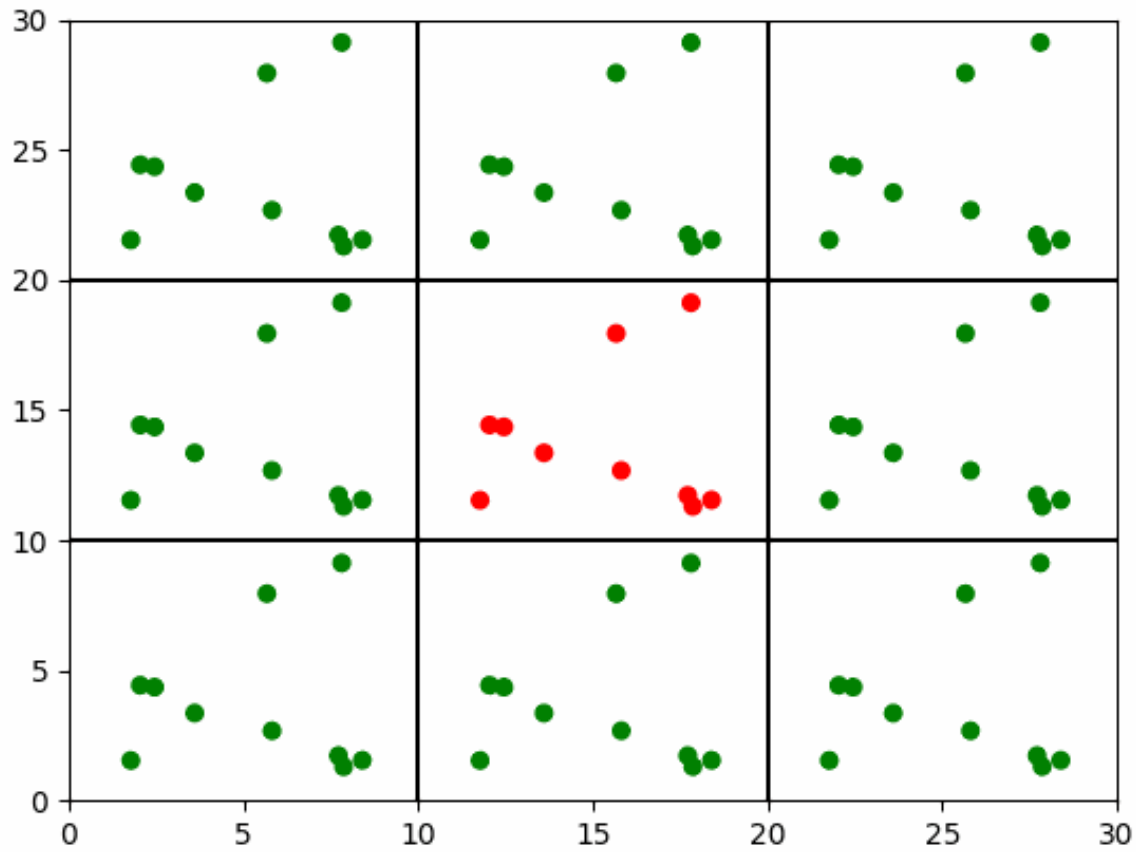
Periodic Boundary Conditions

- Grey box is the central/primary simulations box; often called as unit cell
- Neighbouring A, B, C, D, E, F, G, and H – 8 such boxes in 2-D periodic system are called images
- For 3-D case central box to be surrounded by 26 images
- The number density ($\frac{N}{V}$) in the central box is conserved



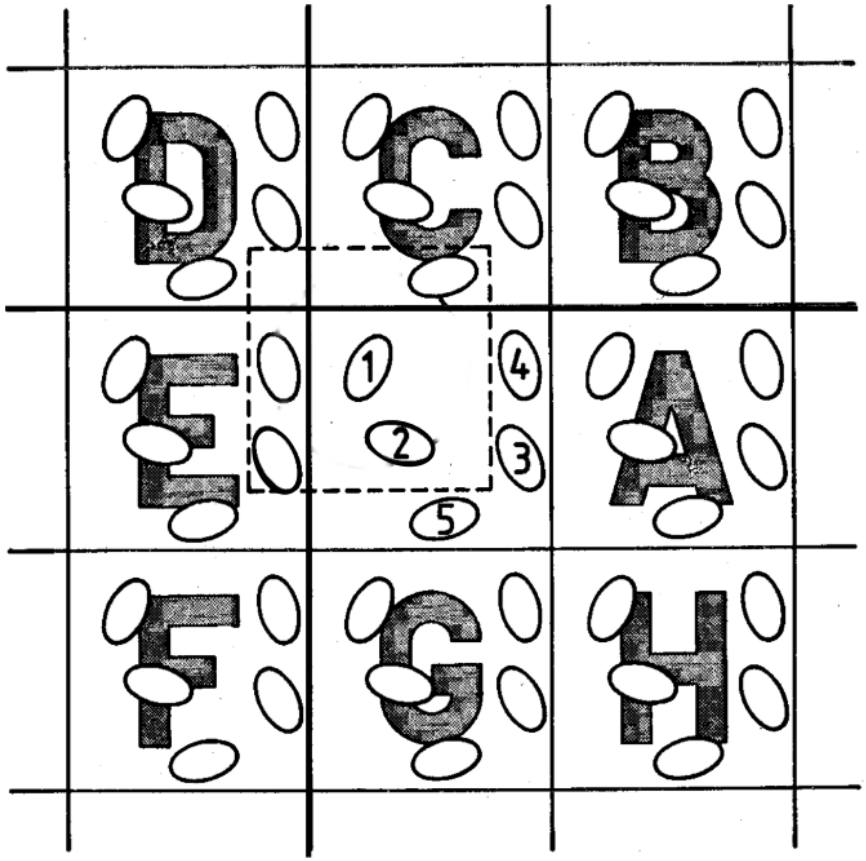
A 2-dimensional periodic system

Periodic Boundary Conditions



The Minimum Image Convention

- Particles interact only with the closest periodic image of the other (N-1) particles:
  - Molecule **1** can interact with (N-1) every other i^{th} molecule in the simulation box.
  - Also, with i_A, i_B, i_C $\cdots$ i_H surrounding images.

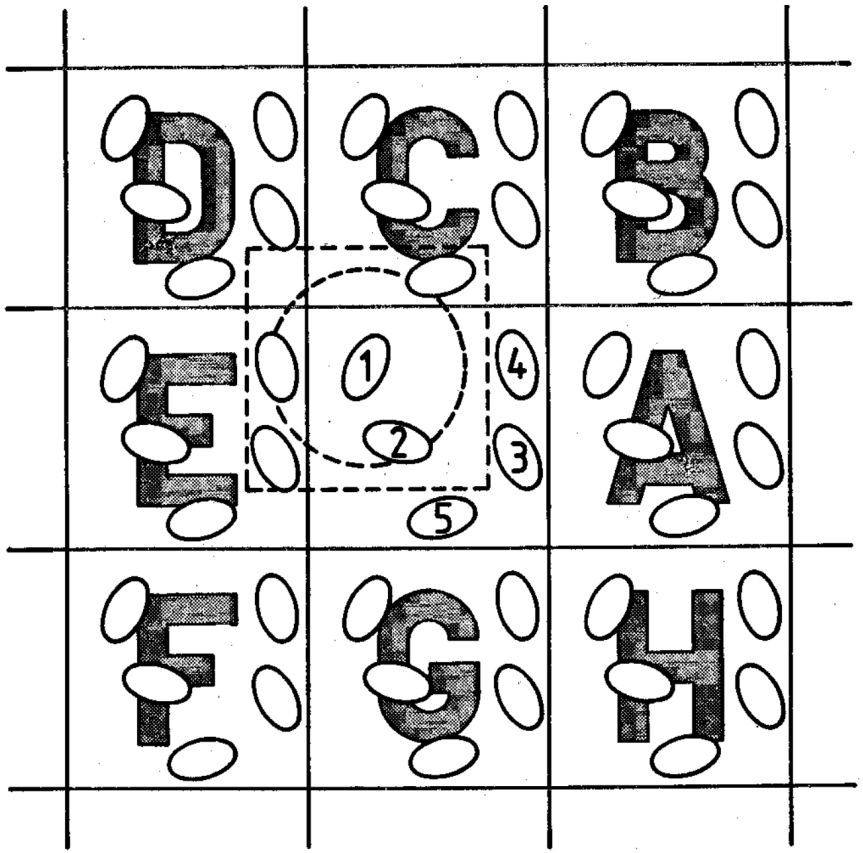


Within the minimum image convention Molecule **1** is interacting with 2, 3_E, 4_E and 5_C

Allen, M. P., & Tildesley, D. J. (2017). *Computer simulation of liquids.* Oxford university press.

Minimum Image and Spherical Cutoff

- The most time consuming part: Computing the nonbonded (vdW & electrostatic) energies and forces
- For a pair additive potential there are N^2 such interactions
- Regularly minimum images and spherical cutoffs are used together
- Applying spherical cutoff sets pair potential $v(r_{ij})$ to zero for $r_{ij} \geq r_c$, where r_c is the cutoff distance



Within the minimum image and spherical cutoff Molecule **1** is interacting with 2, and 4_E, but not with 3_E and 5_C

Minimum Image and Spherical Cutoff

- In a cubic simulation box of dimension L, the number of neighbours explicitly considered is now reduced approximately by a factor of r_c^3/L^3
- The r_c must be no greater than $\frac{1}{2}$L to avoid an unphysical self-interaction; be consistent with the minimum image convention
- Application of an energy cutoff will create a discontinuity in the energy function at the cutoff point; introduces very large artificial forces into the system. Because, $v(r_{ij}) \sim r_{ij}^{-1}$
- How to deal with this?

Outline

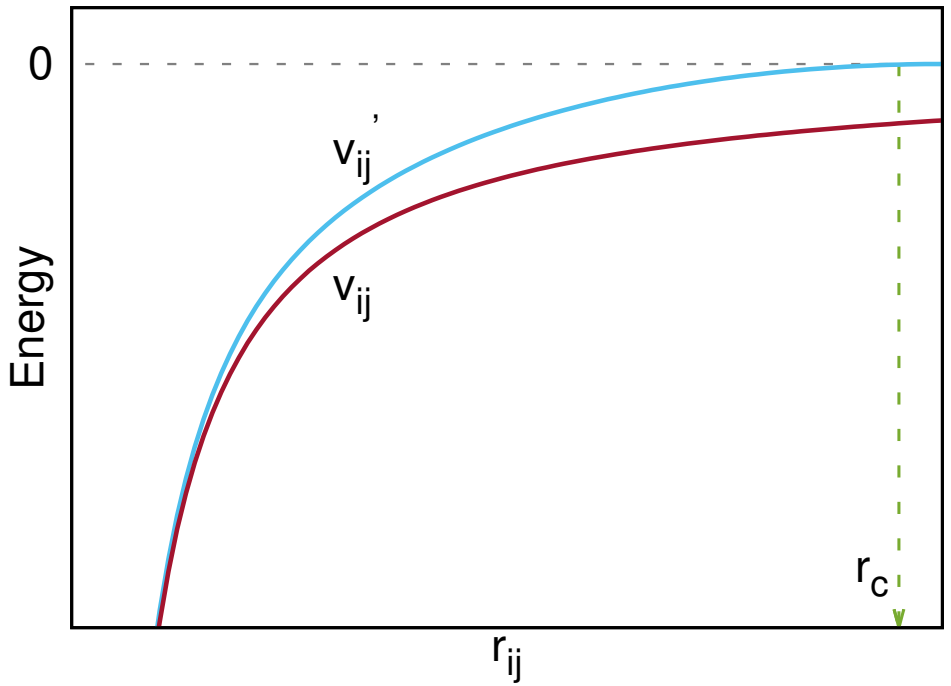
Truncating scheme for nonbonded interaction potential

- To avoid an infinitely large artificial force at the cutoff point energy truncation must be introduced gradually over a range of distances

$$v'_{ij}(r_{ij}) = \begin{cases} v_{ij}(r_{ij}), & \text{if } r_{ij} \leq r_c \\ 0, & \text{if } r_{ij} > r_c \end{cases}$$

Shift truncation function

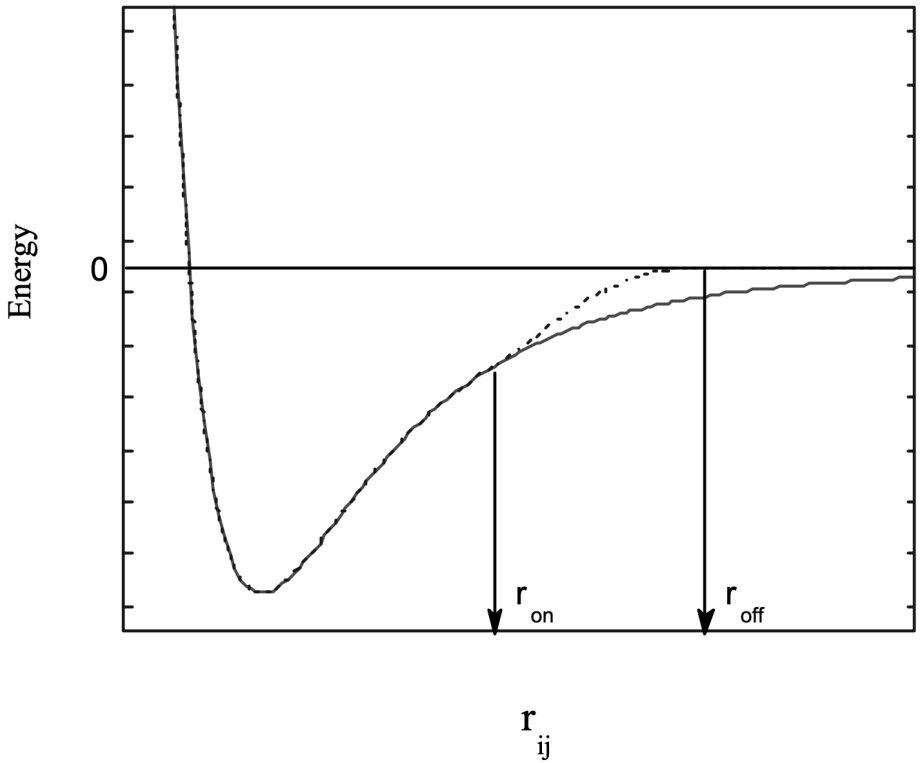
$$sh(r_{ij}, r_c) = \begin{cases} \left[1 - \frac{2r_{ij}^2}{r_c^2} + \frac{r_{ij}^4}{r_c^4}\right], & \text{if } r_{ij} < r_c \\ 0, & \text{if } r_{ij} > r_c \end{cases}$$



Shift truncation function applied to an electrostatic potential

Switch truncation function

$$sw(r_{ij}, r_{\text{on}}, r_{\text{off}}) = \begin{cases} 1, & \text{if } r_{ij} < r_{\text{on}} \\ \frac{(r_{\text{off}} - r_{ij})^2 (r_{\text{off}} + 2r_{ij} - 3r_{\text{on}})}{(r_{\text{off}} - r_{\text{on}})^2}, & \text{if } r_{\text{on}} < r_{ij} < r_{\text{off}} \\ 0, & \text{if } r_{ij} > r_{\text{off}} \end{cases}$$



Switch truncation function applied to a van der Waals potential