Simulations of Small Systems

Simulations usually performed for $100 \le N \le 10{,}000$ molecules, even though million-atom systems are now feasible.

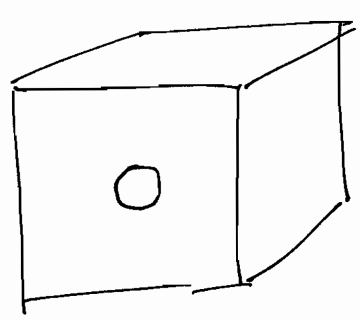
How small is an "acceptable" system?

Box length $\frac{L}{2}$ >
- range of intermolecular interactions
- Correlations in system
- largest feature of interest, e.g. micellar aggregates

Why use small systems?
- memory
- Code speed
- equilibration time ↑ as N ↑

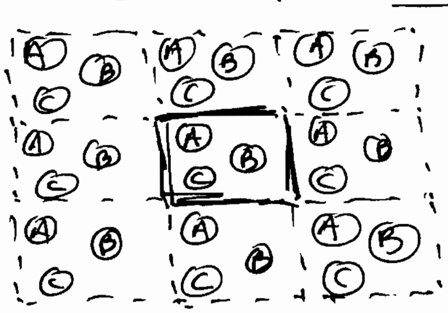
For 1,000 molecules at close-packed density ($\rho^* = O(1)$)

$\Rightarrow L^* = \sqrt[3]{1{,}000} = 10$ → most molecules would be near a wall



- Interactions with walls modify bulk system properties
- Layering near walls over 2-5 σ
- Issue less important in 2D, or for "hard" particles (e.g. PS#4)

Solution: Periodic Boundary Conditions



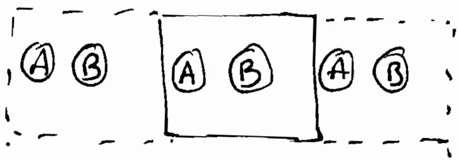
← In 2-D, infinite array of squares replicating central box

Cubic array in 3D

National Brand 42-381 50 SHEETS EYE-EASE 5 SQUARE 42-382 100 SHEETS EYE-EASE 5 SQUARE 42-389 200 SHEETS EYE-EASE 5 SQUARE

Boundary Conditions

Range of Interactions



We would like to perform calculations taking into account only $N \cdot (N-1)/2$ interactions for N particles in the central box.

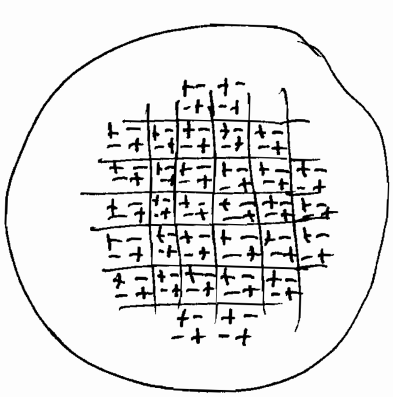
What happens with all the images?

Solution: Truncate (or "cut off") interactions at distances up to $R_{cut} \leq \frac{L}{2}$

→ This guarantees there is at most 1 particle image interacting with any given particle in the central box.

("Minimum Image" convention)

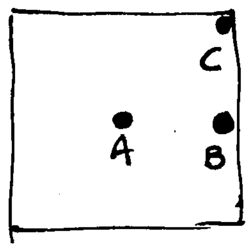
This approach does not work for Coulombic interactions, which decay too slowly to be truncated at L/2. For such systems, special summation methods – Ewald Sums



- Take periodic character of system to be literary true
- Split interactions into short-range (truncated) and long-range (summed to ∞ distance in Fourier space)
- Computationally expensive

An alternative to L/2 cutoff

Theodorou + Suter JCP 82:955 (1985)



- Take into account all interactions "in box" (between minimum image pairs)
- 100% if distance ≤ L/2 (e.g., pair A–B)
- variable fraction determined from intersection of sphere (circle in 2D) with cube (square in 2D)
  - explicit equations worked out for general geometries