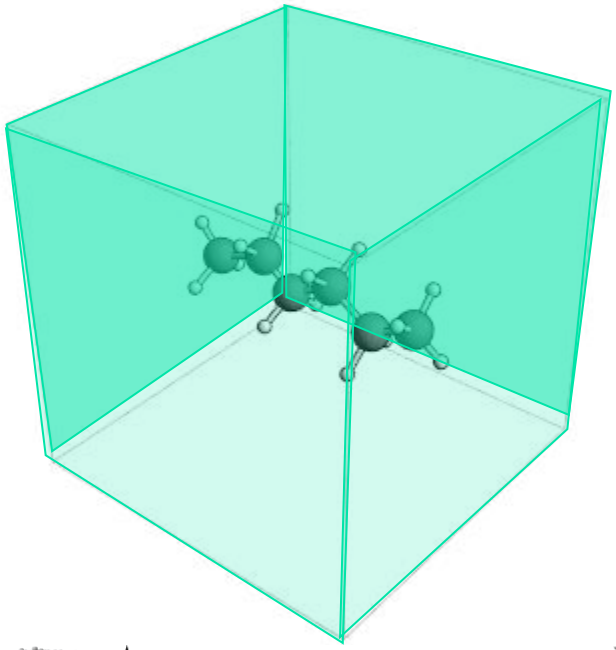
11th i-CoMSE Workshop: Mesoscale Particle-Based Modeling

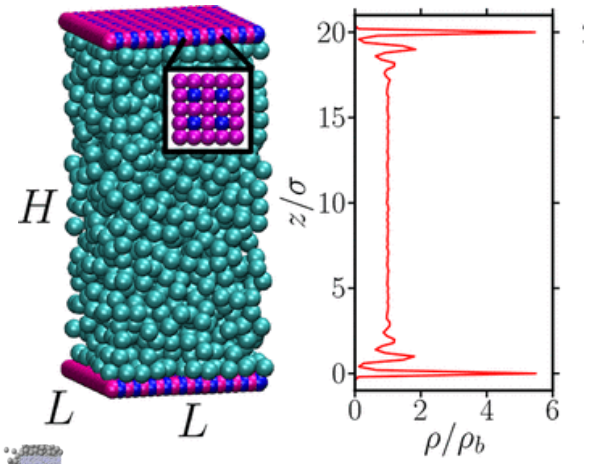
Mississippi State University
July 21–25, 2025

Session 7: Periodic boundary conditions I (structure)

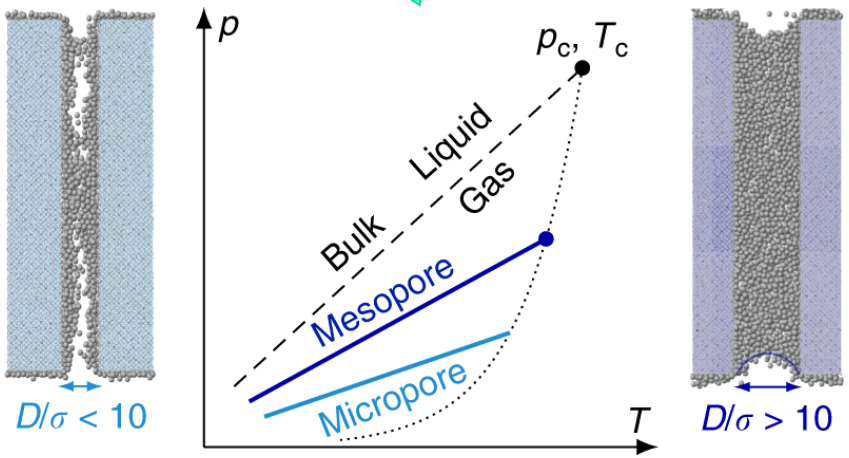
Boundaries in Simulations



What do we do with the edges of the simulation box?



Diffusion under Confinement: Hydrodynamic Finite-Size Effects in Simulation, P. Simonnin, B. Noetinger, C. Nieto-Draghi, V. Marry, B. Rotenberg, JCTC 2017 13 (6), 2881-2889 DOI: 10.1021/acs.jctc.7b00342



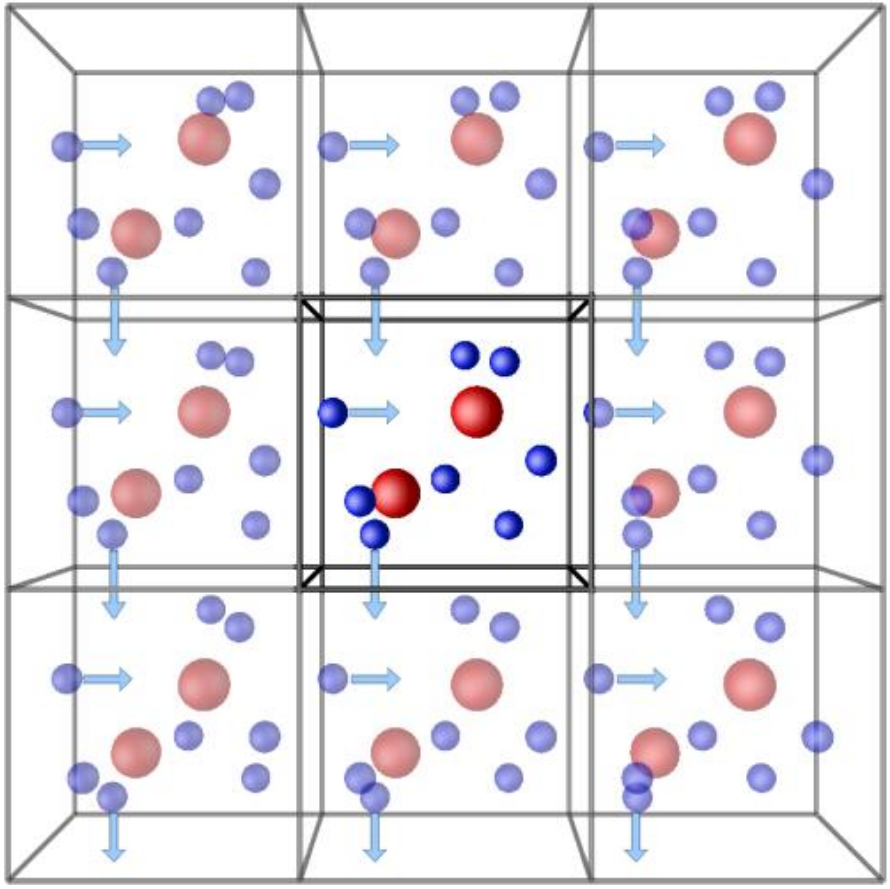
Walls influence:

- Density, critical points, interfacial tensions, diffusion,….

Deroche, I., Daou, T.J., Picard, C. et al. Reminiscent capillarity in subnanopores. Nat Commun 10, 4642 (2019). DOI:10.1038/s41467-019-12418-9

Periodic Boundaries

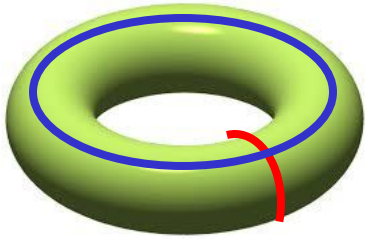
Solution: Periodic Boundary Conditions!



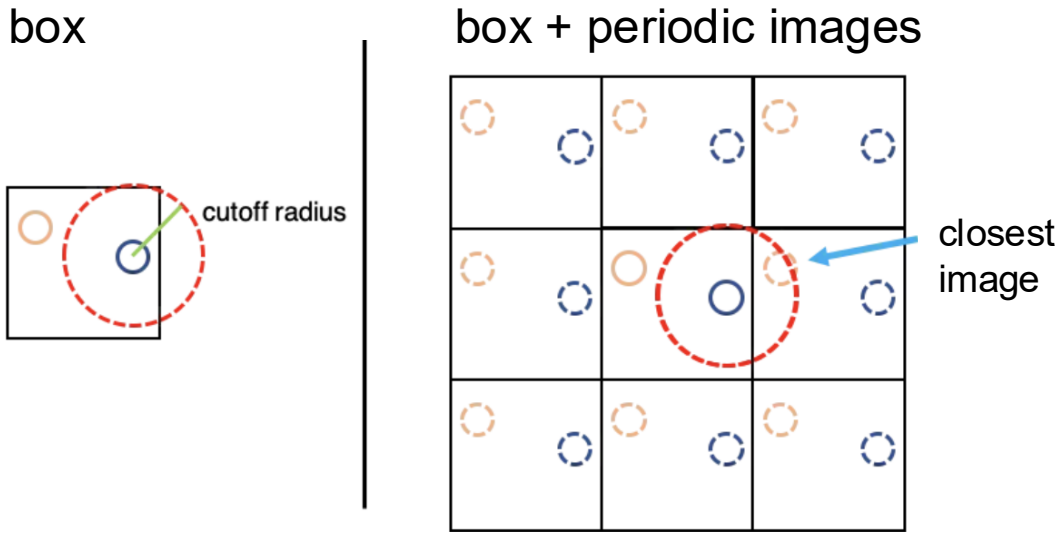
Allen, Michael P., and Dominic J. Tildesley. Computer simulation of liquids. Oxford university press, 2017.

- A way to deal with box edges without walls:
  - Tile space with ”infinite” repeats of the original box
  - If particle leaves on one side of the box, it re-appears on the opposite side with the same velocity

Alternative view:



Minimum Image Convention



Notes:

- Watch out for how the box is defined: $(0, L)$ vs. $(-L/2, L/2)$
- Box needs to be large enough that particles don't interact with themselves
- It is useful to keep track of PBC crossings with so called `images` (arrays of integers)

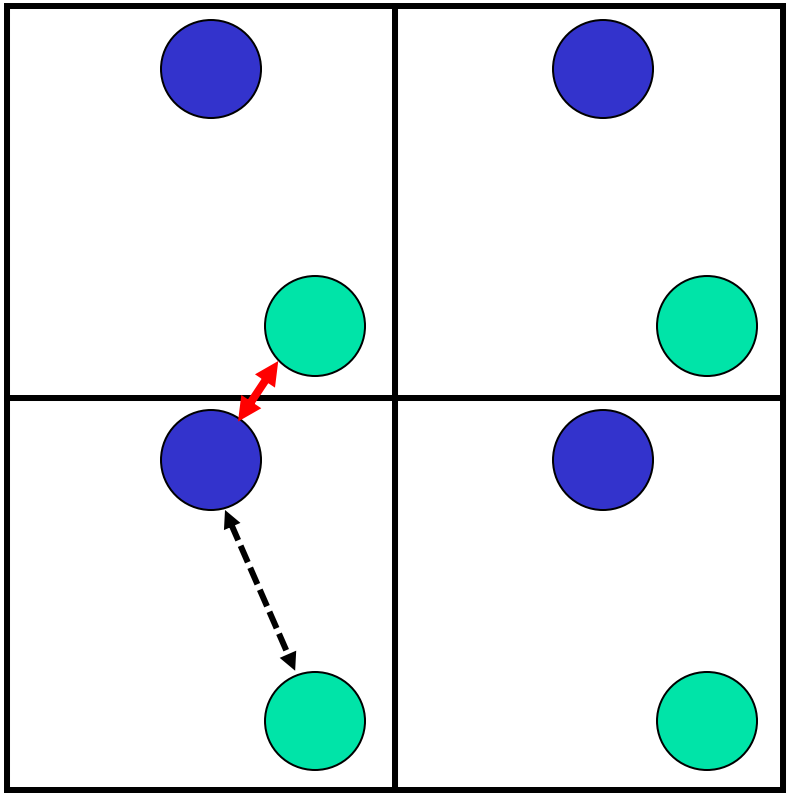
```
if (periodic_x) then
  if (x <  -x_size * 0.5) x = x + x_size
  if (x >=  x_size * 0.5) x = x - x_size
end if
```

or

```
x(i) = x(i) - floor(x(i) / x_size) * x_size
```

Exercise

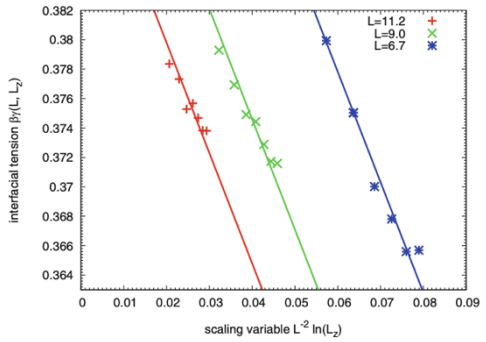
- **Objective:**
  - Learn how to apply the minimum image convention to compute distances



Finite Size Effects

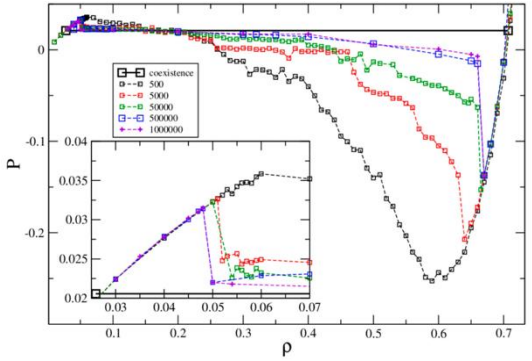
Did we fix everything? **No.**

Interfacial tensions:



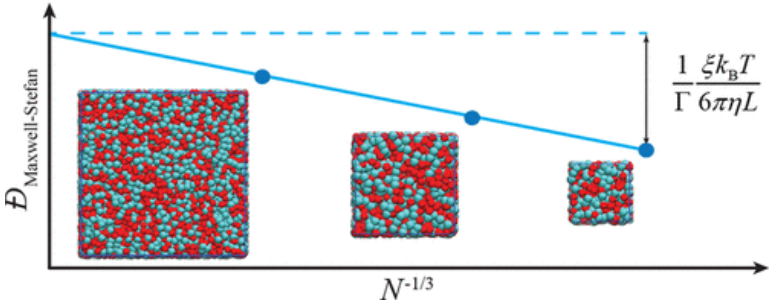
Schmitz, et al. "Investigation of Finite-Size Effects in the Determination of Interfacial Tensions." HPCSE, 2014, 5-18.

Critical Points, transitions, coexistence:



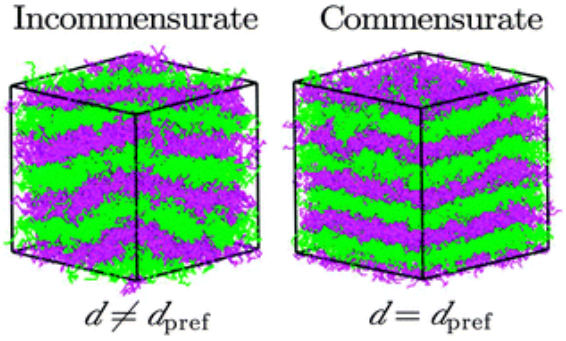
Díaz-Herrera, et al. "Finite size effect on the existence of the liquid–vapour spinodal curve." Molecular Physics 120.4 (2022): e1989071.

Diffusion coefficients:



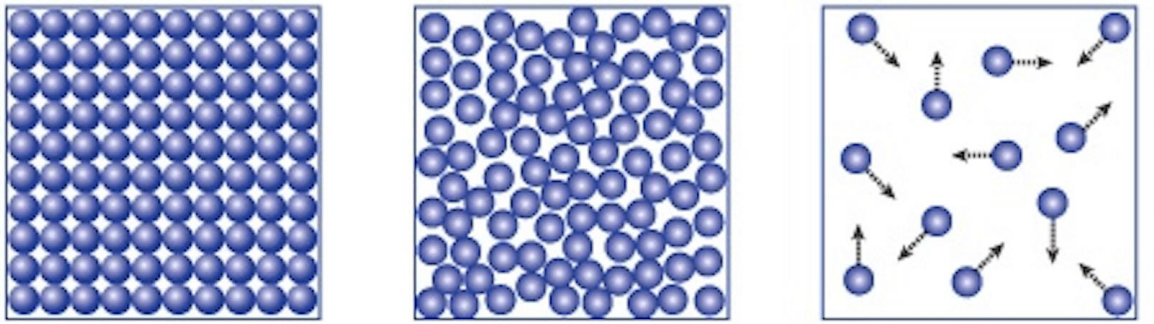
Finite-Size Effects of Binary Mutual Diffusion Coefficients from Molecular Dynamics, S. Jamali et al. JCTC 2018 14 (5), 2667-2677, DOI: 10.1021/acs.jctc.8b00170

Lattice/size mismatches:



Arora et al. "Commensurability and finite size effects in lattice simulations of diblock copolymers." Soft Matter 11.24 (2015): 4862-4867.

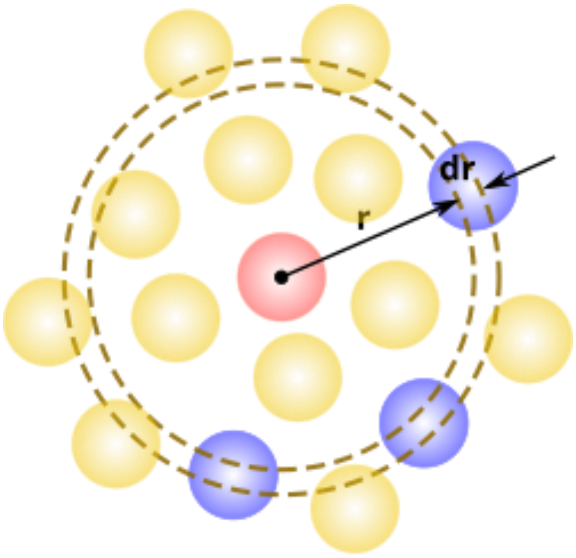
Structure of Simple Models



How to assess local structure and density?

Radial Distribution Function

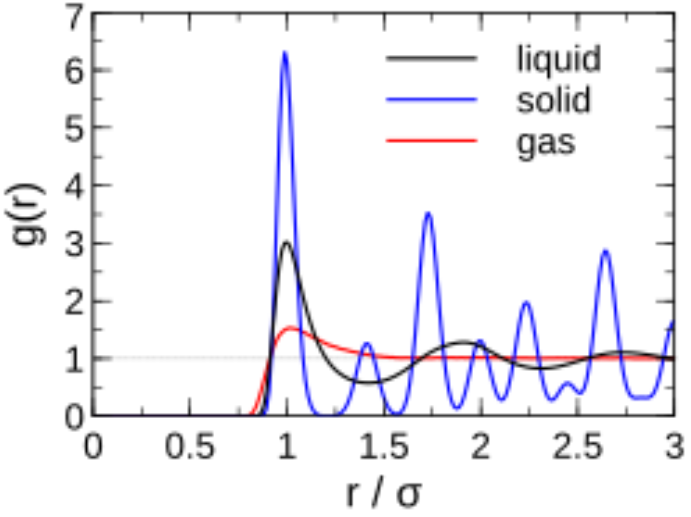
Pair correlation function:



Probability of finding a particle at given distance from another particle:

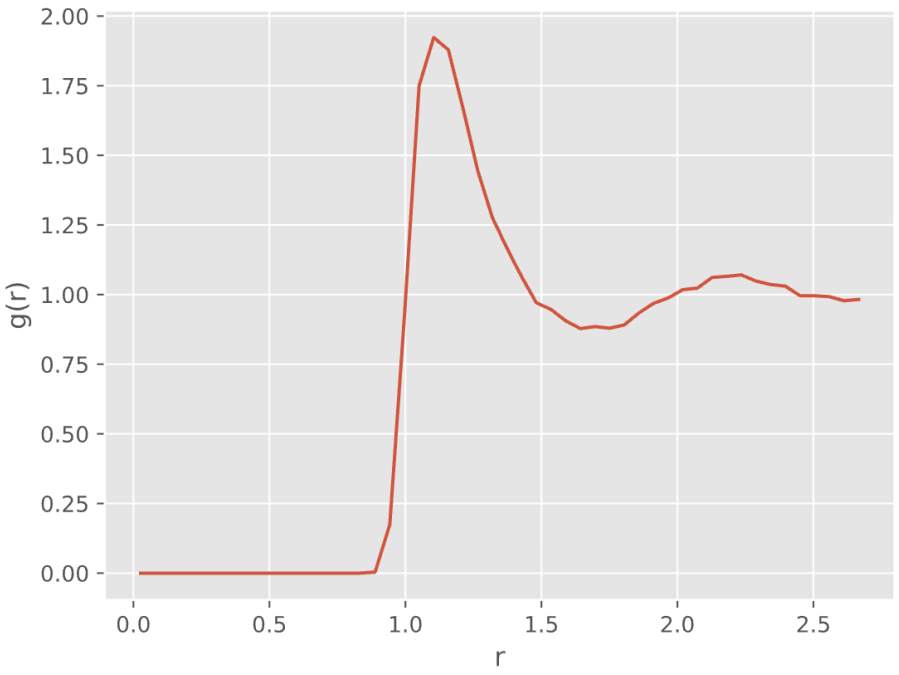
- short distances: nearest neighbors, how particles are packed together
- Intermediate distances: layers around particles, next-nearest neighbors
- large distances: probability of finding two spheres with a given separation is essentially constant – related to overall density (normalize by density)

$$g(r) = \frac{1}{N^2} \sum_i \sum_j \langle \delta(|\vec{r}_i - \vec{r}_j| - r) \rangle$$



Exercise

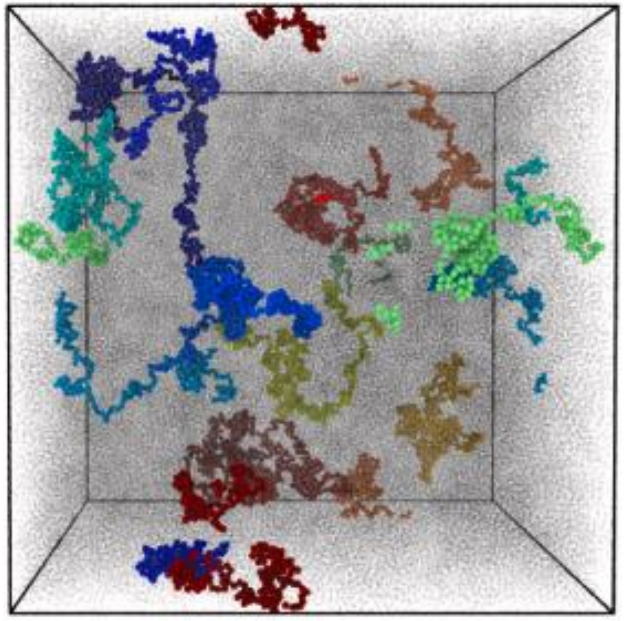
- **Objectives:**
  - Calculate the radial distribution function
  - Learn how to use freud to calculate g(r)



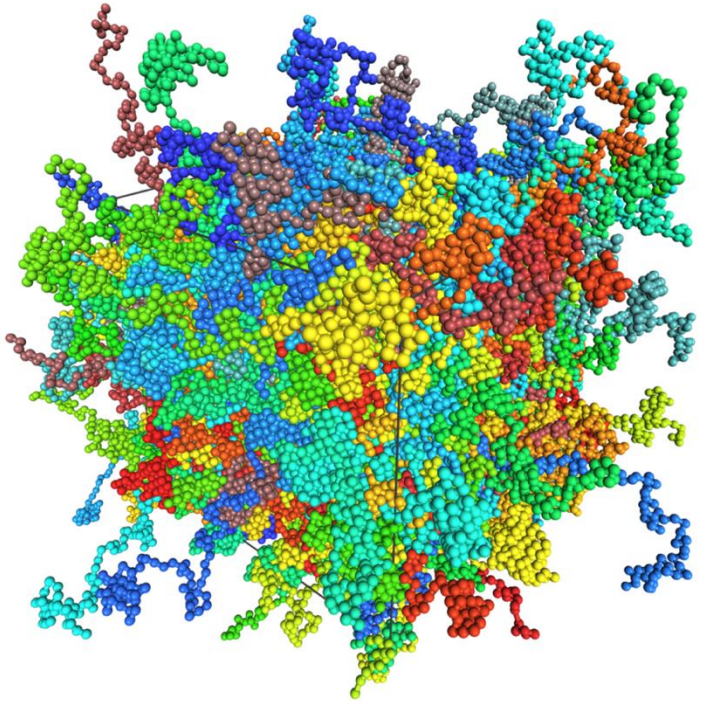
Radial Distribution Function

- Fourier transform of the the structure factor $S(k)$
- Relates bulk density to local density: $\rho(r) = \rho_{bulk} \cdot g(r)$
- Coordination number: $n(r') = 4\pi\rho \int_0^{r'} g(r) r^2 dr$
- Compressibility: $\rho KT \chi_T = 1 + \rho \int_V d\vec{r}\,[g(r) - 1]$
- Potential of mean force: $g(r) = \exp\left[-\frac{w^{(2)}(r)}{kT}\right]$
- …

What about Polymers?



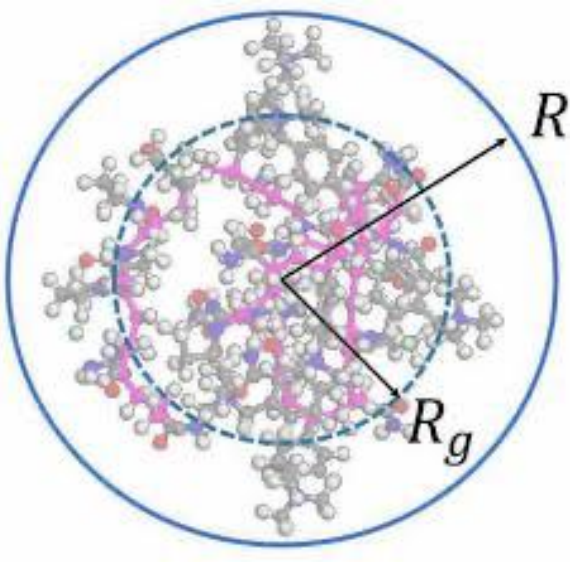
Polymer solutions



Polymer melts

Radius of Gyration of a Polymer

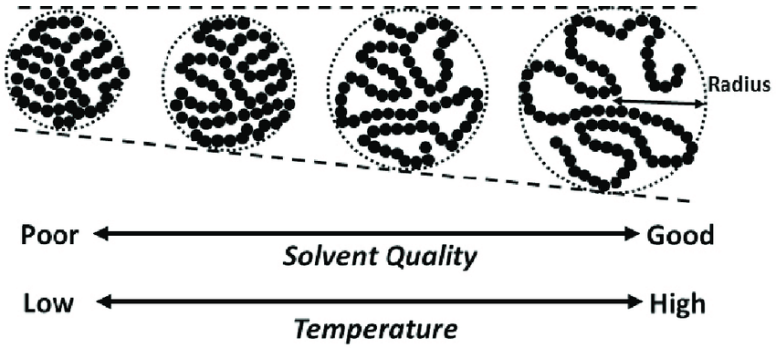
- There are many different sizes one can consider for polymers:
  - End-to-end distance R_{ee}
  - Hydrodynamic radius R_h
  - Radius of gyration R_g
- $R_g^2 = \frac{1}{N}\left\langle \sum_{k=1}^{N} |\vec{r}_k - \vec{r}_{com}|^2 \right\rangle$
- Theory:
  - $< R_{ee}^2 > = Nb^2$ (theta solvent)



N = degree of polymerization

$\vec{r}_k$ = position of monomer k

com = center of mass



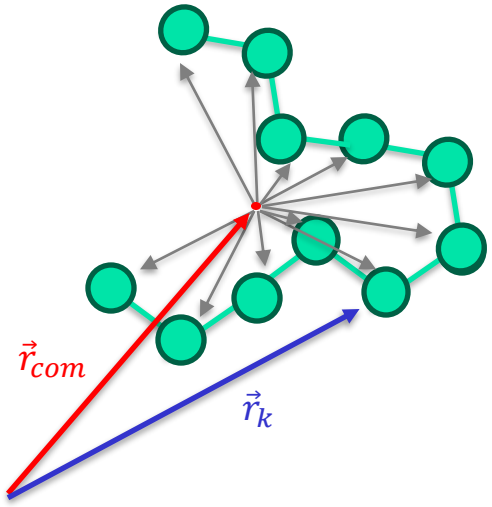
Rubinstein & Colby, Polymer Physics

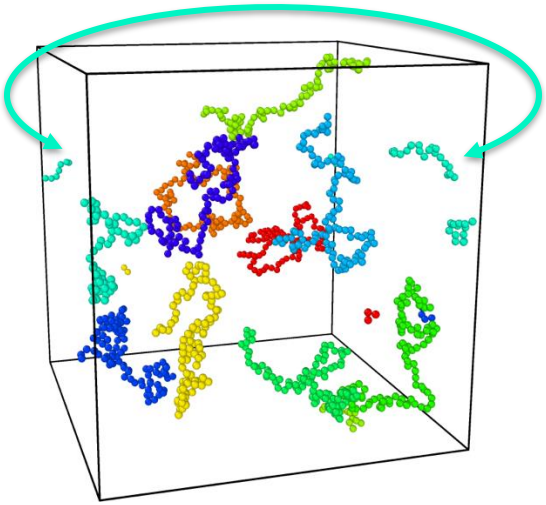
Why R_g?

- Not all polymers have ends (for R_{ee})
- Easy to define, measure, compare
- Structural quantity
- Tells us about how the mass (or monomers) is distributed in an object (polymer)
- Known theoretical relationships (theta solvent):
  - $< R_g^2 > = \frac{<R_{ee}^2>}{6}$
  - $R_h = C\, R_g$
  - ….
- Polymer (solution) behavior depends on its size and concentration. Think about overlap concentration instead of monomer density.

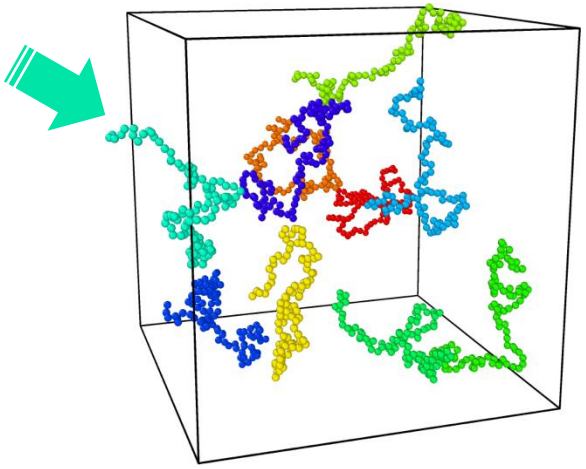
Rubinstein & Colby, Polymer Physics

Center of Mass of a Polymer





unwrap

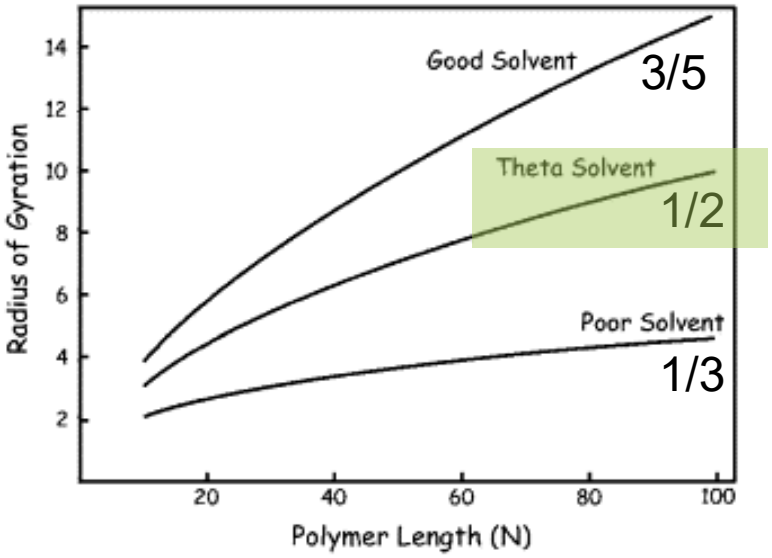


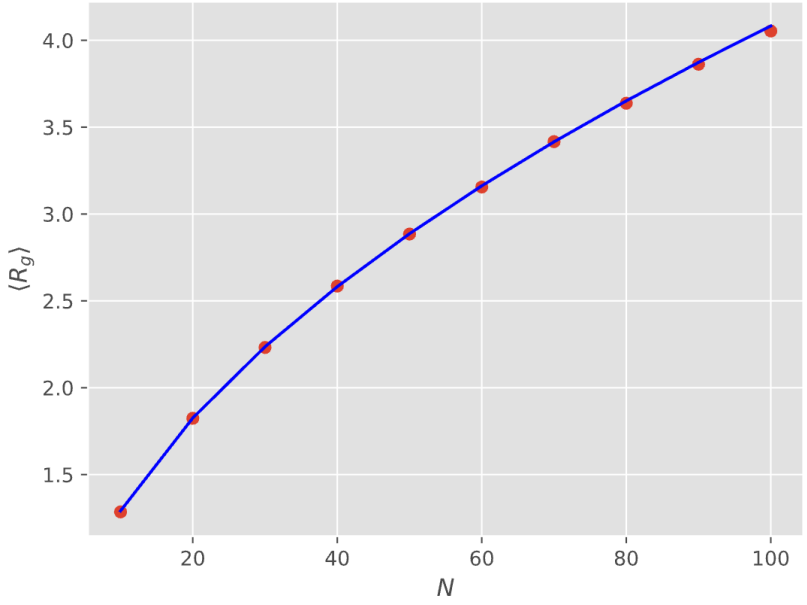
Center of mass (assuming all monomers have mass 1):

$$R_{com} = \frac{1}{N}\sum_k \vec{r}_k$$

Exercise

- **Objectives:**
  - Learn how to unwrap positions
  - Calculate the center of mass of a polymer
  - Calculate the radius of gyration of a polymer (as function of chain length *N*)





Common Pitfalls

- Ignoring finite size effects, using systems that are “too small”
- Forgetting about PBCs (clustering, order parameters, neighbors, …)
- Forgetting to write out images
- $\langle R_g \rangle^2$ $vs.$ $\langle R_g^2 \rangle$ etc.
- Not comparing against theory or scaling predictions