Molecular Dynamics

Analysis of MD trajectory (Part 2)

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Heat-Capacity

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

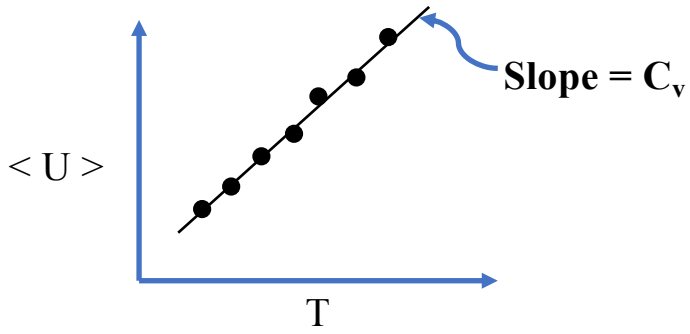
C_v = Heat Capacity at constant volume

U = Internal Energy = (Kinetic Energy + Potential Energy)

T = Temperature

Method I

Simulations
(N, V, T_1)
(N, V, T_2)
(N, V, T_3)
……
(N, V, T_7)



Method II

Single simulation at (N, V, T)

$$C_V = \frac{<(U - <U>)>^2}{K_B T^2}$$

More accurate
Less round of error than,
$< U^2 > - < U >^2$

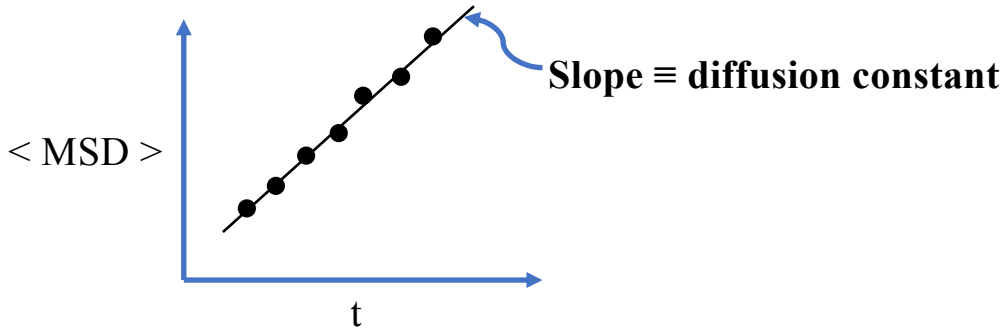
Diffusion coefficient (D)

Step A: Calculate the mean square displacement out of a single trajectory

$$< MSD > = < \frac{1}{N} \sum_{i=1}^{N} (\mathrm{r_i(t)} - \mathrm{r_i}(t = 0)^2 >$$

Step B: Apply Einstein Equation: $3\,\mathbf{D} = \lim_{t \to \infty} \frac{< MSD >}{2\,t}$

Dimension
1, 2, 3 etc



Diffusion coefficient (D)

"D" describes how quickly one material can diffuse through another material.

- Increasing temperature increases the diffusion coefficient.
- Viscosity decreases diffusion coefficient
- **depends on size and shape of molecule**

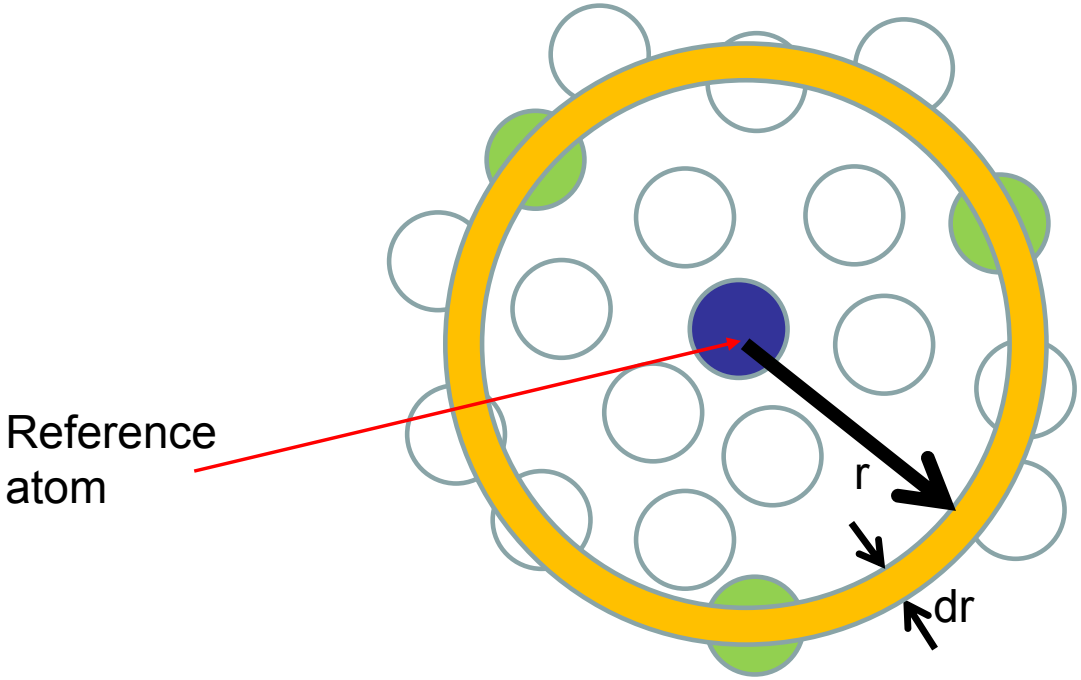
Radial Distribution Function

Many slides taken from:

https://ocw.mit.edu/courses/materials-science-and-engineering/3-021j-introduction-to-modeling-and-simulation-spring-2012/part-i-lectures-readings/MIT3_021JS12_P1_L4.pdf

Formal approach: Radial distribution function (RDF)

Ratio of density of atoms at distance r (in control area dr) by overall density = relative density of atoms as function of radius



$$g(r) = \rho(r) / \rho$$

Formal approach: Radial distribution function (RDF)

The radial distribution function is defined as

$$g(r) = \rho(r) / \overline{\rho}$$

$\overline{\rho}$: Overall density of atoms (volume)

$\rho(r)$: Local density

Provides information about the density of atoms at a given radius r; $\rho(r)$ is the local density of atoms

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Discrete:

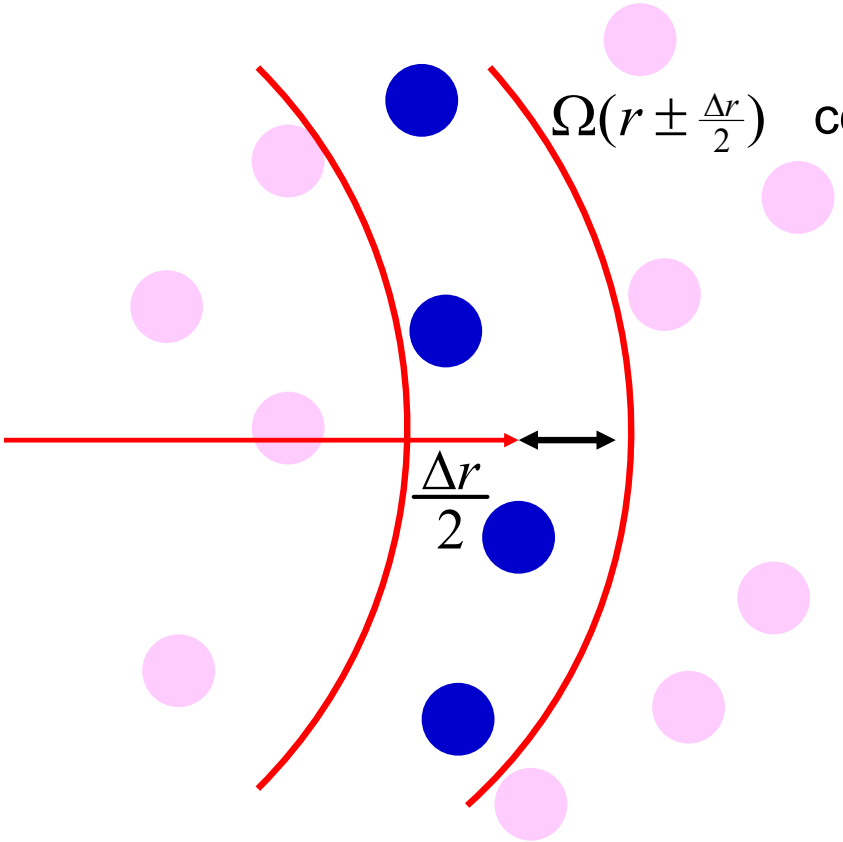
$$g(r) = \frac{< N(r \pm \frac{\Delta r}{2}) >}{\Omega(r \pm \frac{\Delta r}{2})} \frac{1}{\rho}$$

$< N(r \pm \frac{\Delta r}{2}) >$: Number of atoms in the interval $r \pm \frac{\Delta r}{2}$

$\Omega(r \pm \frac{\Delta r}{2})$: Volume of this shell ($dr$)

$g(r)2\pi r^2 dr =$ Number of particles that lie in a spherical shell of radius r and thickness dr

Radial distribution function



considered volume

$$g(r) = \frac{N(r \pm \frac{\Delta r}{2})}{\Omega(r \pm \frac{\Delta r}{2})\rho}$$

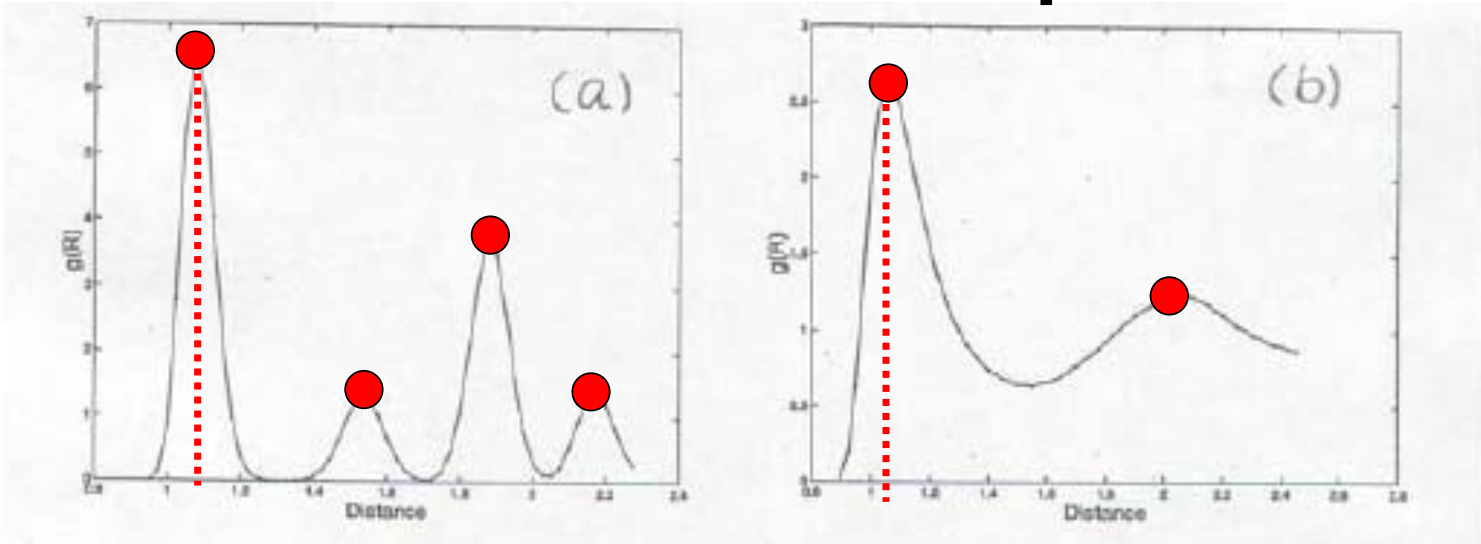
Density

$$\rho = N / V$$

Note: RDF can be measured experimentally using x-ray or neutron-scattering techniques

Radial distribution function:

Which one is solid / liquid?



Interpretation: A peak indicates a particularly favored separation distance for the neighbors to a given particle
Thus, RDF reveals details about the atomic structure of the system being simulated

Java applet:
http://physchem.ox.ac.uk/~rkt/lectures/liqsolns/liquids.html

Radial distribution function: Solid versus liquid versus gas

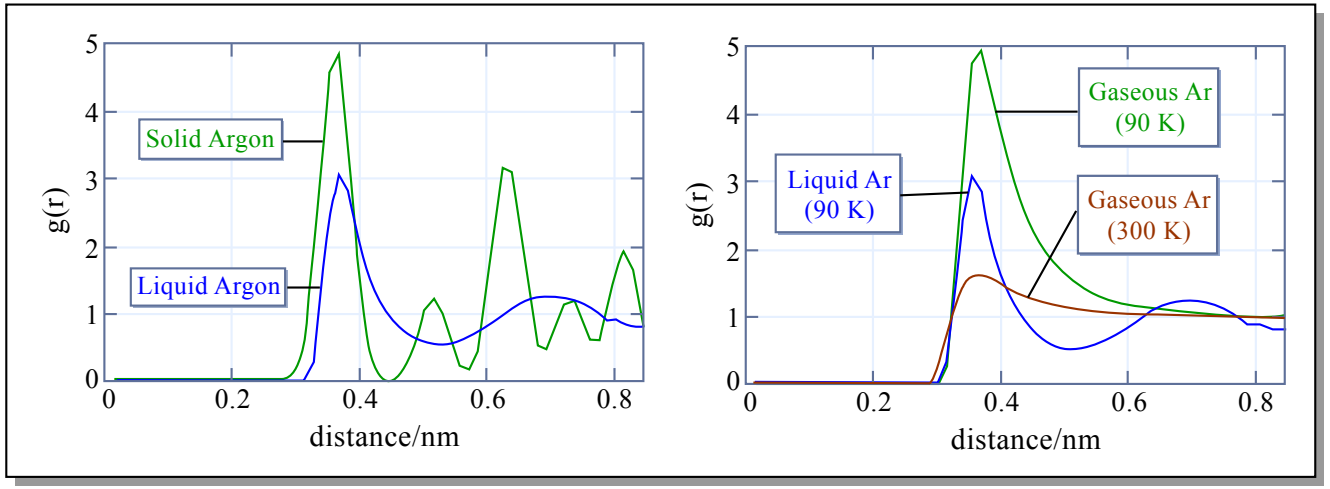


Image by MIT OpenCourseWare.

Note: The first peak corresponds to the nearest neighbor shell, the second peak to the second nearest neighbor shell, etc.

Notes: Radial distribution function (RDF)

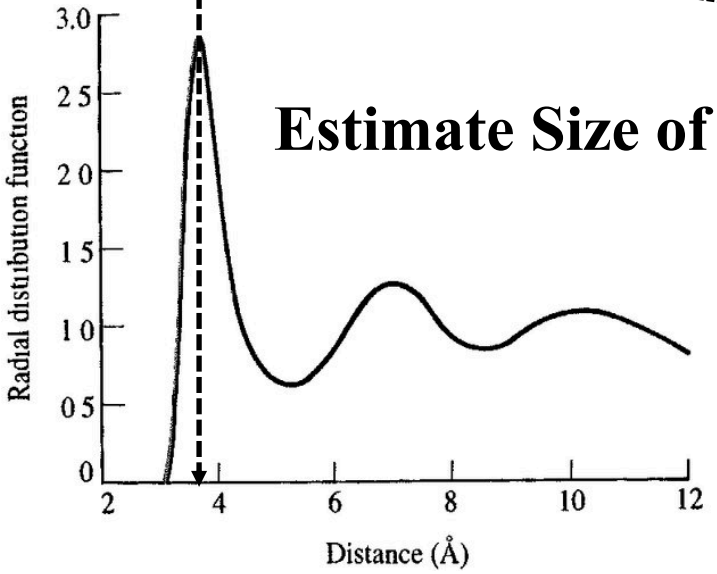
- Pair correlation function (consider only pairs of atoms)
- Provides structural information
- Can provide information about dynamical change of structure, but not about transport properties (how fast atoms move)

Additional comments:

- Describes how - on average - atoms in a system are radially packed around each other
- Particularly effective way of describing the structure of disordered molecular systems (liquids)
- In liquids there is continual movement of the atoms and a single snapshot of the system shows only the instantaneous disorder it is extremely useful to be able to deal with the average structure

Radial Distribution Function

Argon Liquid



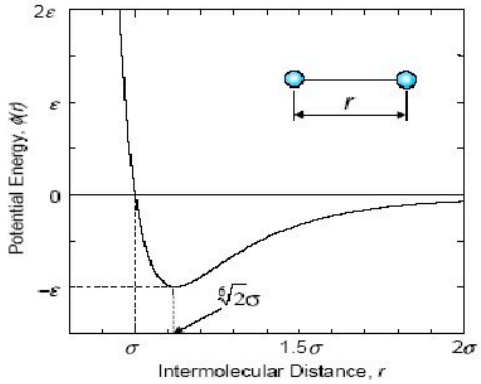
Estimate Size of Argon ?

https://www.researchgate.net/publication/228387451_Molecular_dynamics_of_triglycerides_atomistic_and_coarse-grained_approaches/figures?lo=1

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

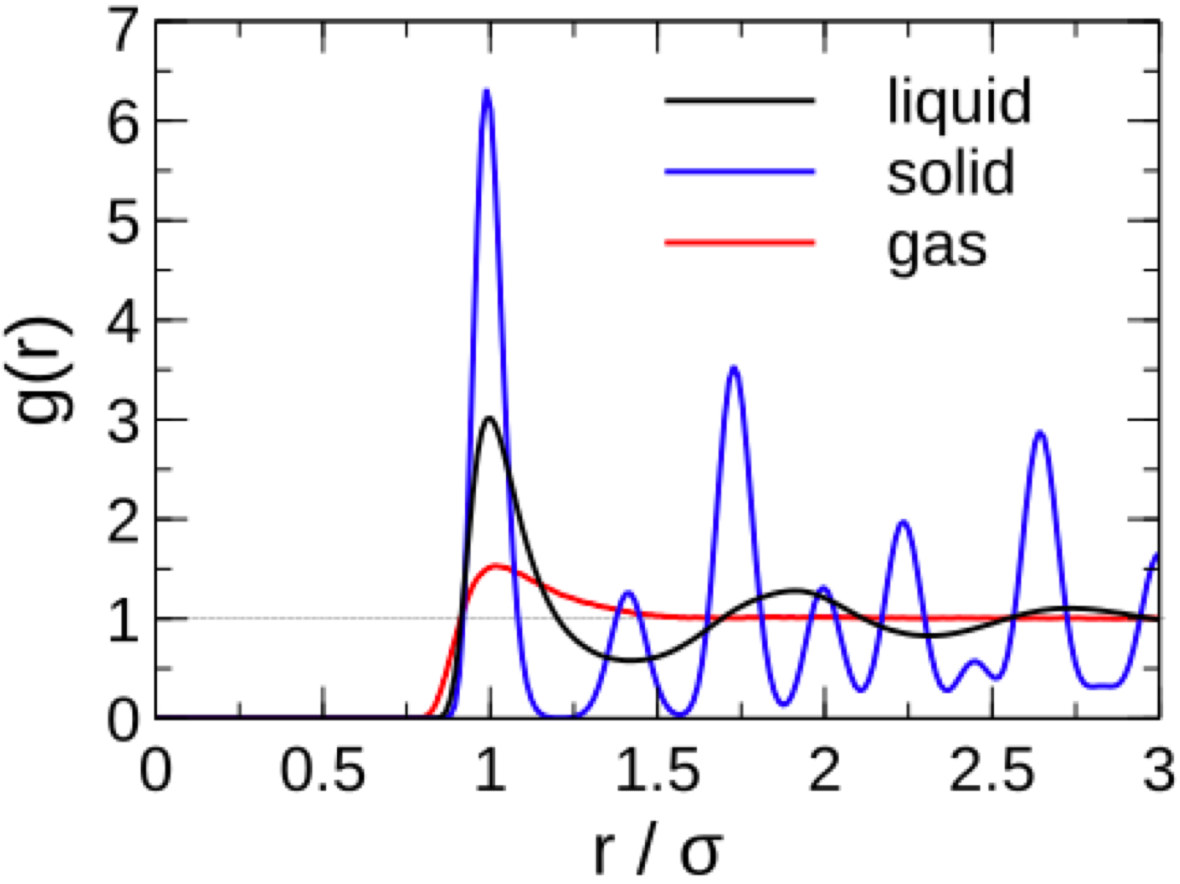
Lennard-Jones Potential: Noble Gas Atoms

	σ [nm]	ε [J]	ε/k_B [K]
Ne		0.50×10^{-21}	36.2
Ar	0.340	1.67×10^{-21}	121
Kr		2.25×10^{-21}	163
Xe	0.398	3.20×10^{-21}	232



https://slidetodoc.com/crystal-binding-bonding-part-vi-more-on-van/

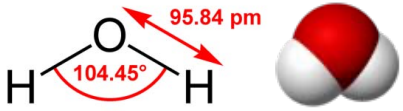
The radial distribution functions of argon
solid (T = 50 K), liquid (T = 80 K), and gas (T = 300 K).

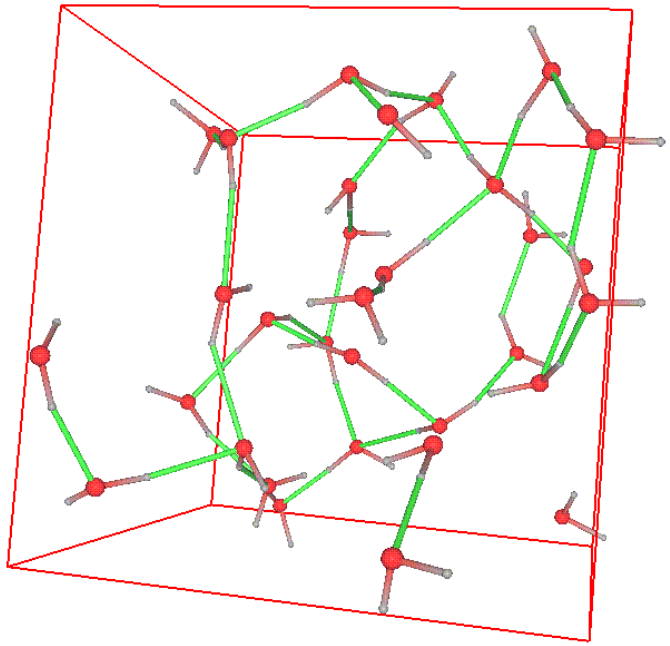


https://en.wikibooks.org/wiki/Molecular_Simulation/Radial_Distribution_Functions

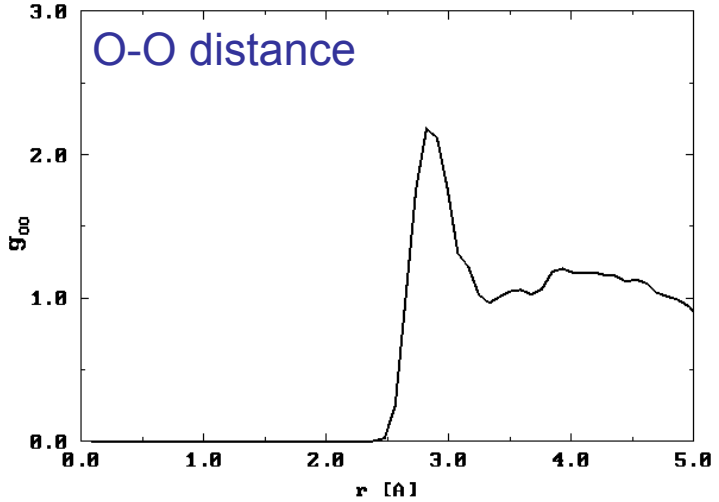
- Sharp peaks at regular interval indicate order

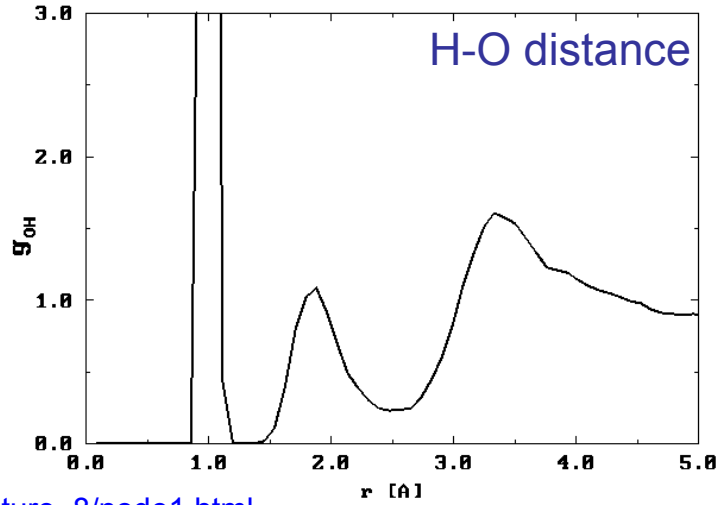
RDF of water (H_2O)





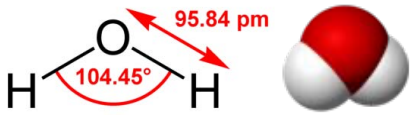
Images courtesy of Mark Tuckerman. Used with permission.

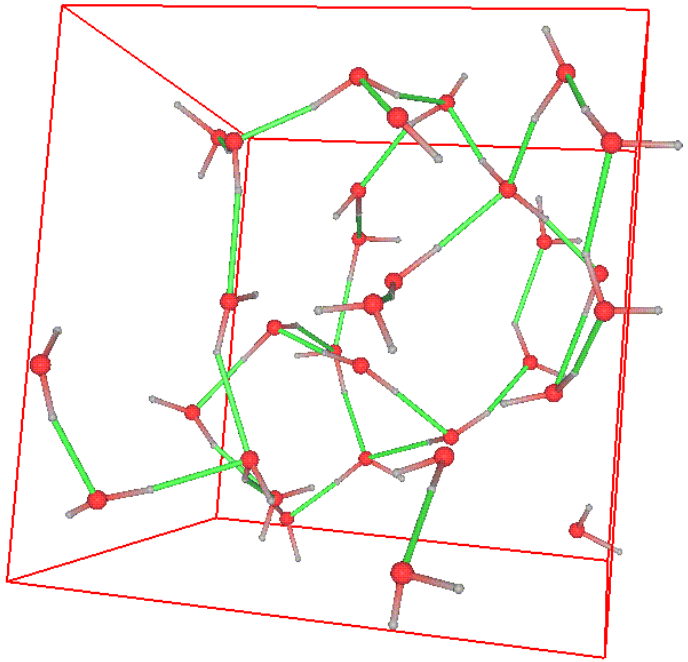




http://www.nyu.edu/classes/tuckerman/stat.mech/lectures/lecture_8/node1.html

RDF of water (H_2O)





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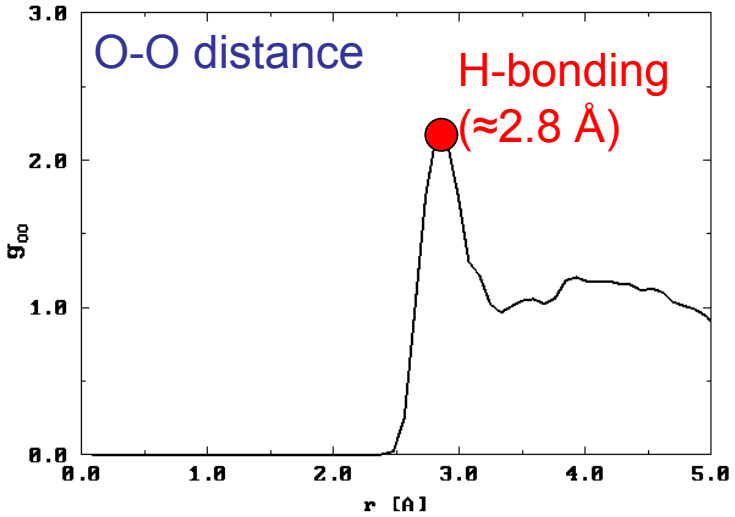

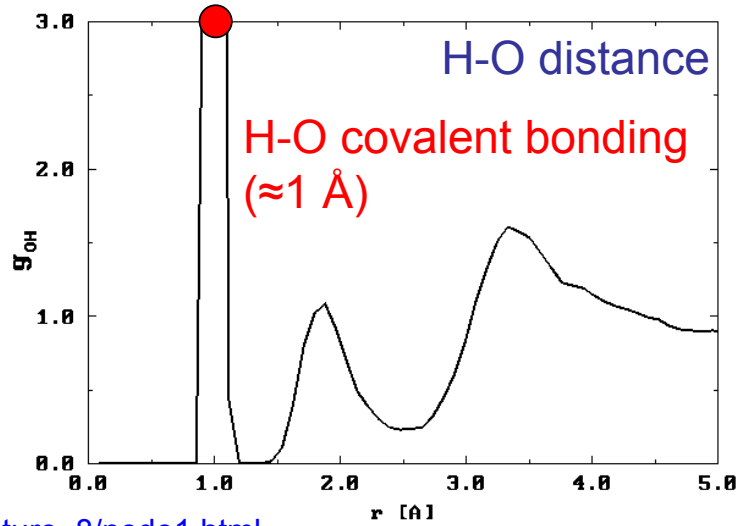

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Radial Distribution Function, g (r)

Fourier Transform

Structure factor, S(r)

Scattering Experiment

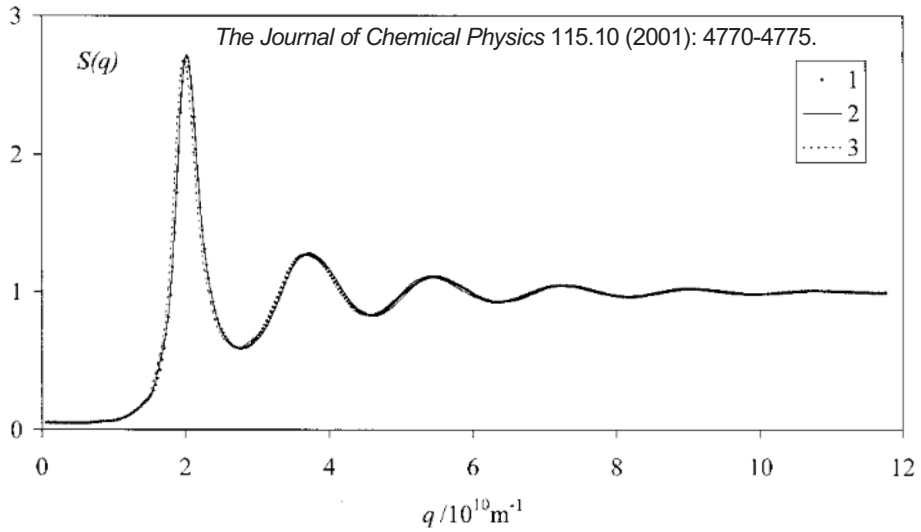

FIG. 4. Structure factor of liquid argon. (1) Experiment, (2) simulation results with our final LJ parameter set, (3) simulation results with the usual LJ parameter set.

Image: https://leverageedu.com/blog/computational-biology/

Next : Connection between MD trajectory and Free Energy