

Lecture 16

CH-4114

Molecular Simulation

“Everything that living things do can be understood in terms of the jigglings and wigglings of atoms.”

- Richard P. Feynman

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More towards MD analysis:
Radial Distribution Function, Scattering
Function and Applications

How to assess “Structure”

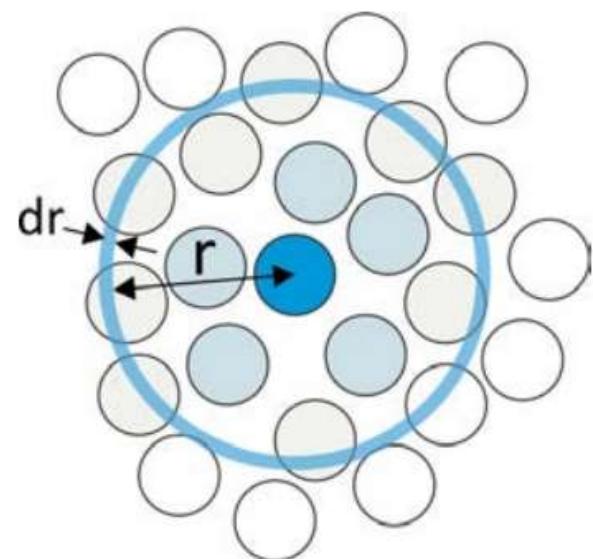
- "Structure" often implies that the positioning of particles is regular and predictable. In simple terms, structure in a fluid means the particles aren't totally random; their positions are somewhat organized over a very short distance. Imagine one particle as your starting point. You can somewhat predict where its immediate neighbors are packed. Because the fluid is constantly moving, we have to average the positions of all the particles to get this information- that statistical average of every snap is called an average correlation function. Over longer distances, this organization disappears, and the particles become totally random again, making the fluid look the same everywhere (homogeneous).
- Short-Range Structure: In a crowd, If you pick one person, you know there will be a few others tightly packed right around them (this is the short-range structure). You can somewhat predict their positions relative to your reference person. Statistical Average: Because everyone is moving, you have to take a photo every second and average all the positions to get a clear picture of this packing—that's the correlation function. Long-Range Disorder: If you try to predict the position of someone standing far away (past the correlation length), you can't; they could be anywhere. At that distance, the crowd just looks like a uniform (homogeneous) mass of people.
- The radial distribution function is most commonly used in gasses, liquids, and solutions, since it can be used to calculate various thermodynamic properties of the system. But is relevant at any size scale, such as packing of colloids, and is useful in complex heterogeneous media, such as the distribution of ions around polyelectrolyte molecules, to name a few.

- The radial distribution function $g(r)$ is the most useful measure of the "structure" of a fluid at molecular length scales. Although it invokes a continuum description, by "fluid" we mean any dense, disordered system which has local variation in the position of its constituent particles but is macroscopically isotropic.

$g(r)$ provides a statistical description of the local packing and particle density of the system, by describing the average distribution of particles around a central reference particle. We define the radial distribution function as:

$$g(r) = \frac{\langle \rho(r) \rangle}{\rho}$$

This is a ratio of the average local number density of particles $\langle \rho(r) \rangle$ at a distance r , to the bulk density of particles, ρ .



Let's look a little deeper, considering particles of the same type, as in an atomic liquid or granular material. If there are N particles in a volume V , and the position of the i th particle is \bar{r}_i , then the local number density is described by the position of particles:

$$\rho(\bar{r}) = \sum_{i=1}^N \delta(\bar{r} - \bar{r}_i) \rightarrow \text{This gives the spatial distribution of particles at position } \mathbf{r}.$$

For a homogeneous system, this is uniform:

$$\rho(\mathbf{r}) = \frac{N}{V} = \rho$$

The average of a radially varying property given by $X(r)$ is determined by

$$\langle X(r) \rangle = \frac{1}{V} \int_V X(r) 4\pi r^2 dr$$

Integrating $\rho(\bar{r})$ over a volume gives the particle number in that volume.

$$\int_V \rho(r) 4\pi r^2 dr = N$$

When the integral is over the entire volume, we can use this to obtain the average particle density:

$$\frac{1}{V} \int_0^\infty \rho(r) 4\pi r^2 dr = \frac{N}{V} = \rho$$

Next, we can consider the spatial correlations between two particles, i and j . The two-particle density correlation function is

$$\rho(\bar{r}, \bar{r}') = \left\langle \sum_{i=1}^N \delta(\bar{r} - \bar{r}_i) \sum_{j=1}^N \delta(\bar{r}' - \bar{r}_j) \right\rangle$$

This describes the conditional probability of finding particle i at position r_i and particle j at position r_j . We can expand and factor $\rho(\bar{r}, \bar{r}')$ into two terms depending on whether $i=j$ or $i \neq j$:

$$\begin{aligned}\rho(\bar{r}, \bar{r}') &= N \langle \delta(\bar{r} - \bar{r}_i) \delta(\bar{r} - \bar{r}_i) \rangle + N(N-1) \langle \delta(\bar{r} - \bar{r}_i) \delta(\bar{r}' - \bar{r}_j) \rangle \\ &= \rho^{(1)} + \rho^{(2)}(\bar{r}, \bar{r}')\end{aligned}$$

The first term describes the self-correlations, of which there are N terms: one for each atom.

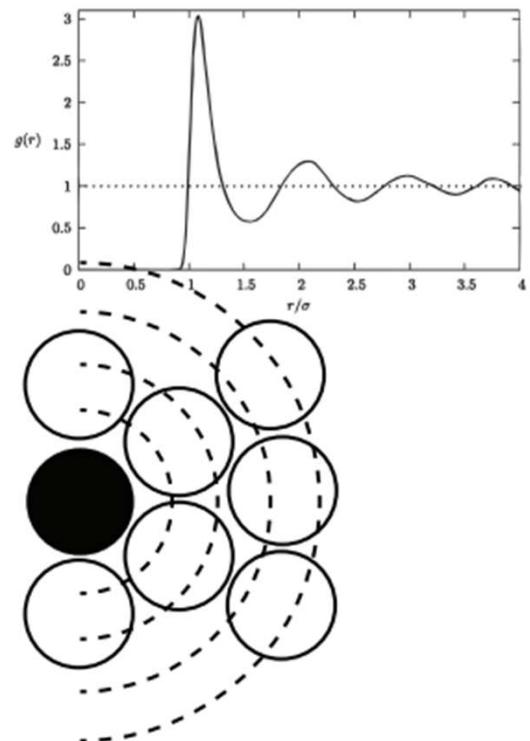
$$\rho^{(1)} = N \langle \delta(\bar{r} - \bar{r}_i) \delta(\bar{r}' - \bar{r}_i) \rangle = \rho$$

The second term describes the two-body correlations, of which there are $N(N-1)$ terms.

$$\begin{aligned}\rho^{(2)}(\bar{r}, \bar{r}') &= N(N-1) \langle \delta(\bar{r} - \bar{r}_i) \delta(\bar{r}' - \bar{r}_j) \rangle \\ &= \frac{N^2}{V^2} g(\bar{r}, \bar{r}') = \rho^2 g(\bar{r}, \bar{r}')\end{aligned}$$

$g() = \rho^{(2)}(\bar{r}, \bar{r}') / \rho^2$ is the two-particle distribution function, which describes spatial correlation between two atoms or molecules. For isotropic media, it depends only on distance between particles, $g(|\bar{r}, \bar{r}'|) = g(r)$, and is therefore also called the radial pair-distribution function.

- In a dense system, $g(r)$ starts at zero (since it does not count the reference particle), rises to a peak at the distance characterizing the first shell of particles surrounding the reference particle (i.e., the solvation shell), and approaches 1 for long distances in isotropic media. The probability of finding a particle at a distance (r) in a shell of thickness dr is $P(r) = 4\pi r^2 g(r) dr$.



Notes for normalization & counting from simulation data

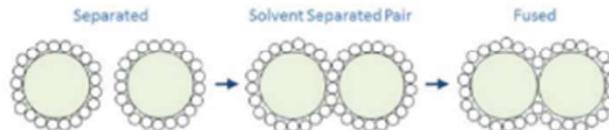
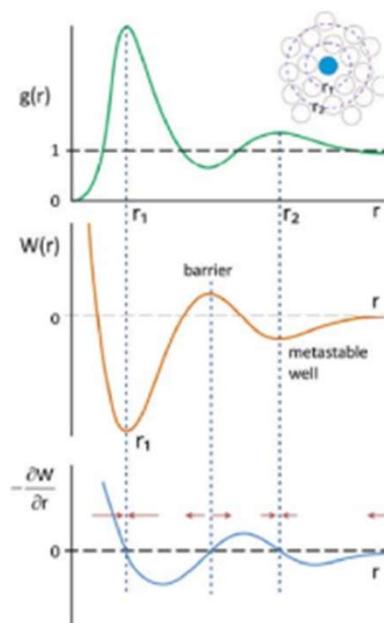
- For finite systems you may prefer the normalized histogram estimator used in MD/MC:

$$g_{AB}(r) = \frac{V}{N_A N_B 4\pi r^2 \Delta r} \langle n_{AB}(r, r + \Delta r) \rangle,$$

where n_{AB} is the number of A-B pairs with separations in $[r, r + \Delta r]$. For $A = B$ replace $N_A N_B$ by $N_A(N_A - 1)$ if counting ordered pairs is not intended.

or by $N_A \rho_A$ when they present sample-averaged histograms to be consistent with whether you count ordered or unordered pairs when computing "g" from simulation data.

Potential of Mean Force



One can use $g(r)$ to describe the free energy for bringing two particles together as

$$W(r) = -k_B T \ln g(r)$$

For detail you may look into:
Statistical Mechanics, D. A. McQuarrie,
University Science Books, California, USA.

$W(r)$ is known as the potential of mean force. We are taking a free energy which is a function of many internal variables and projecting it onto a single coordinate. $W(r)$ is a potential function that can be used to obtain the mean effective forces that a particle will experience at a given separation $f = -\partial W / \partial r$.

Compressibility

The isothermal compressibility κ_T is defined as:

$$\kappa_T \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_{T,N}$$

From thermodynamics it is known that κ_T can be linked to spontaneous fluctuations in the number of particles in an open volume V ,

$$\langle N \rangle \rho k_B T \kappa_T = \langle (N - \langle N \rangle)^2 \rangle = \langle N^2 \rangle - \langle N \rangle^2,$$

where the pointy brackets indicate a long time average or an average over many independent configurations commensurate with the thermodynamic conditions (in this case constant temperature T and volume V).

$$\int_V d^3r_1 \int_V d^3r_2 \rho^2 g(r_{12}) = \langle N(N-1) \rangle = \langle N^2 \rangle - \langle N \rangle.$$

We can use this to link the compressibility to the radial distribution function:

$$\begin{aligned}\langle N \rangle \rho k_B T \kappa_T &= \rho \int_V d^3r_1 \rho \int_V d^3r_2 g(r_{12}) + \langle N \rangle - \rho \int_V d^3r_1 \rho \int_V d^3r_2 \\ &= \rho \int_V d^3r_1 \rho \int_V d^3r_2 (g(r_{12}) - 1) + \langle N \rangle \\ &= \rho \int_V d^3r_1 \rho \int_{\mathbb{R}^3} d^3r (g(r) - 1) + \langle N \rangle\end{aligned}$$

Dividing by $\langle N \rangle$ we find

$$\boxed{\rho k_B T \kappa_T = 1 + \rho \int_{\mathbb{R}^3} d^3r (g(r) - 1)}.$$

This so-called compressibility equation shows that the compressibility of a fluid is intimately connected to the radial distribution function of its constituent molecules.

Density fluctuations in a fluid can be described by means of their Fourier components

$$\begin{aligned}\rho(\mathbf{r}) &= \rho + \frac{1}{(2\pi)^3} \int d^3k \hat{\rho}(\mathbf{k}) \exp \{-i\mathbf{k} \cdot \mathbf{r}\}, \\ \hat{\rho}(\mathbf{k}) &= \int d^3r \{\rho(\mathbf{r}) - \rho\} \exp \{i\mathbf{k} \cdot \mathbf{r}\}.\end{aligned}$$

The microscopic variable corresponding to a density Fourier component

$$\hat{\rho}(\mathbf{k}) = \int d^3r \left\{ \sum_{j=1}^N \delta(\mathbf{r} - \mathbf{r}_j) - \rho \right\} \exp \{i\mathbf{k} \cdot \mathbf{r}\},$$

where $\delta(\mathbf{r}) = \delta(x)\delta(y)\delta(z)$ is the three-dimensional Dirac delta-function.

$$\begin{aligned}\hat{\rho}(\mathbf{k}) &= \sum_{j=1}^N \exp \{i\mathbf{k} \cdot \mathbf{r}_j\} - \rho \int d^3r \exp \{i\mathbf{k} \cdot \mathbf{r}\} \\ &= \sum_{j=1}^N \exp \{i\mathbf{k} \cdot \mathbf{r}_j\} - (2\pi)^3 \rho \delta(\mathbf{k}).\end{aligned}$$

Density fluctuations in a fluid can be measured experimentally by means of scattering of light, neutrons, or X-rays (depending on the scale of interest),

. The scattered intensity also depends on details such as wave polarization and scattering strength or form factor, but generally scattering experiments measure correlation functions of Fourier components of the density. The correlation function of $\hat{\rho}(\mathbf{k})$ with its complex conjugate $\hat{\rho}^*(\mathbf{k}) = \hat{\rho}(-\mathbf{k})$, i.e. the mean square of the density fluctuation with wave vector \mathbf{k} , is a real function of the wavevector, called the *structure factor* $S(\mathbf{k})$:

$$S(\mathbf{k}) \equiv \frac{1}{N} \langle \hat{\rho}(\mathbf{k}) \hat{\rho}^*(\mathbf{k}) \rangle .$$

The division by N leads to a quantity which for large enough systems is independent of system size (that is to say, the mean square density fluctuations grow linearly with system size). The structure factor gives a lot of information about the structure of a fluid. It is essentially a Fourier transform of the radial distribution function, as can be shown as follows:

$$\begin{aligned} S(\mathbf{k}) &= \frac{1}{N} \left\langle \sum_{j=1}^N \sum_{k=1}^N \exp \{i\mathbf{k} \cdot (\mathbf{r}_j - \mathbf{r}_k)\} \right\rangle - \frac{\rho^2}{N} \int d^3r \int d^3r' \exp \{i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')\} \\ &= 1 + \frac{1}{N} \left\langle \sum_{j=1}^N \sum_{k \neq j}^N \exp \{i\mathbf{k} \cdot (\mathbf{r}_j - \mathbf{r}_k)\} \right\rangle - \rho \int d^3r \exp \{i\mathbf{k} \cdot \mathbf{r}\} \\ &= 1 + \rho \int d^3r [g(r) - 1] \exp \{i\mathbf{k} \cdot \mathbf{r}\}. \end{aligned}$$

Comparison with Eq. (1.17) shows, perhaps surprisingly, that the compressibility of a fluid can be obtained not only by compressing the fluid and measuring the pressure, but also by performing a scattering experiment:

$$\rho k_B T \kappa_T = \lim_{k \rightarrow 0} S(k).$$