Radial Distribution Function Algorithm

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1 Acknowledgements

The following numerical formulation was adapted from Professor M. Scott Shell's Notes from the course, *CHE210D: Principles of modern molecular simulation methods, F19*, at the University of California Santa Barbara. The link to the course site is provided here: https://sites.engineering.ucsb.edu/ shell/che210d/index.html.

2 Numerical Formulation

The radial distribution function (RDF) can be interpreted as the probability of finding an atom in a spherical shell at a distance $|\Delta R_{ij}|$ away relative to the probability of finding a particle in the same shell at the bulk density, ρ. Mathematically, this statement can be written as:

$$g(\Delta R_{ij}) = \frac{< \rho(\Delta R_{ij}) >}{\rho} \tag{1}$$

We can formalize the definition more clearly in order to develop a practical method to compute $g(R)$. First, the expectation value in Equation (1) is with respect to the frames in the trajectory and the number of pair separations. Additionally, if we wish to compute $< \rho(\Delta R_{ij}) >$ systematically, then we can do this by computing the volume a single particle occupies in a spherical shell relative to the volume a single particle occupies in the bulk density. Equation (1) simplifies to:

$$g(\Delta R_{ij}) = \frac{< \rho(\Delta R_{ij}) >}{\rho} = \frac{< N_{shell}/V_{shell} >}{N_{bulk}/V_{bulk}} = N_{shell} < \frac{1}{V_{shell}} > \frac{1}{\rho} =< \frac{1}{V_{shell}} > \frac{1}{\rho} \tag{2}$$

The RHS of Equation (2) allows us to practically compute the RDF by histograming the pair separations. The Equation can then be simplified further as:

$$g(\Delta R_{ij}) =< \frac{1}{V_{shell}} > \frac{1}{\rho} = P(1/V_{shell})\frac{1}{\rho V_{shell}} \tag{3}$$

If we designate the bin width for our histogram of pair separations, ΔR_{ij}, as β we can cast Equation (3) in a numerical form:

$$V_{shell} = \frac{4}{3}\pi((i+1)^3(\beta)^3 - (i\beta)^3) \tag{4}$$

$$V_{shell} = \frac{4}{3}\pi\beta^3((i+1)^3 - i^3) \tag{5}$$

where $i\beta$ corresponds to the ith bin's pair separation value($\Delta R_{ij} = i\beta$). Plugging the above equation for V_{shell} into Equation (3) yields the following simplified expression for $g(\Delta R_{ij})$:

$$g(i\beta) = P(1/V_{shell})\frac{\rho^-1}{\frac{4}{3}\pi\beta^3((i+1)^3 - i^3)} \tag{6}$$

Since the volume of the shell is a function of the pair separation values,$V_{shell} \equiv f(\Delta R_{ij}) = f(i\beta)$, then we can make the assumption that:

$$P(1/V_{shell}) \propto P(\Delta R_{ij}) = P(i\beta) \tag{7}$$

Furthermore, if we denote the number of points in the histogram for the pair separation $i\beta$ as H_i then the probability can be written as:

$$P(i\beta) = \frac{H_i}{\sum_i H_i} \tag{8}$$

Plugging Equation (8) into Equation (6) yields:

$$g(i\beta) = \frac{H_i}{\sum_i H_i}\frac{\rho^-1}{\frac{4}{3}\pi\beta^3((i+1)^3 - i^3)} \tag{9}$$

It turns out that the normalization constant, $\sum_i H_i$, can be written as a product of the number of particles, N, with the number of frames, n_f. If the pair separation, ΔR_{ij}, is computed for every ij pair where $i \neq j$, then for a single frame there are $N(N-1)/2$ measurements. This corresponds to the upper triangle of the pair separation matrix.

$$\Delta R_{ij} = \begin{bmatrix} 0 & \Delta R_{12} & \Delta R_{13} & \dots & \Delta R_{1N} \\ \Delta R_{21} & 0 & \Delta R_{23} & \dots & \Delta R_{2N} \\ \Delta R_{31} & \Delta R_{32} & 0 & \dots & \Delta R_{3N} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \Delta R_{N1} & \Delta R_{N2} & \Delta R_{N3} & \dots & 0 \end{bmatrix} \tag{10}$$

If we carryout the binning of $N(N-1)/2$ for each frame, then $\sum_i H_i$ becomes:

$$\sum_i H_i = \frac{N(N-1)}{2} n_f \tag{11}$$

Substitution our expression for the normalization constant, Equation (11), into Equation 9 gives us the final form of the RDF at a given pair separation $i\beta$:

$$g(i\beta) = \frac{H_i}{\frac{N(N-1)}{2} n_f} \frac{\rho^- 1}{\frac{4}{3}\pi\beta^3((i+1)^3 - i^3)} \tag{12}$$

Equation (12) will be the Equation that is numerically evaluated to get an estimate for $g(\Delta R_{ij})$. This concludes the Numerical Formulation section.

3 Algorithm

(1) Create a nested matrix with 1 row and n_f columns with each element equal to a $N \times 3$ matrix where each column corresponds to the particles' position $< x, y, z >$.

(2) For each frame in this nested matrix, bin the pair separations, ΔR_{ij}, into their corresponding $i\beta$ bins using a floor function.

(3) Compute the bins' corresponding shell volume, $\frac{4}{3}\pi\beta^3((i+1)^3 - i^3)$, and compute the probability of the pair separation occurring $\frac{H_i}{\frac{N(N-1)}{2} n_f}$.

(4) Evaluate Equation (12) and plot the array of $g(i\beta)$ values against the pair separations $i\beta$ to get a RDF plot.