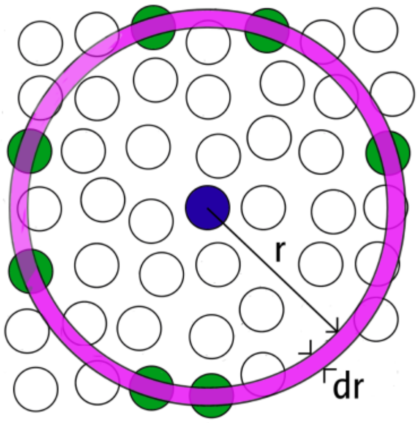

Figure 9.1: Visualization of the radial distribution function

Radial distribution function

The radial distribution function is defined as

$$g(r) = \frac{\rho(r)}{\rho} \, ,$$

where $\rho(r)$ is the particle number density at a distance r from an arbitrary atomic origin and $\rho = \frac{N}{V}$ is the number density of the unit cell. A visual representation of this quantity is shown in Figure Formally this can be found from atomic positions

$$g(r) = \frac{1}{N\rho} \left\langle \sum_{i}^{N} \sum_{i \neq j} \delta(r - r_{ij}) \right\rangle$$

where i and j are particle indices and r_{ij} is the distance between particle i and j. N is the total number of particles and the brackets denote an ensemble average. Due to the delta function, this expression is not particularly useful when analysing MD trajectories of discrete particle positions. To overcome this, we define $n(r, \mathrm{d}r)$ as a function that counts the number of particles at a distance r within a spherical shell of thickness $\mathrm{d}r$.

$$g(r) = \frac{2 \langle n(r, \mathrm{d}r) \rangle}{N \rho V_{\mathrm{s}}(r, \mathrm{d}r)} \, , \tag{9.1}$$

where $V_{\mathrm{s}}(r, \mathrm{d}r) \approx 4\pi r^2 \mathrm{d}r$ is the thickness of the spherical shell. Due to the ergodic hypothesis, the ensemble average is replaced with a time average, so that

$$\langle n(r, \mathrm{d}r) \rangle = \frac{1}{M} \sum_{k=1}^{M} n_k(r, \mathrm{d}r)$$

where M is the number of time steps. In practice n_k is evaluated by creating a list of all particle-particle distances in the frame k and generating a histogram with bin size $\mathrm{d}r$. The factor of two in equation (9.1) comes from the fact that n_k only counts each pair once.

The $g(r)$ we just defined treats all particle pairs on an equal footing. In order to compare simulations with neutron scattering data it is necessary to weigh distinct particle pairs by the product of their neutron cross sections. First, we define the partial radial distribution function $g_{\alpha\beta}(r)$ as the probability of finding a particle with label β at a distance r away from a particle with label α plus the probability of finding a particle with label α at a distance r away from a particle with label β.

$$\begin{aligned} g_{\alpha\beta}(r) &= \frac{\langle n_{\alpha\beta}(r, \mathrm{d}r) \rangle}{N_\alpha \rho_\beta V_{\mathrm{s}}(r, \mathrm{d}r)} + \frac{\langle n_{\alpha\beta}(r, \mathrm{d}r) \rangle}{N_\beta \rho_\alpha V_{\mathrm{s}}(r, \mathrm{d}r)} \\ &= \frac{2V}{N_\alpha N_\beta} \frac{\langle n_{\alpha\beta}(r, \mathrm{d}r) \rangle}{V_{\mathrm{s}}(r, \mathrm{d}r)} \, , \end{aligned}$$

where N_i is the number and ρ_i is the density of particle species i. The reason to define it in 'both directions' is that $n_{\alpha\beta}$ is symmetric to exchange of particles. From the partial pair distribution functions, $g(r)$ can be trivially computed and optionally weighted by neutron cross sections :

$$g(r) = \frac{1}{b_{\text{avg}}} \sum_{\alpha=1,\beta\geq\alpha} c_\alpha c_\beta \bar{b_\alpha} \bar{b_\beta} g_{\alpha\beta}(r)\,,$$

where $c_i = \frac{N_i}{N}$ is the number concentration and $\bar{b_i}$ is the coherent neutron cross section of species i and $b_{\text{avg}} = \langle \bar{b}_\alpha \bar{b}_\beta \rangle$.