

# **M6 Supervision 1**

Oli Bridge, *St Catharine's College*

# 1 Integrators

## 1.1 Momentum conservation without Noether

The total linear momentum of an  $N$ -particle system is given by

$$\mathbf{P} = \sum_{i=1}^N \mathbf{p}_i \quad (1)$$

where  $\mathbf{p}_i$  is the momentum of particle  $i$ . Taking the time derivative of Equation (1) gives

$$\begin{aligned} \frac{d\mathbf{P}}{dt} &= \frac{d}{dt} \left[ \sum_{i=1}^N \mathbf{p}_i \right] \\ &= \sum_{i=1}^N \frac{d\mathbf{p}_i}{dt} = \sum_{i=1}^N \dot{\mathbf{p}}_i \\ &= \sum_{i=1}^N m_i \ddot{\mathbf{r}}_i \\ &= - \sum_{i=1}^N \frac{\partial U(\mathbf{r}^N)}{\partial \mathbf{r}_i} \end{aligned} \quad (2)$$

where the fourth line uses Newton's second law,  $m_i \ddot{\mathbf{r}}_i = \mathbf{f}_i(\mathbf{r}^N)$ . The potential  $U(\mathbf{r}^N)$  for pairwise interactions is written as a sum over all pairs of particles:

$$U(\mathbf{r}^N) = \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i} u_{ij}(r_{ij}) \quad (3)$$

The derivative of  $U(\mathbf{r}^N)$  with respect to the  $i^{\text{th}}$  particle position  $\mathbf{r}_i$  is given by

$$\begin{aligned} \frac{\partial U(\mathbf{r}^N)}{\partial \mathbf{r}_i} &= \frac{1}{2} \sum_{j \neq i} \left( \frac{\partial u_{ij}(r_{ij})}{\partial \mathbf{r}_i} + \frac{\partial u_{ji}(r_{ji})}{\partial \mathbf{r}_i} \right) \\ &= \sum_{j \neq i} \frac{\partial u_{ij}(r_{ij})}{\partial \mathbf{r}_i} \\ &= \sum_{j \neq i} \mathbf{f}_{ij} \end{aligned} \quad (4)$$

where the second line uses the fact that  $r_{ij} = r_{ji}$ . The pairwise force  $\mathbf{f}_{ij}$  satisfies Newton's third law,  $\mathbf{f}_{ij} = -\mathbf{f}_{ji}$ . Thus, the time derivative for the total momentum is

$$\begin{aligned}\frac{d\mathbf{P}}{dt} &= \sum_{i=1}^N \sum_{j \neq i} \mathbf{f}_{ij} \\ &= 0\end{aligned}\tag{5}$$

which sums to zero due to cancellations from the pairwise additive forces. This shows that the total momentum is conserved, given that there are no external forces.

## 1.2 Leap-Frog algorithm

In the Leap-Frog algorithm, the velocities are given by

$$\mathbf{v}_i(t + \delta t/2) = \frac{\mathbf{r}_i(t + \delta t) - \mathbf{r}_i(t)}{\delta t}\tag{6}$$

$$\mathbf{v}_i(t - \delta t/2) = \frac{\mathbf{r}_i(t) - \mathbf{r}_i(t - \delta t)}{\delta t}\tag{7}$$

and the integration step is given by

$$\mathbf{v}_i(t + \delta t/2) = \mathbf{v}_i(t - \delta t/2) + \frac{\delta t}{m_i} \mathbf{f}_i(t)\tag{8}$$

$$\mathbf{r}_i(t + \delta t) = \mathbf{r}_i(t) + \delta t \mathbf{v}_i(t + \delta t/2)\tag{9}$$

Substituting (8) into (9) gives

$$\begin{aligned}\mathbf{r}_i(t + \delta t) &= \mathbf{r}_i + \delta t \left[ \mathbf{v}_i(t - \delta t/2) + \frac{\delta t}{m_i} \mathbf{f}_i(t) \right] \\ &= \mathbf{r}_i + \delta t \left[ \frac{\mathbf{r}_i(t) - \mathbf{r}_i(t - \delta t)}{\delta t} + \frac{\delta t}{m_i} \mathbf{f}_i(t) \right] \\ &= 2\mathbf{r}_i(t) - \mathbf{r}_i(t - \delta t) + \frac{\delta t^2}{m_i} \mathbf{f}_i(t)\end{aligned}\tag{10}$$

which is exactly equivalent to the verlet algorithm:

$$\mathbf{r}_i(t + \delta t) = 2\mathbf{r}_i(t) - \mathbf{r}_i(t - \delta t) + \frac{\delta t^2}{m_i} \mathbf{f}_i(t)\tag{11}$$

### 1.3 Harmonic motion

The autocorrelation function for  $A(t)$  is given by

$$C_{AA}(\tau) = \frac{1}{\Delta t - \tau} \int_0^{\Delta t - \tau} dt A(t + \tau) A(t) \quad (12)$$

For  $A(t) = \cos \omega t$  and  $\Delta t \gg 2\pi/\omega$ , the autocorrelation function is evaluated as

$$\begin{aligned} C_{AA}(\tau) &= \frac{1}{\Delta t - \tau} \int_0^{\Delta t - \tau} dt \cos(\omega(t + \tau)) \cos \omega t \\ &= \frac{1}{\Delta t - \tau} \int_0^{\Delta t - \tau} dt \cos(\omega t + \omega \tau) \cos \omega t \\ &= \frac{1}{\Delta t - \tau} \int_0^{\Delta t - \tau} dt \frac{1}{2} (\cos(2\omega t + \omega \tau) + \cos \omega \tau) \\ &= \frac{1}{\Delta t - \tau} \int_0^{\Delta t - \tau} dt \frac{1}{2} (\underbrace{\cos(2\omega t + \omega \tau) + \cos \omega \tau}_{\text{this term integrates to zero on average for large } \Delta t}) \end{aligned} \quad (13)$$

$$= \frac{\cos \omega \tau}{2(\Delta t - \tau)} \int_0^{\Delta t - \tau} dt$$

$$= \boxed{\frac{1}{2} \cos \omega \tau}$$

For  $A(t) = \underbrace{a_1 \cos \omega_1 t}_{B(t)} + \underbrace{a_2 \cos \omega_2 t}_{C(t)}$ , the autocorrelation function is

$$\begin{aligned} C_{AA}(\tau) &= \frac{1}{\Delta t - \tau} \int_0^{\Delta t - \tau} dt (B(t + \tau) + C(t + \tau))(B(t) + C(t)) \\ &= C_{BB}(\tau) + C_{CC}(\tau) + C_{BC}(\tau) + C_{CB}(\tau) \\ &= \frac{a_1^2}{2} \cos \omega_1 \tau + \frac{a_2^2}{2} \cos \omega_2 \tau + C_{BC}(\tau) + C_{CB}(\tau) \end{aligned} \quad (14)$$

The cross-correlation functions  $C_{AB}(\tau)$  and  $C_{BA}(\tau)$  are of the following form:

$$C_{BC}(t) = \frac{a_1 a_2}{\Delta t - \tau} \int_0^{\Delta t - \tau} dt \cos(\omega_1(t + \tau)) \cos \omega_2 t$$

$$= 0 \quad \text{for } \Delta t \gg 2\pi/\omega \text{ and } \omega_1 \neq \omega_2$$
(15)

Thus,  $C_{AB}(\tau)$  and  $C_{BA}(\tau)$  are equal to zero, since sinusoidal waves of differing frequencies are uncorrelated.  $C_{AA}(\tau)$  is therefore

$$C_{AA}(\tau) = \frac{a_1^2}{2} \cos \omega_1 t + \frac{a_2^2}{2} \cos \omega_2 t$$

(16)

## 2 Structural descriptors: Radial distribution function

### 2.1 RDF of an ideal gas

The radial distribution function (RDF) for a system of  $N$  particles in a volume  $V$  can be calculated as follows:

$$g(r) = \frac{V}{N^2 v_{\text{shell}}(r, \Delta r)} \sum_{i=1}^N n_i(r, \Delta r)$$
(17)

where  $n_i(r, \Delta r)$  is the average number of particles within a shell of radius  $r$ , thickness  $\Delta r$  and volume  $v_{\text{shell}}(r, \Delta r)$ . For the ideal gas system ('ideal.xyz') the following RDF was obtained:

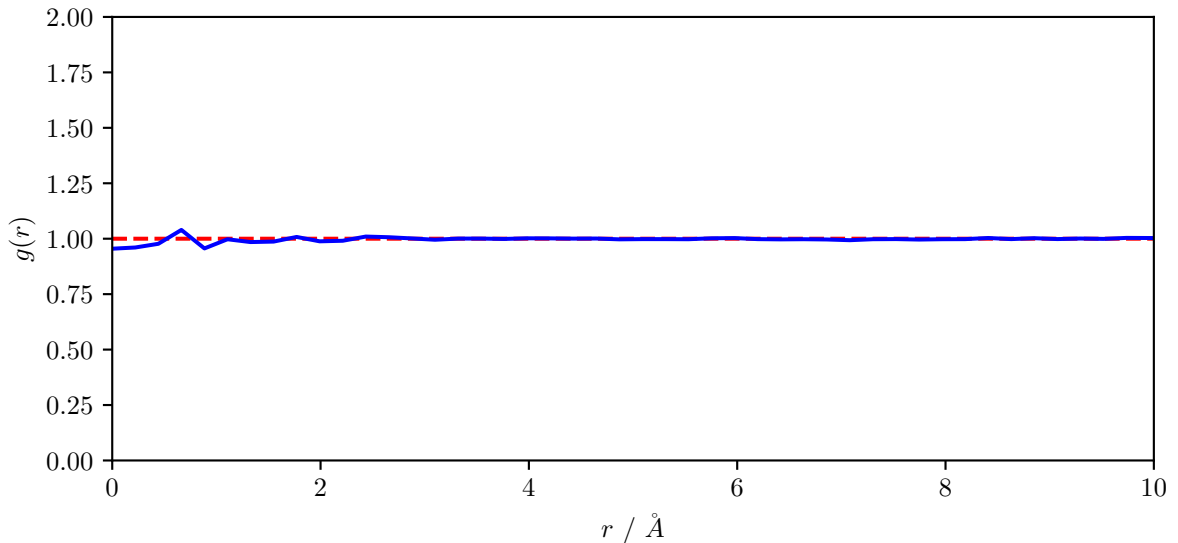


Figure 1:  $g(r)$  for ideal gas system, computed from 'ideal.xyz'

As expected for an ideal gas, the RDF is (approximately) equal to 1 for all values of  $r$ .

Typically for RDFs,  $v_{\text{shell}}(r, \Delta r) = 4\pi r^2 \Delta r$ . For my code, I used the more accurate formula  $v_{\text{shell}}(r, \Delta r) = 4\pi((r + \Delta r)^3 - r^3)/3$ . The only difference to the plots is the behaviour right at  $r = 0$ , which is fairly unimportant in most cases (see water/colloidal systems).

## 2.2 RDF of bulk liquid water

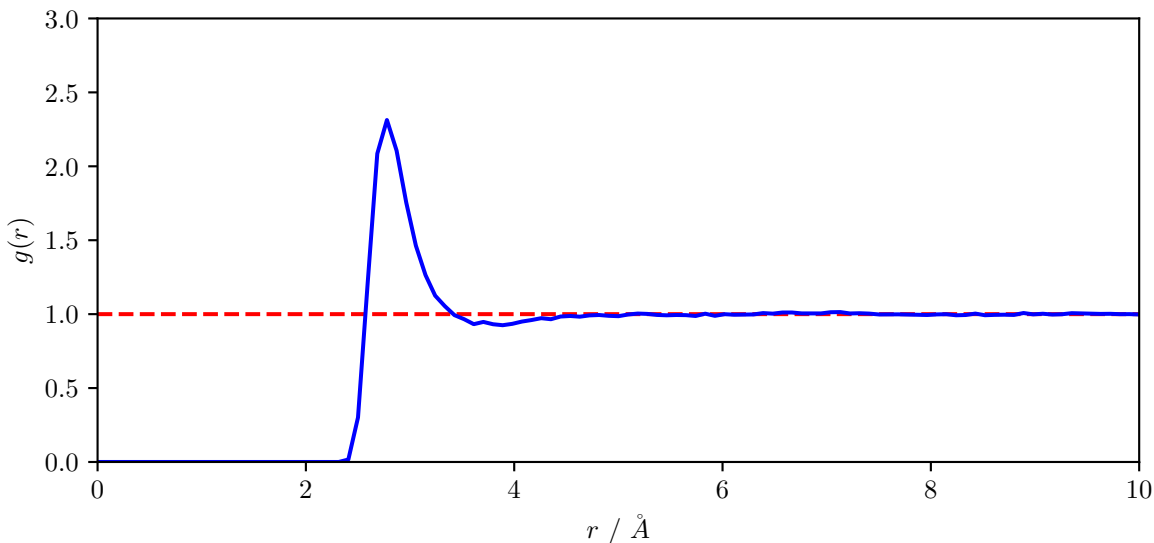


Figure 2:  $g_{\text{OO}}(r)$  for water, computed from ‘water.xyz’

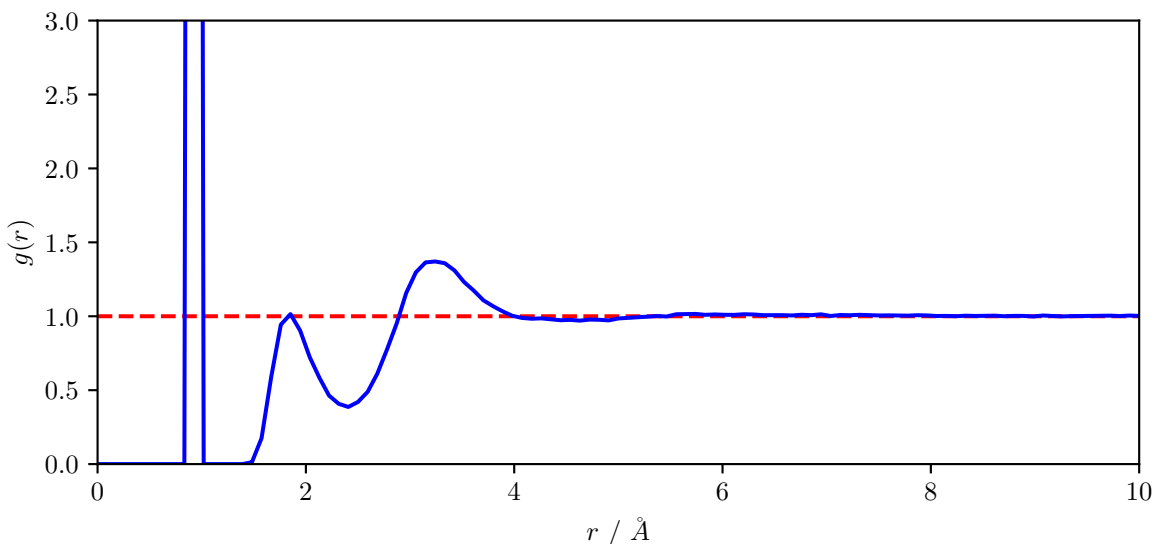


Figure 3:  $g_{\text{OH}}(r)$  for water, computed from ‘water.xyz’

It is clear that for the oxygen-hydrogen RDF, the sharp peak at around 1 Å is due to the two hydrogen atoms on the same molecule as a given oxygen atom.

## 2.3 Characterising different crystal and liquid phases through their RDFs

Fig. 4 shows a colloidal system in the liquid phase, which is clear due to the RDF's smoother shape. Fig. 5 and 6 show crystal phase colloidal systems.

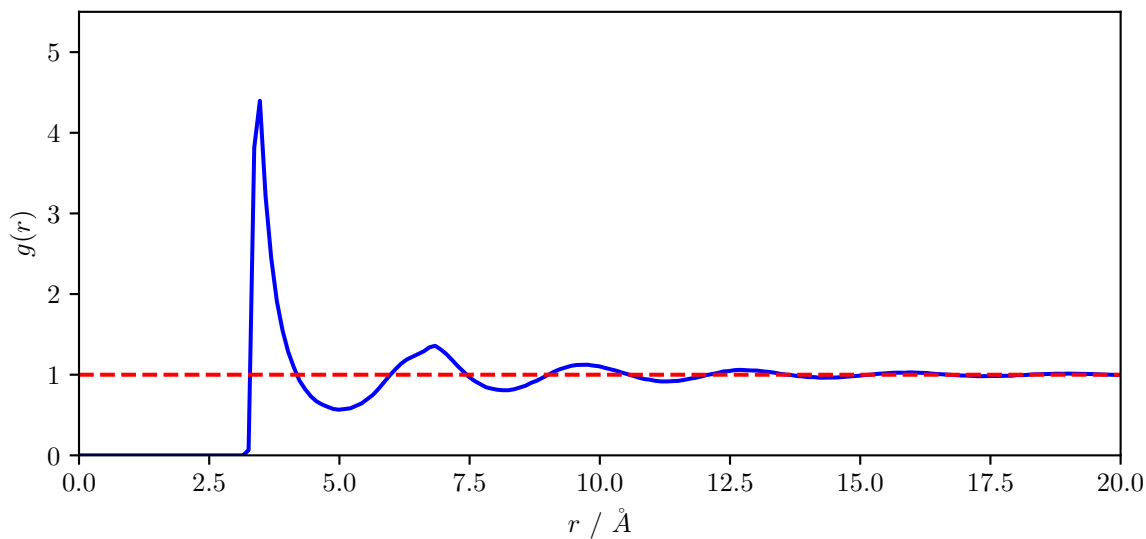


Figure 4:  $g(r)$  for a colloidal system, computed from 'set1.xyz'

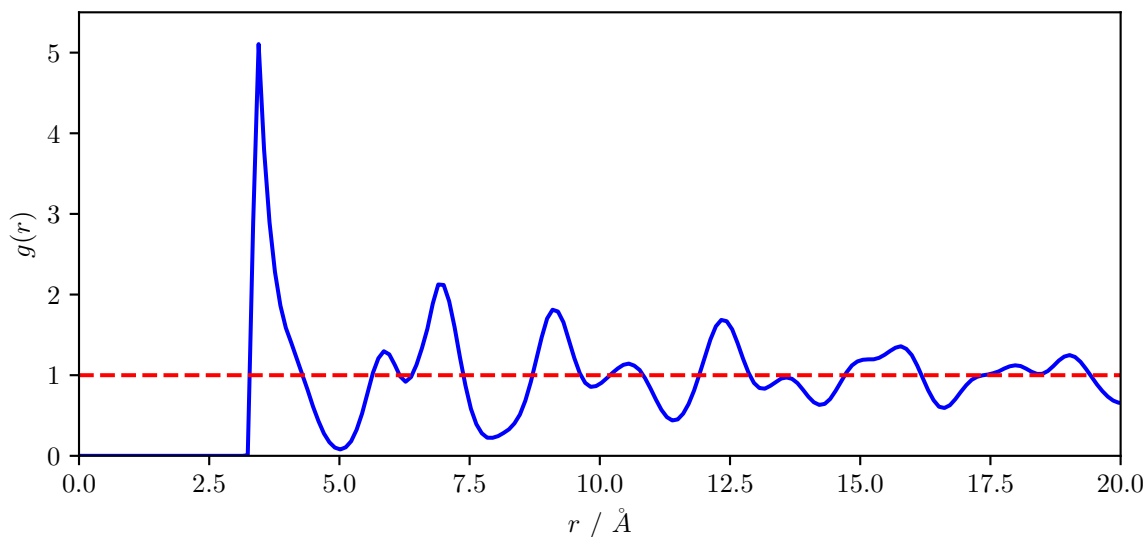


Figure 5:  $g(r)$  for a colloidal system, computed from 'set2.xyz'

The coordination number around an atom at a distance  $r_c$  can be calculated as

$$z(r_c) = 4\pi\rho \int_0^{r_c} dr r^2 g(r) \quad (18)$$

This can be computed by performing numerical integration on the RDF up to a specific point  $r_c$ . Computing the coordination number for Fig. 5 for its first shell ( $r_c \approx 5\text{\AA}$ ) gives  $z(r_1) = 14$ .

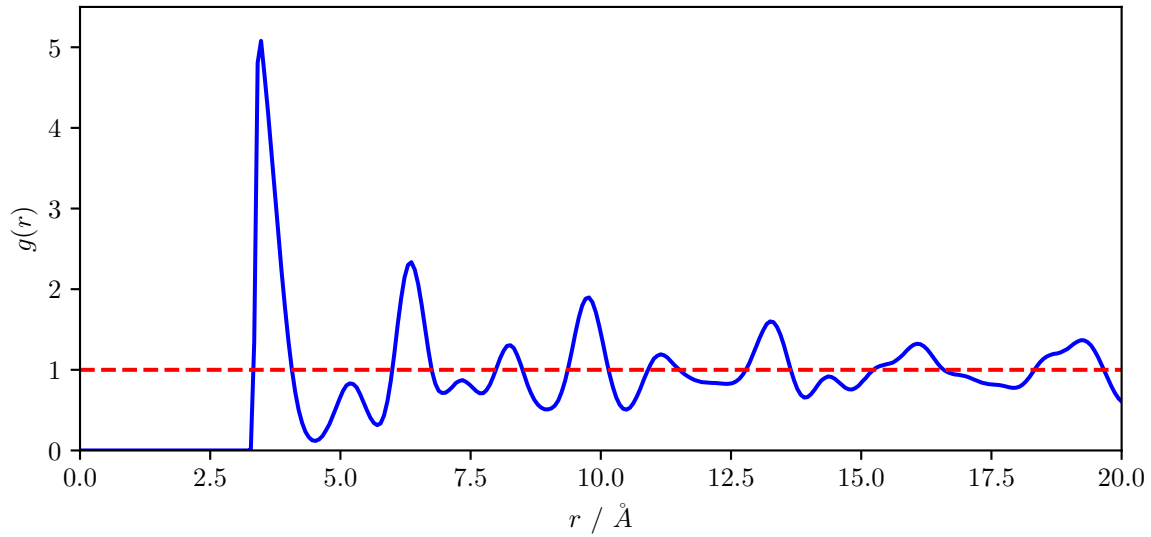


Figure 6:  $g(r)$  for a colloidal system, computed from ‘set3.xyz’

Computing the coordination number for Fig. 6 for its first and second shells gives  $z(r_1) = 12$  and  $z(r_2) = 18$  respectively. This suggests that the crystalline colloidal system in Fig. 6 is face-centred cubic (FCC).