

## 7.6: The Pair Correlation Function

Of particular importance is the case  $n=2$ , or the correlation function  $g^{(2)}(r_1, r_2)$  known as the *pair correlation function*. The explicit expression for  $g^{(2)}(r_1, r_2)$  is

$$\begin{aligned} g^{(2)}(r_1, r_2) &= \frac{V^2 N!}{N^2 (N-2)!} \langle \delta(r_1 - r'_1) \delta(r_2 - r'_2) \rangle \\ &= \frac{V^2 (N-1)}{N Z_N} \int dr_3 \cdots dr_N e^{-\beta U(r_1, \dots, r_N)} \\ &= \frac{N(N-1)}{p^2} \langle \delta(r_1 - r'_1) \delta(r_2 - r'_2) \rangle_{r'_1, \dots, r'_N} \end{aligned}$$

In general, for homogeneous systems in equilibrium, there are no special points in space, so that  $g^{(2)}$  should depend only on the relative position of the particles or the difference  $r_1 - r_2$ . In this case, it proves useful to introduce the change of variables

$$\begin{aligned} r &= r_1 - r_2, R = \frac{1}{2}(r_1 + r_2) \\ r_1 &= R + \frac{1}{2}r, r_2 = R - \frac{1}{2}r \end{aligned}$$

Then, we obtain a new function  $\tilde{g}^{(2)}$ , a function of  $r$  and  $R$ :

$$\begin{aligned} \tilde{g}^{(2)}(r, R) &= \frac{V^2 (N-1)}{N Z_N} \int dr_3 \cdots dr_N e^{-\beta U(R + \frac{1}{2}r, R - \frac{1}{2}r, r_3, \dots, r_N)} \\ &= \frac{N(N-1)}{p^2} \left\langle \delta\left(R + \frac{1}{2}r - r'_1\right) \delta\left(R - \frac{1}{2}r - r'_2\right) \right\rangle_{r'_1, \dots, r'_N} \end{aligned}$$

In general, we are only interested in the dependence on  $r$ . Thus, we integrate this expression over  $R$  and obtain a new correlation function  $\tilde{g}(r)$  defined by

$$\begin{aligned} \tilde{g}(r) &= \frac{1}{V} \int dR \tilde{g}^{(2)}(r, R) \\ &= \frac{V(N-1)}{N Z_N} \int dR dr_3 \cdots dr_N e^{-\beta U(R + \frac{1}{2}r, R - \frac{1}{2}r, r_3, \dots, r_N)} \\ &= \frac{(N-1)}{p Z_N} \int dR dr_3 \cdots dr_N e^{-\beta U(R + \frac{1}{2}r, R - \frac{1}{2}r, r_3, \dots, r_N)} \end{aligned}$$

For an isotropic system such as a liquid or gas, where there is no preferred direction in space, only the magnitude or  $r$ ,  $|r| \equiv r$  is of relevance. Thus, we seek a choice of coordinates that involves  $r$  explicitly. The spherical-polar coordinates of the vector  $r$  is the most natural choice. If  $r = (x, y, z)$  then the spherical polar coordinates are

$$\begin{aligned} x &= r \sin \theta \cos \phi \\ y &= r \sin \theta \sin \phi \\ z &= r \cos \theta \\ dr &= r^2 \sin \theta dr d\theta d\phi \end{aligned}$$

where  $\theta$  and  $\phi$  are the polar and azimuthal angles, respectively. Also, note that

$$r = rn$$

where

$$n = (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)$$

Thus, the function  $g(r)$  that depends only on the distance  $r$  between two particles is defined to be

$$\begin{aligned} g(r) &= \frac{1}{4\pi} \int \sin\theta d\theta d\phi \tilde{g}(r) \\ &= \frac{(N-1)}{4\pi p Z_N} \int \sin\theta d\theta d\phi dR dr_3 \cdots dr_N e^{-\beta U(R + \frac{1}{2}r, R - \frac{1}{2}r, rR, \dots, rN)} \\ &= \frac{(N-1)}{4\pi p} \left\langle \frac{\delta(r-r')}{rr'} \right\rangle_{r^t, \theta^t, \phi^t, R^t, r_3^t, \dots, r_N^t} \end{aligned}$$

Integrating  $g(r)$  over the radial dependence, one finds that

$$4\pi p \int_0^\infty dr r^2 g(r) = N - 1 \approx N$$

The  $g(r)$  function is important for many reasons. It tells us about the structure of complex, isotropic systems, as we will see below, it determines the thermodynamic quantities at the level of the pair potential approximation, and it can be measured in neutron and X-ray diffraction experiments. In such experiments, one observes the scattering of neutrons or X-rays from a particular sample. If a detector is placed at an angle  $\theta$  from the wave-vector direction of an incident beam of particles, then the intensity  $I(\theta)$  that one observes is proportional to the structure factor

$$\begin{aligned} I(\theta) &\sim \frac{1}{N} \left\langle \left| \sum_m e^{ik \cdot r_m} \right|^2 \right\rangle = \frac{1}{N} \left\langle \sum_m e^{ik \cdot (r_m - r_n)} \right\rangle \\ &\equiv S(k) \end{aligned}$$

where  $k$  is the vector difference in the wave vector between the incident and scattered neutrons or X-rays (since neutrons and X-rays are quantum mechanical particles, they must be represented by plane waves of the form  $\exp(ik \cdot r)$ ). By computing the ensemble average (see problem 4 of problem set #5), one finds that  $S(k) = S(k)$  and  $S(k)$  is given by

$$S(k) = 1 + \frac{4\pi p}{k} \int_0^\infty dr r \sin(kr) g(r)$$

Thus, if one can measure  $S(k)$ ,  $g(r)$  can be determined by Fourier transformation.

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