

### 7.5 Measurement of $g(r)$ by Diffraction

Let us now consider how pair correlation functions can be measured. The measurement will have to probe distances of the order of or smaller than Angstroms. Thus, if radiation is used, its wavelength must be smaller than 1 Å; such wavelengths are obtained with X-rays or neutrons. The elementary theory of X-ray scattering is similar to that for neutrons. We treat X-rays here.

A schematic view of an X-ray scattering experiment is shown in Fig. 7.7. The scattered wave at the detector due to scattering from one atom at  $\mathbf{R}_s$  is

$$\left[ \begin{array}{c} \text{atomic scattering} \\ \text{factor} \end{array} \right] |\mathbf{R}_D - \mathbf{R}_s|^{-1} \exp \{i[\mathbf{k}_{in} \cdot \mathbf{R}_s + \mathbf{k}_{out} \cdot (\mathbf{R}_D - \mathbf{R}_s)]\}.$$

(This is the spherical wave, first Born approximation.) If the detector is far from the scattering center,

$$|\mathbf{R}_D - \mathbf{R}_s| \approx |\mathbf{R}_D - \mathbf{R}_c|,$$

where  $\mathbf{R}_c$  is the center of the scattering cell. For that case, the scattered wave at the detector is

$$f(k) |\mathbf{R}_D - \mathbf{R}_c|^{-1} e^{i\mathbf{k}_{out} \cdot \mathbf{R}_D} e^{-i\mathbf{k} \cdot \mathbf{R}_s},$$

where

$$\mathbf{k} = \mathbf{k}_{out} - \mathbf{k}_{in}$$

is the momentum transfer (within a factor of  $\hbar$ ) for the scattered X-ray, and  $f(k)$  is the atomic scattering factor. (It depends upon  $k$ . Why?) Now consider the vector diagram in Fig. 7.8. Since photons scatter nearly elastically,  $|\mathbf{k}_{in}| \approx |\mathbf{k}_{out}|$ . As a result,

$$k = |\mathbf{k}| = (4\pi/\lambda_{in}) \sin(\theta/2).$$

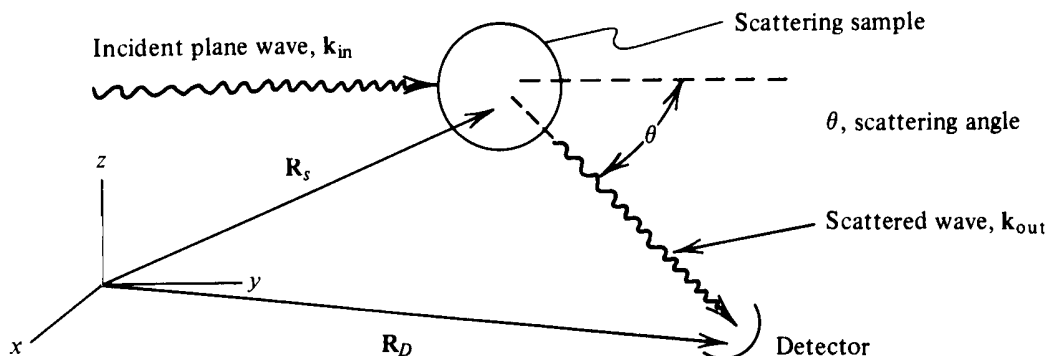


Fig. 7.7. X-ray scattering.

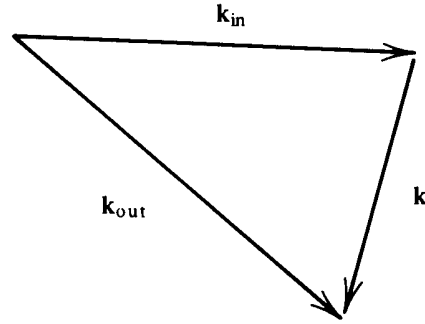


Fig. 7.8. Vector addition.

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**Exercise 7.15** Derive this formula for elastic scattering.

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Since each atom in the system scatters, we have a superposition of waves at the detector:

$$(\text{total scattered wave}) = f(k) \frac{e^{i\mathbf{k}_{\text{out}} \cdot \mathbf{R}_D}}{|\mathbf{R}_c - \mathbf{R}_D|} \sum_{j=1}^N e^{-i\mathbf{k} \cdot \mathbf{r}_j},$$

where  $\mathbf{r}_j$  is the position of the  $j$ th atom. The intensity is the square of the magnitude of the total wave, and the *observed* intensity is the ensemble average of that square:

$$\begin{aligned} I(\theta) &= \text{observed intensity at detector} \\ &= [|f(k)|^2 / |R_c - R_D|^2] NS(k), \end{aligned}$$

where

$$S(k) = N^{-1} \left\langle \sum_{l,j=1}^N \exp [i\mathbf{k} \cdot (\mathbf{r}_l - \mathbf{r}_j)] \right\rangle.$$

The quantity  $S(k)$  is called the *structure factor*. It is related in a simple way to the Fourier transform of  $g(r)$ .

To see why, expand the sum over particles in  $S(k)$  into self,  $l = j$ , and distinct,  $l \neq j$ , parts. There are  $N$  of the former and  $N(N - 1)$  of the latter. Thus,

$$\begin{aligned} S(k) &= 1 + N^{-1}N(N - 1) \langle e^{i\mathbf{k} \cdot (\mathbf{r}_1 - \mathbf{r}_2)} \rangle \\ &= 1 + N^{-1} \frac{N(N - 1) \int d\mathbf{r}^N e^{i\mathbf{k} \cdot (\mathbf{r}_1 - \mathbf{r}_2)} e^{-\beta U}}{\int d\mathbf{r}^N e^{-\beta U}} \end{aligned}$$

$$\begin{aligned}
 &= 1 + N^{-1} \underbrace{\int d\mathbf{r}_1 \int d\mathbf{r}_2}_{\int d\mathbf{r}_1 \int d\mathbf{r}_{12}} \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \underbrace{e^{i\mathbf{k} \cdot (\mathbf{r}_1 - \mathbf{r}_2)}}_{\rho^2 g(r_{12})} \\
 &= 1 + \rho \int d\mathbf{r} g(r) e^{i\mathbf{k} \cdot \mathbf{r}}.
 \end{aligned}$$

As a result, the measured structure factor determines the Fourier transform of  $g(r)$ . Since Fourier transforms are unique,  $S(k)$  can be inverted to determine  $g(r)$ .

**Exercise 7.16** Verify the algebraic details in this derivation and continue the reduction to show that

$$S(k) = 1 + (4\pi\rho/k) \int_0^\infty dr \sin(kr) r g(r).$$

## 7.6 Solvation and Chemical Equilibrium in Liquids

One of the most important aspects of liquid state science in the fields of biophysics and chemistry is the role of liquid environments in affecting conformational and chemical equilibria of solutes in solution. This is the subject of solvation, and here, too, reduced distribution functions are closely related to experimental observations of solvation.

To describe the relationship, we begin by deriving a formula for the chemical potential for a simple structureless solute species dissolved in a fluid at low solute concentrations. The total partition function is

$$\begin{aligned}
 Q &= Q_S^{(\text{id})} Q_A^{(\text{id})} V^{-(N_A + N_S)} \int d\mathbf{r}^{N_A} \int d\mathbf{r}^{N_S} \\
 &\quad \times \exp[-\beta U_S(\mathbf{r}^{N_S}) - \beta U_{AS}(\mathbf{r}^{N_S}, \mathbf{r}^{N_A})],
 \end{aligned}$$

where  $Q_S^{(\text{id})} Q_A^{(\text{id})}$  is the ideal gas partition function for the solvent-solute mixture (it depends upon the numbers of solute and solvent molecules,  $N_A$  and  $N_S$ , respectively, the volume  $V$ , and temperature  $T$ ), the potential energy  $U_S$  is the potential energy for the pure solvent (it is a function of the solvent configurations,  $\mathbf{r}^{N_S}$ ), and  $U_{AS}$  is the contribution to the potential energy due to the coupling between solvent and solute species. In this equation for the partition function we have left out a contribution to the potential energy due to the