2. DIFFRACTION GEOMETRY AND ITS PRACTICAL REALIZATION

contrast of the rest of the complex with respect to the solvent. In practice, it would be wise to follow the same considerations as with triangulation.

2.6.2.8. *Dense systems*

Especially in the case of polymers, but also in alloys, the scattering from the sample can often no longer be described, as in the previous section, as originating from a sum of isolated particles in different orientations. There may be two reasons for this: either the number concentration c of one of the components is higher than about 0.01, leading to excluded-volume effects, and/or there is an electrostatic interaction between components (for example, in solutions of polyelectrolytes, latex, or micelles). In these cases, it is usually the information about the *structure* of the sample caused by the interactions that is to be obtained rather than the shape of the inhomogeneities or particles in the sample, unless the interactions can be regarded as a weak disturbance.

An excellent introduction to the treatment of dense systems is found in the article of Hayter (1985). A detailed description of the theoretical interpretation of correlations in charged macro-molecular and supramolecular solutions has been published by Chen, Sheu, Kalus & Hoffmann (1988).

The scattering from densely packed particles can be written as the product of the structure factor or structure function $S(Q)$, describing the arrangement of the inhomogeneities with respect to each other, in mathematical terms the interference effects of correlations between particle positions, in the sample,

$$S(Q) = \left\langle \sum \sum \exp[i\mathbf{Q}(\mathbf{r}_j - \mathbf{r}_k)] \right\rangle / N, \qquad (2.6.2.14)$$

and of the form factor $P(Q)$ of the inhomogeneities (as before):

$$I(Q) = P(Q)S(Q). \qquad (2.6.2.15)$$

Hayter & Penfold (1981) were the first to describe an analytic structure factor for macro-ion solutions.

If $P(Q)$ can be obtained from a measurement of a dilute solution of the particles under study, then the pure structure factor can be calculated by dividing the high-concentration intensity curve by the low-concentration curve. This procedure requires the form factor not to change with concentration, which is not necessarily the case for loosely arranged particles such as polymers. A technique that avoids this problem is contrast variation (see Subsection 2.6.2.2): introducing a fraction of a deuterated molecule into a bulk of identical protonated molecules (or *vice versa*, with the advantage of reduced incoherent background) yields the scattering of the 'isolated' labelled particle at high-concentration conditions.

Partial structure factors can be obtained from a contrast-variation series of a given system at different volume fractions of the particles. Similarly to equation (2.6.2.4), the structure factor can be decomposed into a quadratic function. In the ternary alloy Al–Ag–Zn, for example, the scattering has been decomposed into the contributions from the two minor species Ag and Zn, and their interference, *i.e.* the partial structure functions for Zn–Zn, Zn–Ag, and Ag–Ag, by using the scattering from three samples with different silver isotopes, and identical sample treatment (Salva-Ghilarducci, Simon, Guyot & Ansara, 1983).

references