

2. DIFFRACTION GEOMETRY AND ITS PRACTICAL REALIZATION

describe the situation by introducing a radial interparticle distribution function $P(r)$ (Zernicke & Prins, 1927; Debye & Menke, 1930). Each particle has the same surroundings. We consider one central particle and ask for the probability that another particle will be found in the volume element dV at a distance r apart. The mean value is $(N/v) dV$; any deviation from this may be accounted for by a factor $P(r)$. In the range of impenetrability ($r < D$), we have $P(r) = 0$ and in the long range ($r \gg D$) $P(r) = 1$. So the corresponding equation takes the form

$$I(h) = NI_1(h) \left[1 + \frac{N}{V} \int_0^\infty 4\pi r^2 [P(r) - 1] \frac{\sin(hr)}{hr} dr \right]. \quad (2.6.1.53)$$

The second term contains all interparticle interferences. Its predominant part is the 'hole' of radius D , where $[P(r) - 1] = -1$. This leads to a decrease of the scattering intensity mainly in the central part, which results in a liquid-type pattern (Fig. 2.6.1.11). This can be explained by the reduction of the contrast caused by the high number of surrounding particles. Even if a size distribution for the spheres is assumed, the effect remains essentially the same (Porod, 1952). Up to now, no exact analytical expressions for $P(r)$ exist. The situation is even more complicated if one takes into account attractive or repulsive interactions or non-spherical particle shapes (orientation).

If we have a system of spheres with known size D , we can use equation (2.6.1.37) for $I_1(h)$ in equation (2.6.1.53), divide by this function, and calculate $P(r)$ from experimental data by Fourier inversion. The interference term can be used to study particle correlations of charged macromolecular solutions (Chen, Sheu, Kalus & Hoffmann, 1988).

If there are attractive forces, there will be a tendency for aggregation. This tendency may, for instance, be introduced by some steps in the procedure of preparation of biological samples. Such aggregation leads to an increase of the intensity in the central part (gas type). In this case, we will finally have a polydisperse system of monomers and oligomers. Again, there exist no methods to analyse such a system uniquely.

Elimination of concentration effects – liquid type. In most cases, the interference effect is a perturbation of our experiment where we are only interested in the particle scattering function. Any remaining concentration effect would lead to errors in the resulting parameters. As we have seen above, the effect is essential at low h values, thus influencing $I(0)$, R_g , and the PDDF at large r values.

The problem can be handled for the liquid-like type in the following way. We measure the scattering function $I(h)$ at different concentrations (typically from a few mg ml^{-1} up to about 50 mg ml^{-1}). The influence of the concentration can be seen in a common plot of these scattering curves, divided by

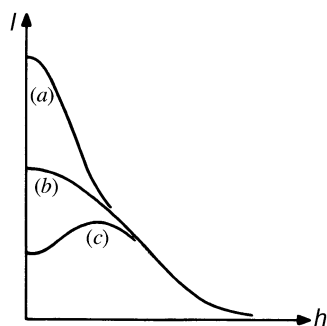


Fig. 2.6.1.11. Characteristic types of scattering functions: (a) gas type; (b) particle scattering; (c) liquid type.

their concentrations. For large h values, these curves are identical. In the low- h range, the curves must be extrapolated to zero concentration. It depends on the problem as to whether a linear fit is sufficient or whether a second-degree polynomial has to be used. The extrapolation can be performed in a standard $I(h)/c$ versus h plot or in a Zimm plot $[I(h)/c]^{-1}$ versus h (Cleemann & Kratky, 1960; Kirste & Oberthür, 1982). The Zimm plot should be preferred when working with highly concentrated solutions (Pilz, 1982).

As mentioned above, the innermost part of the scattering function is lowered and the apparent radius of gyration decreases with increasing concentration. The length of the linear range of the Guinier plot can be extended by the interference effect for non-spherical particles. Thus, an elongated linear Guinier plot is no guarantee of the completeness of the elimination of the concentration effect. Remaining interparticle interferences cannot be recognized in reciprocal space.

The PDDF is affected considerably by interparticle interference (Glatter, 1979). It is lowered with increasing distance r , goes through a negative minimum in the region of the maximum dimension D of the particle, and the oscillations vanish at larger r values. This is shown for the hard-sphere model in Fig. 2.6.1.12. The oscillations disappear when the concentration goes to zero.

The same behaviour can be found from experimental data even in the case of non-spherical data (Pilz, Goral, Hoylaerts, Witters & Lontie, 1980; Pilz, 1982).

In some cases, it may be impossible to carry out experiments with varying concentrations. This will be the case if the structure of the particles depends on concentration. Under certain circumstances, it is possible to find the particle parameters by neglecting the innermost part of the scattering function influenced by the concentration effect (Müller & Glatter, 1982).

Aggregates – gas type. When the particles show a tendency to aggregation with increasing concentration, we can follow the same procedures as discussed for the liquid type, *i.e.* perform a concentration series and extrapolate the $I(h)/c$ curves to zero concentration.

However, in most cases, the tendency to aggregation exists at any concentration, *i.e.* even at very high dilution we have a certain number of oligomers coexisting with monomers. There is no unique way to find the real particle parameters in these cases. It is not sufficient just to neglect the innermost part of the

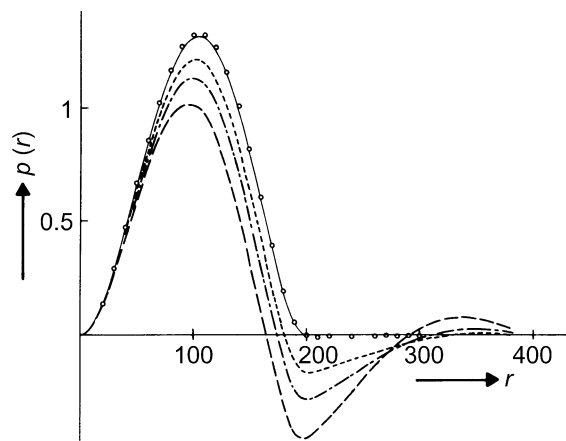


Fig. 2.6.1.12. Distance distribution – hard-sphere interference model. Theoretical $p(r)$ functions: — $\theta = 0$; - - - $\theta = 0.25$; — · — $\theta = 0.5$; — — — $\theta = 1.0$. Circles: results from indirect transformation: $\theta = 0.5$, $h_1R = 2.0$. 2% statistical noise, $D_{\max} = 300 \text{ \AA}$, $\Delta R_g = 0.5\%$, $\Delta I_0 = 1.2\%$.