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can be interpreted as a residual constant background (including the self-term of the constant nuclear 'form factor'), which may be used for slightly correcting the estimated background and consequently improving the quality of the data. For mono-dispersed particles, a particle surface can be deduced from the overall surface. The value of the surface area so determined depends on the maximal Q to which the scattering curve can be obtained with good statistics. This depends also on the magnitude of the background. At least for weakly scattering particles in mixtures of ^1H_2O and ^2H_2O, and even more in pure ^1H_2O, the incoherent background level often cannot be determined precisely enough for interpreting the tail of the scattering curve in terms of the surface area.

2.6.2.7. *Single-particle scattering*

Single-particle scattering in this context means scattering from isolated structures (clusters in alloys, isolated polymer chains in a solvent, biological macromolecules, *etc.*) randomly distributed in space and sufficiently far away from each other so that interparticle contributions to the scattering (see Subsection 2.6.2.8) can be neglected. The tendency of polymerization of single particles, for example the monomer–dimer equilibrium of proteins or the formation of higher aggregates, and long-range (*e.g.* electrostatic) interactions between the particles disturb single-particle scattering. In the absence of such effects, samples with solute volume fractions below about 1% can be regarded as free of volume-exclusion interparticle effects for most purposes. For (monodispersed) protein samples, for example, this means that concentrations of about $5 \, mg \, ml^{-1}$ are often a good compromise between sufficient scattering intensity and concentration effects. In many cases, series of scattering measurements with increasing particle concentrations have been used for extrapolating the scattering to zero concentration. In the following, we assume that particle interactions are absent.

2.6.2.7.1. *Particle shape*

All X-ray and neutron small-angle scattering curves can be approximated by a parabolic fit in a narrow Q range near $Q = 0$ (Porod, 1951): $I(Q) \simeq I(0) \, (1 - a^2 Q^2/3 + \ldots)$. In the case of single-particle scattering, a Gaussian approximation to the scattering curve is even more precise (Guinier & Fournet, 1955) in the zero-angle limit:

$$I(Q) \simeq I(0) \exp(-Q^2/3R_G^2), \qquad (2.6.2.10)$$

where R_G is the radius of gyration of the particle's excess scattering density.

The concept of R_G and the validity of the Guinier approximation is discussed in more detail in the SAXS section of this volume (§2.6.1). It might be mentioned here that the frequently used $QR_G < 1$ rule for the validity of the Guinier approximation is no more than an indication and should always be tested by a scattering calculation with the model obtained from the experiment: Spheres yield a deviation of 5% of the Gaussian approximation at $QR_G = 1.3$, rods at $QR_G = 0.6$; ellipsoids of revolution with an elongation factor of 2 can reach as far as $QR_G = 3$.

More detailed shape information requires a wider Q range. As indicated before, Fourier transforms may help to distinguish between conflicting models. In many instances (*e.g.* hollow bodies, cylinders), it is much easier to find the shape of the scattering particle from the distance distribution function than from the scattering curve [see §2.6.2.7.3].

2.6.2.7.2. *Particle mass*

With $N = CN_A V_s/M_r$, where N_A is Avogadro's number, C is the mass concentration of the solute in $g \, l^{-1}$, and V_s is the sample volume in cm^{-3} (we assume N identical particles randomly distributed in dilute solution), we find that the relative molecular mass M_r of a particle can be determined from the intensity at zero angle, $I(0)$ in equation (2.6.2.10), using the relation (Jacrot & Zaccai, 1981), where the particle mass concentration C (in $mg \, ml^{-1}$) is omitted:

$$I(0)/\{CI[H_2O](0)\}$$
$$= 4\pi f \, T_s M_r N_A d_s \, 10^{-3} \left[\left(\sum b_i - \rho_s V \right)/M_r \right]^2 /(1 - T[H_2O]).$$
$$(2.6.2.11)$$

d_s is the sample thickness. Note that $\sum b_i/M_r$ may depend on solvent exchange; in a given solvent, especially ^1H_2O, it is rather independent of the exact amino acid composition of proteins (Jacrot & Zaccai, 1981).

An alternative presentation of equation (2.6.2.11) is

$$I(0)/\{CI[H_2O](0)\}$$
$$= 4\pi f \, T_s M_r d_s \, 10^{-3} (v\Delta\rho)^2 /N_A(1 - T[H_2O]), \quad (2.6.2.11a)$$

where $\Delta\rho = \rho_p(\rho_s) - \rho_s$ is the contrast; ρ_p is the particle scattering-length density (depending on the scattering-length density ρ_s of the solvent, in general) and v is the partial specific volume of the particle. Expression (2.6.2.11a) is of advantage when $(v\Delta\rho)$, which is a linear function of ρ_s, is known for a class of particles.

A thermodynamic approach to the particle-size problem, in view of the complementarity of different methods, has been given Zaccai, Wachtel & Eisenberg (1986) on the basis of the theory of Eisenberg (1981). It permits the determination of the molecular mass, of the hydration, and of the amount of bound salts.

2.6.2.7.3. *Real-space considerations*

The scattering from a large number of randomly oriented particles at infinite dilution, and as a first approximation that of particles at sufficiently high dilution (see above), is completely determined by a function $p(r)$ in real space, the distance-distribution function. It describes the probability p of finding a given distance r between any two volume elements within the particle, weighted with the product of the scattering-length densities of the two volume elements.

Theoretically, $p(r)$ can be obtained by an infinite sine Fourier transform of the isolated-particle scattering curve

$$I(Q) = \int_0^\infty [p(r)/Qr] \sin(Qr) \, dr. \qquad (2.6.2.12)$$

In practice, the scattering curve can be measured neither to $Q = 0$ (but an extrapolation is possible to this limit), nor to $Q \to \infty$. In fact, neutrons allow us to measure more easily the sample scattering in the range near $Q = 0$; X-rays are superior for large Q values. Indirect iterative methods have been developed that fit the finite Fourier transform

$$I(Q) = \int_0^{D_{max}} [p(r)/Qr] \sin(Qr) \, dr \qquad (2.6.2.12a)$$

of a $p(r)$ function described by a limited number of parameters between $r = 0$ and a maximal chord length D_{max} within the particle to the experimental scattering curve. It differs from the $p(r)$ of Section 2.6.1 by a factor of 4π.

references