1.3.6. Spherically Symmetric Body

When $\varphi(\mathbf{r}) = \varphi(r)$ $(r = |\mathbf{r}|)$, then using spherical coordinates in equation (1.8) one may write

$$f(s) = 4\pi \int_0^\infty \varphi(r) \frac{\sin(sr)}{sr} r^2 dr \tag{1.25}$$

where we recall that $s = 2\pi q = (4\pi \sin\theta)/\lambda$. This variable s is convenient for writing relationships in the case of isotropic scattering and most small-angle scattering problems. It is clear that for spherically symmetric bodies the scattering patterns also have spherical symmetry. For scattering by a homogeneous solid sphere

$$\varphi(r) = \Pi(r - R) = \begin{cases} 1, & r \leqslant R \\ 0, & r > R \end{cases} \tag{1.26}$$

and one may obtain the following important relationship by direct calculation:

$$f(s) = 3(sR)^{-3}[\sin(sR) - sR\cos(sR)] = \phi(sR) \tag{1.27}$$

where $f(0) = 1$ (normalized scattering amplitude).

These examples illustrate the application of Fourier transforms and convolution integrals to the solution of certain scattering problems. The relationships given above will be used later when analyzing certain general problems of small-angle scattering.

<N>: average number of particles

caused by interparticle interference

2.3.3. Concentrated and Dilute Systems

General expression (2.9) shows that the scattering intensity consists of two terms: the first depends only on particle structure, while the second is also a function of their statistical distribution $P(r)$ and the volume v_1 per particle. Moreover, function $P(r)$ itself should also depend on v_1: $P(r) = P(r, v_1)$. If equation (2.9) is expressed in the form

$$I(s) = \langle N \rangle \langle F^2(\mathbf{s}) \rangle - \langle F(\mathbf{s}) \rangle^2 \frac{\langle N \rangle^2}{V} \int_0^\infty [1 - P(r, v_1)] \frac{\sin(sr)}{sr} 4\pi r^2 dr \quad (2.13)$$

one can see that the first term corresponds to independent scattering from $\langle N \rangle$ particles, while the second term, proportional to $\langle N \rangle^2$, is caused by interparticle interference.

The interference effects are unlikely to be treated rigorously, the main difficulty being just the dependence of P on v_1. It was stressed by Guinier and Fournet (1955) that contradiction is inevitable in those approaches where P is assumed to be independent of v_1, because when studying $I(s)$ as a function of concentration one should not believe that one of the most important functions describing $I(s)$ is independent of this parameter.

For single-phase liquids and gases, it is possible to describe interparticle interference with the help of an equation of state (see Section 2.5.1). Debye (1927) calculated $I(s)$ for the simplest model of nonpenetrating solid spheres. Taking $P(r, v_1)$ in the form

$$P(r, v_1) = P(r) = \begin{cases} 0, & 0 \leqslant r \leqslant 2R \\ 1, & r > 2R \end{cases}$$

where R is the radius of a sphere, one obtains

$$I(s) = \langle N \rangle \phi^2(sR) \left[1 - \frac{8V}{v_1} \phi(2sR) \right]$$

where $V = 4\pi R^3/3$ is the sphere volume and $\phi(sR)$ is its normalized scattering amplitude [equation (1.27)]. This relation describes interference effects satisfactorily at low concentrations. At high concentrations, however, the already-mentioned contradiction manifests itself clearly, so that for $V/v_1 > \frac{1}{8}$ pointless negative values of $I(0)$ are obtained. It should be noted that no correct treatment of interference effects based on equation (2.13) has yet been presented. There are also other approaches to this problem [in particular, the "surrounding function" of Porod (1972)], but they only give qualitative results.

As the concentration increases, the scattering curve begins to alter owing to interparticle interference. The interference effects may be described qualitatively as follows:

1. They increase with concentration.
2. They are significant only at the very beginning of the curve, because the function $\sin(sr)$ at larger values of s starts oscillating rapidly compared with $P(r, v_1)$, and the integral in equation (2.13) tends to zero very quickly.
3. They decrease the observed scattering intensity, since $P(r, v_1) \leqslant 1$ for all r.

For solutions of intermediate concentration ($V/v_1 \sim 0.1$) it is possible to reduce these effects by performing measurements on the samples with different concentration (see Section 3.3.1).

For highly concentrated solutions, interference effects become quite significant. As a matter of fact, they are paracrystalline structures rather than disordered systems (see Hosemann and Bagchi, 1962). Fibrous structures, liquid crystals, and solid polymers are examples of such objects. To study such samples other methods, different from those employed to investigate isotropic solutions, are required. Some of them will be considered in Chapter 6.

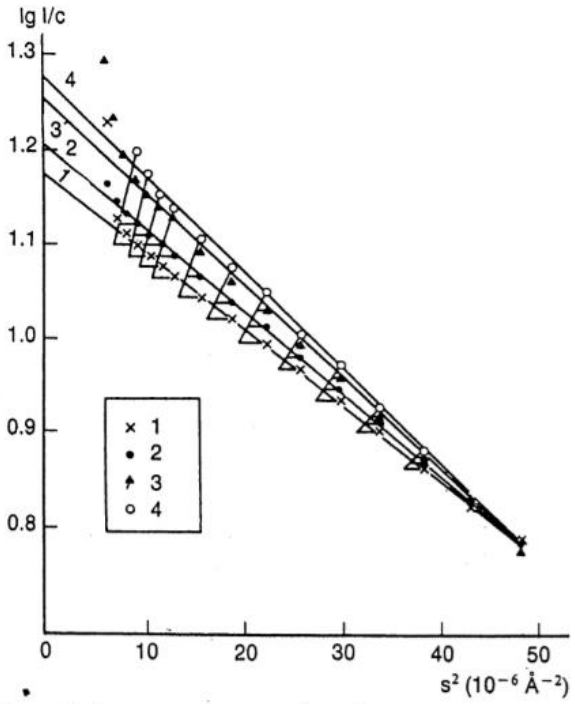


Figure 3.2. Extrapolation to zero concentration of the scattering curve for bacteriophage f7 (Rolbin *et al.*, 1980): (1)–(4) denote concentrations $c = 24$ mg/ml, 18 mg/ml, 6 mg/ml, and "infinite dilution" $c = 0$, respectively.

A. Consideration on Concentration Dependency (added by Takahashi)

In the formula (2.13), interpreting <N>, the average number of particles, as a proxy of the concentration and focusing our attention to the relation between intensity and concentration, we get the following equivalent formula,

$$I(\mathrm{s}) = C \cdot A(\mathrm{s}) + C^2 \cdot B(s)$$

where $A(\mathrm{s})$ and $B(s)$ are to be taken fittingly.
Therefore, from a serial measurement varying concentration, we have the following multiple relations, where the data of intensities $I_i(\mathrm{s})$ and concentration C_i are available while $A(\mathrm{s})$ and $B(s)$ are yet hidden.

$$\begin{aligned} I_1(\mathrm{s}) &= C_1 \cdot A(\mathrm{s}) + {C_1}^2 \cdot B(s) \\ I_2(\mathrm{s}) &= C_2 \cdot A(\mathrm{s}) + {C_2}^2 \cdot B(s) \\ &\vdots \\ I_n(\mathrm{s}) &= C_n \cdot A(\mathrm{s}) + {C_n}^2 \cdot B(s) \end{aligned}$$

For a fixed value of s, determining A and B is a multivariate regression problem. If we assume linearity for simplicity, we can easily get $A(\mathrm{s})$ and $B(s)$ for each s, which can be used to extrapolate to any desired concentration.
After we have determined $A(\mathrm{s})$ and $B(s)$ for all values of s, these two functions can be used for further stages of analysis.