SHORT COMMUNICATIONS

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Spatial correlation functions of radially distributed quantities applied to small-angle scattering

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Abstract

Spatial auto- and cross-correlation functions of quantities distributed radially over spheres of different radii are presented in analytical form. In terms of its application to small-angle (neutron and X-ray) scattering, the distance distribution function is calculated for two-shell ionic micelles and for a spherical Gaussian contrast distribution.

1. Introduction

In many applications, the small-angle scattering (SAS) intensity $I(Q)$ can be decomposed into the product of form and structure factors $F(Q)$ and $S(Q)$, respectively: $I(Q) \approx n_pF(Q)S(Q)$, where n_p is the number of particles per unit volume (Hayter & Penfold, 1981, 1983; Cabane *et al.*, 1985). The form factor equals the Fourier transform of $\Delta\tilde{\rho}^2(r)$, the autocorrelation function of the mean scattering contrast $\Delta\rho(r)$ of the individual scatterers: $F(Q) = 4\pi\int_0^\infty \Delta\tilde{\rho}^2(r)r^2[\sin(Qr)/Qr]\,dr$ and $p(r) = r^2\Delta\tilde{\rho}^2(r)$ is called the distance distribution function (Guinier & Fournet, 1955; Glatter & Kratky, 1982; Svergun & Feigin, 1986).

The inverse Fourier transform $(n_p/2\pi^2) \times \int_0^\infty F(Q)S(Q)Q^2[\sin(Qr)/Qr]\,dQ$ of the scattering intensity results in $\Delta\tilde{\rho}^2_{\rm sys}(r)$; in dilute systems, *i.e.* for $S(Q) \approx 1$, it reflects the properties of the internal structure of the individual scatterers: $\Delta\tilde{\rho}^2_{\rm sys}(r) \simeq n_p\Delta\tilde{\rho}^2(r)$. In X-ray scattering, because one-dimensional detectors produce scattering patterns in necessarily fine Q steps, $\Delta\tilde{\rho}^2_{\rm sys}(r)$ can reliably be determined from experiments (Glatter, 1982, 1988; Glatter & Gruber, 1993) and it serves as the basis for structural analysis – regardless of the difficulties of the conceptual and practical nature involved (Porod, 1982).

In spite of its central role, $\Delta\tilde{\rho}^2(r)$ is applied to interpreting scattering patterns only under very limited conditions. In the classical problem of uniform homogeneous spheres of radii R (Guinier & Fournet, 1955; Porod, 1982), we have $\Delta\tilde{\rho}^2(r) = \Delta\rho^2\Delta V_{R,R}(r)$, where $\Delta\rho$ is constant and $\Delta V_{R,R}(r)$ is the volume of the intersection of spheres at distance r. Glatter & Hainisch (1984) generalized this result for radially distributed $\Delta\rho$ and approximated $\Delta\tilde{\rho}^2$ by a finite linear combination of step functions. The aim of this paper is to derive an exact analytical expression for the cross- and autocorrelation functions of radially distributed scattering contrast functions.

2. Correlation functions of radially distributed quantities

The cross-correlation function of quantities $f_1(r_1)$ and $f_2(r_2)$, distributed radially over spheres of radii R_1 and R_2, is given by the following integral:

$$\tilde{f}^2_{12}(r) = \int\limits_{\Delta V_{R_1,R_2}(r)} f_1(r_1)f_2(r_2)\,dV(r_1, dr_1, r_2, dr_2; r) \quad (1)$$

taken over the volume $\Delta V_{R_1,R_2}(r)$ of intersection of the spheres; for notation see Fig. 1. The intersection volume, after Glatter & Hainisch (1984), is expressed by

$$\Delta V_{R_1,R_2}(r) = (2\pi/3)[R_1^3 + R_2^3 - (3r/4)(R_1^2 + R_2^2) - (3/8r)(R_2^2 - R_1^2)^2 + (r^3/8)] \quad (2)$$

and the use of bipolar coordinates when evaluating the integral in (1) is avoided by calculating the elementary volume dV from (2) as

$$\begin{aligned} dV(r_1, dr_1, r_2, dr_2; r) &= \Delta V_{r_1,r_2}(r) - \Delta V_{r_1,r_2-dr_2}(r) \\ &\quad - \Delta V_{r_1-dr_1,r_2}(r) + \Delta V_{r_1-dr_1,r_2-dr_2}(r) \\ &\rightarrow (2\pi r_1^2r_2^2/r)(dr_1\,dr_2/r_1r_2) \\ &\quad \text{for } dr_1, dr_2 \rightarrow 0. \end{aligned} \quad (3)$$

This result leads to the following form suitable for practical purposes, in particular numerical applications:

$$\tilde{f}^2_{12}(r) = (2\pi/r)\int\limits_{\max(0,r-R_1)}^{R_2} f_2(r_2)r_2\,dr_2 \int\limits_{|r-r_2|}^{\min(R_1,r+r_2)} f_1(r_1)r_1\,dr_1. \quad (4)$$

By setting $f_1(r) = f_2(r) = f(r)$, (4) results in the autocorrelation function of $f(r)$.

3. Applications to SAS

In many SAS applications, the objects to be studied (*e.g.* colloids, vesicles *etc.*) are considered as spherical particles divided into two spherical shells of radii R_1, R_2 with constant scattering contrast $\Delta\rho_1$, $\Delta\rho_2$ inside. Such contrast distributions

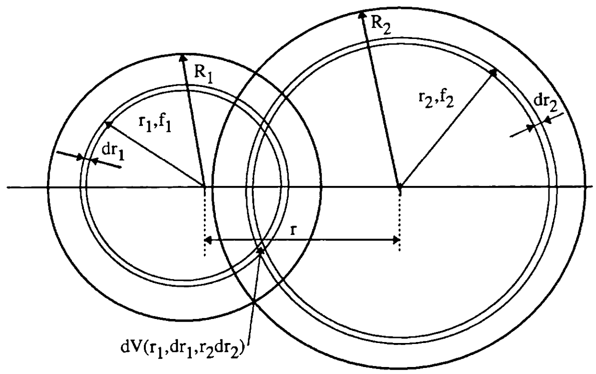

Fig. 1. Notations for calculating the cross-correlation function $\tilde{f}^2_{12}(r)$ of quantities $f_1(r_1)$ and $f_2(r_2)$, distributed radially on spheres of radii R_1 and R_2, respectively.

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are described by step functions plotted in Fig. 2(*a*); by setting them in (4), the following form results for the autocorrelation function of the scattering contrast:

$$\Delta\tilde{\rho}^2(r) = (\Delta\rho_2)^2 \Delta V_{R_2,R_2}(r) + 2(\Delta\rho_1 - \Delta\rho_2)\Delta\rho_2 \Delta V_{R_1,R_2}(r) + (\Delta\rho_1 - \Delta\rho_2)^2 \Delta V_{R_1,R_1}(r). \quad (5)$$

In the particular case of a finite number of step functions, this result follows directly from (2) and (3).

Equation (5) is applied to calculate $p(r)$ of a hypothetical caesium dodecyl sulfate (CsDDS) micelle of aggregation number $n_{ag} = 76$ for X-rays and neutrons. The inner radius (of the micellar core) is determined by the aggregation number and $R_1 = 1.86$ nm; the outer is chosen with some degree of arbitrariness: $R_2 = 3.86$ nm (Vass *et al.*, 1997). Neutron scattering-length data are taken from Sears (1984), X-ray data are calculated from the classical electron radius. Radial distributions of the scattering contrast are plotted in Fig. 2(*a*) and the corresponding $p(r)$ functions in Fig. 2(*b*); the curves show the difference between the information gained by SAXS and SANS from the same system.

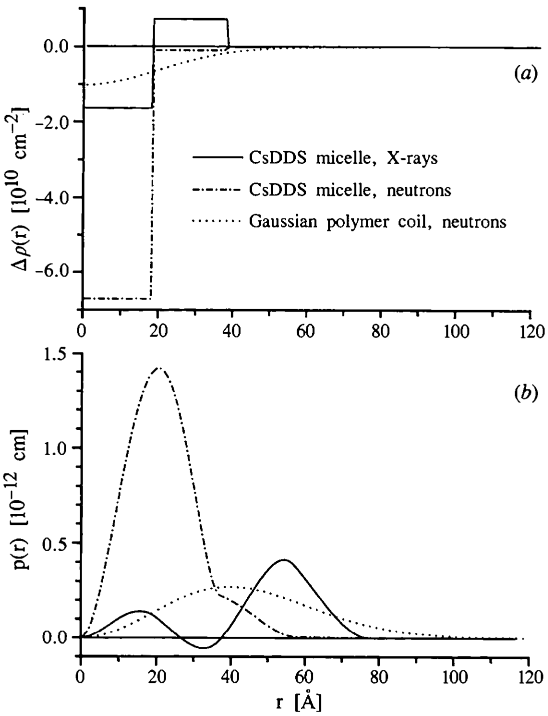

Fig. 2. (*a*) Distribution of scattering-length density in a CsDDS micelle and in a Gaussian particle; (*b*) corresponding spatial autocorrelation functions.

In general applications of (4), the correlation function cannot be expressed by a finite linear combination of overlapping volumes. Let us assume that the scattering contrast has a hypothetical Gaussian distribution of amplitude ρ_0 and width σ: $\Delta\rho(r) = [\rho_0/(2\pi)^{1/2}\sigma] \exp -(r/2^{1/2}\sigma)^2$. For $\Delta\tilde{\rho}^2(r)$, we have

$$\begin{aligned}\Delta\tilde{\rho}^2(r) &= 2\rho_0^2\pi^{1/2}\sigma \exp -(r/2^{1/2}\sigma)^2 \operatorname{erf}[(2R - r)/2\sigma] \\ &\quad - (4\rho_0^2\sigma^2/r) \exp -(R/2^{1/2}\sigma)^2 \\ &\quad \times \{\exp -[(r - R)/2^{1/2}\sigma]^2 \\ &\quad - \exp -(R/2^{1/2}\sigma)^2\}. \end{aligned} \quad (6)$$

Calculations were made with $\rho_0 = 3.51 \times 10^9$ cm^{-2} and $\sigma =$ 2 nm; results for $\Delta\rho(r)$ and $p(r)$ are respectively plotted in Figs. 2(*a*) and (*b*).

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