

Deviations from the Porod Law due to Parallel Equidistant Interfaces

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Abstract

It is proved that the second-order derivative of the correlation function, relevant to an amorphous N -component sample, can have a first-order discontinuity at a point r_0 ($\neq 0$) only when the interfaces have the following geometrical property: there exists a *finite-area* subset of one phase boundary, say S_i , such that any point P_1 of this is far away, r_0 , from a point P_2 , belonging to another boundary, say S_j , and moreover the segment P_1P_2 is orthogonal both to S_i and to S_j . The explicit integral expression of the discontinuity is obtained. The relevance of this result to the analysis of scattered intensities showing a systematic deviation from the Porod–Debye law is pointed out.

I. Introduction

The standard intensity [$i(\mathbf{h})$] of the radiation scattered by a sample is related to the so-called correlation function $\gamma(\mathbf{r})$ of the latter by the relation

$$i(\mathbf{h}) = \int \exp(i\mathbf{h} \cdot \mathbf{r}) \gamma(\mathbf{r}) \, d\mathbf{r}. \quad (\text{I.1})$$

In the case of amorphous samples, $\gamma(\mathbf{r})$ depends only on r and thus (I.1) becomes

$$i(h) = (4\pi/h) \int_0^\infty r \gamma(r) \sinh r \, dr. \quad (\text{I.2})$$

The behaviour of $i(h)$ at very large momentum transfers h is related to the discontinuities of the derivatives of the correlation function. In fact three subsequent partial integrations of (I.2), together with the hypotheses that $\dot{\gamma}(r)$, the first-order derivative of $\gamma(r)$, is continuous and that $\gamma(r)$ and its derivatives decrease sufficiently fast at infinity, yield

$$i(h) = -4\pi \left[2\dot{\gamma}(0^+) + \sum_1^N \delta_i \cos(h\delta_i) \Delta^{(2)}(\delta_i) \right] / h^4 + o(h^4). \quad (\text{I.3})$$

Here

$$\Delta^{(2)}(\delta_i) \equiv \dot{\gamma}(\delta_i^+) - \dot{\gamma}(\delta_i^-) \quad (\text{I.4})$$

represents the value of the first-order discontinuity of $\dot{\gamma}(r)$ at the point δ_i . Porod (1951, 1982) and Debye, Anderson & Brumberger (1957) have obtained the

explicit relation between $\dot{\gamma}(0^+)$ and the areas of inter-phase surfaces and thus (I.3), once one considers only the first contribution on the r.h.s., is known as the Porod–Debye law.

The second term on the r.h.s. is usually neglected on the basis of the fact that almost all the samples one actually deals with are polydisperse ones. However this argument is not completely satisfactory since we do not exactly know the explicit relation between the possible discontinuities of $\dot{\gamma}(r)$ and the geometrical shape of interfaces. Up to now in fact some configurations are known where discontinuities are present. In fact, they have been found in the correlation function of a spherical particle, with radius R , at the point $r=2R$ (Guinier & Fournet, 1955) as well as in that of a cubic particle, with edge L , at the point $r=L$ (Goodisman, 1980). These examples clearly support the former statement. In fact, since these discontinuities are related to the dimensions of the particles, one expects that, on the r.h.s. of (I.3), N is so large that the sum of all the oscillatory contributions washes out.

We emphasize however that the former argument cannot be considered satisfactory in as far as we do not know a sufficiently general answer to the question: what are the geometrical conditions that generate the first-order discontinuities in the second-order derivative of the correlation function?

Wu & Schmidt (1974) in a very interesting paper addressed a question much more general than the former. They tried to determine how the coefficients A_i and μ_i that appear in the asymptotic expansion $\sum_i A_i h^{-\mu_i}$ of the scattered intensity are related to the geometrical shape of the particles. They actually succeeded in obtaining both the exponents μ_i and the way the coefficients A_i are related to some geometrical features of particles near the so-called extremal chords. By so doing, however, they made some assumptions that considerably restrict the field over which their results apply. In fact they only considered particles with a strictly convex shape and neglected any possible crossed interference effect.

In this paper we analyse the above question by using the general formalism developed by Ciccariello, Cocco, Benedetti & Enzo (1981). We shall prove that the second-order derivative of the so-called stick

probability function (SPF) $P_{ij}(\mathbf{r})$ relevant to the phase pair (i, j) has a first-order discontinuity at a particular value r_0 ($r_0 \neq 0$) when there exists a finite-area subset \hat{S}_i of the i th phase boundary S_i whose distance from S_j is r_0 . By that we mean that, if one considers the straight line orthogonal to S_i at a particular point, P_i , the former line is also orthogonal to S_j and it intersects the latter at a point P_j such that $|P_i P_j| = r_0$. The explicit relation between the geometrical configuration and the value of the discontinuity is worked out in the case of elliptical contact points and represents the main result of the paper.

This is organized as follows. In the next section (§ II) we review and generalize slightly the definitions of SPFs. In § III we report the general integral expressions of the lowest-order derivatives of the oriented stick probability functions (oSPF). The geometrical conditions that generate the first-order discontinuities of the oSPFs are obtained in § IV. In the next section (§ V) we prove the result mentioned above, while in the last section (§ VI) we discuss briefly the usefulness of this result for interpreting the 'anomalous' behaviour shown by the intensities scattered by some coal samples (Schiller & Méring, 1967; Perret & Ruland, 1968). More details on the mathematical derivations of some of our results are contained in two Appendices.*

II. General definitions

The main hypothesis of small-angle-scattering (SAS) theory is that the sample is conceived as made up of a suitable number (N) of phases, which are characterized by a constant electronic† density. More definitely, sets V and V_i relevant to the sample and to the i th constituting phase, respectively, are related as follows:

$$V = \bigcup_1^N V_i \quad (\text{II.1})$$

while the electronic density $n(\mathbf{r})$ of the sample can be written as

$$n(\mathbf{r}) = \sum_1^N n_i \rho_{V_i}(\mathbf{r}). \quad (\text{II.2})$$

Here $\rho_{V_i}(\mathbf{r})$, the function characteristic of set V_i , is defined as

$$\rho_{V_i}(\mathbf{r}) = \begin{cases} 1 & \text{when } \mathbf{r} \in V_i \\ 0 & \text{when } \mathbf{r} \notin V_i \end{cases} \quad (\text{II.3})$$

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† We emphasize that although we shall make explicit reference to X-ray scattering for greater concreteness, our results also hold true for neutron scattering. We shall follow closely the notation of the paper by Ciccariello *et al.* (1981), to which one should refer for details.

and n_i denotes the (bulk) electronic density of the i th phase.

The standard correlation function $\gamma(\mathbf{r})$ of the sample is defined as (Debye & Bueche, 1949)

$$\gamma(\mathbf{r}) = (\langle \eta^2 \rangle V)^{-1} \int \eta(\mathbf{r}_1) \eta(\mathbf{r}_1 + \mathbf{r}) d\mathbf{v}_1, \quad (\text{II.4})$$

where $\eta(\mathbf{r})$, the electronic density fluctuation, reads

$$\begin{aligned} \eta(\mathbf{r}) &\equiv n(\mathbf{r}) - \langle n \rangle \rho_V(\mathbf{r}) \\ &= \sum_1^N (n_i - \langle n \rangle) \rho_{V_i}(\mathbf{r}). \end{aligned} \quad (\text{II.5})$$

$\langle n \rangle$ denotes the average electronic density of the sample, which is given by

$$\langle n \rangle = \sum_1^N n_i \varphi_i, \quad (\text{II.6})$$

where $\varphi_i \equiv V_i/V$ is the volume fraction of the i th phase.

$\gamma(\mathbf{r})$ is related to the standard scattered intensity by (I.1). From (II.4) and (II.5) it can be written as

$$\gamma(\mathbf{r}) = \sum_{i,j=1}^N [(n_i - \langle n \rangle)(n_j - \langle n \rangle) / \langle \eta^2 \rangle] \mathcal{P}_{ij}(\mathbf{r}). \quad (\text{II.7})$$

Here, $\mathcal{P}_{ij}(\mathbf{r})$ is the oriented stick probability function (oSPF) relevant to the pair of phases i and j . It is defined as follows:

$$\mathcal{P}_{ij}(\mathbf{r}) = \int_{R_3} d\mathbf{v}_1 \rho_{V_i}(\mathbf{r}_1) \rho_{V_j}(\mathbf{r}_1 + \mathbf{r}) / V. \quad (\text{II.8})$$

It is easy to show that the $\mathcal{P}_{ij}(\mathbf{r})$'s obey the following conditions.

$$\mathcal{P}_{ij}(\mathbf{r}) = \mathcal{P}_{ji}(-\mathbf{r}) \geq 0 \quad (\text{II.9a})$$

$$\mathcal{P}_{ij}(0) = \varphi_i \delta_{ij} \quad (\text{II.9b})$$

$$\int_{R_3} \mathcal{P}_{ij}(\mathbf{r}) d\mathbf{v} / V = \varphi_i \varphi_j \quad (\text{II.9c})$$

$$\int_{R_3} \mathcal{P}_{i,S}(\mathbf{r}) d\mathbf{v} / V = \varphi_i \quad (\text{II.9d})$$

$$\int_{R_3} \mathcal{P}_S(\mathbf{r}) d\mathbf{v} / V = 1. \quad (\text{II.9e})$$

Here we have used the following definitions:

$$\mathcal{P}_{i,S}(\mathbf{r}) \equiv \sum_1^N \mathcal{P}_{ij}(\mathbf{r}) = \int_{R_3} \rho_{V_i}(\mathbf{r}_1) \rho_V(\mathbf{r}_1 + \mathbf{r}) d\mathbf{v}_1 / V \quad (\text{II.9f})$$

$$\mathcal{P}_S(\mathbf{r}) \equiv \sum_1^N \mathcal{P}_{i,S}(\mathbf{r}) = \int_{R_3} \rho_V(\mathbf{r}_1) \rho_V(\mathbf{r}_1 + \mathbf{r}) d\mathbf{v}_1 / V. \quad (\text{II.9g})$$

The former equations generalize well-known relations (Goodisman & Brumberger, 1971; Ciccariello *et al.*, 1981) to the case of finite and anisotropic samples. They could be useful for analysing the accuracy of the simplifying assumption that real amorphous samples can be considered infinitely large, homogeneous and isotropic. This assumption yields

the following identities:

$$\mathcal{P}_{ij}(\mathbf{r}) \equiv \mathcal{P}_{ij}(r\hat{\omega}_1) = \mathcal{P}_{ij}(r\hat{\omega}_2), \forall \hat{\omega}_1, \hat{\omega}_2 \quad (\text{II.10a})$$

$$\mathcal{P}_{iS}(\mathbf{r}) \equiv \varphi_i; \quad \mathcal{P}_S(\mathbf{r}) \equiv 1. \quad (\text{II.10b, c})$$

However, if one defines the (ij) SPF as the angular average of the corresponding oSPF,

$$P_{ij}(r) \equiv (4\pi)^{-1} \int \mathcal{P}_{ij}(r\hat{\omega}) d\hat{\omega}, \quad (\text{II.11})$$

one finds that the former assumption also implies that oSPFs and SPFs become identically equal. In that case the expression for the correlation fraction simplifies noticeably and reads

$$\gamma(r) = 1 - \sum_{i < j=1}^N (n_i - n_j)^2 P_{ij}(r) / \langle \eta^2 \rangle. \quad (\text{II.12})$$

Equations (II.7) and (II.12) show that the problem of finding the discontinuities of the correlation functions $\gamma(\mathbf{r})$ and $\gamma(r)$ is tantamount to finding those of the oSPFs and of the SPFs, respectively. However, since the SPFs are related to the oSPF by (II.11), the knowledge of the discontinuities of the latter yields that of the former. For that reason, in the next two sections we shall deal with oSPFs.

III. Integral expressions for the derivatives of the oSPFs

Similarly to the SPFs, the oSPFs can be looked at both as density probability functions (Debye *et al.*, 1957) and as volumes of some intersection sets (Porod, 1951). Since the last point of view will often be referred to in the following, we shall briefly describe it. Equation (II.8) shows that $V\mathcal{P}_{ij}(\mathbf{r})$ is the volume of the intersection of the set V_i with the set that is obtained by translating V_j by the quantity $-\mathbf{r}$. Let us denote by $T(\mathbf{r})$ the linear operator that translates the space by $-\mathbf{r}$. $T(\mathbf{r})^*$ transforms the set V_j into a new set, which will be denoted by $T(\mathbf{r})V_j$ and consequently one could rewrite (II.8) as

$$V\mathcal{P}_{ij}(\mathbf{r}) = \text{volume}\{V_i \cap [T(\mathbf{r})V_j]\}. \quad (\text{III.1})$$

This expression makes the continuity of $\mathcal{P}_{ij}(\mathbf{r})$ evident if one assumes that each set V_i is made up of a finite number of internally connected sets and each of these has a boundary that is almost everywhere regular. In other words the set of points where the boundaries have contact points and/or do not have a unique tangent plane has a null (two-dimensional) measure.†

* We recall that $T(\mathbf{r})$ is defined by the following functional mapping

$$g(\mathbf{r}_1) = [T(\mathbf{r})f](\mathbf{r}_1) \equiv f(\mathbf{r}_1 + \mathbf{r}),$$

where f is an arbitrary function defined on R_3 .

† This assumption apparently does not look very strong, particularly as far as the volume of the sample is finite. However, when the latter goes to infinity, the former hypothesis could fail. Actually it should fail if one believes in fractal dimensions (Bale & Schmidt, 1984).

Once one has chosen this rather conservative point of view, one can easily obtain some useful integral expressions of the oSPF derivatives.

III.1. First-order derivatives

The use of Dirac's three-dimensional δ function allows us to rewrite (II.8) as

$$\mathcal{P}_{ij}(\mathbf{r}) = \int_{V_i} dv_i \int_{V_j} dv_j \delta(\mathbf{r}_i + \mathbf{r} - \mathbf{r}_j) / V. \quad (\text{III.2})$$

By applying to both sides of (III.2) the differential operator $(\hat{\nu} \cdot \nabla)$, where $\hat{\nu}$ is an arbitrary unit vector, and by using Gauss' theorem one gets

$$\begin{aligned} (\hat{\nu} \cdot \nabla)\mathcal{P}_{ij}(\mathbf{r}) &= \int_{S_i} (d\mathbf{S}_i \cdot \hat{\nu}) \rho_{V_i}(\mathbf{r}_i + \mathbf{r}) / V \\ &= - \int_{S_j} (d\mathbf{S}_j \cdot \hat{\nu}) \rho_{V_j}(\mathbf{r}_j - \mathbf{r}) / V. \end{aligned} \quad (\text{III.3})$$

In the former integral, \mathbf{r}_i denotes the position vector of the infinitesimal subset $d\mathbf{S}_i$ of S_i , the boundary of the i th phase, while the direction of $d\mathbf{S}_i$ is taken orthogonal to $d\mathbf{S}_i$ and (locally) external to V_i . (The meaning of the symbols in the latter integral is quite similar.)

The hypothesis on the regularity of phase boundaries makes (III.3) mathematically meaningful. Equation (III.3) represents the sought integral expression of the first-order derivative of oSPFs. Besides, from (III.3) it appears evident that the $\mathcal{P}_{ij}(\mathbf{r})$ first-order derivative represents the area of the projection, on a plane perpendicular to $\hat{\nu}$, of the S_i subset that lies inside the set $T(\mathbf{r})V_j$.

III.2. Second-order derivative

By applying $(\hat{\nu} \cdot \nabla)$ to both sides of (III.2) and by performing the same manipulations that led us to (III.3), one gets the following expression for the second-order derivative along two arbitrary directions $\hat{\mu}$ and $\hat{\nu}$:

$$\begin{aligned} (\hat{\mu} \cdot \nabla)(\hat{\nu} \cdot \nabla)\mathcal{P}_{ij}(\mathbf{r}) &= - \int_{S_i} (d\mathbf{S}_i \cdot \hat{\mu}) \int_{S_j} (d\mathbf{S}_j \cdot \hat{\nu}) \delta(\mathbf{r}_i + \mathbf{r} - \mathbf{r}_j) / V \\ &= - \int_{S_i} (d\mathbf{S}_i \cdot \hat{\nu}) \int_{S_j} (d\mathbf{S}_j \cdot \hat{\mu}) \delta(\mathbf{r}_i + \mathbf{r} - \mathbf{r}_j) / V. \end{aligned} \quad (\text{III.4})$$

The presence of the δ function implies that (III.4) can be expressed as an integral of a suitable function on the geometrical variety $S_i \cap [T(\mathbf{r})S_j]$ or equivalently on the set $S_j \cap [T(-\mathbf{r})S_i]$. In general these varieties, being the intersection of two surfaces, will correspond to curves in a three-dimensional space, although one cannot *a priori* exclude the most complicated case that the former intersection sets are made up of isolated contact points, of curves and of surfaces. Leaving the discussion of the general case

to § IV, we shall now explicitly show how (III.4) can be converted into a one-dimensional integral when the set $S_i \cap [T(\mathbf{r})S_j]$ is a curve.

Let

$$\mathbf{r}_i = \mathbf{r}_i(u_i, v_i) \quad (III.5a)$$

$$\mathbf{r}_j = \mathbf{r}_j(u_j, v_j) \quad (III.5b)$$

be the parametric equations of surfaces S_i and S_j , respectively. The δ function requires that

$$\mathbf{R}(u_i, u_j; v_i, v_j; \mathbf{r}) \equiv \mathbf{r}_i(u_i; v_i) + \mathbf{r} - \mathbf{r}_j(u_j; v_j) = 0. \quad (III.6)$$

Let, for definiteness,

$$\begin{aligned} u_i &= \hat{u}_i(v_i, \mathbf{r}) \\ u_j &= \hat{u}_j(v_i, \mathbf{r}) \\ v_j &= \hat{v}_j(v_i, \mathbf{r}) \end{aligned} \quad (III.7)$$

be the solutions of (III.6) and let

$$J(v_i, \mathbf{r}) \equiv |\partial(R_x, R_y, R_z)/\partial(u_i, u_j, v_j)| \quad (III.8)$$

denote the absolute value of the Jacobian. The following formulae of differential geometry (e.g. Smirnov, 1964):

$$dS_i \equiv dS_i \hat{\sigma}_i \quad (III.9a)$$

$$\hat{\sigma}_i = \left(\frac{\partial \mathbf{r}_i}{\partial u_i} \times \frac{\partial \mathbf{r}_i}{\partial v_i} \right) / (E_i G_i - F_i^2)^{1/2} \quad (III.9b)^*$$

$$dS_i = (E_i G_i - F_i^2)^{1/2} du_i dv_i \quad (III.9c)$$

$$E_i \equiv \frac{\partial \mathbf{r}_i}{\partial u_i} \cdot \frac{\partial \mathbf{r}_i}{\partial u_i}; \quad F_i \equiv \frac{\partial \mathbf{r}_i}{\partial u_i} \cdot \frac{\partial \mathbf{r}_i}{\partial v_i}; \quad G_i \equiv \frac{\partial \mathbf{r}_i}{\partial v_i} \cdot \frac{\partial \mathbf{r}_i}{\partial v_i}; \quad (III.9d)$$

allow us to express integral (III.6) in terms of variables $\{u, v\}$. Then the use of the identity

$$\delta(\mathbf{R}) = J^{-1} \delta(u_i - \hat{u}_i) \delta(u_j - \hat{u}_j) \delta(v_j - \hat{v}_j) \quad (III.10)$$

makes the integration with respect to u_i, u_j and v_j immediate. One finds

$$\begin{aligned} &(\hat{\mu} \cdot \nabla)(\hat{v} \cdot \nabla) \mathcal{P}_{ij}(\mathbf{r}) \\ &= -V^{-1} \int dv_i \left\{ \left(\hat{\mu} \cdot \frac{\partial \mathbf{r}_i}{\partial u_i} \times \frac{\partial \mathbf{r}_i}{\partial v_i} \right) \right. \\ &\quad \left. \times \left(\hat{v} \cdot \frac{\partial \mathbf{r}_j}{\partial u_j} \times \frac{\partial \mathbf{r}_j}{\partial v_j} \right) / J \right\}. \end{aligned} \quad (III.11)$$

The vertical bar reminds us that the integrand must be evaluated by using solutions (III.7). Equation (III.11) represents the looked for expression. In fact we can choose v_i as the curvilinear coordinate of a point belonging to the curve $S_i \cap [T(\mathbf{r})S_j]$. Consequently, (III.11) expresses the second-order deriva-

tive of $P_{ij}(\mathbf{r})$ as an integral of a known function, i.e. the expression inside curly brackets, along the former curve.

IV. Geometrical configurations yielding first-order discontinuities in the derivatives of oSFPs

It has already been emphasized that oSPFs are continuous functions since the phase boundaries have been assumed to be almost everywhere regular. Their derivatives however can be discontinuous as will appear clear from the following discussion. Our attention will focus on first-order discontinuities since they determine the coefficients of the leading terms in the asymptotic expansion of $i(\mathbf{h})$ at large h . The first-order discontinuity of a function $f(\mathbf{r})$ will be defined as

$$\lim_{\varepsilon \rightarrow 0^+} f(\mathbf{r} + \varepsilon \hat{\omega}) - \lim_{\varepsilon \rightarrow 0^+} f(\mathbf{r} - \varepsilon \hat{\omega}). \quad (IV.1)$$

This definition makes the dependence of the discontinuity value on the direction $\hat{\omega}$, along which one approaches to the discontinuity point, evident.

IV.1. First-order derivative

If we put

$$S_{ij}(\mathbf{r}) \equiv S_i \cap [T(\mathbf{r})V_j] \quad (IV.2)$$

(III.3) can be written as

$$(\hat{v} \cdot \nabla) \mathcal{P}_{ij}(\mathbf{r}) = \int_{s_{ij}(\mathbf{r})} dS_i \cdot \hat{v} / V. \quad (IV.3)$$

This equation shows very clearly that discontinuities can arise only from those of $S_{ij}(\mathbf{r})$. On the other hand, the latter can exist only when the set obtained by translating S_j by $-\mathbf{r}$ superposes on an S_i subset having a non-null area. More explicitly

$$s_{ij}(\mathbf{r}) \equiv S_i \cap [T(\mathbf{r})S_j] \quad (IV.4)$$

must exist as a two-dimensional variety. Let us define now the two-limit subsets

$$s_{ij}^{\pm}(\hat{\omega}, \mathbf{r}) \equiv \lim_{\varepsilon \rightarrow 0^+} s_{ij}(\mathbf{r}) \cap [T(\mathbf{r} \pm \varepsilon \hat{\omega})V_j]. \quad (IV.5)$$

Clearly the regularity of phase boundaries yields the following properties

$$s_{ij}^+(\hat{\omega}, \mathbf{r}) \cap s_{ij}^-(\hat{\omega}, \mathbf{r}) = \Phi \quad (IV.6a)$$

$$s_{ij}^+(\hat{\omega}, \mathbf{r}) \cup s_{ij}^-(\hat{\omega}, \mathbf{r}) \subseteq s_{ij}(\mathbf{r}), \quad (IV.6b)$$

where Φ is a set having a null two-dimensional measure. By combining (IV.5), (IV.1) and (IV.3), the expression for the first-order discontinuity $\Delta_{ij}^{(1)}(\hat{v}, \hat{\omega}, \mathbf{r})$ of the (ij) oSPF follows immediately:

$$V \Delta_{ij}^{(1)}(\hat{v}, \hat{\omega}, \mathbf{r}) = \int_{s_{ij}^+(\hat{\omega}, \mathbf{r})} \hat{v} \cdot dS_i - \int_{s_{ij}^-(\hat{\omega}, \mathbf{r})} \hat{v} \cdot dS_i. \quad (IV.7)$$

Thus the existence of a first-order discontinuity is related to the existence of the set $s_{ij}(\mathbf{r})$. The value of the discontinuity will depend on $\hat{\omega}$ and \hat{v} as is shown by (IV.7). Fig. 1 illustrates a typical configuration.

* It is here understood that the labelling of variables $\{u\}$ and $\{v\}$ has been performed in such a way that the orientation of $\hat{\sigma}_i$ coincides with the one defined below (III.3).

One has two subsets in the r space where $(\hat{v}, \hat{V})\mathcal{P}_{ij}(\mathbf{r})$ has first-order discontinuities. The first subset is made up of the r values, which yield (partial) 'translational overlapping' of the half-circular cylindrical surface S_1 with the equally shaped surface S'_1 . This subset is made up of the point P having coordinates $(r_1, 0, z)$ with $-H \leq z \leq H$ and thus it is a linear subset. The second subset is originated by the (partial) 'translational overlapping' of planar surfaces S_2 and S'_2 . This subset is a planar one since the translation r values, yielding a superposition, are $\{r_2, y, z\}$ with $-L \leq y \leq L$ and $-H \leq z \leq H$.

IV.2. Second-order derivative

By a subsequent differentiation of (IV.3), the discontinuity found will give rise to a (one-dimensional) δ -like contribution. It will appear clear later that these contributions do not give rise to first-order discontinuities in the derivatives of the correlation function of amorphous samples. These discontinuities in fact arise from one of the two possible kinds of genuine first-order discontinuities of the second-order derivatives of oSPFs.

From (III.4) and (III.11) it appears clear that the two geometrical configurations that can originate a first-order discontinuity are: (i) one of the boundaries, say S_j , has a sharp edge $e_{ij}(\mathbf{r})$, which, after being translated by $-\mathbf{r}$, superposes itself on S_i ; (iii) S_j , once it has been translated by $-\mathbf{r}$, is tangent to S_i at a point of the latter and moreover the tangent plane is orthogonal to \mathbf{r} .

We stress that in both cases, after the translation, one obtains the same geometrical configurations that are responsible for a non-null second-order derivative value of SPF's at the origin (Ciccariello *et al.*, 1981; Ciccariello & Benedetti, 1982, 1985a).

Let us first discuss case (i).

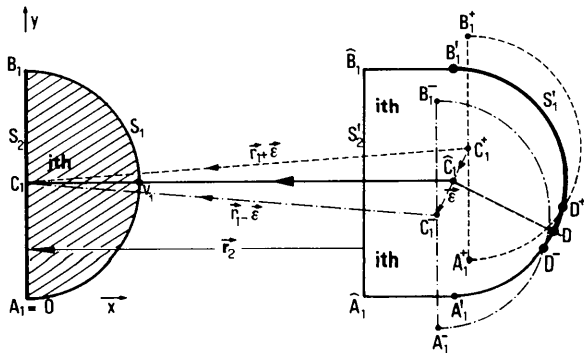


Fig. 1. The continuous curves $A_1B_1V_1$ and $\hat{A}_1\hat{B}_1\hat{V}_1A'_1$ represent the normal sections of two cylindrical particles made up of different phases but having the same height, the same curvature radius, and their lower bases on the (xy) plane. $B_1^+D_1^+A_1^+$ and $B_1^-D_1^-A_1^-$ represent the configurations of the first particle once this has been translated by $-(\mathbf{r}_1 + \epsilon\hat{\omega})$ and $-(\mathbf{r}_1 - \epsilon\hat{\omega})$. B_1DA_1 , $B_1^+D_1^+A_1^+$ and $DD^-A_1^-$ represent $s_{ij}(\mathbf{r}_1)$, $s_{ij}^+(\mathbf{r}_1, \hat{\omega})$ and $s_{ij}^-(\mathbf{r}_1, \hat{\omega})$, respectively. (D denotes the intersection of the straight line orthogonal to $\hat{\omega}$ at C_1 with the half-circle.)

The presence of the edge $e_{ij}(\mathbf{r})$ allows us to look at S_j as made up of two smooth surfaces: $S_{j,1}$ and $S_{j,2}$, which meet along $e_{ij}(\mathbf{r})$. This fact, on the one hand, implies that (III.11) is ambiguous since one does not know whether the parametric equation of $S_{j,1}$ or that of $S_{j,2}$ must be used when one performs the integral along $e_{ij}(\mathbf{r})$. On the other hand, it shows that, by letting \mathbf{r} change infinitesimally, the new intersection curve $S_i \cap [T(\mathbf{r} + \epsilon\hat{\omega})S_j]$ will be partly on $S_{j,1}$ and partly on $S_{j,2}$, but, eventually, for sets having zero length. (See Fig. 2, which shows a typical configuration.) The limiting integral value will depend of course on the chosen $\hat{\omega}$ direction as we let ϵ go to zero. In this way the origin of the discontinuity is explained and one can obtain the integral expression of the discontinuity. To this end let us define the limiting one-dimensional sets

$$e_{ij,1}^\pm(\hat{\omega}, \mathbf{r}) \equiv e_{ij}(\mathbf{r}) \cap (\lim_{\epsilon \rightarrow 0} S_i \cap [T(\mathbf{r} \pm \epsilon\hat{\omega})S_{j,1}]). \quad (IV.8)$$

In a quite similar way one defines $e_{ij,2}^\pm(\hat{\omega}, \mathbf{r})$. If we denote by $F_1(v)$ and by $F_2(v)$ the integrand of (III.11), once we have used there the parametric equations of $S_{j,1}$ or of $S_{j,2}$, respectively, the sought for discontinuity value $\Delta_{ij}^{(2)}(\dots)$ reads

$$\begin{aligned} \Delta_{ij}^{(2)}(\hat{\mu}, \hat{v}, \hat{\omega}, \mathbf{r}) &= -V^{-1} \left\{ \int_{e_{ij,1}^+(\hat{\omega}, \mathbf{r})} dv F_1(v) \right. \\ &\quad \left. - \int_{e_{ij,1}^-(\hat{\omega}, \mathbf{r})} dv F_1(v) \right\} + [1 \leftrightarrow 2]. \quad (IV.9) \end{aligned}$$

Now we turn to the analysis of case (ii).

After having translated S_j , the geometrical configuration of S_i and of $T(\mathbf{r})S_j$ is essentially that of the case considered by Ciccariello & Benedetti (1982). The only differences are that now we do not have to

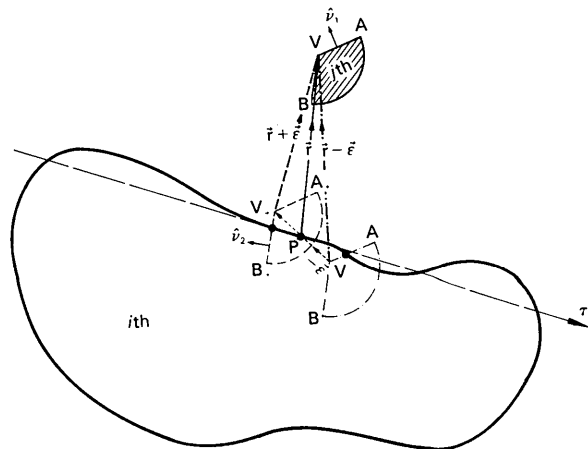


Fig. 2. The continuous lines represent the normal sections of two cylindrical particles. V denotes the sharp edge, which after translation by $-\mathbf{r}$, is superimposed on the i th particle boundary at P . The figure shows that in (III.5) one must use the parametric equation of surface VB or VA depending on whether the limiting configuration is reached along V_+P or V_-P , respectively.

perform the $\hat{\omega}$ integration and that we must pay some attention to the nature of the contact point P_0 . This can correctly be called parabolic when the tangency condition is of higher order than first. In the other cases, we must distinguish the two situations: (i) $T(\mathbf{r})S_j$ lies completely inside or completely outside V_i in a sufficiently small neighbourhood of P_0 ; or (ii) $T(\mathbf{r})S_j$ lies partly inside and partly outside V_i . In the two cases, P_0 is called elliptic or hyperbolic, respectively. Let us choose the origin of a Cartesian system of axes at the contact point, the z axis parallel to \mathbf{r} , and let us denote by $z = f_i(x, y)$ and by $z = f_j(x, y)$ the parametric equations of the two surfaces S_i and $T(\mathbf{r})S_j$, respectively. The equation

$$z = F(x, y) = f_j(x, y) - f_i(x, y)$$

will represent the parametric equation of the surface Σ defined as 'the difference' between $T(\mathbf{r})S_j$ and S_i . By following now the procedure of the paper referred to above one can show that each elliptic contact point yields a first-order discontinuity given by

$$\begin{aligned} \Delta_{ij}^{(2)}(\hat{\mu}, \hat{\nu}, \hat{\omega}, \mathbf{r}) \\ = -2\pi \text{sign}(\mathbf{r} \cdot \hat{\omega}) \text{sign}(\Sigma_{ij})(\hat{\mu} \cdot \hat{\sigma}_i) \\ \times (\hat{\nu} \cdot \hat{\sigma}_j) / H^{1/2}(\mathbf{r}) V. \end{aligned} \quad (\text{IV.10})$$

Here $H(\mathbf{r})$ denotes the Hessian of $F(x, y)$ at origin, while $\text{sign}(\Sigma_{ij})$, $\hat{\sigma}_i$, $\hat{\sigma}_j$ denotes the sign of the surface Σ , *i.e.* of $F(x, y)$, next to the origin, and the unit vectors orthogonal, at the contact point, to S_i and S_j , respectively.

When the contact point is a hyperbolic point of Σ , the limits of the second-order derivative of $P_{ij}(\mathbf{r} + \varepsilon\hat{\omega})$, as $\varepsilon \rightarrow 0^\pm$, are no more finite, although the Cauchy first-order discontinuity is still finite. The behaviour in the case of a parabolic point is more involved. We refer to Appendix A* for a more detailed discussion of all these cases.

V. Discontinuities of SPF derivatives in the case of amorphous samples

The oSPFs relevant to macroscopically isotropic and homogeneous samples coincide with their angular averages, see (II.11). Therefore we shall now analyse the continuity property of the latter. The continuity of $P_{ij}(r)$ follows from that of $\mathcal{P}_{ij}(\mathbf{r})$. It is immediately shown from (II.11) that the n th-order derivative of $P_{ij}(r)$ can be written as

$$d^n P_{ij}(r) / dr^n = (4\pi)^{-1} \int (\hat{\omega} \cdot \nabla)^n \mathcal{P}_{ij}(r\hat{\omega}) d\hat{\omega}. \quad (\text{V.1})$$

In this way the discontinuities of the derivatives of SPFs can be immediately found by performing the angular averages of the discontinuities of the corresponding oSPF derivatives.

Let us first discuss the case of the first-order derivatives. According to our former analysis, the first-order

derivative of the (i, j) oSPF can have a first-order discontinuity only when $S_i \cap [T(r\hat{\omega})S_j]$ has a finite area. From (V.1), with $n=1$, one concludes that the corresponding (ij) SPF derivative will have a discontinuity at the point r only when the former condition is satisfied on a set of $\hat{\omega}$ directions that has a non-null measure. However, an infinitesimally slight rotation of \mathbf{r} , but for the case $r=0$, is such that the new intersection set $S_i \cap \{T[r(\hat{\omega} + \delta\hat{\omega})]S_j\}$ is generally* a line. Thus one concludes that $P_{ij}(r)$ cannot have first-order discontinuities when $r \neq 0$.

We turn now to the analysis of second-order derivatives. Equation (V.1) with $n=2$ and the results of § IV.3 allow us to conclude that first-order discontinuities can be present in $\ddot{P}_{ij}(r)$, with $r \neq 0$, only when we have 'translational sharp edge' and/or 'translational contact points' for a set of translations $r\hat{\omega}$, such that the measure of the corresponding $\hat{\omega}$ set is non-null. Once more the standard shape of boundaries rules out the possibility that 'translational sharp edges' could yield a finite contribution. By contrast, one can have translational contact points associated to a set of translations $r\hat{\omega}$ such that the measure of the $\hat{\omega}$ set is finite. A well-known example is the case of a spherical particle. Let R denote its radius. It is evident that, by translating this particle by $2R\hat{\omega}$, for any $\hat{\omega}$ the translated particle will be tangent to the initial sphere. Besides, the tangent plane is orthogonal to $\hat{\omega}$ and the contact point is elliptical for the corresponding 'difference surface'. In order to evaluate the discontinuity of $\ddot{P}_{11}(r)$ ('1' denotes the phase inside the spherical particle that coincides with the sample) one must simply average $\Delta_{11}^{(2)}(\hat{\omega}, \hat{\omega}, \hat{\omega}, 2R\hat{\omega})$, given by (IV.10) over all possible directions. We recall now that the Hessian of the surface 'difference' of two spheres in contact and having radii R_1 and R_2 , is equal to $(R_2^{-1} - R_1^{-1})^2$ or to $(R_2^{-1} + R_1^{-1})^2$ depending on whether the sphere centres lie on the same side or on the opposite sides of the contact point, respectively. By substituting the second value in (IV.10) one gets

$$\begin{aligned} \Delta_{11}^{(2)}(2R) &\equiv \lim_{\varepsilon \rightarrow 0} \ddot{P}_{11}(2R + \varepsilon) - \lim_{\varepsilon \rightarrow 0} \ddot{P}_{11}(2R - \varepsilon) \\ &= -3/4R^2. \end{aligned} \quad (\text{V.2})$$

This result can be immediately checked by evaluating the second-order derivative of the correlation function relevant to a spherical particle (Guinier & Fournet, 1955).

It must be emphasized that the constraint on the nature of the contact point can be considerably

* Of course we are excluding the fact that the boundary of each phase has such a folded and winding structure that one can have overlapping on a finite set of $\hat{\omega}$ directions when we let the volume of the sample become infinitely large. Once more one can confidently expect that this phenomenon could take place in samples which become 'fractals' as their size becomes infinitely large.

* See deposition footnote.

weakened. To this aim, we write (V.1), when $n=2$, in a more explicit way by using (III.4):

$$\begin{aligned} \ddot{P}_{ij}(r) = & -(1/4\pi V) \int d\hat{\omega} \int_{S_i} (dS_i \cdot \hat{\omega}) \int_{S_j} (dS_j \cdot \hat{\omega}) \\ & \times \delta(\mathbf{r}_i + r\hat{\omega} - \mathbf{r}_j). \end{aligned} \quad (\text{V.3})$$

We denote by $\hat{\Omega}(r)$ the subset of $\hat{\omega}$'s such that the translations of S_j by $-r\hat{\omega}$ yield a contact point with S_i . The symmetry of (V.3) allows us to think that we have a spherical surface $r\Omega$ and that, after S_j has been translated by the quantity $-\mathbf{r}_j = \mathbf{r} - \mathbf{r}_i$, the translated set $T(\mathbf{r}_i)S_j$ has a contact point with the spherical surface $r\Omega$. In other words we are interchanging the role between \mathbf{r} and \mathbf{r}_i . In this way we first analyse the \mathbf{r}_i -translation contact points between S_j and the spherical surface $r\Omega$ and subsequently we perform the average over S_i . By so doing it can happen that the translational contact point between $r\Omega$ and S_j be elliptical and thus we can safely apply (A.16) with the appropriate changes. Before discussing an interesting example let us write down our general result. To this aim we introduce a new index, o , which will be appended to all the quantities that refer to the aforesaid spherical surface having radius equal to r . Then the general integral expression of the first-order discontinuity, generated by the fact that we have a finite area subset of S_i that is at an 'orthogonally translated distance r^* ' from S_j , is given by

$$\begin{aligned} \Delta \ddot{P}_{ij}(r) \equiv \Delta_{ij}^{(2)}(r) \\ = -(1/2Vr^2) \int_{\hat{S}_i} dS_i \text{sign} \left[\sum_{mn} (\hat{\sigma}_i r) \right] (\hat{\sigma}_i \cdot \hat{\sigma}_m) \\ \times (\hat{\sigma}_i \cdot \hat{\sigma}_n) / H_{mn}^{1/2}(\hat{\sigma}_i r). \end{aligned} \quad (\text{V.4})$$

In this equation (l, m, n) is one of the particular choices of indices (i, j, o) such that the translational contact point between S_m and S_n is an elliptical one. The integral is performed over that subset \hat{S}_i of the remaining surface S_i , which ensures that one has an r -translational contact point.

An interesting application of this result is that of a sample having a cubic shape of size L . Clearly when one shifts the cube by L along the direction of one edge, two faces will superpose. Thus $\ddot{P}_{11}(r)$ could have a first-order discontinuity only at $r=L$. However, (V.4) cannot be used if one considers the choice $(l, m, n) = (0, 1, 1)$: the $\hat{\Omega}$ set reduces to only one direction whilst the integrand does not exist, since $H(L) = 0$. However the choice $(l, m, n) = (1, 0, 1)$ is quite meaningful. Indeed, the contact point between the sphere, having radius L , and the face of the cube, opposite to the face where the sphere's centre lies, is elliptical. By recalling that a planar set has only one

curvature radius that is equal to $+\infty$, we can apply the former expression for the Hessian. By substituting in (V.4) one gets

$$\Delta_{11}^{(2)}(L) = -(1/2L^3L^2)[-6L^2/(1/L)] = 3/L^2. \quad (\text{V.5})$$

The correlation function of a cube has been recently evaluated by Goodisman (1980). If one measures with a rule the height of the discontinuity shown in the figure of that paper at the point $(r/L) = 1$, one finds results (V.5).*

Equation (V.4) represents the main result of this paper. It shows that the discontinuities in the second-order derivative of an SPF can arise at a point r only when a non-null subset of one phase boundary superimposes on a second phase boundary once it has been orthogonally translated by r .

It should be underlined that the particles are no longer required to have a strictly convex shape and that the boundaries we have always spoken of do not refer to a single particle but to a phase.

The only constraint required for the validity of (V.4) is that contact points are elliptical for at least two of the three surfaces involved. Although this constraint could be physically violated in some cases, it does not appear unreasonable to think that the violation takes place only in sets having a null measure.

The last remark deals with the sign of the discontinuity value. Equation (V.4) shows clearly that the sign, through the difference surface Σ , depends on the relative shape of S_i and S_j . In fact, in the cases of a sphere and of a cube we have found that the discontinuity turns out negative (V.2) and positive (V.5), respectively. A further application of (V.4) is given by the case of a particle having the shape of a spherical shell whose radii are R_1 and R_2 ($R_1 < R_2$). This particle is clearly a non-convex one. The discontinuities of $\ddot{P}_{11}(r)$ will be located at $r = 2R_1$, $R_2 - R_1$, $R_2 + R_1$ and $2R_2$. The corresponding values can be easily found from (V.4). They are $-2\pi/V(2/R_1)$, $4\pi/V(1/R_1 - 1/R_2)$, $4\pi/V(1/R_1 + 1/R_2)$, $-2\pi/V(2/R_2)$, where $V \equiv 4\pi(R_2^3 - R_1^3)/3$.

* Actually the check can be carried through exactly by evaluating the second-order derivatives of (5) and (6) of the above-quoted paper at the point $r=L$. One finds: $\ddot{P}_{11}(L^+) = 3/L^2 + 5/2\pi L^2$ and $\ddot{P}_{11}(L^-) = 5/2\pi L^2$. The difference in these results is equal to (V.5). It is also interesting to note that the second-order derivative of the SPF relevant to a cubic particle cannot have further first-order discontinuities, since the condition of the 'finite-area overlapping consequent to orthogonal translations' is realized only for a translation equal to the edge of the cube. By contrast, the figure referred to above shows a further spike at $r = 2^{1/2}L$. This spike is probably an artifact due to rounding-off errors. In fact one can check that this discontinuity is not present, either by evaluating the second-order derivative of the difference of integral expression (7) and (6) as $r \rightarrow 2^{1/2}L^+$ [note that the quantity defined by (6) is C^∞ around $2^{1/2}L$], or by evaluating the derivatives of (8) and (6). The first route yields a null value, while the second one yields $\ddot{P}_{11}(2^{1/2}L^+) = (3/2)2^{1/2} - 17/4\pi 2^{1/2}/L^2 = \ddot{P}_{11}(2^{1/2}L^-)$.

* By this expression we mean that any of the straight lines going orthogonally to S_i from each point of the former subset will normally intersect S_j after a distance r .

Finally we recall that the results for the case $r=0$ are already known. For completeness however their discussion is carried through in Appendix B.*

VI. Concluding remarks

We would like to conclude this paper by showing the usefulness of the former results for achieving a better understanding of the apparent violation of the Porod-Debye relation.

On the one hand the discussion of the previous sections has shown that (I.3) represents the right asymptotic expansion of the scattered intensity *provided* one assumes that the phase boundaries are smooth except for null sets. On the other hand, (I.3) shows that $h^4 i(h)$ cannot be constant in the asymptotic region only because it can contain oscillatory contributions. These are related to the presence of 'parallel equidistant surfaces' and, moreover, the distance δ_i between the latter determines the 'oscillatory frequency' of the cosine factor in the h space.

The asymptotic h region for SAXS experiments lies in the range $0.05\text{--}0.5 \text{ \AA}^{-1}$. Many reported graphs of $h^4 i(h)$ show more than one oscillation in this region with respect to the Porod-Debye horizontal asymptotic although the amplitudes are generally so small to be considered as experimental uncertainties. However, one cannot exclude that, in more favourable cases, by using (I.3) one can estimate the area of the parallel equidistant surfaces and their relative distance. A more interesting application of (I.3) deals with the so-called violation of the Porod law. This phenomenon consists in the fact that it is necessary to consider a dependence on h for a satisfactory fit of $h^4 i(h)$ in the asymptotic region. Usually one assumes that $h^4 i(h)$ behaves as $A + Bh^2$, where A and B are suitable numerical coefficients (Schiller & Méring, 1967). This fact indicates that experimentally one does not observe a complete large oscillation in $h^4 i(h)$. Consequently δ must have such a value that $h\delta$ does not change appreciably (say less than π) in the asymptotic region. In this way $\delta \approx \pi/2h_{\max} \lesssim 5 \text{ \AA}$. This value is so small that it cannot be related to the typical dimensions of particles that make up our samples. In a very interesting paper, Ruland (1971) has shown that the aforesaid linear h^2 behaviour of $h^4 i(h)$ can be obtained provided one assumes that the electronic density changes smoothly around each interface as we go from one phase to the other. This fact suggests that a more satisfactory idealization of the sample can be realized only if we assume that between phases '1' and '2' we have a further phase '3', whose electronic density is half-way between the bulk ones. In this way we substitute interface S_{12} for

two interfaces S_{13} and S_{23} (see Fig. 3). These are constructed in the following way: for each point Q of S_{12} one considers the straight line l orthogonal to S_{12} . On each side of l we consider the two points Q_1 and Q_2 , which are far away ($\delta/2$) from Q . But for very small sets, S_{13} and S_{23} will be made up of the points Q_1 and Q_2 , respectively. By this construction, S_{13} and S_{23} will be equidistantly parallel and thus they will contribute a term proportional to $\cos(h\delta)$ in the asymptotic expansion of $h^4 i(h)$.

One can now show that the resulting coefficient in front of $\cos(h\delta)$ turns out positive (Ciccariello & Benedetti, 1985b). Consequently by expanding $\cos(h\delta)$ up to terms $o(h^2)$ one finds a negative deviation from the Porod law.

Positive deviations are produced by the fluctuations of the electronic density inside the particles of the sample. These fluctuations are present when the sample has a certain degree of crystallinity (Ruland, 1971). In this case each particle will be more accurately described if it is seen as an ordered sequence of quasi-parallelepipedic regions with two electronic densities. The resulting parallel equidistant interfaces will produce oscillatory deviations. That relevant to the smallest distance is the most important one and yields a positive deviation. Thus, by combining these

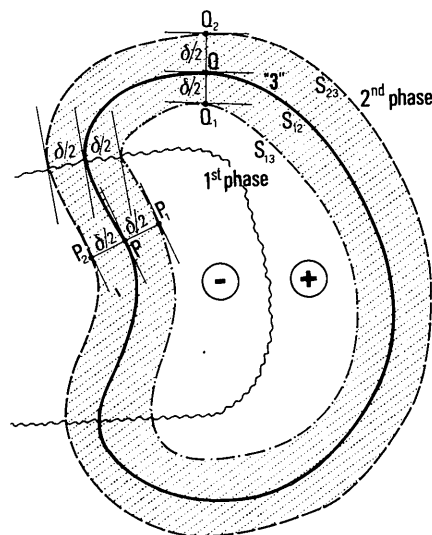


Fig. 3. The figure shows how one can go from a two-phase description to a three-phase one. The former corresponds to assuming that the electronic density is n_1 inside the continuous line and n_2 outside. The latter assumes that in the grey region the electronic density is n_3 with $n_2 < n_3 < n_1$. The new phase has a thickness δ and its boundaries S_{13} and S_{23} are obtained as the envelopes of points P_1, Q_1, \dots and P_2, Q_2, \dots respectively. We note that $P_1 P_2$ is orthogonal to S_{12} at P and that $P_1 P = P P_2 = \delta/2$. For any direction $\hat{\omega}$, the shift of S_{13} by $\delta \hat{\omega}$ will yield a contact with S_{23} . However the sign of the 'difference surface', for the $\hat{\omega}$ directions relevant to region (-) (i.e. the concave part of the boundary), is equal to that of region (+).

* See deposition footnote.

two effects, one ought to succeed in reproducing scattered intensities.*

I am grateful to Dr A. Benedetti for friendly discussions.

* A quantitative analysis of the intensities scattered by some carbon samples is now under way (Ciccariello & Benedetti, 1985b). One compares the goodness of the fits obtained by parameterizing $i(h)$ either according to (1.3) or to Bale & Schmidt (1984), i.e. $Ah^{-\alpha} + B$. (Actually, in the first case, further changes are required if the intensities refer to slit-defined beams.) Our preliminary results, which refer to the intensities reported in Fig. 1 by Perret & Ruland (1968), show no significant differences in the two cases.

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Relative Absorption Correction for Rotation Film Data

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Abstract

An improved method of implementing the absorption correction procedure of Stuart & Walker [*Acta Cryst.* (1979), **A35**, 925–933] is presented. This method scales measured reflections to a partial reference data set of corrected intensities by determining, for each crystal, a transmission surface representing the relative transmission as a function of secondary beam directions. By reformulating the observational equations and by introducing eigenvalue filtering of the least-squares normal equations, the problems of correlation between parameters defining the transmission surface are reduced.

Introduction

Absorption effects can create serious problems in macromolecular crystallography especially with the method of isomorphous replacement, which depends on accurate determination of small intensity differences between reflections recorded from different crystals. A method has been described (Stuart & Walker, 1979; Walker & Stuart, 1983) for dealing with this source of systematic error. The method depends upon

having a reference data set that has been previously corrected for absorption effects and to which the uncorrected measurements are to be scaled, that is

$$I_{\text{ref}}^i = T_{ps} I_{\text{raw}}^i, \quad (1)$$

where I_{ref}^i is the absorption-corrected intensity of the i th reflection, I_{raw}^i is the uncorrected measurement, and T_{ps} is the transmission factor parameterized by the primary and secondary beam directions \mathbf{p} and \mathbf{s} .

In principle, the transmission surface T_{ps} can be determined if a reasonably well distributed set of I_{ref}^i is available. This reference data set ideally consists of data that have been corrected by an empirical method (e.g. Kopfmann & Huber, 1968; North, Phillips & Mathews, 1968), such as partial diffractometer data, which includes a uniformly distributed sample of strong reflections throughout reciprocal space. Alternatively, heavy-atom-derivative data may be scaled to native data, or calculated intensities can be used (Walker & Stuart, 1983).

In this paper we extend the usefulness of the original method and make its application more straightforward. These improvements deal solely with the solution of the least-squares equations and not with any fundamental assumptions of the approach.