

(i) Of the three *MULTAN80* procedures, procedure III is found to be the best in one out of nine cases for the determination of k and in one out of nine cases for the determination of B . It is interesting to note that procedure I turns out to be preferable to procedure III in three out of nine cases for the determination of k and two out of nine cases for the determination of B .

(ii) The new techniques are found to lead to significantly better values of k and B than *MULTAN80* procedures in eight out of nine cases. Even in the rare situations where *MULTAN80* values are better, the new techniques are only slightly inferior. Thus, it appears that the new techniques could be used profitably.

(iii) To obtain an overall idea, the global average values of the percentage-error magnitudes in the estimated values of k and B for the various crystals are also given in Table 4. These also show that the new techniques are in general preferable to the *MULTAN80* procedures.

(iv) It may incidentally be noted that all ten new techniques and the three *MULTAN80* procedures underestimate the value of B in most cases. Furthermore, the new techniques overestimate the values of k in most cases while the *MULTAN80* procedures lead to overestimated values in all the cases.

7. Concluding remarks

From the above considerations it appears that the \bar{X} -data method could be used profitably in practice. The new procedure is likely to be particularly useful in the field of protein crystallography where one has access to intensity data from crystals of homologous proteins. However, further work needs to be carried out on the data from actual protein crystals to confirm this conclusion.

One can also employ the maximum-entropy principle to tackle the present problem instead of the procedures discussed in this paper. Work in this direction is in progress.

The authors thank Dr M. N. Ponnuswamy and Mr S. Eswaramoorthy for providing raw intensity data for some crystals used in the test of the theoretical results. Thanks are also due to the Council of Scientific and Industrial Research, India, for the award of a Senior Research Fellowship to KS.

References

- ALLEN, F. H., KENNARD, O. & TAYLOR, R. (1983). *Acc. Chem. Res.* **16**, 146–151.
- BERNSTEIN, F. C., KOETZLE, T. F., WILLIAMS, G. J. B., MEYER, D. F. JR, BRICE, M. D., RODGERS, J. R., KENNARD, O., SHIMANOUCI, T. & TASUMI, M. (1977). *J. Mol. Biol.* **112**, 535–542.
- ESWARAMOORTHY, S., PONNUSWAMY, M. N. & RAJU, K. S. (1991). Personal communication.
- EVERITT, B. S. (1987). *Introduction to Optimization Methods and their Application in Statistics*. London, New York: Chapman & Hall.
- HAMMING, R. W. (1989). *Introduction to Applied Numerical Analysis*. New York: Hemisphere.
- HIGH, D. F. & KRAUT, J. (1966). *Acta Cryst.* **21**, 88–96.
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures for X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.
- MAZUMDAR, S. K. & SRINIVASAN, R. (1964). *Curr. Sci. (India)*, **33**, 573–575.
- PANNEERSELVAM, K. & CHACKO, K. K. (1990). *Int. J. Pept. Protein Res.* **35**, 460–464.
- PANNEERSELVAM, K., CHACKO, K. K. & VEENA, R. (1989). *Int. J. Pept. Protein Res.* **33**, 191–194.
- ROGERS, D. (1965). In *Computing Methods in Crystallography*, edited by J. S. ROLLETT. Oxford: Pergamon Press.
- SEKAR, K. & PARTHASARATHY, S. (1992). Personal communication.
- SEKAR, K., PARTHASARATHY, S. & RADHAKRISHNAN, T. R. (1990). *Acta Cryst.* **C46**, 1338–1340.
- SEKAR, K., PARTHASARATHY, S. & RADHAKRISHNAN, T. R. (1993). *Acta Cryst.* **C49**, 93–95.
- SEKAR, K., PARTHASARATHY, S. & RAJALINGAM, P. (1990). *Acta Cryst.* **C46**, 1153–1155.
- WEEKS, C. M., COOPER, A., NORTON, D. A., HAUPTMAN, H. & FISHER, J. (1971). *Acta Cryst.* **B27**, 1562–1572.
- WILSON, A. J. C. (1942). *Nature (London)*, **150**, 152–154.

Acta Cryst. (1993). **A49**, 398–405

Edge Contributions to the Kirste–Porod Formula: the Truncated Circular Right Cone Case

BY S. CICCARIELLO

Dipartimento di Fisica 'G. Galilei' and sez. INFN, via Marzolo 8, I-35131 Padova, Italy

(Received 5 June 1992; accepted 23 September 1992)

Abstract

The wide-angle correlation function $\gamma(r)$ of a dilute system of particles, shaped as truncated circular right

cones, is evaluated in closed form. The angular average of the contribution proportional to r^3 gives $\gamma'''(0^+)$, the value at the origin of the third derivative with respect to r of the corresponding small-angle

correlation function. The value differs from that obtained by the Kirste–Porod formula by a negative contribution that arises from the two circular edges. Moreover, $\gamma'''(0^+)$ turns out to be divergent in the case of circular right cones.

I. Introduction

The Kirste–Porod (KP) formula (Kirste & Porod, 1962) gives an explicit relation between $\gamma'''(0)$, the value at the origin of the third derivative with respect to the distance r of the sample correlation function (CF), and the surface integral of an appropriate combination of the Gaussian curvature and the squared mean curvature of the interphase surface of an isotropic two-phase system. The KP formula has been obtained for smooth interfaces. (A surface is smooth when no edges, no vertices and no contact points are present on it.) At present, it is not known how the formula should be modified when particles have corners and/or sharp edges. Recently, however, Sobry, Ledent & Fontaine (1991) analyzed the case of prism-shaped particles. They found that the edges yield no extra contribution but the corners do and the contribution from each corner is negative. Since the analysis of general singular interfaces does not appear simple, the CF of a truncated circular right cone was calculated to see whether the circular edges contribute. It was found that they do. Hence, the $\gamma'''(0)$ value, relevant to a generic interface with edges and corners, will contain, besides the KP contribution, further terms related to these singularities.

In this paper, the derivation of this result is reported as follows. Firstly, the relations existing between the asymptotic behavior of the scattered intensity and the singularities of the CF derivatives as well as the relations between these singularities and some geometrical features of the interphase surfaces are briefly reviewed. In particular, the similarity of the analysis of the peak profiles, measured by wide-angle X-ray scattering (WAXS) experiments, with that of the intensities, measured in small-angle X-ray scattering (SAXS) experiments, will be emphasized. To an approximation, the SAXS results given by the Porod–Debye relation, the so-called angularity and the Kirste–Porod relation, respectively, correspond to angularly averaging, over all possible reflex directions, the so-called variance Scherrer constant (Tournarie, 1956), the taper parameter (Wilson, 1962) and the rotundity parameter (Mitra, 1964; Wilson, 1971). In § III, the SAXS CF of the truncated circular right cone is derived. In § IV, the third derivative of the corresponding SAXS CF is evaluated at $r = 0$ and the result is compared with that obtained by the KP formula. Some technical points of the mathematical

derivation are discussed in detail in Appendices A, B and C.*

II. Geometrical properties of the interface and asymptotic behavior of the intensities

According to a general result of the theory of Fourier transforms (FT) (Erdélyi, 1956), the asymptotic behavior at large momenta of the FT of a function $f(x)$ is related to the singularities of $f(x)$ and its derivatives. For this reason, the behavior of $I(\mathbf{h})$ (the X-ray or neutron intensity scattered by a sample) at large momentum transfers $h = |\mathbf{h}|$ will be intimately related to the behavior of $\gamma(r)$ (the CF of the sample) around $r = 0$ and around those distances where the derivatives of $\gamma(r)$ become singular. The further assumption that the electron (or the scattering-length) density $n(\mathbf{r})$ can be fairly well approximated by a discrete-valued function implies that $\gamma(r)$ is mainly determined by the boundaries of the regions V_i where the density assumes the i th value n_i . (In the following, for simplicity, only two-phase samples will be considered, so that $i = 1, 2$.) In this way, the asymptotic behavior of $I(\mathbf{h})$ will reflect some of the geometrical properties of the interphase boundaries. Over the past fifty years, many researchers have tried to make such relations clear. A report of the full list of references would be lengthy, thus only a sketch of the present theory will be made. The theory of both SAXS and WAXS from powder samples, where the main source of the peak-profile broadening is the finite size of sample crystallites, is of interest. Indeed, when stacking faults and strain effects can be sensibly neglected in WAXS analyses and, inside each crystallite, the electron density is close to the average, the inverse (one-dimensional) Fourier transform of each peak profile yields the volume $V_k(r)$ common to the sample crystallites and to their ghosts, resulting from the shift of the sample by a distance r along the k th considered reflection. On the other hand, the three-dimensional inverse Fourier transform of the SAXS intensity yields $\gamma(r)$, the so-called (isotropic component of the) CF of the sample. $\gamma(r)$ is related to the average of the $V_k(r)$ with respect to k , i.e. to the angular average of $V_k(r)$. $V_k(r)$ is simply proportional to the sample CF, defined as

$$\gamma(r\hat{\omega}) = (V\langle n^2 \rangle)^{-1} \int d\mathbf{v}_1 n(\mathbf{r}_1)n(\mathbf{r}_1 + r\hat{\omega}), \quad (1)$$

where $\hat{\omega}$ and $\langle n^2 \rangle$ denote the direction of the k th reflection and the mean square electron density of the sample whose volume is V . For this reason, $\gamma(r\hat{\omega})$

* Appendices A, B and C have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55587 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

will be referred to as the WAXS CF. [The notation $\gamma(\mathbf{r})$ or $\gamma(r, \theta, \varphi)$, with θ and φ denoting the polar angles of $\mathbf{r} = r\hat{\omega}$ with respect to a convenient coordinate system, will be used.] The SAXS CF $\gamma(r)^*$ is related to the WAXS CF by the angular average

$$\gamma(r) = (4\pi)^{-1} \int_{\Omega} d\hat{\omega} \gamma(r\hat{\omega}). \quad (2)$$

A recent paper (Ciccariello, 1990) gives a detailed discussion of this relation and led to the re-enunciation of some WAXS results.† The former relation having been emphasized, it is no surprise that many of the theoretical results, related to the geometrical meaning of the coefficients of the expansions of $V_k(r)$ and $\gamma(r)$ around the origin, have been independently discovered by workers in both WAXS and SAXS theory. The well known Porod-Debye result (Porod, 1951; Debye, Anderson & Brumberger, 1957) that 'the derivative of the SAXS CF at $r = 0$ is proportional to the total area of the sample interface, i.e. $\gamma'(0) = -S/(4V\varphi_1\varphi_2)$ ' (S denotes the area of the sample interface while $\varphi_i = V_i/V$, $i = 1, 2$, are the volume fractions of the constituting phases), corresponds to the WAXS result obtained by Wilson (1949, pp. 43-44) that ' $-V'_k(0)/V$ represents the total area (per unit sample volume) of the projection of the sample interface on the plane orthogonal to the k th reflection direction'. From (1), by averaging $-V'_k(0)/V$ [which is also known as the variance-slope Scherrer constant (Langford & Wilson, 1977)] over all possible reflection directions, one recovers the Porod-Debye result. Similarly, the statements that 'the second-order derivative of $\gamma(r)$, evaluated at $r = 0^+$, is equal to zero when the interface is smooth' (Kirste & Porod, 1962) and 'otherwise it is positive' (Porod, 1967, p. 13) correspond to the interpretation of $V''_k(0)/V$ given by Wilson (1962). Wilson called the reciprocal of the latter quantity (multiplied by the square of a suitable length) the taper parameter of the sample interface, to emphasize its relation with the presence of edges and vertices. In other words, the angularity and the taper parameter are essentially the same and, by an appropriate normalization, the former is obtained by the angular average of the latter. Finally, the measurability of the value at the origin of the third r derivative

of the CF was first noticed by Kirste & Porod (1962) in the SAXS case and a few years later by Mitra (1964) in the WAXS regime.

These brief historical notes show that the WAXS and SAXS fields progressed almost simultaneously, although quite separately, in this theoretical subject until the early seventies. Later, interest survived mainly in the SAXS realm for physically evident reasons: firstly, in WAXS the corrections related to strain and strain gradient are a problem; secondly, the fluctuations in the local electron density of the sample phases can be more safely neglected in SAXS experiments than in WAXS ones, owing to the smaller spatial resolution of the former. Moreover, when the average particle size exceeds $\sim 100 \text{ \AA}$, the h range in which the asymptotic behavior of $I(h)$ should be applicable is large enough to yield accurate determination of both $\gamma'(0)$ and $\gamma''(0^+)$ by the use of the Porod law

$$I(h)/V\langle\eta^2\rangle \approx -8\pi\gamma'_s(0)/h^4 = 2\pi S/(V\varphi_1\varphi_2h^4) \quad (3)$$

and of the Porod (1967) sum rule

$$\gamma''_s(0^+) = (1/6\pi^2) \int_0^\infty [-8\pi\gamma'_s(0) - h^4 I(h)/V\langle\eta^2\rangle] dh. \quad (4)$$

The first practical application of (4) was made by Tchoubar & Méring (1969). The explicit relations between the $\gamma''(0^+)^*$ value and the singularities of the interphase surface were obtained by Ciccariello, Cocco, Benedetti & Enzo (1981) for the case of sharp edges and by Ciccariello & Benedetti (1982) for the case of contact points and vertices were shown not to contribute. The derivation of these results was made possible by the use of the two general integral expressions of $\gamma'(r)$ and $\gamma''(r)$ obtained by Ciccariello *et al.* (1981). These relations were further generalized to yield the integral expressions of $\nabla\gamma(r)$ and $\nabla\nabla\gamma(r)$ (Ciccariello, 1985).

All these relations are particularly useful in finding the geometrical configurations of the interfaces that yield a singular behavior of the CF derivatives at particular distances ($\delta, \bar{\delta}$) in both the SAXS and the WAXS domains. It has already been shown that $\gamma'(0)$ is related to the leading asymptotic term of $I(h)$, which decreases as h^{-4} [see (3)]. The important questions about the general asymptotic expansion of $I(h)$ and the way the coefficients of the expansion are related to the phase boundaries were tackled by Schmidt and co-workers in many papers (in particular, Miller & Schmidt, 1962; Schmidt, 1965, 1967; Wu & Schmidt, 1974) and, more recently, by Ciccariello (1985, 1989, 1991). The main conclusions are as follows.

* Note that the SAXS CF is defined here in terms of the electronic density and not in terms of the local electronic density fluctuation $\eta(\mathbf{r}) \equiv n(\mathbf{r}) - \langle n \rangle$. The two quantities are simply related by $\gamma(r) = \langle \eta^2 \rangle \gamma_s(r) / (\langle n^2 \rangle + \langle n \rangle^2)$, where index s refers to the standard definition in terms of η . Moreover, a previous paper by Ciccariello (1985) gave the general integral expressions of $\gamma_s(r)$ and of its lowest partial derivatives and discussed the latter's continuity properties.

† The results are relevant to the geometrical meaning of the values of the first (Wilson, 1949, pp. 43-44) and the second (Wilson, 1962) $V_k(r)$ derivatives evaluated at the origin, to the h^{-2} behavior of the peak profile [$I(h)$] in the tail region (Patterson, 1939) and to the $V_k(r)$ relevant to spherical, cubic and cylindrical particles (Wilson, 1969, 1970). The author is grateful to Professor A. J. C. Wilson for having kindly brought these references to his attention.

* To simplify the notation, index s is no longer used; nonetheless, SAXS CFs can still be distinguished from WAXS CFs because the former have only one argument.

(i) $\gamma''(r)$ can be singular only when part of the interface is parallel to itself. In particular, $\gamma''(r)$ either has a finite discontinuity (Miller & Schmidt, 1962; Ciccariello, 1985) at $r = \delta$ or it has the logarithmic behavior $\ln|r - \delta|$ around $r = \delta$ (Schmidt, 1965; Ciccariello, 1989), where δ is the distance between the parallel surfaces. The two possible behaviors yield, in the asymptotic expansion of $I(h)$, two contributions proportional to $(\cos h\delta)/h^4$ and to $(\sin h\delta)/h^4$, respectively. The coefficients of these terms have known integral expressions (Ciccariello, 1991).

(ii) Around other distances, denoted $\bar{\delta}$, $\gamma''(r)$ behaves as $|r - \bar{\delta}|^\alpha$ or $|r - \bar{\delta}|^\alpha \ln(|r - \bar{\delta}|)$ with $\alpha > 0$ (Wu & Schmidt, 1974). More precisely, they showed that, with the assumption that each particle is smooth and strictly convex,* $\bar{\delta}$ is the so-called extremal chord of the particle and α obeys the inequalities $0 < \alpha \leq 1$. By use of either the Erdélyi (1956) theorem or its generalization by Jones & Kline (1958), Wu & Schmidt showed that the aforementioned behaviors of $\gamma''(r)$ determine the next asymptotic terms of $I(h)$. They turn out to be linear combinations of the functions $(\cos h\bar{\delta})/h^{4+\alpha}$ and $(\sin h\bar{\delta})/h^{4+\alpha}$. The values of α as well as the values of the coefficients of these damped oscillatory terms depend on the behavior of the surface around the extremal chords. Wu & Schmidt (1974) evaluated these quantities in some typical cases.

From a practical point of view, the main conclusion of this analysis is that the damped oscillatory terms can generally be neglected when the particles do not have high symmetry and when their polydispersity is not small. In these cases, there are a very large number of extremal chords and, consequently, a large number of oscillatory terms whose sum will probably average to zero. It is stressed that this conclusion is physically sound only when the number of oscillatory terms is large and when their coefficients are approximately equal. Indeed, some physically interesting cases have been found where most of the extremal chords are close to a particular value and clear oscillations in the Porod plot [$h^4 I(h)$ or $h^3 I(h)$ vs h , depending on the collimation geometry] of the intensities are observed (Ciccariello & Benedetti, 1986; Benedetti & Ciccariello, 1993). However, when no clear oscillations are observed, it appears natural to assume that the intensities are well approximated only by the asymptotic nonoscillatory terms in the region of large h . The first contribution is the well known Porod h^{-4} term, given by (3). It is to be expected that, if account is made for the next contribution, a better approximation is obtained, though the outer part of the large- h

region must be considered because the expansion is asymptotic. Integration by parts of the defining relation

$$i(h) \equiv I(h)/V\langle\eta^2\rangle = (4\pi/h) \int_0^\infty r\gamma(r) \sin(hr) dr,$$

and neglect of possible contributions arising from the discontinuities of $\gamma''(r)$ and of $\gamma'''(r)$, for the reason just explained, readily leads to

$$i(h) \approx -8\pi\gamma'(0)/h^4 + 16\pi\gamma'''(0)/h^6 + o(h^{-6}). \quad (5)$$

Thus, the term next to the leading nonoscillatory term decreases as h^{-6} and its coefficient is related to $\gamma'''(0^+)$. Kirste & Porod (1962) have shown that, for a system made up of smooth particles,

$$\gamma'''(0) = (1/4 V\varphi_1\varphi_2)\mathcal{K} \quad (6a)$$

with

$$\begin{aligned} \mathcal{K} &\equiv \int_S dS (3/R_m^2 + 2/R_m R_M + 3/R_M^2)/16 \\ &= \frac{1}{4} \int_S dS (3H^2 - \kappa_G). \end{aligned} \quad (6b)$$

Here R_m and R_M denote the principal curvature radii of the interface S , while $H = (1/R_m + 1/R_M)/2$ and $\kappa_G = 1/R_m R_M$ are the mean and Gaussian curvatures. Thus, from (6b), \mathcal{K} is a dimensionless quantity obtained by integration of the Gaussian and the squared mean curvature of the surface. From (6a), $\gamma'''(0)$ is directly proportional to \mathcal{K} and (6) will be referred to as the Kirste–Porod (KP) formula. Provided the particles are smooth, the integrand of (6b) also makes sense when $\kappa_G < 0$. Moreover, the integrand in (6b) can be written as $2/R_m^2 + (1/R_m + 1/R_M)^2 + 2/R_M^2$, hence \mathcal{K} is a positive quantity.* It is worth commenting briefly on the relation between \mathcal{K} and M , the so-called rotundity parameter (Wilson, 1971). Comparison of equation (2) of Wilson (1971) with (4) gives $-M = V\gamma'''(0^+, \hat{\omega})$. Thus, from (2) and (6a), $-\langle M \rangle_{\text{ang}} = V\gamma'''(0^+) = \mathcal{K}/4$, where the volume fractions are omitted since the sample comprises a single particle. The first equality of this last expression shows that $V\gamma'''(0^+)$ is the opposite of the angular average of the rotundity parameter, while the second, relating them to the curvature radii of the surface, has a self-evident geometrical meaning. Moreover, the numerical values of the rotundity, obtained by Wilson (1971), Edwards & Toman (1971) and Langford & Louër (1982)† for simple particle

* When the samples have more than two phases, the interfaces in general are no longer closed surfaces and their boundaries consist of closed curves. The integrand of (6b) may be singular or undefined on these curves. However, the area of these curves is zero and thus (6b) could still be considered true. Thus, \mathcal{K} is always non-negative.

† The author acknowledges A. J. C. Wilson for assistance with the literature and information on the rotundity-parameter definition.

* Strictly convex means that the remaining points of any linear segment having its ends on the particle boundary are internal to the particle. A particle chord is any segment having its ends on the particle boundary. A chord is said to be extremal when the two planes orthogonal to it at its ends are tangent to the particle at these points.

shapes, allow one to estimate the corresponding $V\gamma'''(0^+)$ values.

A natural question is whether the KP formula can also be generalized to the case of particles that have sharp corners and/or edges. In an interesting and recent paper, Sobry, Ledent & Fontaine (1991) analyzed the right prism and the right circular cylinder. In the latter case, using the small-distance expansion of the relevant $\gamma(r)$, obtained by Méring & Tchoubar (1968), they found that $\gamma'''(0)$ is related to the \mathcal{K} value as in the KP formula. By contrast, for prismatic particles, they have found that $\gamma'''(0)$ differs from the KP formula (which yields $\mathcal{K} = 0$) by a contribution that can be expressed as a sum of contributions, each owing to a corner of the prism. More precisely, they concluded that, when the interface is made up of planar facets, each linear edge does not yield an extra contribution with respect to the KP formula while each vertex does. The corresponding contribution has been explicitly evaluated in the case of corners having two right angles.

Since the cylinder has only sharp edges and no corner and since the KP formula works exactly in this case, it may be supposed that the extra contributions arise only in the presence of sharp corners.

Determination of the generalization of the KP formula to the case of generic interfaces with sharp edges is not simple. However, the extra contribution found by Sobry *et al.* (1991) is proportional to $\cot \beta$, where β is the dihedral angle [see their equations (23) and (24)]. In the case of the cylinder, $\beta = \pi/2$, thus the absence of an extra contribution might be related to the $\cot \beta$ term. For this reason, to answer the above question, the WAXS CF relevant to a truncated circular right cone (TCRC) has been evaluated. The TCRC appears to be one of the simplest particle shapes with closed edges characterized by dihedral angles different from $\pi/2$.

The results of these calculations are now reported.

III. WAXS CF of a truncated circular right cone

With reference to Fig. 1, let 2α and h ($=AD'$) denote respectively the opening angle and the height of a TCRC, obtained from a cone of height H ($=AT'$). The points belonging to the TCRC considered satisfy

$$0 \leq z \leq h, \quad (7a)$$

$$x^2 + y^2 \leq R^2(z) = (H - z)^2 \tan^2 \alpha. \quad (7b)$$

It is convenient to choose the unit length to be equal to H . Thus, (7b) becomes

$$x^2 + y^2 \leq R^2(z) = (1 - z)^2 \tan^2 \alpha \quad (7b')$$

and h satisfies $0 < h \leq 1$. The volume of the TCRC is

$$V = \pi(\tan^2 \alpha)[1 - (1 - h)^3]/3. \quad (8)$$

The WAXS CF is given by

$$\gamma(\mathbf{r}) = V^{-1} \int_V \rho(\mathbf{r}_1)\rho(\mathbf{r}_1 + \mathbf{r}) d\mathbf{v}_1, \quad (9)$$

where $\rho(\mathbf{r})$ is defined as being 1 when \mathbf{r} fulfills conditions (7a, b') and 0 elsewhere. [Note that the factor $(\varphi_1\varphi_2)^{-1}$ is absent since the sample comprises a single particle.] The integral in (9) represents the volume of the region common to the given TCRC and to its image resulting from its translation by \mathbf{r} . Clearly, $\gamma(\mathbf{r}) = \gamma(-\mathbf{r})$. Moreover, $\gamma(\mathbf{r})$ is invariant as \mathbf{r} is rotated around the z axis (see Fig. 1). Therefore, only the \mathbf{r} 's lying in the first quadrant of the xz plane need be considered. In other words, with use of a system of polar coordinates with the polar axis along \hat{z} and φ being the longitudinal angle from the xz plane, it is only required to consider

$$\mathbf{r} = (r \sin \theta, 0, r \cos \theta) \quad \text{with } 0 \leq \theta \leq \pi/2, \quad (10)$$

while the noted symmetry properties of the TCRC CF imply that $\gamma(\mathbf{r})$ depends only on r and θ . Thus, instead of $\gamma(\mathbf{r})$, the more explicit notation $\gamma(r, \theta)$ will be adopted.

The shape of the intersection region between the given particle and its ghost depends on the actual values of θ and r as well as on those of α and h . In

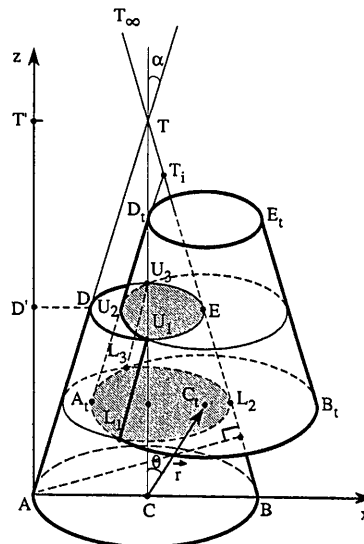


Fig. 1. $ABED$ represents a truncated right circular cone, whose height and opening angle are $h = AD'$ and 2α , respectively. The length unit has been chosen to be the height AT' ($=H$) of the right circular cone ATB . A translation of $ABED$ by \mathbf{r} yields the TCRC $A_t B_t E_t D_t$, which shares with the original TCRC the truncated right cone delimited by the two gray regions $U_1 E U_3 U_2$ and $A_t L_1 L_2 L_3$. The shape of the intersection region changes with the orientation (θ) and length (r) of \mathbf{r} . When $\theta > \alpha$ (as shown in the figure), the upper surface of the intersection region becomes smaller with increasing r . Thus, the intersection region will become a simple right cone provided θ is close to $\pi/2$. In contrast when $\theta < \alpha$, the intersection region, if it exists, will be a truncated circular right cone.

fact, the shape of the intersection region can be: (i) a truncated circular right cone (TCRC); (ii) a truncated right cone (TRC) whose generic section orthogonal to the z axis is the intersection between two circles of different radii (R_1 and R_2) and with their centers at a relative distance d (see Fig. 1); (iii) a simple right cone (RC), whose sections are similar to those specified above. Such a RC results from a TRC whose top surface, *e.g.* that delimited by the arcs of circles $U_3U_2U_1$ and U_1EU_3 , shrinks to a point. For small r , these intersection configurations become possible only when h and θ are respectively close to 1 and $\pi/2$. However, when $h \neq 1$, these configurations become impossible as r approaches zero. Nonetheless, it is convenient to take them into account explicitly so that the limit $h \rightarrow 1$ may be taken, corresponding to the case of particles having the shape of a circular right cone (CRC). From the thorough discussion in Appendix C* of the θ ranges when r is not small, only the following three angular regions

$$\text{I: } 0 \leq \theta \leq \alpha \quad (11a)$$

$$\text{II: } \alpha \leq \theta \leq \theta_1 \equiv \arcsin [2(1-h)(\sin \alpha)/r] + \alpha \quad (11b)$$

$$\text{III: } \theta_1 \leq \theta \leq \pi/2 \quad (11c)$$

are considered. From Fig. 1, it appears clear that the intersection region is a TCRC in range I, a TRC in range II and a RC in range III. The determination of θ_1 will be given later. Region III exists provided

$$r \geq 2(1-h) \tan \alpha, \quad (12)$$

which can be satisfied for infinitesimal r 's only when $h = 1$, *i.e.* when the particle is a CRC. In such a case, region II does not exist.

Let the volume of the intersection region, with θ belonging to region I, be evaluated. The lower and upper surfaces of the resulting TCRC are circles, whose radii are equal to $(1-r \cos \theta) \tan \alpha$ and to $(1-h) \tan \alpha$, respectively. Thus, the volume is $\pi(\tan^2 \alpha)[(1-r \cos \theta)^3 - (1-h)^3]/3$ and the WAXS CF is

$$\gamma_I(r, \theta) = [\pi(\tan^2 \alpha)/3V][(1-r \cos \theta)^3 - (1-h)^3]. \quad (13)$$

For greater clarity, the polar coordinates of \mathbf{r} are used as arguments of γ , while the index I is a reminder that θ lies in region I.

Now consider region II. The volume of the overlapping region, which is a TRC, is given by

$$\int_{z_1}^{z_2} \mathcal{S}(d, R_1, R_2) d\bar{z}, \quad (14)$$

where $\mathcal{S}(d, R_1, R_2)$ denotes the area of the section of the TRC with the plane $z = \bar{z}$ and z_1 and z_2 are

respectively the z ordinates of the lower and upper surfaces of the TRC. Clearly,

$$z_1 = r \cos \theta \quad \text{and} \quad z_2 = h. \quad (15a, b)$$

$\mathcal{S}(d, R_1, R_2)$ is the area of the region shared by two coplanar circles having radii R_1 and R_2 with centers a distance d apart. It is easy to prove that

$$\mathcal{S}(d, R_1, R_2) = R_1^2 \mathcal{A}[\mathcal{R}(d, R_1, R_2)] + R_2^2 \mathcal{A}[\mathcal{R}(d, R_2, R_1)] \quad (16)$$

where

$$\mathcal{A}(x) \equiv \arccos x - x(1-x^2)^{1/2} \quad \text{with } |x| \leq 1 \quad (17)$$

and

$$\mathcal{R}(d, R_1, R_2) \equiv (d^2 + R_1^2 - R_2^2)/2dR_1. \quad (18)$$

These circles result from the intersection of the plane $z = \bar{z}$ with the TCRC particle and its ghost. Therefore, the radii R_1 and R_2 are

$$R_1 = (1-\bar{z}) \tan \alpha \quad \text{and} \quad R_2 = (1+r \cos \theta - \bar{z}) \tan \alpha, \quad (19a, b)$$

and the distance between their centers is

$$d = r \sin \theta. \quad (19c)$$

The method to obtain the value of θ_1 reported in (11b) can now be explained. The upper surface of the intersection TRC shrinks to a point when $R_1 + R_2 = d$. At fixed (and small) r , the smallest θ angle ($\equiv \theta_1$) at which this condition occurs is that corresponding to the highest possible value of \bar{z} , *i.e.* $\bar{z} = h$.

By use of (19), (18) and (17), $\mathcal{S}(d, R_1, R_2)$ can be obtained as a function of \bar{z} and then the integral (14) can be evaluated. The details are reported in Appendix A.* With use of the definitions

$$\xi \equiv r(\sin \theta)/2 \tan \alpha, \quad \tau \equiv \tan \alpha / \tan \theta \quad (20a, b)$$

and

$$\mathcal{T} \equiv (1-\tau^2)^{1/2}, \quad (20c)$$

$\gamma_{II}(r, \theta)$ can be written as

$$\begin{aligned} \gamma_{II}(r, \theta) = & [(\tan^2 \alpha)/3V][\mathcal{B}(1, \tau, \xi) - \mathcal{B}(1-h, -\tau, \xi) \\ & - 2\xi^3 \mathcal{T}^3 \ln \{ (1-h + \tau\xi + [(1-h + \tau\xi)^2 \\ & - \xi^2]^{1/2}) \{ 1 - \tau\xi + [(1-\tau\xi)^2 - \xi^2]^{1/2} \}^{-1} \}], \end{aligned} \quad (21a)$$

where

$$\begin{aligned} \mathcal{B}(\kappa, \tau, \xi) \equiv & \kappa^3 \mathcal{A}(\tau + \mathcal{T}^2 \xi / \kappa) \\ & + (\kappa - 2\tau\xi)^3 \mathcal{A}[-\tau + \mathcal{T}^2 \xi / (\kappa - 2\tau\xi)] \\ & - 2\xi \mathcal{T}^3 (\kappa - \tau\xi) [(\kappa - \tau\xi)^2 - \xi^2]^{1/2}. \end{aligned} \quad (21b)$$

To complete the derivation of the WAXS CF of the TCRC particle, it is required to evaluate the

* See deposition footnote.

* See deposition footnote.

volume of the intersection RC when θ belongs to region III. Equation (A14) of Appendix A,* which is the closed-form expression of integral (14), can be used provided

$$z_2 = 1 - r(\sin \theta)/2 \tan \alpha + r(\cos \theta)/2, \quad (22)$$

which represents the z ordinate of the tip of the intersection RC. Thus, it is found that

$$\gamma_{\text{III}}(r, \theta) = [(\tan^2 \alpha)/3V][\mathcal{B}(1, \tau, \xi) + 2\xi^3 \mathcal{F}^3 \times \ln \{1 - \tau\xi + [(1 - \tau\xi)^2 - \xi^2]^{1/2}\}/\xi]. \quad (23)$$

Equations (13), (21) and (23), valid respectively in the angular ranges $[0, \alpha]$, $[\alpha, \theta_1]$ and $[\theta_1, \pi/2]$ when r is sufficiently small, represent the WAXS CF of a TCRC. When $\pi/2 \leq \theta \leq \pi$, the CF is obtained by the symmetry relation $\gamma(r, \theta) = \gamma(r, \pi - \theta)$.

It has already been mentioned that the case of a CRC can be obtained by setting $h = 1$. In this case, region II no longer exists. Therefore, (13) (with $h = 1$) and (23) (which is already h independent) represent the WAXS CF of a CRC.

IV. Generalization of the Kirste-Porod formula

The main reason for having carried through the former calculations is the evaluation of the contribution that must be added to the value obtained from the Kirste-Porod formula in order to recover the correct value of $\gamma'''(0^+)$. The first task will be the evaluation of this last quantity. The noted symmetry properties of the TCRC allow the SAXS CF, defined by (2), to be written as

$$\gamma(r) = \int_0^{\pi/2} \gamma(r, \theta) \sin \theta \, d\theta. \quad (24)$$

The independence of $\gamma(r, \theta)$ from φ makes the φ integration trivial and the symmetry $\gamma(r, \theta) = \gamma(r, \pi - \theta)$ restricts the θ integration to $[0, \pi/2]$. Since it is necessary to examine the behavior of the $\gamma(r)$ derivatives as $r \rightarrow 0$, the case of the TCRC particles must be separated from that of the CRC ones. In the first case, the condition $h \neq 0$ indicates that, once r has become sufficiently small, region III cannot exist. This follows immediately from the dependence of θ_1 on r [see (11b)]. However, from Fig. 1 it can be seen that when $\theta > \alpha$ and r is quite close to 0, whatever the opening and the height of the TCRC, the intersection region is always shaped as a TRC. Therefore, when $r = 0$,

$$\gamma(r) = \int_0^\alpha \gamma_I(r, \theta, 0) \sin \theta \, d\theta + \int_\alpha^{\pi/2} \gamma_{\text{II}}(r, \theta, 0) \sin \theta \, d\theta. \quad (25)$$

A closed-form evaluation of the second integral does

not appear possible. Nevertheless, $\gamma'''(0^+)$ can be obtained if one evaluates $\partial^3 \gamma_{\text{II}}(r, \theta, 0)/\partial r^3$, takes the limit of the latter as $r \rightarrow 0^+$ and finally performs the angular integration (25). The limiting value of $\partial^3 \gamma_{\text{II}}(r, \theta, 0)/\partial r^3$ as $r \rightarrow 0^+$ is

$$\begin{aligned} & [\partial^3 \gamma_{\text{II}}(r, \theta)/\partial r^3]_{r=0^+} \\ &= -2\pi(\tan^2 \alpha)(\cos^3 \theta)/V \\ & \quad - \mathcal{F}^3(\theta)(\sin^3 \theta) \ln(1-h)/2V \tan \alpha. \end{aligned} \quad (26)$$

The second term on the right-hand side (r.h.s.) is straightforwardly obtained from the logarithmic contribution on the r.h.s. of (21), owing to the presence of the factor $\xi^3 \propto r^3$. The first term is obtained from the remaining terms in (21). Its derivation follows rather easily by use of a symmetry property, as shown in Appendix B.* In region I, it follows from (13) that

$$[\partial^3 \gamma_I(r, \theta)/\partial r^3]_{r=0^+} = -2\pi(\tan^2 \alpha)(\cos^3 \theta)V. \quad (27)$$

Equations (26) and (27) give the value at the origin of the third partial r derivative of the WAXS CF, which, after multiplication by $-V$, yields the rotundity parameter of TCRCs. From (25), its integral will yield the required result

$$\begin{aligned} \gamma'''(0^+) &= -\pi(\tan^2 \alpha)/2V - 3\pi[\ln(1-h)] \\ & \quad \times (\cos^2 \alpha)/32V \sin \alpha. \end{aligned} \quad (28)$$

This result must be compared with that obtained by the KP formula to see whether the sharp circular edges contribute. Thus \mathcal{K} , defined by (6b), needs to be evaluated. Since $R_m = R_M = \infty$ on the two bases of the TCRC, the latter yield no contribution to the integral. Thus, \mathcal{K} will only depend upon the lateral surface of the TCRC. By parameterization of the surface with

$$\begin{aligned} z &= h(1-t), & 0 \leq t \leq 1, \\ x &= R(t) \cos \varphi, & 0 \leq \varphi < 2\pi, \\ y &= R(t) \sin \varphi, \\ R(t) &\equiv (1-h-h t) \tan \alpha, \end{aligned}$$

it is found that $dS = [hR(t)/\cos \alpha] dt d\varphi$, $R_M = \infty$ and, by the Meusnier theorem (Smirnov, 1970), $R_m = R(t)/\cos \alpha$. In this way it can be seen that

$$\mathcal{K}_{\text{KP}} = -3\pi \ln(1-h)(\cos^2 \alpha)/8 \sin \alpha, \quad (29)$$

which is a positive quantity, while the suffix KP is a remainder that the quantity was obtained by the KP formula. Since 1 must be substituted for the factor $\varphi_1 \varphi_2$ in (6a) when the sample is made up of a single particle,

$$\gamma'''_{\text{KP}}(0^+) = -3\pi(\cos^2 \alpha) \ln(1-h)/32V \sin \alpha. \quad (30)$$

$\gamma'''_{\text{KP}}(0^+)$ denotes the contribution to $\gamma'''(0^+)$ coming

* See deposition footnote.

* See deposition footnote.

from the Kirste–Porod formula. By comparison of (30) with (28), it is concluded that the two circular edges of the TCRC are responsible for the contribution

$$-\pi(\tan^2 \alpha)/2V, \quad (31)$$

which is always negative.

Let

$$\mathcal{S} \equiv 4V\gamma'''(0^+) - \mathcal{H}_{\text{KP}}. \quad (32)$$

Provided \mathcal{H}_{KP} exists, \mathcal{S} can be taken as a measure of the sharpness of the interfaces. In fact, by the result of Sobry *et al.* (1991) and by (31), \mathcal{S} is nonzero only when the particle surfaces have edges and/or vertices, while \mathcal{H}_{KP} describes the smooth contribution to $\gamma'''(0^+)$ related to the surface curvatures. However, it must be stressed that \mathcal{H}_{KP} must be finite for the separation between \mathcal{S} and \mathcal{H}_{KP} to be meaningful. In this respect, the discussion of the remaining case, *viz* that of CRC particles, is illuminating. The tip of the cone yields both a logarithmically divergent \mathcal{H}_{KP} value and a logarithmic singularity in $\gamma'''(r)$ as $r \rightarrow 0^+$. The first property is evident if the limit $h \rightarrow 1$ is taken in (29). The second follows from the fact that the leading behavior of $\gamma'''_{\text{CRC}}(r, \theta)$ {the third partial r derivative of the WAXS CF of a CRC [$\equiv \gamma_{\text{CRC}}(r, \theta)$] obtained at the end of § III} is $-\mathcal{T}^3(\theta)(\sin^3 \theta) \times (\ln r)/(2V \tan \alpha)$ at very small r 's. The angular average of the latter gives $-[3\pi(\cos^2 \alpha) \ln r]/(32V \sin \alpha)$, which is equal to the aforementioned \mathcal{H}_{KP} limit once $\ln r$ is identified with $\ln(1-h)$. Although such an identification would yield a well defined sharpness value by (32), the evident arbitrariness of the assumption, combined with the fact that it does not guarantee that the full tip contribution is accounted for by \mathcal{S} , shows that the decomposition (32) is sensible only when \mathcal{H}_{KP} is not divergent. Clearly, for \mathcal{H}_{KP} to be divergent, the particle surface should have points (the tip of the cone for CRC particles) where at least one of the curvature radii becomes infinitesimally small. Finally, it should also be noted that divergence of $\gamma'''(0^+)$ would easily be noticed since $h^6[I(h) + 8\pi\gamma'_s(0)V(\eta^2)/h^4]$ would be divergent as h increases.

The author thanks Mr A. Rampazzo for drawing the figure. Financial support of MURST through 60% and 40% Funds is acknowledged.

References

- BENEDETTI, A. & CICCARIELLO, S. (1993). In preparation.
 CICCARIELLO, S. (1985). *Acta Cryst.* **A41**, 560–568.
 CICCARIELLO, S. (1989). *Acta Cryst.* **A45**, 86–99.
 CICCARIELLO, S. (1990). *Acta Cryst.* **A46**, 175–186.
 CICCARIELLO, S. (1991). *Phys. Rev. A*, **44**, 2975–2983.
 CICCARIELLO, S. & BENEDETTI, A. (1982). *Phys. Rev. B*, **26**, 6384–6389.
 CICCARIELLO, S. & BENEDETTI, A. (1986). *J. Appl. Cryst.* **19**, 195–197.
 CICCARIELLO, S., COCCO, G., BENEDETTI, A. & ENZO, S. (1981). *Phys. Rev. B*, **23**, 6474–6485.
 DEBYE, P., ANDERSON, H. R. & BRUMBERGER, H. (1957). *J. Appl. Phys.* **28**, 679–683.
 EDWARDS, H. J. & TOMAN, K. (1977). *J. Appl. Cryst.* **4**, 319–321.
 ERDÉLYI, A. (1956). *Asymptotic Expansions*, ch. II. New York: Dover.
 JONES, D. S. & KLINE, M. (1958). *J. Math. Phys. (Cambridge, Mass.)* **37**, 1–28.
 KIRSTE, R. & POROD, H. (1962). *Kolloid Z.* **184**, 1–7.
 LANGFORD, J. I. & LOUËR, D. (1982). *J. Appl. Cryst.* **15**, 20–26.
 LANGFORD, J. I. & WILSON, A. J. C. (1977). *J. Appl. Cryst.* **11**, 102–113.
 MÉRING, J. & TCHOUBAR, D. (1968). *J. Appl. Cryst.* **1**, 153–165.
 MILLER, A. & SCHMIDT, P. W. (1962). *J. Math. Phys. (NY)*, **3**, 92–96.
 MITRA, B. G. (1964). *Br. J. Appl. Phys.* **15**, 917–921.
 PATTERSON, A. L. (1939). *Phys. Rev.* **56**, 972–977.
 POROD, G. (1951). *Kolloid Z.* **124**, 83–87.
 POROD, G. (1967). *Small-Angle X-ray Scattering: Proceedings of the Syracuse Conference*, edited by H. Brumberger, pp. 1–14. New York: Gordon and Breach.
 SCHMIDT, P. W. (1965). *J. Math. Phys. (NY)*, **6**, 424–431.
 SCHMIDT, P. W. (1967). *J. Math. Phys. (NY)*, **8**, 475–477.
 SMIRNOV, V. (1970). *Cours de Mathématiques Supérieures*, Vol. II. Moscow: MIR.
 SOBRY, R., LEDENT, J. & FONTAINE, F. (1991). *J. Appl. Cryst.* **24**, 516–525.
 TCHOUBAR, D. & MÉRING, J. (1969). *J. Appl. Cryst.* **2**, 128–135.
 TOURNARIE, M. (1956). *C. R. Acad. Sci.* **242**, 2016–2018.
 WILSON, A. J. C. (1949). *X-ray Optics*. London: Methuen.
 WILSON, A. J. C. (1962). *Proc. Phys. Soc. London*, **80**, 286–294.
 WILSON, A. J. C. (1969). *J. Appl. Cryst.* **2**, 181–183.
 WILSON, A. J. C. (1970). *Elements of X-ray Crystallography*, ch. 10. Reading, MA: Addison-Wesley.
 WILSON, A. J. C. (1971). *J. Appl. Cryst.* **4**, 440–443.
 WU, H. & SCHMIDT, P. W. (1974). *J. Appl. Cryst.* **7**, 131–146.