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Reconstruction of the form of a particle from its three-dimensional asymptotic form factor

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The form of a particle, which is homogeneous, finite, strictly convex, smooth and centrosymmetric, can uniquely be determined if the leading asymptotic term of its form factor is known along each direction of reciprocal space. If the central symmetry is lacking, all the admissible particle forms are among the solutions of a partial differential equation with given boundary conditions. The possible practical relevance of this result is discussed.

It is well known that the scattering density of a sample cannot uniquely be determined from its scattering intensity. This, in fact, determines only the modulus of the scattering amplitude while the amplitude's phase remains fully unknown. However, this ambiguity can drastically be reduced and, in favourable cases, completely removed if one requires that the scattering density has some definite mathematical properties. For instance, in the one-dimensional case, it is possible to determine all the scattering densities that reproduce a given scattering intensity when it is known that they refer to a linear finite object (Burge *et al.*, 1976; Requicha, 1980). (For the three-dimensional case, see Baker *et al.*, 1993.) Similarly, the knowledge of an appropriate finite subset of the diffraction pattern of a periodic crystal is sufficient to determine all the atomic configurations that reproduce the scattering intensity (Cervellino & Ciccariello, 2001) if one assumes that the unit cell of the crystal consists of a finite number of *point-like* atoms.

In the realm of small-angle scattering (SAS), the scattering density is assumed to be a two-value function (Debye *et al.*, 1957). If we confine ourselves to the case of a dilute sample consisting of a monodisperse collection of identical particles equally oriented inside the sample, the observed scattering intensity $I(\mathbf{q})$ takes the form (Guinier & Fournet, 1955)

$$I(\mathbf{q}) = \mathcal{N}_p(\Delta n)^2 F(\mathbf{q}), \tag{1}$$

where $\mathbf{q}$ is the scattering vector, $(\Delta n)^2$ the contrast, $\mathcal{N}_p$ the particle number and $F(\mathbf{q})$ the geometrical form factor of the particle. $F(\mathbf{q})$ is related to $\mathcal{A}(\mathbf{q})$, the scattering amplitude of the particle, by

$$(\Delta n)^2 F(\mathbf{q}) = |\mathcal{A}(\mathbf{q})|^2, \tag{2}$$

with $\mathcal{A}(\mathbf{q})$ defined by

$$\mathcal{A}(\mathbf{q}) = (\Delta n) \textstyle\int \rho(\mathbf{r}) \exp(i\mathbf{q}\cdot\mathbf{r})\, \mathrm{d}v. \tag{3}$$

Here, $\rho(\mathbf{r})$ defines the particle form since it is defined as being equal to one when the tip of $\mathbf{r}$ is internal to the particle and equal to zero elsewhere. Clearly, the knowledge of $\mathcal{A}(\mathbf{q})$ uniquely determines $(\Delta n)\rho(\mathbf{r})$, the two functions being related by a Fourier transformation. But, according to (2), the observed $I(\mathbf{q})$ does not determine $\mathcal{A}(\mathbf{q})$. It only determines $F(\mathbf{q})$ aside from the trivial constant $\mathcal{C} \equiv \mathcal{N}_p(\Delta n)^2$. Nonetheless, *the knowledge of the asymptotic form factor along any direction of reciprocal space allows us to say whether it refers to a finite, homogeneous, strictly convex, smooth and centrosymmetric particle or not and, in the affirmative case, to determine uniquely the particle form*. [It is recalled that a particle is smooth when no edges or corner points are present on its surface and it is strictly convex when each segment having its two ends on the particle boundary has the remaining points in the particle interior.]

To prove this statement, referred to as property I in the following, it is recalled that, according to equation (11) of Ciccariello *et al.* (2000), the asymptotic behaviour of $\mathcal{A}(q\hat{\mathbf{q}})$ reads

$$\mathcal{A}(q\hat{\mathbf{q}}) = -\frac{2\pi\Delta n}{q^2}\left\{\frac{\exp(iq\delta_+)}{[\kappa_{\rm G}(\hat{\mathbf{q}})]^{1/2}} + \frac{\exp(iq\delta_-)}{[\kappa_{\rm G}(-\hat{\mathbf{q}})]^{1/2}}\right\} + o(q^{-2}). \tag{4}$$

Here, $q\,(\equiv|\mathbf{q}|)$ and $\hat{\mathbf{q}}\,(\equiv \mathbf{q}/q)$ denote the modulus and the direction of the scattering vector $\mathbf{q}$, $o(q^{-2})$ a contribution decreasing faster than q^{-2} as $q\to\infty$ and $\kappa_{\rm G}(\hat{\mathbf{q}})$ ($\kappa_{\rm G}(-\hat{\mathbf{q}})$) the value of the Gaussian curvature of the particle surface Σ at the point P_+ (P_-), where the unit normal $\hat{\boldsymbol{\nu}}$, pointing outward to the particle, is parallel (antiparallel) to $\hat{\mathbf{q}}$. Finally, δ_+ (δ_-) is the algebraic distance from the origin to the plane tangent to Σ at P_+ (P_-). The assumptions of strict convexity and smoothness ensure that, whatever $\hat{\mathbf{q}}$, the (unit) normal to Σ is equal to $\hat{\mathbf{q}}$ at only one point of Σ and that $\kappa_{\rm G}(\mathrm{P}) > 0$ whatever the considered point P of Σ. The first of these properties implies that one can write $\mathrm{P} = \mathrm{P}(\hat{\mathbf{q}})$ as well as $\hat{\mathbf{q}} = \hat{\mathbf{q}}(\mathrm{P})$. Here, $\mathrm{P}(\hat{\mathbf{q}})$ denotes the point of Σ where the unit normal is equal to $\hat{\mathbf{q}}$, and $\hat{\mathbf{q}}(\mathrm{P})$ denotes the direction of reciprocal space equal to $\hat{\boldsymbol{\nu}}(\mathrm{P})$, the normal to Σ at P. Moreover, $\mathrm{P}(\hat{\mathbf{q}})$ and $\hat{\mathbf{q}}(\mathrm{P})$ respectively span the total surface Σ and all the directions of reciprocal space, as $\hat{\mathbf{q}}$ ranges over the latter and P over Σ. Define now the function $\delta(\hat{\mathbf{q}})$ by setting $\delta(\hat{\mathbf{q}}) \equiv \delta_+(\hat{\mathbf{q}})$. The particle being finite and smooth, $\delta(\hat{\mathbf{q}})$ exists and is finite whatever $\hat{\mathbf{q}}$. Furthermore, one has $\delta_-(\hat{\mathbf{q}}) = -\delta(-\hat{\mathbf{q}})$ because, in defining $\delta_+(\hat{\mathbf{q}})$ and $\delta_-(\hat{\mathbf{q}})$, the distances of the tangent planes from the origin are evaluated along the straight line oriented along $\hat{\mathbf{q}}$ and going through the origin. This definition also implies that $\delta_+(\hat{\mathbf{q}}) > \delta_-(\hat{\mathbf{q}})$, whatever $\hat{\mathbf{q}}$. After substituting (4) into (2), the leading asymptotic behaviour of the particle form factor reads

$$F(q\hat{\mathbf{q}}) = \frac{4\pi^2}{q^4}\left[\frac{1}{\kappa_G(\hat{\mathbf{q}})} + \frac{1}{\kappa_G(-\hat{\mathbf{q}})} + \frac{2\cos[q(\delta(\hat{\mathbf{q}}) + \delta(-\hat{\mathbf{q}}))]}{[\kappa_G(\hat{\mathbf{q}})\kappa_G(-\hat{\mathbf{q}})]^{1/2}}\right] + o(q^{-4}). \tag{5}$$

As expected, this expression is centrosymmetric since it is the asymptotic leading term of the Fourier transform of the autoconvolution of a real function. It simplifies further in the case of a centrosymmetric particle. In this case, we have $\kappa_G(\hat{\mathbf{q}}) = \kappa_G(-\hat{\mathbf{q}})$ and, after choosing a reference frame with its origin set at the particle's centre, $\delta(\hat{\mathbf{q}}) = \delta(-\hat{\mathbf{q}})$. Thus, for a centrosymmetric particle one finds that

$$q^4F(q\hat{\mathbf{q}}) = \frac{8\pi^2}{\kappa_G(\hat{\mathbf{q}})}\{1 + \cos[2q\delta(\hat{\mathbf{q}})]\} + \varepsilon, \tag{6}$$

where ε is a contribution approaching zero as $q \to \infty$. The three-dimensional (3D) Porod plot (Porod, 1951) of the form factor is obtained by plotting $q^4F(q\hat{\mathbf{q}})$ *versus* $\mathbf{q}$. Hence, the 3D Porod plot of the form factor of a homogeneous, strictly convex, smooth, finite and centrosymmetric particle, which for conciseness will be named *simple* in the following, must show, in the outer q region, the analytic dependence reported on the right hand side (r.h.s.) of (6). Each of the aforesaid particle properties is related to a mathematical feature of (6). In fact, the homogeneity is related to the fact that $q^4F(q\hat{\mathbf{q}})$ does not decrease as q increases. The smoothness and the finiteness reflect into the existence and the finiteness of both $\kappa_G(\hat{\mathbf{q}})$ and $\delta(\hat{\mathbf{q}})$. The strict convexity implies that the r.h.s. of (6) remains finite whatever the considered $\hat{\mathbf{q}}$ (it is recalled that a smooth non-convex particle necessarily has points where $\kappa_G = 0$) and that the tip of the vector $\hat{\mathbf{q}}\delta(\hat{\mathbf{q}})$ spans a closed smooth (and simply connected) surface as $\hat{\mathbf{q}}$ takes all possible values. Finally, the central symmetry is responsible for the property that, for each $\hat{\mathbf{q}}$, the amplitude of the oscillatory contribution $\cos[2q\delta(\hat{\mathbf{q}})]$ is equal to the 'constant' contribution, *i.e.* the Porod term equal to $8\pi^2/\kappa_G(\hat{\mathbf{q}})$. (For discussion of the case of non-centrosymmetric particles, we refer to Appendix *A*.) This property has an interesting implication: the r.h.s. of (6) becomes infinitesimal with ε in a family of $\mathbf{q}$ regions that, as q increases, approach the surfaces $q = q_N(\hat{\mathbf{q}})$, $q_N(\hat{\mathbf{q}})$ being defined by

$$q_N(\hat{\mathbf{q}})\delta(\hat{\mathbf{q}}) = (2N+1)\pi/2, \tag{7a}$$

with N integer and sufficiently large. Geometrically, each $q_N(\hat{\mathbf{q}})$ represents a surface of reciprocal space where the intensity becomes closer and closer to zero as N increases. Moreover, $q_N(\hat{\mathbf{q}})$ is a smooth closed surface since, as reported above, the same property applies to $\delta(\hat{\mathbf{q}})$. Observe now that both $q_N(\hat{\mathbf{q}})$ and $\delta(\hat{\mathbf{q}})$ can be determined knowing at least two next-neighbour regions of the 3D Porod plot where $q^4F(q\hat{\mathbf{q}}) \approx 0$. One concludes that by looking at the properties of the 3D Porod plot of the form factor of a particle it is possible to state whether the particle is simple or not. In this way, the first part of property I is proven.

To prove the second part, it will be shown that the knowledge of $\delta(\hat{\mathbf{q}})$ allows us to determine the particle boundary. To this aim, it is first observed that from (7*a*) it follows that

$$\delta(\hat{\mathbf{q}}) = (2N+1)\pi/2q_N(\hat{\mathbf{q}}), \tag{7b}$$

so that the knowledge of the zero iso-intensity surfaces, observed in the asymptotic region of the Porod plot, determines $\delta(\hat{\mathbf{q}})$. [It is noted that a fair independence of the r.h.s. of (7*b*) on N ensures that the considered $\mathbf{q}$ region is asymptotic.] If the zero iso-intensity surfaces are smooth, finite and closed and if the r.h.s. of (7*b*) is (almost) independent of N, then $\delta(\hat{\mathbf{q}})$ refers to a simple particle. According to our previous remarks, $\delta(\hat{\mathbf{q}})$ is the distance from the origin to the plane tangent to the particle surface at the point where the normal points along $\hat{\mathbf{q}}$. Besides, as already reported, for a smooth and strictly convex particle, the points of Σ can be parametrized in terms of $\hat{\mathbf{q}}$ as $\mathrm{P} = \mathrm{P}(\hat{\mathbf{q}})$, and this relation can be inverted as $\hat{\mathbf{q}} = \hat{\mathbf{q}}(\mathrm{P})$. On the other hand, $\hat{\mathbf{q}}$ can be parametrized as

$$\hat{\mathbf{q}}_x = \hat{\boldsymbol{\nu}}_x = \cos(\varphi)\sin(\theta), \quad \hat{\mathbf{q}}_y = \hat{\boldsymbol{\nu}}_y = \sin(\varphi)\sin(\theta),$$
$$\hat{\mathbf{q}}_z = \hat{\boldsymbol{\nu}}_z = \cos(\theta), \tag{8a}$$

where φ and θ denote the polar angles of $\hat{\mathbf{q}}$. Consider the following unit vectors:

$$\hat{\boldsymbol{\tau}} \equiv (\cos(\varphi)\cos(\theta), \sin(\varphi)\cos(\theta), -\sin(\theta)), \tag{8b}$$
$$\hat{\boldsymbol{\mu}} \equiv (-\sin(\varphi), \cos(\varphi), 0), \tag{8c}$$

Whatever (θ, φ), vectors $\hat{\boldsymbol{\nu}}(\theta,\varphi)$, $\hat{\boldsymbol{\tau}}(\theta,\varphi)$ and $\hat{\boldsymbol{\mu}}(\theta,\varphi)$ are orthogonal to each other and such that $\hat{\boldsymbol{\mu}} = \hat{\boldsymbol{\nu}} \times \hat{\boldsymbol{\tau}}$, the last relation remaining true when the involved vectors are circularly permuted. We also have

$$\hat{\boldsymbol{\nu}}_{,\theta}(\theta,\varphi) \equiv \frac{\partial\hat{\boldsymbol{\nu}}(\theta,\varphi)}{\partial\theta} = \hat{\boldsymbol{\tau}}(\theta,\varphi), \tag{9a}$$
$$\hat{\boldsymbol{\nu}}_{,\varphi}(\theta,\varphi) \equiv \frac{\partial\hat{\boldsymbol{\nu}}(\theta,\varphi)}{\partial\varphi} = \sin(\theta)\hat{\boldsymbol{\mu}}(\theta,\varphi), \tag{9b}$$
$$\hat{\boldsymbol{\tau}}_{,\theta} = -\hat{\boldsymbol{\nu}}, \quad \hat{\boldsymbol{\tau}}_{,\varphi} = \cos(\theta)\hat{\boldsymbol{\mu}}, \tag{9c,d}$$
$$\hat{\boldsymbol{\mu}}_{,\theta} = 0, \quad \hat{\boldsymbol{\mu}}_{,\varphi} = -\sin(\theta)\hat{\boldsymbol{\nu}} - \cos(\theta)\hat{\boldsymbol{\tau}}. \tag{9e,f}$$

Let $\mathbf{R}(\hat{\mathbf{q}}) = \mathbf{R}(\theta,\varphi)$ denote the position vector of $\mathrm{P}(\mathbf{q})$, the point of the particle surface where the normal is equal to $\hat{\mathbf{q}}$. On general grounds, one can write

$$\mathbf{R}(\theta,\varphi) = \delta(\theta,\varphi)\hat{\boldsymbol{\nu}}(\theta,\varphi) + \xi(\theta,\varphi)\hat{\boldsymbol{\tau}}(\theta,\varphi) + \eta(\theta,\varphi)\hat{\boldsymbol{\mu}}(\theta,\varphi), \tag{10}$$

where $\xi(\theta,\varphi)$ and $\eta(\theta,\varphi)$ are as yet unknown functions. However, these must be such that the normal to the surface defined by (10) be equal to $\hat{\boldsymbol{\nu}}$. By a well known formula of differential geometry (Smirnov, 1970), the normal to the surface is given by

$$\hat{\boldsymbol{\nu}}(\theta,\varphi) = \mathbf{R}_{,\theta} \times \mathbf{R}_{,\varphi}/||\mathbf{R}_{,\theta} \times \mathbf{R}_{,\varphi}||, \tag{11}$$

where, with the same convention adopted in (9), $\mathbf{R}_{,\theta}$ ($\mathbf{R}_{,\varphi}$) denotes the partial derivative of $\mathbf{R}$ with respect to θ (φ). Thus, it must result that $\hat{\boldsymbol{\nu}}(\theta,\varphi) \cdot \mathbf{R}_{,\theta}(\theta,\varphi) = \hat{\boldsymbol{\nu}}(\theta,\varphi) \cdot \mathbf{R}_{,\varphi}(\theta,\varphi) = 0$.

These two conditions, applied to the $\mathbf{R}_{,\theta}$ and $\mathbf{R}_{,\varphi}$ expressions obtained by evaluating the relevant derivatives of (10), yield

$$\xi(\theta,\varphi) = \delta_{,\theta}(\theta,\varphi) \tag{12a}$$

$$\eta(\theta,\varphi) = \delta_{,\varphi}(\theta,\varphi)/\sin(\theta). \tag{12b}$$

In this way, the knowledge of $\delta(\theta,\varphi)$ implies that of $\xi(\theta,\varphi)$ and $\eta(\theta,\varphi)$. Thus, $\mathbf{R}(\theta,\varphi)$ turns out to be fully determined and property I fully proven. An analytical illustration of this result is reported in Appendix *B*.

It is now remarked that, since the knowledge of $\delta(\theta,\varphi)$ fully determines the particle geometry, $\delta(\theta,\varphi)$ must also determine the Gaussian curvature of the particle surface. In fact, after putting

$$A(\theta,\varphi) \equiv (\delta + \delta_{,\theta^2}), \quad B(\theta,\varphi) \equiv \left(\frac{\delta_{,\varphi}}{\sin(\theta)}\right)_{,\theta}, \tag{13a,b}$$

$$C(\theta,\varphi) \equiv \frac{\delta_{,\varphi^2} - \cos(\theta)\delta_{,\varphi}}{\sin(\theta)}, \tag{13c}$$

$$D(\theta,\varphi) \equiv \frac{\delta_{,\varphi^2}}{\sin(\theta)} + \sin(\theta)\delta + \cos(\theta)\delta_{,\theta}, \tag{13d}$$

from (10) and (12), one gets

$$\mathbf{R}_{,\theta} = A(\theta,\varphi)\hat{\boldsymbol{\tau}}(\theta,\varphi) + B(\theta,\varphi)\hat{\boldsymbol{\mu}}(\theta,\varphi), \tag{14a}$$

$$\mathbf{R}_{,\varphi} = C(\theta,\varphi)\hat{\boldsymbol{\tau}} + D(\theta,\varphi)\hat{\boldsymbol{\mu}}, \tag{14b}$$

$$\mathbf{R}_{,\theta^2} = -A\hat{\boldsymbol{\nu}} + A_{,\theta}\hat{\boldsymbol{\tau}} + B_{,\theta}\hat{\boldsymbol{\mu}}, \tag{14c}$$

$$\mathbf{R}_{,\theta\varphi} = -B\sin(\theta)\hat{\boldsymbol{\nu}} + [A_{,\varphi} - B\cos(\theta)]\hat{\boldsymbol{\tau}} + [B_{,\varphi} + A\cos(\theta)]\hat{\boldsymbol{\mu}}, \tag{14d}$$

$$\mathbf{R}_{,\varphi^2} = -D\sin(\theta)\hat{\boldsymbol{\nu}} + [C_{,\varphi} - D\cos(\theta)]\hat{\boldsymbol{\tau}} + [D_{,\varphi} + C\cos(\theta)]\hat{\boldsymbol{\mu}} \tag{14e}$$

and the Gaussian curvature in terms of $\delta(\theta,\varphi)$ reads

$$\kappa_{\rm G}(\hat{\mathbf{q}}) = \frac{AD\sin(\theta) - B^2\sin^2(\theta)}{(A^2+B^2)(C^2+D^2) - (AC+BD)^2}, \tag{15}$$

as it immediately follows from the previous expressions using some basic formulae of differential geometry (Smirnov, 1970), *viz* $\kappa_{\rm G}(\hat{\mathbf{q}}) = [LN - M^2]/[EG - F^2]$, with $E \equiv \mathbf{R}_{,\theta}\cdot\mathbf{R}_{,\theta}$, $F \equiv \mathbf{R}_{,\theta}\cdot\mathbf{R}_{,\varphi}$, $G \equiv \mathbf{R}_{,\varphi}\cdot\mathbf{R}_{,\varphi}$, $L \equiv \mathbf{R}_{,\theta^2}\cdot\hat{\boldsymbol{\nu}}$, $M \equiv \mathbf{R}_{,\theta\varphi}\cdot\hat{\boldsymbol{\nu}}$ and $N \equiv \mathbf{R}_{,\varphi^2}\cdot\hat{\boldsymbol{\nu}}$. One concludes that the knowledge of $\delta(\hat{\mathbf{q}})$ fully determines the leading asymptotic term of the form factor of a simple particle. Thus, from the Porod plot of the observed intensity, one finds that the 'constant' term (that in the anisotropic case depends on $\hat{\mathbf{q}}$) in the asymptotic region is $\mathcal{P}_{\rm PD}(\hat{\mathbf{q}}) = 8\pi^2\mathcal{N}_p(\Delta n)^2/\kappa_{\rm G}(\hat{\mathbf{q}})$ as it immediately follows by combining (1) and (6). Since $\kappa_{\rm G}(\hat{\mathbf{q}})$ is known in terms of $\delta(\hat{\mathbf{q}})$ by (15), the knowledge of $\mathcal{P}_{\rm PD}(\hat{\mathbf{q}})$ determines $\mathcal{N}_p(\Delta n)^2$.

These results show that, for a dilute and monodisperse system of *simple* particles that are equally oriented inside the sample, the phase problem for the particle shape can uniquely be solved when the scattering intensity is accurately known in the asymptotic region. Actually, the assumption that the system be diluted could be substituted with the weaker assumption that the correlation length of the 3D radial distribution function not be large. In such a case, the asymptotic region of the scattering intensity, in comparison to the dilute case, moves farther in reciprocal space but could still be observed. Then, the particle form could be uniquely determined, while the inner part of the scattering intensity determines, *via* a Fourier transformation, the radial distribution function (Hansen & McDonald, 1986) no longer equal to one as in the dilute case.

Two questions appear now quite natural. First, is it possible to generalize property I to particles with a more general shape? Second, which are the conditions to be fulfilled for property I to have a practical usefulness? As explained in Appendix *A*, the answer to the first question is negative. There, in fact, it is shown that, when lacking the central symmetry, the particle forms can be obtained as the solutions of a partial differential equation with specified boundary conditions, a rather awkward mathematical problem indeed. On the contrary, the second question can be answered in the affirmative under favourable circumstances that will now be detailed.

To this aim, we refer to Fig. 1 showing a 'theoretical' illustration of property I. Here is considered the case of a simple particle bounded by the revolution surface obtained by rotating the continuous line, shown in Fig. 1(*a*), around axis *z*. The curve is the section of the particle surface with the plane $y = 0$. Its analytic expression is

$$x = R(|\phi|)\cos(|\phi|), \qquad z = R(|\phi|)\sin(\phi) \tag{16a,b}$$

with

$$R(|\phi|) \equiv R_0\exp[\Gamma(|\phi|)], \quad \Gamma(|\phi|) \equiv \phi^2(G_1 + G_2|\phi| + G_3\phi^2), \tag{16c,d}$$

where

$$G_1 \equiv a\pi/4, \quad G_2 \equiv -a(1 - b\pi/2)/3,$$
$$G_3 \equiv -ab/4, \quad a \equiv -6\log(R_1/R_0)/[(1 + b\pi/4)(\pi/2)^3]$$

and ϕ ($\in [-\pi/2, \pi/2]$) is equal to the angle formed by $\mathbf{r} = (x, z)$ with axis *x*. The figure refers to the choices $b = -1$ and $R_1 = 1.1$ u, while $R_0 = R(\pi/2) = 1$ u, u denoting an arbitrary length. The broken and the dotted curves respectively show the sections of $\mathrm{u}/\delta(\hat{\mathbf{q}})$ and $[\mathrm{u}^2\kappa_{\rm G}(\hat{\mathbf{q}})]^{-1/4}$ with the reciprocal-space plane $q_y = 0$. The first and the second curves respectively show the shape of $q_N(\hat{\mathbf{q}})$, defined by (7*b*), and that of the asymptotic iso-intensity line when the only monotonic contribution is considered on the r.h.s. of (6). Fig. 1(*b*) shows the two-dimensional (2D) Porod plot of the particle form factor on the same plane with the scale of greys reported on the right. The full 3D Porod plot as well as the full 3D shape of $\mathrm{u}/\delta(\hat{\mathbf{q}})$ and $[\mathrm{u}^2\kappa_{\rm G}(\hat{\mathbf{q}})]^{-1/4}$ are obtained by rotating Fig. 1(*b*) and Fig. 1(*a*) around axis *z*, owing to the assumed rotational symmetry. $F(q\hat{\mathbf{q}})$ was obtained by numerical integration of (3), as appears evident from the small squares in the figure that originate from making discrete the integral domains. The (broken and continuous) black curves are the iso-values of $q^4F_{\rm as}(q\hat{\mathbf{q}})$, $F_{\rm as}(q\hat{\mathbf{q}})$ denoting the asymptotic expression given by (6), and range from 0 (broken curve) to 250 with a step of 50. The figure makes it evident that the agreement between $q^4F(q\hat{\mathbf{q}})$ and $q^4F_{\rm as}(q\hat{\mathbf{q}})$ is already satisfactory beyond the first white annulus. Moreover, the shape of the broken curve of Fig.

1(a) and that of the broken ones internal to the white annuli of Fig. 1(b) are quite similar. The last curves are the plots of the sections of $q_N(\hat{\mathbf{q}})$, with $N = 2, 3, \ldots$, and defined by (7b), with the plane $q_y = 0$. The white annuli present in the 2D Porod plot make an approximate determination of these curves rather simple and unambiguous. Then the rotational symmetry and the use of (7a) make the particle determination possible, since the conditions required for the validity of property I are met.

This example indicates that an approximate determination of the particle form becomes practically possible if: (i) the sample is known to consist of particles with a rotational axis parallel to the detector plane, and if the 2D SAS intensity approximately fulfils the following two conditions: (ii) its 2D Porod plot shows at least two 'white' annuli where $q^4 I(q\hat{\mathbf{q}}) \approx 0$, and (iii) it is possible to draw, inside each annulus, a closed continuous curve such that the ratio $q_2(\hat{\mathbf{q}})/q_1(\hat{\mathbf{q}}) = (2N+1)/(2N-1)$ be independent of $\hat{\mathbf{q}}$ and equal to the ratio of the next two odd integers. [Here, $q_i(\hat{\mathbf{q}})$, with $i = 1, 2$, denote the distances, along direction $\hat{\mathbf{q}}$, from the origin to the the inner and outer curve, respectively.] If these conditions are reasonably fulfilled, $\delta(\hat{\mathbf{q}})$ is obtained by (7b) and by the rotational symmetry. Then the knowledge of $\delta(\hat{\mathbf{q}})$, *via* (10), (12a), (12b), allows us to determine $\mathbf{R}(\hat{\mathbf{q}})$, the parametric equation of the particle surface. Moreover, one can use the knowledge of the oscillation amplitude [*viz* $4\mathcal{N}_p(\Delta n)^2\pi^2/\kappa_G(\hat{\mathbf{q}})$], resulting from the best fit of the considered 2D Porod plot, to check whether (15) is obeyed or not, and to conclude that only in the first case is the particle determination reliable.

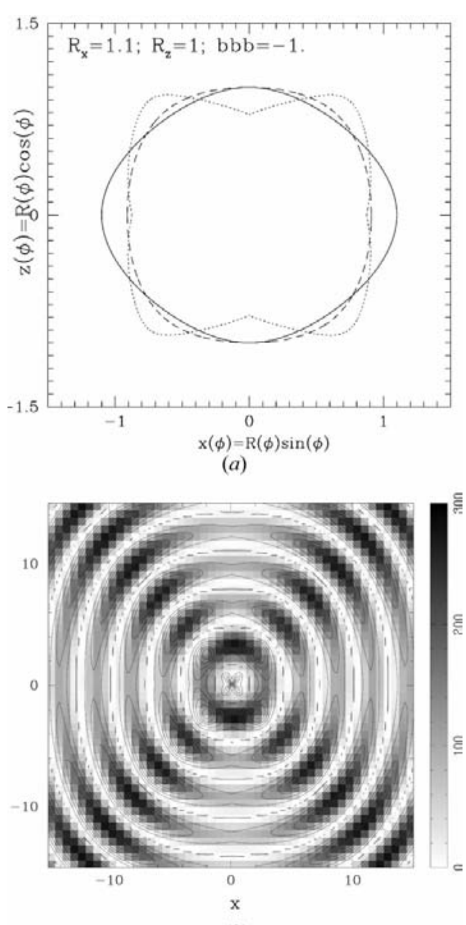

Figure 1
(a) The continuous line shows the section, with the plane $y = 0$, of the considered particle surface which is a revolution surface around z. The broken and the dotted curves represent $\mathrm{u}/\delta(\hat{\mathbf{q}})$ and $[\mathrm{u}^2\kappa_G(\hat{\mathbf{q}})]^{-1/4}$, respectively. ($b$) The section with the reciprocal-space plane $q_y = 0$ of the 3D Porod plots of the corresponding exact (in grey) and asymptotic form factors (tiny black lines). The values reported on axes x and z refer to $q_x\mathrm{u}$ and $q_z\mathrm{u}$, u being an arbitrary length unit.

One concludes that property I can be practically useful for analysing samples where conditions (i)–(iii) are obeyed. It is now observed that samples obeying condition (i) have recently been observed (Ciccariello, 2002). Moreover, the asymptotic analysis of some isotropic intensities (Ciccariello & Sobry, 1999) indicates that condition (ii) holds practically true even in the presence of a polydispersity smaller than 20% and one can confidently expect that (ii) applies also in the presence of a small particle misalignment. Finally, condition (iii) is no longer necessary when the mean particle size exceeds 200 Å because, in this case, the SAS behaviour will be fairly independent of interparticle interference in the outer q range $[0.1 - 0.3]$ Å^{-1}. The previous remarks indicate that samples obeying conditions (i)–(iii), if not already found, might be found in the future so as to make the application of property I practically useful.

Summarizing, it has been shown that the asymptotic behaviour of the form factor allows us to say whether it is relevant to a homogeneous, finite, smooth, strictly convex and centrosymmetric particle or not and, in the affirmative case, to uniquely determine the latter form. When the particle is not centrosymmetric, from the asymptotic behaviour of the form factor it is possible to obtain a partial differential equation with appropriate boundary conditions, whose solutions yield all the possible particle forms able to reproduce the given form factor. In favourable conditions, property I can usefully be applied to determine the particle form from the asymptotic behaviour of its scattering intensity. Finally, the fact that the previous analysis apparently avoids the ambiguities related to the crystallographic phase problem is not surprising because the aforesaid procedure fully exploited the condition that the solution refers to a homogeneous particle.

APPENDIX *A*
Non-centrosymmetric particles

We discuss now the case of a strictly convex particle that is not centrosymmetric. The asymptotic behaviour, given by (5), can be written as

$$q^4 F(q\hat{\mathbf{q}}) = \frac{8\pi^2}{\Xi(\hat{\mathbf{q}})}\{f(\Upsilon(\hat{\mathbf{q}})) + \cos[q\Delta(\hat{\mathbf{q}})]\} + \varepsilon, \qquad (17)$$

where we have put

$$\Xi(\hat{\mathbf{q}}) \equiv [\kappa_G(\hat{\mathbf{q}})\kappa_G(-\hat{\mathbf{q}})]^{1/2}, \quad \Upsilon(\hat{\mathbf{q}}) \equiv [\kappa_G(-\hat{\mathbf{q}})/\kappa_G(\hat{\mathbf{q}})]^{1/2}, \qquad (18a,b)$$

and

$$\Delta(\hat{\mathbf{q}}) \equiv \delta(\hat{\mathbf{q}}) + \delta(-\hat{\mathbf{q}}), \quad f(x) \equiv (1/2)(x + 1/x). \qquad (18c,d)$$

It is observed that, in the physically relevant region $\Upsilon > 0$, $f(\Upsilon)$ is minimum at $\Upsilon = 1$, where it results that $f(1) = 1$. Consequently, as q varies, the expression inside square brackets on the r.h.s. of (17) is never equal to zero except for those $\hat{\mathbf{q}}$ directions where it may result that $\Upsilon(\hat{\mathbf{q}}) = 1$, *i.e.* $\kappa_G(\hat{\mathbf{q}}) = \kappa_G(-\hat{\mathbf{q}})$. It is concluded that the absence of closed surfaces of zeros in the Porod plot of the form factor is the signature that the particle is not centrosymmetric. In principle, the knowledge of $F(q\hat{\mathbf{q}})$ allow us to determine both $\kappa_G(\hat{\mathbf{q}})$ and $\Delta(\hat{\mathbf{q}})$ by (17). In fact, by best-fitting the r.h.s. of (17) to the given $q^4F(q\hat{\mathbf{q}})$ at fixed $\hat{\mathbf{q}}$ and large q's, one determines the three quantities there present, *i.e*: $X_1 \equiv f(\Upsilon(\hat{\mathbf{q}}))/\Xi(\hat{\mathbf{q}})$, $X_2 \equiv 1/\Xi(\hat{\mathbf{q}})$ and $X_3 \equiv \Delta(\hat{\mathbf{q}})$. The first two relations can be solved and yield

$$\kappa_G(\hat{\mathbf{q}}) = \frac{X_1(\hat{\mathbf{q}}) \pm [X_1^2(\hat{\mathbf{q}}) - X_2^2(\hat{\mathbf{q}})]^{1/2}}{X_2^2(\hat{\mathbf{q}})} \qquad (19a)$$

$$\kappa_G(-\hat{\mathbf{q}}) = \frac{X_1(\hat{\mathbf{q}}) \mp [X_1^2(\hat{\mathbf{q}}) - X_2^2(\hat{\mathbf{q}})]^{1/2}}{X_2^2(\hat{\mathbf{q}})}. \qquad (19b)$$

It is now observed that $F(q\hat{\mathbf{q}})$ is always an even function. This fact implies that $X_1(\hat{\mathbf{q}}) = X_1(-\hat{\mathbf{q}})$ and $X_2(\hat{\mathbf{q}}) = X_2(-\hat{\mathbf{q}})$, as appears evident from their definitions. For (19*a*) to match continuously into (19*b*), $X_1^2(\hat{\mathbf{q}}) - X_2^2(\hat{\mathbf{q}}) = 0$ must hold for the $\hat{\mathbf{q}}$'s that form closed curves on the unit sphere. Assume, for simplicity, we have only one curve denoted by Γ. In this case, a solution is given by $\kappa_G(\hat{\mathbf{q}}) = \kappa_G^{(+)}(\hat{\mathbf{q}})$ for the $\hat{\mathbf{q}}$'s lying on the left of Γ and by $\kappa_G(\hat{\mathbf{q}}) = \kappa_G^{(-)}(-\hat{\mathbf{q}})$ for the $\hat{\mathbf{q}}$'s on the right. Here superscripts $(+)$ and $(-)$ refer to the signs present in front of the square roots in (19*a*) and (19*b*), respectively. The other solution is $\kappa_G(\hat{\mathbf{q}}) = \kappa_G^{(-)}(\hat{\mathbf{q}})$ and $\kappa_G(\hat{\mathbf{q}}) = \kappa_G^{(+)}(-\hat{\mathbf{q}})$, respectively on the left and on the right of Γ. The existence of two solutions, denoted in the following by superscripts 1 and 2, is physically evident: if a particle with form function $\rho(\mathbf{r})$ has Gaussian curvature $\kappa_G^{(1)}(\hat{\mathbf{q}})$, then the particle with form function $\rho(-\mathbf{r})$ will have Gaussian curvature $\kappa_G^{(2)}(\hat{\mathbf{q}}) = \kappa_G^{(1)}(-\hat{\mathbf{q}})$, while the autocorrelation functions, and consequently the form factors, of $\rho(\mathbf{r})$ and $\rho(-\mathbf{r})$ coincide. One wonders now on the possible implications that follow from the knowledge of $\Delta(\hat{\mathbf{q}})$. The lack of central symmetry does not allow one to obtain $\delta(\hat{\mathbf{q}})$ from $\Delta(\hat{\mathbf{q}})$. On general grounds, one can only write that

$$\delta(\hat{\mathbf{q}}) = \Delta(\hat{\mathbf{q}})/2 + \sigma(\hat{\mathbf{q}}), \qquad (20)$$

where $\sigma(\hat{\mathbf{q}})$ is an arbitrary odd function of $\hat{\mathbf{q}}$. Equation (20) is the general solution of the equation $\delta(\hat{\mathbf{q}}) + \delta(-\hat{\mathbf{q}}) = \Delta(\hat{\mathbf{q}})$. Besides, we can choose the origin at the midpoint of the particle diameter pointing along a particular direction $\hat{\mathbf{q}}_0$, so that $\sigma(\hat{\mathbf{q}}_0) = 0$. By the same considerations reported between (7*a*) and (15), after adopting the same parametrization in terms of (θ, φ), (15) yields a partial differential equation for $\sigma(\theta, \varphi)$. Its solutions, which fulfil the condition $\sigma(\hat{\mathbf{q}}_0) = 0$ and yield a continuous and *closed* $\mathbf{R}(\theta, \varphi)$, determine the particle forms that reproduce the asymptotic behaviour of the considered form factor. This appears to be the largest amount of information that can be extracted from the asymptotic behaviour of the form factor relevant to a strictly convex and homogeneous particle. In order to emphasize the role of the continuity argument, let us consider the case of a particle with C_∞ symmetry along a particular axis which will be chosen as polar axis. Then, $\sigma(\hat{\mathbf{q}}) = \sigma(\theta)$ and the former partial differential equation converts into an ordinary second-order differential equation. Moreover, the oddness of $\sigma(\hat{\mathbf{q}})$ becomes $\sigma(\theta) = -\sigma(\pi - \theta)$ and the origin can be fixed by requiring that $\sigma(0) = 0$. Equation (15) yields

$$\left\{\sin(\theta)\left[\frac{\Delta(\theta)}{2} + \sigma(\theta)\right] + \cos(\theta)\left[\frac{\Delta_{,\theta^2}(\theta)}{2} + \sigma_{,\theta^2}(\theta)\right]\right\} \times \left[\frac{\Delta(\theta)}{2} + \sigma(\theta) + \frac{\Delta_{,\theta^2}(\theta)}{2} + \sigma_{,\theta^2}(\theta)\right] = \frac{\sin(\theta)}{\kappa_G(\theta)}. \qquad (21)$$

The oddness of $\sigma(\theta)$ implies that we have to solve (21) in the θ range $[0, \pi/2]$. The continuity of $\kappa_G(\theta)$ at $\theta = 0$ requires that $[\Delta_{,\theta^2}(\theta)/2 + \sigma_{,\theta^2}(\theta)] \to 0$ as $\theta \to 0$. This condition does not determine the second initial condition, *i.e.* $\sigma_{,\theta}(0)$, which together with the condition $\sigma(0) = 0$ would ensure a unique solution. However, the continuity of $\delta(\theta)$ and the oddness of $\sigma(\theta)$ require that $\sigma(\pi/2) = 0$. Thus, we must look for the solutions of (21) that fulfil the two boundary conditions $\sigma(0) = 0$ and $\sigma(\pi/2) = 0$. In our case, we know that this problem must have at least one solution, *viz* the one relevant to the particle form from which the form factor was evaluated. But it can also happen that other solutions exist for $\sigma(\theta)$, so as to have more than one particle form with the given asymptotic form factor. Even though we are not able to state that all the $\sigma(\theta)$'s, solutions of the aforesaid problem, yield the given form factor (in fact, it could happen that the form factor be reproduced only asymptotically), certainly the particle forms having the considered form factor are among these solutions.

APPENDIX *B*
Ellipsoidal particles

An illustration of the application of the anisotropic Porod law to the case of ellipsoidal particles was recently presented by Ciccariello *et al.* (2002). Using the analytic expression of the form factor of this kind of particle, it is easy to obtain a rather straightforward application of the procedure discussed in this paper. In fact, according to (37) of the paper just quoted, the form factor of an ellipsoid reads

$$F_e(q\hat{\mathbf{q}}) = \left[\frac{16\pi^2(abc)^2}{q^4\Lambda^4}\right]\left[\cos(q\Lambda) - \frac{\sin(q\Lambda)}{q\Lambda}\right]^2, \qquad (22)$$

where a, b and c are the ellipsoid's semiaxis lengths along axes x, y and z, respectively, and Λ is defined as

$$\Lambda \equiv [(a\sin\theta\cos\phi)^2 + (b\sin\theta\sin\phi)^2 + (c\cos\theta)^2]^{1/2}, \qquad (23)$$

θ and ϕ being the polar angles of $\hat{\mathbf{q}}$. The asymptotic leading term of $F_e(q\hat{\mathbf{q}})$ is

$$F_e(q\hat{\mathbf{q}}) \approx \left[\frac{8\pi^2(abc)^2}{q^4\Lambda^4}\right][1+\cos(2q\Lambda)]. \qquad (24)$$

It is identical to that of a sphere except for the fact that Λ is not constant since it depends on θ and ϕ as described in (23). The comparison of (24) with (6) shows that

$$\delta(\hat{\mathbf{q}}) = \Lambda(\theta, \phi). \qquad (25)$$

It is now a matter of simple algebra to show that (10), together with (12*a*), (12*b*) and (8*a*)–(8*c*), yields the equation

$$x^2/a^2 + y^2/b^2 + z^2/c^2 = 1$$

of the ellipsoid with semiaxes a, b and c.

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