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Particle Shapes and Oscillatory Deviations from the Porod Law: the Hyperbolic Contact Point Case

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Abstract

The leading term in the asymptotic expansion of the isotropic component of the X-ray intensity scattered by a homogeneous right circular cylindrical particle (of height H and diameter D) can be written as: $\mathscr{C}h^{-4}[S_T-2S_B\cos(hH)-S_L\sin(hD)]$. Here S_L, S_B and S_T denote respectively the lateral, the base and the total surface area of the cylinder, while $\mathscr{C}$ is a normalization factor. From this expression one is led to conjecture that the oscillatory deviations from the Porod law, originated by the two interface subsets which have the same normal and are separated by δ, are proportional to $\cos(h\delta)$ or to $\sin(h\delta)$ depending on whether the tangency points between one of the interphase subsets and the spheres of radius δ centred on the opposite subset are elliptical or hyperbolic respectively. It is proved that the conjecture is true and general expressions for the coefficients in front of the two oscillatory functions are obtained.

Introduction

Knowledge of the leading term in the asymptotic expansion of the small-angle X-ray intensity $[\equiv I(h)]$ scattered by an amorphous sample can be very useful in order to analyse experimental data. Recently Ciccariello & Benedetti (1986) have shown that the oscillations observed in the Porod plots of the intensities scattered by some glasses undergoing a demixing process (Williams, Rindone & McKinstry, 1981) are due to the spherical particles which originated from an Ostwald ripening mechanism of nucleation and growth inside the metastable region.* The aforesaid analysis used the theoretical result (Ciccariello, 1985†) that, under some assumptions to be specified later, the leading term in the asymptotic expansion of the SAXS intensity can be written as

$$I(h)/4\pi V\langle\eta^2\rangle \simeq \frac{2S_T}{4V\Phi_1\Phi_2}\frac{1}{h^4}+\frac{2S_\parallel}{4V\Phi_1\Phi_2}\frac{\cos(h\delta)}{h^4}+o. \tag{1}$$

* A comparison of the currently available theoretical methods of analysis of the SAXS intensities scattered by demixing glasses can be found in a more recent paper (Benedetti, Ciccariello & Fagherazzi, 1988) where further examples of oscillatory deviations are reported.

† This paper will be referred to as I in the following.

On the r.h.s. of (1),* the first contribution corresponds to the well known Porod law (Porod, 1952; Debye, Anderson & Brumberger, 1957) while the second one represents an oscillatory *deviation* from the latter. One should note that in the Porod plot of the intensity [*i.e.* the plot of $h^4I(h)$ *versus* h], the amplitude of the deviation does not fade away as h increases. Accordingly, we shall use *deviation* for any contribution to the asymptotic expansion of the intensity which is different from the Porod term and shares the aforesaid property.

In this paper we address ourselves to the question of finding out the functional dependence of the deviations as well as the interphase features which originate them.

Of course, in order to find an answer to this question we have to assume that the interphase surface obeys some regularity conditions. Thus, we shall assume that the h^{-4} behaviour is due to a fractal dimension of the interphase surface equal to two (Bale & Schmidt, 1984; Rojanski *et al.*, 1986), in order that we might speak of a genuine Porod law. More definitely, we shall assume that the sample is made up of particles which are neither too small nor too large and that their boundaries are smooth but, possibly, for a *finite* number of corner and edges. We must now recall that in this framework the problem is related to a much more general problem, namely how the asymptotic behaviour of the intensity scattered by a *single* particle is determined by the latter's shape. On the one hand this problem is much more difficult than the former since it requires the determination of all the asymptotic terms. On the other hand it is too restrictive, requiring that the sample be dilute.

* The meaning of the symbols involved in the equation is the following: V is the sample volume, Φ_1 and Φ_2 are the volume fractions of the two phases where the electronic density can be assumed to be constant, $\langle\eta^2\rangle$ denotes the mean squared electronic density fluctuation and S_T is the total interphase surface area. The complete definition of δ and $S_\parallel$ will be given later (see note on p. 89). Here we note only that they have the physical dimensions of a length and of a surface, respectively. Moreover, for a critical discussion on the assumption of a two-valued electronic density as well as on the meaning of asymptotic behaviour we refer to Ciccariello, Goodisman & Brumberger (1988). Finally, according to standard mathematical terminology, throughout the paper the symbol o will denote a contribution which, as $h\to\infty$, decreases faster than the ones written down explicitly, while $O(h^{-\alpha})$ denotes a contribution decreasing as $h^{-\alpha}$.

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This problem has been studied in a series of important papers* by Schmidt and collaborators throughout the sixties and the early seventies. In particular, Miller & Schmidt (1962) first pointed out that the asymptotic expansion of the intensity scattered by a cylindrical particle of arbitrary cross section shows oscillatory deviations from the Porod law when the right cross section has polygonal portions with sides which are *parallel* and *opposite*. They noted also that the resulting deviation from the Porod law was proportional to $\cos(h\delta)$, with δ equal to the distance between the two opposite sides. In a subsequent paper, Schmidt (1965) showed that an oscillatory deviation is present also in the case of the right circular cylinder and that in this case it is proportional to $\sin(h\delta)$, where δ now represents the diameter of the cylinder. In obtaining these results the cylindrical structure played an important role. Subsequently Wu & Schmidt removed this condition and, assuming that the particles had a *convex* and *smooth* shape (*i.e.* with no edges and corners), they worked out the leading terms of the scattered intensity up to contributions $O(h^{-6})$. However, the hypothesis of convexity and smoothness rules out many interesting cases as, for instance, hollow spheres, tori and cylinders, and thus the problem of deviations from the Porod law does not find a complete and immediate answer from these results. However, the results of Miller and Schmidt on cylinders show the existence of deviations proportional both to $\cos(h\delta)$ and to $\sin(h\delta)$. Besides, Miller & Schmidt (1962) showed that the first behaviour arises from a *finite* discontinuity in the second-order derivative [$\equiv\gamma_0''(r)$] of the correlation function of a cylinder, while Schmidt (1965) has shown that the second behaviour arises from a *logarithmic* divergence, present at $r=D$, in the $\gamma_0''(r)$ relevant to a right circular cylinder with diameter D.

We recall now that in paper I we singled out the geometrical features of the interphase surface which yield discontinuities in $\gamma_0''(r)$ under the more general assumptions stated at the beginning. We showed that, so long as a quantity ($\equiv\mathscr{H}$) to be defined later [see (8)] is different from zero, one can have either finite discontinuities (called first order in order to stress the existence of *finite* left and right limits) or logarithmic divergences. Moreover, in the first case, the explicit expression of the discontinuity was also reported and thus we can conclude that the deviation proportional to $\cos(h\delta)$ has already been determined in paper I. Since the term proportional to $\sin(h\delta)$ found by Schmidt (1965) resulted from a logarithmic divergence in $\gamma_0''(r)$, one should expect that this deviation will also be present in the more general situation we have considered in I. However, we have to be sure that the procedure can be applied to these more general geometrical configurations and we have to find the analytical expression of the coefficient in front of $\sin(h\delta)$. In this paper we carry through this job. It turns out that, but for a trivial modification, the coefficient coincides with the one obtained in I. Owing to the constraint on the quantity $\mathscr{H}$ alluded to above, strictly speaking this result does not give the complete answer to the problem of determining the most general deviation from the Porod law. However, we do not know any geometrical configuration not obeying the mentioned constraint (*i.e.* $\mathscr{H}\neq 0$) and thus we are inclined to think that the answer to the problem can be considered physically exhaustive.

The plan of the paper is as follows. In the next section, after reporting the general integral expressions of the second-order derivative of the correlation function, we discuss the conditions which are responsible for a discontinuous behaviour of $\gamma_0''(r)$. There we show how the behaviour depends on the nature of the contact points between some surfaces. In particular, we show that elliptical contact points generate finite discontinuities while hyperbolic contact points generate logarithmic divergences. The leading term in the asymptotic expansion of $\gamma_0''(r)$ near the logarithmic singularity is evaluated in Appendix *A*. The r dependence is such that, like Schmidt (1965), one could use the lemma of Jones & Kline (1958) and quickly obtain the final result. However, we preferred a longer way with the hope that a more detailed discussion will make these issues easier and more familiar. In the third section we reobtain the correlation function for a right cylindrical particle so as to apply the results of the second section on the location of the discontinuities and on their amplitudes. In the fourth section, we show how the logarithmic divergence is tackled and we evaluate the leading asymptotic term of the corresponding scattered intensity. In the final section, combining the previous analysis and the results of the second section, we obtain the general expression of the deviations from the Porod law.

General results on discontinuities

For a two-component isotropic system the correlation function $\gamma_0(r)$ is given by [Debye *et al.* (1957) and equation (I.II.12)]

$$\gamma_0(r)=1-P_{12}(r)/\Phi_1\Phi_2 \tag{2a}$$

$$P_{12}(r)\equiv(4\pi V)^{-1}\int_{R^3}\mathrm{d}v_1\int_{\Omega}\rho_1(\mathbf{r}_1)\rho_2(\mathbf{r}_1+r\hat{\omega})\,\mathrm{d}\hat{\omega}. \tag{2b}$$

Here $\rho_1(\mathbf{r})$ and $\rho_2(\mathbf{r})$ represent the characteristic functions of phases 1 and 2 [*i.e.* $\rho_1(\mathbf{r})$ is equal to one or to zero depending on whether $\mathbf{r}$ is inside or outside

* A complete list can be obtained from the references cited by Schmidt (1967) and Wu & Schmidt (1974). I am grateful to a referee for having brought to my attention the first papers of the series.

phase 1], and $\hat{\omega}$ is a unit vector which ranges over the set Ω of all possible directions. Ciccariello, Cocco, Benedetti & Enzo (1981) have shown that the second-order derivative of the correlation function is given by

$$\gamma_0''(r) = (4\pi V\Phi_1\Phi_2)^{-1} \int_\Omega d\hat{\omega} \int_\Sigma dS_1 \int_\Sigma dS_2[\hat{\sigma}_1(\mathbf{r}_1).\hat{\omega}] \times [\hat{\sigma}_2(\mathbf{r}_2).\hat{\omega}]\, \delta(\mathbf{r}_1 + r\hat{\omega} - \mathbf{r}_2), \quad (3)$$

which is equivalent to

$$\gamma_0''(r) = (4\pi Vr^2\Phi_1\Phi_2)^{-1} \int_\Sigma dS_1 \oint_{\Gamma(\mathbf{r}_1, r)} dl([\hat{\sigma}_1.\hat{\omega}(l)] \times \cot\{\arc\cos[\hat{\sigma}_2(l).\hat{\omega}(l)]\}). \quad (4a)$$

In (3) and (4a), Σ denotes the interphase surface, $\hat{\sigma}_1$ and $\hat{\sigma}_2$ are the unit vectors orthogonal to the infinitesimal surface elements dS_1 and dS_2 of Σ and oriented externally to phases 1 and 2 respectively, $\delta(\ )$ denotes the Dirac function, while $\Gamma(\mathbf{r}_1, r)$ denotes the curve* resulting from the intersection of Σ with the spherical surface $[\equiv \mathcal{S}(\mathbf{r}_1, r)]$, with radius r and centred at $\mathbf{r}_1$. Consequently, l represents the curvilinear coordinate on Γ of the point P_2 where the corresponding dS_2 in (3) is located, $\hat{\sigma}_2(l)$ represents the normal to this element and $\hat{\omega}(l)$ is the unit vector of the direction going from dS_1 to dS_2. The integrand of (4a) diverges only when $\hat{\sigma}_2(l)$ is parallel or antiparallel to $\hat{\omega}(l)$. However, the former divergence does not necessarily yield a divergence or a discontinuity in $\gamma_0''(r)$ since we have still to integrate over dl and dS_1. Exploiting the symmetry of (3) with respect to the exchange $1\rightleftarrows 2$, one sees that the former divergence is harmless when $\hat{\sigma}_1.\hat{\omega}(l) \neq \pm 1$. In these cases in fact, integrating (3) first with respect to $\mathbf{r}_2$, one would have obtained

$$\gamma_0''(r) = (4\pi Vr^2\Phi_1\Phi_2)^{-1} \int_\Sigma dS_2 \oint_{\Gamma(\mathbf{r}_2, r)} dl([\hat{\sigma}_2.\hat{\omega}(l)] \times \cot\{\arc\cos[\hat{\sigma}_1(l).\hat{\omega}(l)]\}). \quad (4b)$$

In this way the geometry of the two infinitesimal surfaces dS_1 at P_1 and dS_2 at P_2 separated by a distance r can be described either by the infinitesimal element dl at P_2 and the integrand of (4a) for dS_1, or by the infinitesimal element dl at P_1 and the integrand of (4b) for dS_2. In the latter case the integrand is not divergent and thus in the first case the divergence will cancel by integration. Clearly the argument can no longer be applied when $\hat{\sigma}_1.\hat{\omega}(l) = \pm 1$. Geometrically this condition means that the surface elements dS_1 and dS_2 have the *same* normal and thus $\hat{\sigma}_1$, $\hat{\sigma}_2$ and $\hat{\omega}(l)$ are either parallel or antiparallel. The former geometry can also be characterized by saying that if we translate dS_1 along its normal straight line by r, dS_1 superimposes on dS_2 or equivalently that the sphere $\mathcal{S}(\mathbf{r}_1, r)$ is tangent to dS_2 and that the line connecting dS_2 with the sphere's centre is orthogonal to dS_1. More briefly we shall say that dS_1 and dS_2 are *opposite* and *parallel*. From now on the r values where this condition takes place, so that both the integrand of (4a) and that of (4b) are divergent, will be denoted by δ. In order to see whether this divergence survives after integration, we have to study the limit as $r \to \delta$ of the linear integral appearing on the r.h.s. of (4a), *i.e.*

$$\mathcal{L}(\mathbf{r}_1, r) \equiv \oint_{\Gamma(\mathbf{r}_1, r)} ([\hat{\sigma}_1.\hat{\omega}(l)] \times \cot\{\arc\cos[\hat{\sigma}_2(l).\hat{\omega}(l)]\})\, dl. \quad (5)$$

The behaviour of this integral depends crucially on the nature of the contact between Σ and $\mathcal{S}(\mathbf{r}_1, \delta)$. Since $\mathcal{L}(\mathbf{r}_1, r)$ is a scalar quantity, we momentarily choose a Cartesian system with the origin at P_1 and the z axis parallel to the direction going from P_1 to P_2. The surfaces Σ and $\mathcal{S}(\mathbf{0}, \delta)$ will be tangent at the point P_2, located on the positive z axis at a distance δ from the origin. In a suitable neighbourhood of the latter, the two surfaces can be represented by the equations

$$z = f_\Sigma(x, y) \quad (6a)$$

$$z = f_\mathcal{S}(x, y) = (\delta^2 - x^2 - y^2)^{1/2}. \quad (6b)$$

Let us introduce the function $F(x, y)$ defined as

$$z = F(x, y) \equiv f_\Sigma(x, y) - f_\mathcal{S}(x, y). \quad (7)$$

Now, in a small neighbourhood of the contact point P_2 and excluding the latter, it can happen that: (1a) the contact is *simple* [the latter's definition will be given below (8)] and Σ always lies above $\mathcal{S}(\mathbf{0}, \delta)$, and then $F(x, y) > 0$; (1b) the contact is *simple* and Σ lies always below $\mathcal{S}(\mathbf{0}, \delta)$ and then $F(x, y) < 0$; (2) the contact is *simple* and Σ lies partly above and partly below $\mathcal{S}(\mathbf{0}, \delta)$; or (3) the contact is not *simple*.

In cases (1), (2) and (3) one says that the contact point is *elliptical*, *hyperbolic* and *parabolic*, respectively. In cases (1a) and (1b) the origin represents respectively a local minimum or a local maximum of $F(x, y)$, while in case (2) it is a saddle point. From the theory of the extremal points of a function of many variables, the determinant $[\equiv \mathcal{H}(x, y)]$ of the matrix

$$\mathcal{H} \equiv \begin{pmatrix} \partial_x^2 F & \partial_{xy}^2 F \\ \partial_{xy}^2 F & \partial_y^2 F \end{pmatrix} \quad (8)$$

evaluated at the origin is positive in case (1), negative in case (2) and null in case (3). This property gives us the operational definition of a *simple* contact point: it is a point where the first-order partial derivatives are null and the *Hessian* [*i.e.* $\mathcal{H}(x, y)$] of F is different from zero.

* Note that in general this will be formed by different closed curves. Therefore we should add an index to Γ for distinguishing them and add a summation on the r.h.s. of (4a). In order to simplify the notation we avoid this complication.

We can now discuss the limit of $\mathscr{L}$, defined by (5), as $r \to \delta$.

(a) Discontinuity due to elliptical contact-point sets

Let us consider first the elliptical contact-point case corresponding to case (1a). Since F has a local minimum, locally Σ lies above $\mathscr{S}(\mathbf{0}, \delta)$ and thus it will also lie above $\mathscr{S}(\mathbf{0}, r)$ when $r < \delta$. In this case $\mathscr{S}(\mathbf{0}, r)$ will not intersect Σ and so $\Gamma(\mathbf{0}, r)$ does not exist. From (5) one concludes that

$$\mathscr{L}(\mathbf{0}, \delta^-) = 0.$$

By contrast, when $r > \delta$, $\mathscr{S}(\mathbf{0}, r)$ will intersect Σ along a closed curve which shrinks to a point as $r \to \delta^+$. In that limit, the integrand diverges and simultaneously the length of the integration domain tends to zero. In Appendix A we show that

$$\mathscr{L}(\mathbf{0}, \delta^+) \equiv \lim_{r \to \delta^+} \mathscr{L}(\mathbf{0}, r) = 2\pi \mathscr{H}^{-1/2} (\hat{\sigma}_1 . \hat{\sigma}_0)(\hat{\sigma}_2 . \hat{\sigma}_0)$$

where $\hat{\sigma}_0$ denotes the unit vector of the direction going from $\mathrm{d}S_1$ to $\mathrm{d}S_2$. One concludes that $\mathscr{L}(\mathbf{0}, r)$ has a finite discontinuity at $r = \delta$ in case (1a). The discussion of case (1b) is quite similar. We have only to exchange the inequalities involving r and δ and thus the discontinuity of $\mathscr{L}(\mathbf{0}, r)$ will have the opposite sign. In conclusion, recalling that $\hat{\sigma}_1$, $\hat{\sigma}_2$ and $\hat{\sigma}_0$ can be parallel or antiparallel, one has

$$\begin{aligned} &\mathscr{L}(\mathbf{r}_1, \delta^+) - \mathscr{L}(\mathbf{r}_1, \delta^-) \\ &\quad = 2\pi \mathscr{H}^{-1/2}(\mathbf{r}_1, \delta) \\ &\quad\quad \times \{\hat{\sigma}_1(\mathbf{r}_1) . \hat{\sigma}_2[\mathbf{r}_1 + \delta \hat{\sigma}_0(\mathbf{r}_1)]\} \operatorname{sign}(F) \end{aligned} \tag{9}$$

where we have removed the unnecessary condition that $\mathrm{d}S_1$ be located at the origin and we have explicitly indicated that the value of the Hessian depends on $\mathbf{r}_1$ and on δ, since the contact takes place at $\mathbf{r}_1 + \delta \hat{\sigma}_0(\mathbf{r}_1)$. The finite discontinuity (9) results from a pair of *parallel* and *opposite* infinitesimal surface elements of Σ at a relative distance δ and characterized by an *elliptical* contact point between one of these elements and the sphere of radius δ centred on the opposite element. Clearly, the infinitesimal contributions sum to a finite discontinuity of $\gamma_0''(r)$ only when the condition of *opposite equidistant elliptical parallelism* is realized on a *finite-area* subset of the interphase surface. In particular, if we denote this subset by Σ_δ^E, combining (9) and (4a) we find the general integral expression of the finite discontinuity of the second-order derivative of the correlation function

$$\begin{aligned} \gamma_0''(\delta^+) - \gamma_0''(\delta^-) = (2V\delta^2 \Phi_1 \Phi_2)^{-1} &\int_{\Sigma_\delta^E} \mathrm{d}S_1 \operatorname{sign}(F) \\ &\times \{\hat{\sigma}_1(\mathbf{r}_1) . \hat{\sigma}_2[\mathbf{r}_1 + \delta\hat{\sigma}_0(\mathbf{r}_1)]\} \\ &\times \mathscr{H}^{-1/2}[\mathbf{r}_1 + \delta \hat{\sigma}_0(\mathbf{r}_1)]. \end{aligned}$$

We note that the presence of edges on the particle boundaries implies that $\hat{\sigma}(\mathbf{r}_1)$ does not exist on these curves. By assumption the set of the latter is not dense in Σ and then the integral exists. We can decompose Σ_δ^E in the union of the largest subsets which in their inside have no subsets of the edges, which consequently will form part of the boundaries of the aforesaid subsets of Σ_δ^E. The decomposition of the latter corresponds to writing the former integral as a sum of integrals each evaluated on one of the Σ_δ^E subsets. Inside each of these, $\hat{\sigma}_1(\mathbf{r}_1)$ and $\hat{\sigma}_2[\mathbf{r}_1 + \delta\hat{\sigma}_0(\mathbf{r}_1)]$ are continuous vectors and their scalar product will be continuous too. Since $\hat{\sigma}_1$ and $\hat{\sigma}_2$ are either parallel or antiparallel, if at a point of the subset they are parallel they will remain parallel throughout the subset. In the same way the value of sign (F) cannot change, otherwise we pass from a maximum to a minimum and this requires that the Hessian becomes somewhere null. Thus the scalar product and sign (F) can be taken out of each of the integrals. For notational simplicity we shall omit denoting the summation over the subsets and thus we shall simply write

$$\gamma_0''(\delta^+) - \gamma_0''(\delta^-) = \Delta_E^{(2)}(\delta) \tag{10a}$$

$$\Delta_E^{(2)}(\delta) \equiv \frac{\operatorname{sign}(F)(\hat{\sigma}_1 . \hat{\sigma}_2)}{2V\delta^2 \Phi_1 \Phi_2} \times \int_{\Sigma_\delta^E} \mathrm{d}S_1 \mathscr{H}^{-1/2}[\mathbf{r}_1 + \delta\hat{\sigma}_0(\mathbf{r}_1)]. \tag{10b}$$

But for some simplifications, this result coincides with equation (V.4) of I, where one can also find a discussion of some examples.*

(b) Discontinuity due to hyperbolic contact-point sets

Once one takes into account result (A.25), the discussion of this case is quite similar to the previous one. We shall denote by Σ_δ^H the subset of Σ obeying the condition of *opposite equidistant hyperbolic parallelism, i.e.* Σ_δ^H is made up of infinitesimal surface elements such that each has in Σ_δ^H a *parallel* and *opposite* element at a distance δ, and moreover the sphere with radius δ and centred on it has a hyperbolic contact with the opposite element. Then, by combining (A.25) and (4a) one finds that this set gives rise to a logarithmic divergence in $\gamma_0''(r)$ as $r \to \delta$. More definitely, the general result is

$$\gamma_0''(r) \simeq -\Delta_H^{(2)} \ln|r - \delta| + o \tag{11a}$$

* In particular, when the interphase surface is a sphere the integral is proportional to the area S_δ^E of Σ_δ^E, which was denoted by $S_\|$ in (1). In more general cases each of the contributions (10b), by the theorem of the mean, is equal to $\pm S_\delta^E \langle \mathscr{R}_G \rangle$. From the footnote on p. 96, $\langle \mathscr{R}_G \rangle$ is the mean Gauss radius of the *difference* surface.

where

$$\Delta_H^{(2)} \equiv \frac{(\hat{\sigma}_1 . \hat{\sigma}_2)}{2\pi V \delta^2 \Phi_1 \Phi_2} \times \int_{\Sigma_\delta^H} \mathrm{d}S_1 |\mathcal{H}|^{-1/2}[\mathbf{r}_1 + \delta\hat{\sigma}_0(\mathbf{r}_1)]. \quad (11b)$$

Here o denotes a continuous contribution with an integrable derivative in the neighbourhood of δ and the scalar product has been taken out from the integral since we are using the same convention discussed below (10). If we start from (10) and (11) and use the theorem of Erdélyi (1956) and the lemma of Jones & Kline (1958) it would be easy to show that these contributions give rise to oscillatory deviations proportional to cos ( ) and to sin ( ), respectively. As we have said in the *Introduction*, we prefer to arrive at this conclusion after having discussed the case of a cylindrical particle.

Cylinder correlation function

According to the general SAXS theory (Porod, 1982), the isotropic component of the correlation function of a single particle with uniform electronic density is given by

$$\gamma_0(r) = (4\pi V)^{-1} \iint \rho_1(\mathbf{r}_1)\rho_1(\mathbf{r}_1 + r\hat{\omega})\, \mathrm{d}v_1\, \mathrm{d}\hat{\omega} \quad (12)$$

where V is the volume of the particle and $\rho_1(\mathbf{r})$ is the latter's characteristic function.* We confine ourselves to the case of a right circular cylindrical particle. Equation (12) can easily be evaluated if one recalls that the integral in (12) represents the volume of the region shared by this cylinder and by an identical cylinder translated by $r\hat{\omega}$ (Guinier, 1963). With this aim we choose the origin of the coordinates $\mathbf{r}_1$ at the centre of one of the cylinder's bases and the z_1 axis along the axis of the cylinder. Denoting by α the angle between $r\hat{\omega}$ and the plane $z=0$, from (12) one gets [see Miller & Schmidt (1962), Schmidt (1965) and more recently Gille (1987)]

$$\gamma(x) = \begin{cases} (2/\pi a) \int_{\alpha_m(x)}^{\alpha_n(x)} \cos(\alpha) s(\alpha, x) A(\alpha, x)\, \mathrm{d}\alpha, & x \le (1+a^2)^{1/2} \\ 0, & x \ge (1+a^2)^{1/2}. \end{cases} \quad (13)$$

Here the following definitions have been used:

$$D \equiv 2R,\ x \equiv r/D,\ a \equiv H/D, \quad A(\alpha, x) \equiv a - x \sin\alpha \quad (14)$$

$$s(\alpha, x) \equiv \arccos(x\cos\alpha) - x(1 - x^2\cos^2\alpha)^{1/2}\cos\alpha$$

$$\alpha_m(x) \equiv \begin{cases} 0, & 0 \le x \le \min(a, 1) \\ \max[0, \arccos(1/x)], & \min(a,1) \le x \le \max(a,1) \\ \arccos(1/x), & \max(a,1) \le x \le (1+a^2)^{1/2} \end{cases} \quad (15)$$

$$\alpha_M(x) \equiv \begin{cases} \pi/2, & 0 \le x \le \min(a, 1) \\ \max[\pi/2, \arcsin(1/x)], & \min(a,1) \le x \le \max(a,1) \\ \arcsin(a/x), & \max(a,1) \le x \le (1+a^2)^{1/2}. \end{cases} \quad (16)$$

The second-order derivative of $\gamma(x)$ can easily be obtained by differentiating (13). After some algebraic manipulations, one succeeds in expressing $\gamma''(x)$ in terms of some elliptical and elementary algebraic functions (Abramowitz & Stegun, 1970). In particular, one finds that

$$\gamma''(x) = \begin{cases} (4/3\pi x)[S_1\mathbf{K}(x) - S_2\mathbf{E}(x)] + (1/2\pi a x^3)\mathcal{S}(x), & 0 \le x \le \min(a,1) \\ (4/3\pi)[S_3\mathbf{K}(1/x) - S_2\mathbf{E}(1/x)] + (1/2\pi a x^3)\mathcal{S}(1), & 1 \le a \text{ and } 1 \le x \le a \\ (4/3\pi x)\{-aR_1R_2 + S_1[\mathbf{K}(x) - F(\varphi, x)] - S_2[\mathbf{E}(x) - E(\varphi, x)]\} + \mathcal{G}_1 + \mathcal{D}(x, a), & a \le 1 \text{ and } a \le x \le 1 \\ (4/3\pi)\{-(a/x)R_1R_2 + S_3[\mathbf{K}(1/x) - F(\varphi, 1/x)] - S_2[\mathbf{E}(1/x) - E(\varphi, 1/x)]\} + \mathcal{G}_2 + \mathcal{D}(x, a), & \max(a,1) \le x \le (1+a^2)^{1/2} \\ 0, & (1+a^2)^{1/2} \le x. \end{cases} \quad (17)$$

We have put

$$R_1 \equiv (x^2 - a^2)^{1/2}, \quad R_2 \equiv (1 + a^2 - x^2)^{1/2} \quad (18a)$$

$$S_1 \equiv 2 + x^2, \quad S_2 \equiv 2(1+x^2), \quad S_3 \equiv 1 + 2x^2 \quad (18b)$$

$$\varphi \equiv \arcsin(R_1) \quad (18c)$$

$$\mathcal{D}(a, x) \equiv (2a/\pi x^3)[\arccos(R_1) - 2R_1R_2] \quad (18d)$$

$$\mathcal{S}(x) \equiv [2\sin(2x) - \arcsin x - \tfrac{3}{4}\sin(4x)] \quad (18e)$$

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* See, for more details, Ciccariello *et al.* (1981) and paper I. In particular we note that all the results of these two papers apply also to the case of a single particle, provided one takes $N=1$, $\langle\eta^2\rangle = 1$ and the sample's volume be identified with that of the particle.

$$\mathscr{G}_1 \equiv (1/2\pi a x^3)[\mathscr{S}(x) - \mathscr{S}(R_1)] \quad (18f)$$

$$\mathscr{G}_2 \equiv (1/2\pi a x^3)[\mathscr{S}(1) - \mathscr{S}(R_1)] \quad (18g)$$

while $\mathbf{K}(x)$ and $\mathbf{E}(x)$ are complete elliptic functions of the first and second kinds (Gradshteyn & Ryzhik, 1970). Similarly, $F(\varphi, y)$ and $E(\varphi, y)$ denote the corresponding incomplete elliptic functions and φ and y are the so-called amplitude and modulus respectively.

As we have already emphasized the deviations from the Porod law are determined by the discontinuities of $\gamma_0''(r)$. Therefore we shall now discuss the continuity properties of $\gamma''(x)$ resulting from (17). Apart from $K(\ )$, the other functions appearing on the r.h.s. of (17) are continuous in the reported x range. Thus the discontinuities can appear at $x=1$ where both $K(x)$ and $K(1/x)$ are singular and at the points which separate next intervals provided the left and right limits of $\gamma''(x)$ are different. The only point where this phenomenon occurs is the point $x=a$, since here the contribution $\mathscr{D}(x, a)$ is present only on the right while the remaining quantities are equal. We recover the finite discontinuity already found by Miller & Schmidt (1962), whose value can be easily obtained from (17). One finds that $\gamma''(a^+) - \gamma''(a^-) = \mathscr{D}(a, a) = a^{-2}$. Recalling that $\gamma_0''(r) = D^{-2}\gamma(x)$, one concludes that

$$\gamma_0''(H^+) - \gamma_0''(H^-) = 1/H^2. \quad (19)$$

At $x=1$, the singularity of $\gamma''(x)$ is a logarithmic one (Schmidt, 1965). It can be immediately isolated by using the series representation (8.113.3) of Gradshteyn & Ryzhik for $K(x)$ and $K(1/x)$. One finds that, as $x \to 1^-$,

$$\begin{aligned}\mathbf{K}(x) &\simeq \ln[4(1-x^2)^{-1/2}] + o \\ &= -\tfrac{1}{2}\ln(1-x) + \ln[4(1+x)^{-1/2}] + o \quad (20a)\end{aligned}$$

while, as $x \to 1^+$,

$$\begin{aligned}\mathbf{K}(1/x) &\simeq \ln[4x(x^2-1)^{-1/2}] + o \\ &= -\tfrac{1}{2}\ln(x-1) + \ln[4x(1+x)^{-1/2}] + o. \quad (20b)\end{aligned}$$

Thus, from (17) one finds that the leading term of $\gamma_0''(r)$ as $r \to D$ is

$$\gamma_0''(r) \simeq -(2/\pi D^2)\ln(|1 - r/D|) + o \quad (21)$$

where o denotes the remaining contribution which is continuous and has a derivative with integrable singularities as $r \to D$.

It is instructive to see how results (19) and (21) can be easily obtained by applying the results reported in the previous section. First of all we note that when the sample is made up of a single particle the second-order derivative of the correlation function is given by (Ciccariello *et al.*, 1981)

$$\begin{aligned}\gamma_0''(r) = -(1/4\pi V r^2)\int \mathrm{d}S_1 \oint_{\Gamma(\mathbf{r}_1, r)} \mathrm{d}l([\hat{\sigma}_1 . \hat{\omega}(l)] \\ \times \cot\{\arccos[\hat{\sigma}_1(l) . \hat{\omega}(l)]\}) \quad (22)\end{aligned}$$

where the meaning of the symbols is the same as in (4a). (One should note that formally here one has $\Phi_1\Phi_2 = 1$. This is a consequence of the fact that we have a single particle.) Consequently, the results (10) and (11) will apply also to this case. Accordingly we have first to see whether subsets S_δ^E and S_δ^H exist and then to use (10) and (11).

We note now that the condition of *equidistant and oppositely parallel* subsets can be formulated in terms of the Huygens' principle. In fact, imagine that a subset of the sample's interface be the initial configuration of a wave front. In order to determine the wave front at a later time we have to consider the family of spheres with centre on each point of the subset and with radius equal to the distance travelled by the wave in the time interval considered. The envelope of the spheres gives the new wave front. If this partly superimposes on the initial subset, it appears evident* that the superimposed subset is clearly made up of infinitesimal elements which are *equidistant* and *oppositely parallel.*

Let us apply this construction by assuming that the lower basis of the cylinder be the initial wave front. After the wave has travelled a distance equal to the cylinder's height H, the new wave front superimposes clearly on the top basis and *vice versa.* Similarly, taking as initial wave front the lateral surface of the cylinder, one sees that after the wave has travelled a distance equal to D, the cylinder's diameter, the new wave front again superimposes on the lateral surface. Thus we have two distance values H and D, where the condition of *equidistance* and *opposite parallelism* is met.

In the first case, since each touching sphere lies below the top basis the contact is clearly elliptical. In order to apply (10), we need to know the Hessian. To this aim we choose the z axis parallel to the cylinder's axis and the origin at the point opposite to the contact point. The local parametric equations of the upper basis and of the touching sphere are

$$\begin{aligned} z &= f_\Sigma(x, y) = H \\ z &= f_\mathscr{S}(x, y) = (H^2 - x^2 - y^2)^{1/2}. \end{aligned}$$

Using (7) and (8) one finds that $\mathscr{H}(0) = H^{-2}$. This quantity is the same for any point of the basis. Substituting in (10) and noting that sign $(F) > 0$ and that $\hat{\sigma}_1 . \hat{\sigma}_2 = 1$ one has

$$\gamma_0''(H^+) - \gamma_0''(H^-) = \Delta_E^{(2)}(H) = S_b/VH \quad (23)$$

which is clearly equal to (19).

* One can rigorously prove this property (Ciccariello, 1989).

We evaluate now the contribution to the lateral surface ($\equiv S_L$). From Fig. 1 it appears clear that the contact points are hyperbolic. In fact, when $r<D$, $\Gamma(\mathbf{r}_1, r)$ is equal to the curve Γ_1 shown in Fig. 1. But as $r\to D^-$, the top points Q and Q', approach each other and they meet at P_t, the point opposite the sphere centre P, when $r=D$. At this point, the curve $\Gamma(\mathbf{r}_1, r)$, which was made up of one curve only, is now formed by two closed curves touching each other at P_t. As r becomes larger than D, the intersection curve indeed separates into the two curves Γ_2 of Fig. 1. Clearly, the spherical surface lies inside the cylinder in the regions on the left and on the right of Γ_2 or in the region above Γ_1, while it lies outside the cylinder in the region in between the Γ_2's or below Γ_1. It is evident then that P_t is hyperbolic. We can use (19) in order to obtain the leading asymptotic term of $\gamma_0''(r)$ as $r\to D$. In order to evaluate the Hessian we choose the z axis along a cylinder's diameter and the origin at the lower end of the latter, while its upper end is the contact point. The y axis is parallel to the cylinder's axis. The local parametric equations are

$$z=f_\Sigma(x,y)=D/z+(D^2/4-x^2)^{1/2}$$
$$z=f_{\mathscr{S}}(x,y)=(D^2-x^2-y^2)^{1/2}$$

and the Hessian is $\mathscr{H}(0)=1/D^2$. This quantity does not change if we rotate the cylinder or if we move along the y axis. The calculation of the integral (11b) is immediate and one finds that

$$\begin{aligned}\gamma_0''(r) &\simeq -\frac{S_L}{2\pi VD}\ln(|1-r/D|)+o\\ &\equiv -\Delta_H^{(2)}(D)\ln(|1-r/D|)+o,\end{aligned} \tag{24}$$

which coincides with (21).

Asymptotic behaviour of the intensity

We have now to work out the asymptotic behaviour of the isotropic component of the intensity scattered by the homogeneous cylinder considered above. In the case of a single particle one simply has

$$I(h)=(1/4\pi)\int|\tilde{\rho}(h\hat{\omega})|^2\,d\hat{\omega} \tag{25}$$

where $\tilde{\rho}(\mathbf{h})$ is the Fourier transform (FT) of $\rho(\mathbf{r})$. By direct evaluation (*e.g.* Guinier, 1963), one finds that

$$I(h)=4V^2\int_0^{\pi/2}\sin\theta\left[\frac{\sin(qa\cos\theta)}{qa\cos\theta}\,\frac{J_1(q\sin\theta)}{q\sin\theta}\right]^2 d\theta \tag{26}$$

with $q\equiv hR$. On the other hand, $I(h)$ is also the FT of the sample correlation function. In this way from (12) and (25) one obtains

$$\begin{aligned}I(h)&=(4\pi V/h)\int_0^\infty r\gamma_0(r)\sin(hr)\,dr\\ &=(4\pi VD^3/Q)\int_0^\infty x\gamma(x)\sin(Qx)\,dx\end{aligned} \tag{27}$$

where we have put $Q\equiv hD=2q$.

The leading term in the asymptotic expansion of $I(h)$ will be evaluated starting from the latter expression. Two integrations by parts yield

$$I(h)/4\pi VD^3=-Q^{-3}\int_0^{L_M}\sin(Qx)[d^2x\gamma(x)/dx^2]\,dx \tag{28}$$

where we have used the property that $\gamma(x)\equiv 0$ when $x>L_M\equiv(1+a^2)^{1/2}$ [see (13)]. In order to go one step further we have to take account both of the first-order discontinuity and of the logarithmic singularity of $\gamma''(x)$, located at $x=a$ and at $x=1$, respectively. For definiteness, let us assume that $a>1$. Then we split the integration domain of (28) in two parts: $[0, a_0]$ and $[a_0, L_M]$, where a_0 is such that $1<a_0<a$. Similarly to I, the domain $[a_0, L_M]$ is split into $[a_0, a^-]$ and $[a^+, L_M]$. Inside each of the latter the integrand of (28) is continuously differentiable. Thus one can integrate by parts and one finds

$$\begin{aligned}-Q^{-3}&\int_{a_0}^{L_M}\sin(Qx)\frac{d^2x\gamma(x)}{dx^2}\,dx\\ &=Q^{-4}\left[\cos(Qx)\frac{d^2x\gamma(x)}{dx^2}\bigg|_{a_0}^{a^-}+\cos(Qx)\frac{d^2x\gamma(x)}{dx^2}\bigg|_{a^+}^{L_M}\right]\\ &\quad-Q^{-4}\left[\int_{a_0}^{a^-}\cos(Qx)\frac{d^3x\gamma(x)}{dx^3}\,dx+\int_{a^+}^{L_M}\cos(Qx)\frac{d^3x\gamma(x)}{dx^3}\,dx\right]\\ &=Q^{-4}\left[-\cos(Qa)a\Delta_E^{(2)}(a)-\cos(Qa_0)\frac{d^2a_0\gamma(a_0)}{da_0^2}\right]+o\end{aligned} \tag{29}$$

where the property $\gamma'(L_M)=\gamma''(L_M)=0$, following from (13) and (17), has been accounted for.

In order to handle the logarithmic singularity of $\gamma''(x)$ at $x=1$, we split the domain $[0, a_0]$ in three parts: $[0, 1-\varepsilon]$, $[1-\varepsilon, 1+\varepsilon]$ and $[1+\varepsilon, a_0]$, with ε a sufficiently small real positive number. In the first and in the third domain, the integrand is continuously differentiable and thus one can integrate by parts as before. One gets

$$-Q^{-3}\int_0^{1-\varepsilon}\sin(Qx)\frac{\mathrm{d}^2x\gamma(x)}{\mathrm{d}x^2}\,\mathrm{d}x$$

$$\simeq Q^{-4}\left[-2\gamma'(0)+\cos(Qx)\frac{\mathrm{d}^2x\gamma(x)}{\mathrm{d}x^2}\bigg|_{1-\varepsilon}\right]+o \quad (30)$$

$$-Q^{-3}\int_{1+\varepsilon}^{a_0}\sin(Qx)\frac{\mathrm{d}^2x\gamma(x)}{\mathrm{d}x^2}\,\mathrm{d}x$$

$$\simeq Q^{-4}\left[\cos(Qa_0)\frac{\mathrm{d}^2a_0\gamma(a_0)}{\mathrm{d}a_0^2}\right.$$

$$\left.-\cos(Qx)\frac{\mathrm{d}^2x\gamma(x)}{\mathrm{d}x^2}\bigg|_{1+\varepsilon}\right]+o. \quad (31)$$

The remaining integral contains the logarithmic singularity of $\gamma''(x)$, given by (21). Adding and subtracting this contribution and defining

$$\gamma_R(x)\equiv \mathrm{d}^2x\gamma(x)/\mathrm{d}x^2+(2/\pi)\ln(|1-x|), \quad (32).$$

we find that the aforesaid integral splits into the sum

$$-Q^{-3}\int_{1-\varepsilon}^{1+\varepsilon}\sin(Qx)\gamma_R(x)\,\mathrm{d}x$$

$$+(2/\pi Q^3)\int_{1-\varepsilon}^{1+\varepsilon}\sin(Qx)\ln(|1-x|)\,\mathrm{d}x. \quad (33)$$

The regularized function $\gamma_R(x)$ is such that, by differentiating it once more, the resulting derivative will have integrable singularities at $x=1$, as one can see from (17) and the general properties of the elliptic functions involved. By the theorem reported by Erdélyi (1956), one can integrate by parts the first integral of (34) and one obtains

$$-Q^{-3}\int_{1-\varepsilon}^{1+\varepsilon}\sin(Qx)\gamma_R(x)\,\mathrm{d}x$$

$$\simeq Q^{-4}\cos(Qx)\gamma_R(x)|_{1-\varepsilon}^{1+\varepsilon}+o. \quad (34)$$

In Appendix B we show that the leading asymptotic term of the second integral of (34) is

$$\frac{4}{\pi Q^4}\left\{-\frac{\pi}{2}\sin Q-\tfrac{1}{2}\ln\varepsilon\cos(Qx)\bigg|_{1-\varepsilon}^{1+\varepsilon}\right\}+o. \quad (35)$$

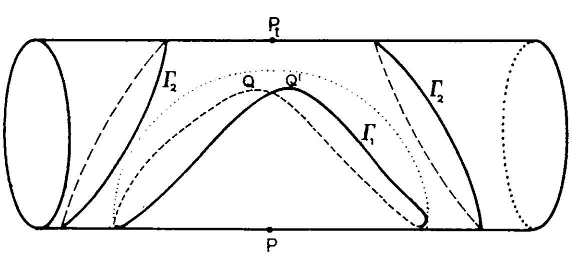
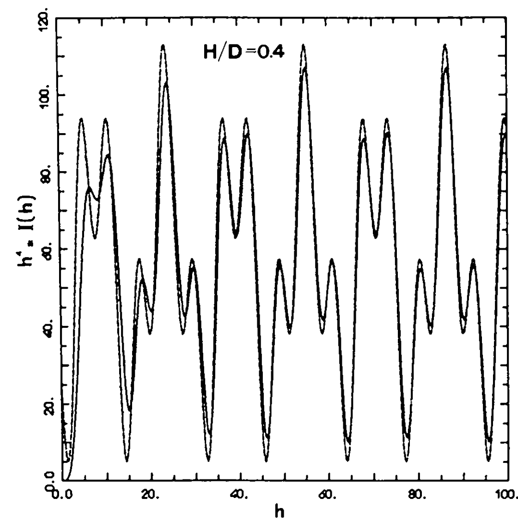
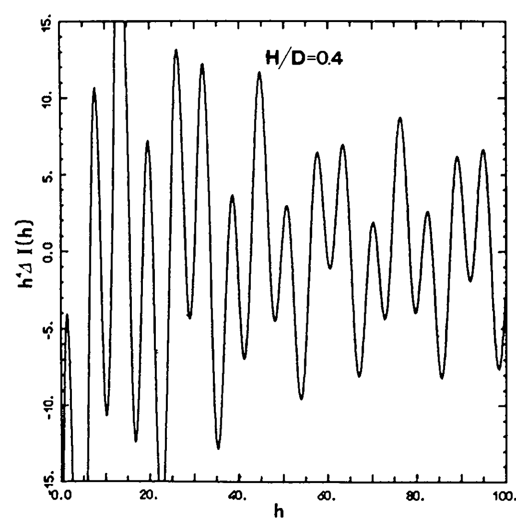


Fig. 1. The curve Γ_1 represents the intersection of the sphere, with radius $r<D$ and centred at P, with the cylinder's lateral surface. As we let the sphere radius increase, the top points Q and Q' move towards P_t. They meet at P_t when the sphere radius becomes equal to the cylinder diameter. In this case P_t becomes a double point of the curve. As the sphere radius becomes still larger, the curve Γ splits into the two curves Γ_2.



(a)



(b)

Fig. 2. (a) Porod plot of the intensity scattered by a cylinder characterized by the ratio $H/D=0{\cdot}4$. The units of h are D^{-1}. The continuous line refers to the theoretical intensity $I_{\rm th}(h)$ obtained from (26), while the dotted line refers to the leading asymptotic approximation $I_{\rm as}(h)$ given by (38). (b) The curve plots the quantity $h^4\,[I_{\rm th}(h)-I_{\rm as}(h)]$. The slow decrease of the curve suggests that the next terms in the asymptotic expansion are characterized by a behaviour $h^{-\alpha}$, with α slightly larger than four, as appears evident from Fig. 5.

Summing contributions (34) and (35) and using (32) one finds

$$-\frac{2}{Q^4}\frac{\sin(Q)}{Q^4}+Q^{-4}\cos(Qx)\left.\frac{d^2x\gamma(x)}{dx^2}\right|_{1-\varepsilon}^{1+\varepsilon}+o. \quad (36)$$

Collecting the results relevant to (29), (30) and (36), one obtains that the leading asymptotic term of the intensity scattered by a cylinder is given by*

$$I(h)\simeq(4\pi VD^3/Q^4)\{-2\gamma'(0)$$
$$-a\Delta_E^{(2)}(a)\cos(Qa)-2\sin Q\}+o. \quad (37)$$

Recalling that $\gamma'(0)=-S_T/4V$ (Debye *et al.*, 1957), and also that $\Delta_E^{(2)}(a)$ is given by (19), we see that the former result can be written in terms of the cylinder surface components as

$$I(h)\simeq\frac{4\pi V}{h^4}\left[\frac{2S_B+S_L}{2V}-\frac{2S_B}{2V}\cos(hH)\right.$$
$$\left.-\frac{S_L}{2V}\sin(hD)\right]+o. \quad (38)$$

Figs. 2-4 allow us to see how result (38) works. There we plot the intensities, as well as the difference between the intensity given by (26) and its asymptotic expansion (38), for three different H/D ratios. In Fig. 5 the relative importance of the next higher order terms $O(h^{-4\cdot5})$ and $O(h^{-5})$, obtained by Schmidt (1965), is shown.

* One should note that any dependence on the physically inessential parameter ε has disappeared. The changes required for the proof of (38), when $a<1$, are obvious.

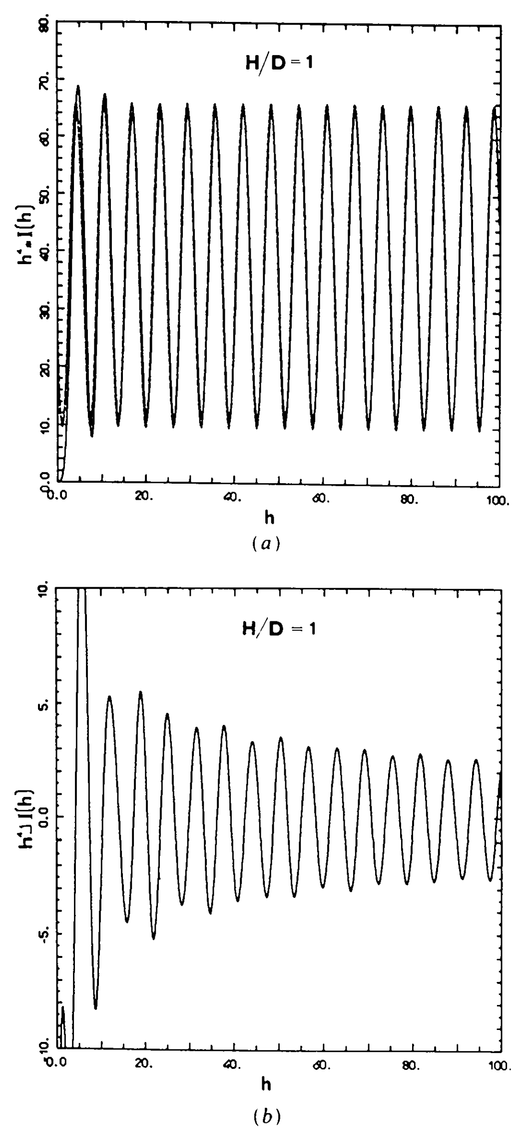


Fig. 3. As in Fig. 2, with $H/D=1$.

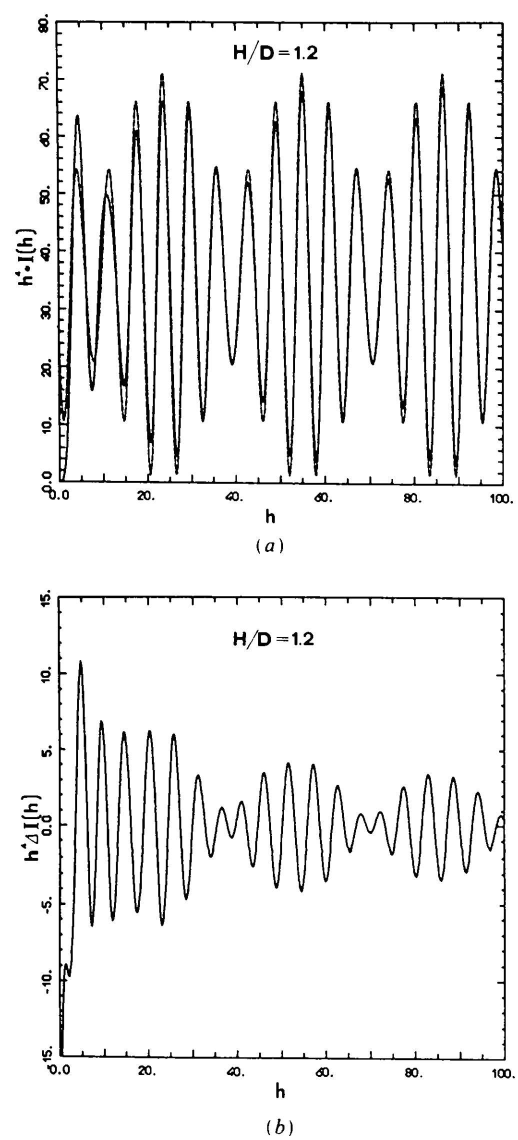


Fig. 4. As in Fig. 2, with $H/D=1\cdot2$.

Concluding remarks

The proof of (38) nowhere depends on the fact that we have a single cylindrical particle. It depends indeed only on the fact that $\gamma''(x)$ has a finite discontinuity (at $x=a$) and a discontinuity (at $x=1$) corresponding to a logarithmic divergence of the kind $\ln(|1-x|)$. The proof that the first discontinuity generates oscillatory deviations proportional to the cosine function depends on the fact that once the integration domain is split at the discontinuity point a, in the resulting two neighbouring integrals the integrand is differentiable [see (29)]. By contrast the proof that the logarithmic singularity gives a contribution proportional to the sine function is more involved. It requires in fact that in the neighbourhood of the singular point we are able to tame the divergence by constructing a regular function, as we have done in (32). The proof given above shows that when the singularity has the behaviour $\simeq \Delta_H^{(2)} \ln(|1-x|)+o$ and o is a continuous contribution with an integrable derivative, the asymptotic behaviour of the singular logarithmic term yields a contribution proportional to the sine function and a further contribution which, added to the one resulting from the regularized function, reproduces the initial function [see (36)]. In this way the contributions due respectively to the upper and lower extrema of the next integrals cancel and only the contribution proportional to the sine function survives. In the second section we have shown

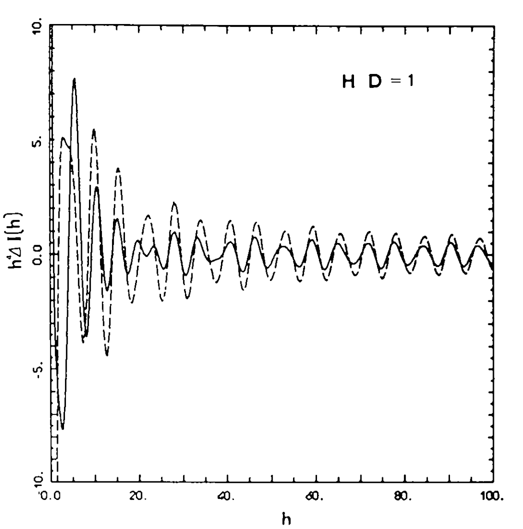


Fig. 5. The broken and the continuous curves show $h^4[I_{\rm th}(h)-I_{\rm as}(h)]$ when $I_{\rm as}(h)$ accounts for the contribution $O(h^{-4.5})$ and $O(h^{-5})$, which are the next higher order ones. They have been obtained by Schmidt (1965) and with our normalization they read

$$(8\pi/h^{4.5})[\cos(Hh+\pi/4)/H^{1/2}+(2/H)^{1/2}\sin(h+\pi/4)/H]$$

and $(-12\pi/h^5)\cos(h)$, respectively. The comparison with Fig. 4(b) shows a good improvement. However, from a practical point of view, Figs. 2-4(a) show that an asymptotic analysis with only Porod deviations can be satisfactory starting beyond the first complete oscillation.

that $\gamma_0''(r)$ behaviour around a hyperbolic singularity obeys the conditions just recalled. Thus the proof yielding result (37) can be applied to each of the singularities of $\gamma_0''(r)$. In order to find the general contribution we express the deviations from the Porod law present in (37) in terms of the coefficients defined by (23) and (24). One finds respectively

$$-(4\pi V/h^4)H\Delta_E^{(2)}(H)\cos(hH) \qquad (39)$$

$$-(4\pi V/h^4)D\pi\Delta_H^{(2)}(D)\sin(hD). \qquad (40)$$

We conclude the paper by summarizing the results.

The most general deviation from the Porod law is

$$\sum_i A_i\cos(h\delta_i)/h^4+\sum_j B_j\sin(h\delta_j)/h^4.$$

Each of these contributions arises from the existence of a subset of the interphase surface which is opposite, parallel to and distant δ_i from itself. Moreover the cos( ) and sin( ) terms arise from those subsets characterized respectively by elliptical or by hyperbolic contact points. Finally, coefficients A_i's and B_j's are related to the coefficients defined by (10) and (11) and to the mean *Gauss* radius, defined in the footnote on p. 89, through

$$A_i=-4\pi V\delta_i\Delta_E^{(2)}(\delta_i)$$
$$=-4\pi V\left[\frac{\mathrm{sign}\,(F)(\hat\sigma_1.\hat\sigma_2)}{2V\Phi_1\Phi_2}S_\delta^E\frac{\langle\mathcal{R}_G\rangle}{\delta}\right]_i \qquad (41a)$$

$$B_i=-4\pi V\delta_i\pi\Delta_H^{(2)}(\delta_i)$$
$$=-4\pi V\left[\frac{(\hat\sigma_1.\hat\sigma_2)}{2V\Phi_1\Phi_2}S_\delta^H\frac{\langle\mathcal{R}_G\rangle}{\delta}\right]_i. \qquad (41b)$$

The index i reminds us that the quantities inside brackets are evaluated at δ_i. The close similarity of the coefficients in the two cases now appears evident. Clearly the usefulness of this analysis lies in the fact that by inspecting the geometrical properties of the interphase one can directly obtain the leading asymptotic term of the intensity.* We hope that the knowledge of these results may be of some help in the interpretation of the wiggles sometimes present in experimental intensities, as has already happened (Ciccariello & Benedetti, 1986).

It is a pleasant duty to thank one of the referees for having brought to my attention the papers by Schmidt (1965) and by Miller & Schmidt (1962) and for having stressed the importance of the paper by Jones & Kline (1958). I am also very grateful to Professor Paul W. Schmidt for enlightening correspondence. Financial support from the Italian

* For instance, if the sample is made up of toroidal particles, then one expects that only a deviation proportional to the sine function is present. Indeed, let D denote the diameter of a small section of the torus, so the toroidal surface is oppositely parallel and distant D from itself and the contact points are hyperbolic (Ciccariello, 1989).

Ministry of Public Education (40% funds) is acknowledged.

APPENDIX *A*

We have to study the limiting behaviour of $\mathscr{L}(\mathbf{r}_1, R)$ as $R \to \delta$. To this aim we follow very closely the procedure illustrated in Appendix *A* of I. Comparing (3) and (4*a*), we see that $\mathscr{L}(\mathbf{r}_1, R)$, defined by (5), can be written as

$$\mathscr{L}(\mathbf{r}_1, R) = \int_{\Omega} R^2\,\mathrm{d}\hat{\omega} \int_{\Sigma} \mathrm{d}S_2(\hat{\sigma}_1.\hat{\omega})(\hat{\sigma}_2.\hat{\omega}) \times \delta(\mathbf{r}_1 + R\hat{\omega} - \mathbf{r}_2). \quad (A.1)$$

We choose the z axis along the direction going from $\mathrm{d}S_1$ to $\mathrm{d}S_2$ and the origin at $\mathrm{d}S_1$. Equation (A.1) becomes

$$\mathscr{L}(\mathbf{0}, R) = \int_{\mathscr{S}} \mathrm{d}\mathscr{S} \int_{\Sigma'} \mathrm{d}S_2[\hat{\sigma}_1.\sigma_0(\mathbf{R})] \times [\hat{\sigma}_2(\mathbf{r}_2).\sigma_0(\mathbf{R})]\,\delta(\mathbf{R} - \mathbf{r}_2) \quad (A.1a)$$

where $\mathbf{R}$ denotes a point on the spherical surface $\mathscr{S}(\mathbf{0}, R)$ and $\sigma_0(\mathbf{R})$ is the unit vector normal to $\mathscr{S}$ at $\mathbf{R}$ and pointing externally to $\mathscr{S}$. Moreover, since we are interested in extracting the singular contribution to $\mathscr{L}(\mathbf{0}, R)$ due to the point P_2, we can confine ourselves to analysing the contribution to the integral due to Σ', a small subset of Σ centred at P_2. Locally, the parametric equations of $\mathscr{S}$ and Σ are

$$Z = Z(X, Y) = (R^2 - X^2 - Y^2)^{1/2} \quad (A.2a)$$

$$z = f_\Sigma(x, y). \quad (A.2b)$$

By the well known Gauss formulae (*e.g.* Smirnov, 1964, § 130)

$$\mathrm{d}\mathscr{S}(\mathbf{R}) = \mu_{\mathscr{S}}(X, Y)\,\mathrm{d}X\,\mathrm{d}Y \quad (A.3a)$$

$$\mathrm{d}S_2(\mathbf{r}) = \mu_\Sigma(x, y)\,\mathrm{d}x\,\mathrm{d}y \quad (A.3b)$$

with

$$\mu_{\mathscr{S}}(X, Y) = (1 + Z_{,X}^2 + Z_{,Y}^2)^{1/2} \quad (A.3c)$$

$$\mu_\Sigma(x, y) = (1 + f_{\Sigma,x}^2 + f_{\Sigma,y}^2)^{1/2} \quad (A.3d)$$

($f_{\Sigma,x}$ denotes the partial derivative of f_Σ with respect to x, *etc.*). The presence of the δ function makes the integration of (A.1a) with respect to X and Y immediate:

$$\mathscr{L}(0, R) = \int_{\Sigma'} \mathrm{d}x\,\mathrm{d}y\,\delta[Z(x, y) - f_\Sigma(x, y)]\,l_r(x, y) \quad (A.4)$$

where $l_r(x, y)$, defined as

$$l_r(x, y) \equiv \mu_{\mathscr{S}}(x, y)\mu_\Sigma(x, y)[\hat{\sigma}_1.\hat{\sigma}_0(x, y, Z)] \times [\hat{\sigma}_2(x, y, f_\Sigma).\hat{\sigma}_0(x, y, Z)] \quad (A.5)$$

is a continuous differentiable function, due to the previous smoothness assumption. Since Σ' is a small region around the origin, expanding there both f_Σ and $Z(x, y)$ one finds

$$f_\Sigma \simeq \delta + (f_{\Sigma,xx}x^2 + 2f_{\Sigma,xy}xy + f_{\Sigma,yy}y^2)/2 + o \quad (A.6a)$$

$$Z \simeq R - (x^2 + y^2)/2R + o \quad (A.6b)$$

where o denotes a contribution infinitesimal with respect to $x^2 + y^2$. By a suitable rotation of the axes in the (x, y) plane, we can write (A.6a) and (A.6b) as*

$$f_\Sigma \simeq \delta + a\xi^2 + b\eta^2 + o \quad (A.7a)$$

$$Z \simeq R - (\xi^2 + \eta^2)/2R + o \quad (A.7b)$$

where ξ and η are the rotated coordinates and a and b can easily be related to the coefficients present in (A.6a). We introduce the function

$$F_R(x, y) \equiv f_\Sigma(x, y) - Z(x, y) \quad (A.8)$$

which becomes equal to the one defined by (7) when $R = \delta$. Moreover, the Hessian of F_R at the origin is equal to

$$\mathscr{H}_R(0) = (f_{\Sigma,xx} + 1/R)(f_{\Sigma,yy} + 1/R) - f_{\Sigma,xy}^2 = (2a + 1/R)(2b + 1/R). \quad (A.9)$$

The last equality follows from the fact that the rotation corresponds to a transformation which diagonalizes the Hessian matrix and consequently leaves invariant its determinant.† In terms of variables ξ and η, the δ function in (A.4a) requires that

$$(a + 1/2R)\xi^2 + (b + 1/2R)\eta^2 = R - \delta. \quad (A.10)$$

(a) *Elliptical point case*

When P_2 is an elliptical point, $\mathscr{H}_\delta(0) > 0$. For the continuity of $\mathscr{H}_R(0)$ with respect to R [see (A.9)], one has also $\mathscr{H}_R(0) > 0$, provided R is sufficiently close to δ. In this situation we have two possibilities:

$$A \equiv a + 1/2R > 0 \quad \text{and} \quad B \equiv b + 1/2R > 0 \quad (A.11a)$$

* We are sure that (A.7a) can be obtained from (A.6a) by a suitable rotation, since (A.7a) represents the surface f_Σ around P_2 with respect to the directions of its principal curvatures, which are also orthogonal (Smirnov, 1964, § 136). One should also note that the rotation does not depend on R.

† It is very interesting to note that $\mathscr{H}_R(0)$ has an important geometrical meaning. In fact (A.8) is the parametric equation of a surface which could be called the *difference* surface between Σ and $\mathscr{S}(\mathbf{0}, R)$. Using ($A$.7$a$) and ($A$.7$b$) one immediately sees that its *principal* curvature radii are $R_1 = (2a + 1/R)^{-1}$ and $R_2 = (2b + 1/R)^{-1}$. Recalling that the so-called Gauss curvature $\mathscr{H}_G$ (Smirnov, 1964, § 134) is given by $\mathscr{H}_G = 1/(R_1R_2)$, one concludes that $\mathscr{H} = \mathscr{H}_G$. This result is important, because the Gaussian curvature is an intrinsic property of a surface [see, for instance, Hilbert & Cohn-Vossen (1953)] and thus its value cannot depend on the coordinate system. From the previous definition, $|\mathscr{H}_G|^{-1/2}$ ($\equiv \mathscr{R}_G$) represents the geometrical mean of the principal curvature radii. For this reason we shall call this quantity the *Gauss* radius of the difference surface.

or

$$A<0 \quad \text{and} \quad B<0. \tag{A.11b}$$

In the second case ($A.10$) cannot be satisfied when $R>\delta$ and thus

$$\mathscr{L}(0, \delta^+) \equiv \lim_{r\to\delta^+} \mathscr{L}(\mathbf{0}, r) = 0. \tag{A.12}$$

By contrast, when $R<\delta$ we can rescale ξ and η as follows:

$$\xi = |A|^{-1/2}\xi_1, \quad \eta = |B|^{-1/2}\eta_1. \tag{A.13}$$

With this substitution ($A.10$) becomes

$$\xi_1^2 + \eta_1^2 = \delta - R + o$$

while

$$\mathrm{d}x\,\mathrm{d}y = |AB|^{-1/2}\,\mathrm{d}\xi_1\,\mathrm{d}\eta_1 = \mathscr{H}_R^{-1/2}(0)\,\mathrm{d}t\,\mathrm{d}\phi$$

where we are using the polar coordinates and so $t = \xi_1^2 + \eta_1^2$. The argument of the Dirac function becomes $t-(\delta - R)$ and since $\delta - R > 0$, the integration with respect to t yields

$$\mathscr{L}(\mathbf{0}, R) = \int_0^{2\pi} \mathrm{d}\phi\, l_r(x, y)|_{t=\delta-R}.$$

The quantity inside the integrand is continuous and has to be evaluated at points which become closer and closer to P_2 as $t\to 0$. Its evaluation at P_2 is trivial since, owing to the fact that the first-order partial derivatives are null there, from ($A.3c$) and ($A.3d$) it follows that $\mu_{\mathscr{S}} = \mu_\Sigma = 1$, and at P_2 one also has that σ_0 points toward the positive z axis while σ_1 and σ_2 are parallel or antiparallel to the latter. In conclusion the result is

$$\mathscr{L}(\mathbf{0}, \delta^-) \equiv \lim_{R\to\delta^-} \mathscr{L}(\mathbf{0}, R) = 2\pi\mathscr{H}^{-1/2}(\hat{\sigma}_1 . \hat{\sigma}_0)(\hat{\sigma}_2 . \hat{\sigma}_0) \equiv \hat{\mathscr{L}}.$$

The discussion for the case ($A.11a$) is quite similar. One finds that

$$\mathscr{L}(0, \delta^+) = \hat{\mathscr{L}} \quad \text{and} \quad \mathscr{L}(0, \delta^-) = 0.$$

Combining the two results one obtains

$$\mathscr{L}(\mathbf{0}, \delta^+) - \mathscr{L}(\mathbf{0}, \delta^-) = 2\pi\mathscr{H}^{-1/2}(0)(\hat{\sigma}_1 . \hat{\sigma}_2)\,\mathrm{sign}\,(A) \tag{A.14}$$

where instead of $\mathrm{sign}\,(A)$ one could also use $\mathrm{sign}\,[F_\delta(x, y)]$, with the understanding that $F_\delta(x, y)$ must be evaluated quite close to the origin.

(b) Hyperbolic contact point

The condition $\mathscr{H}_\delta(0)<0$ implies that $\mathscr{H}_R(0)<0$ in a sufficiently close neighbourhood of P_2, which requires that R is close to δ. From ($A.9$) we have to distinguish two cases:

$$A>0 \quad \text{and} \quad B<0 \tag{A.15a}$$

or

$$A<0 \quad \text{and} \quad B>0. \tag{A.15b}$$

Let us discuss the first case. After rescaling variables as before, ($A.10$) becomes

$$\xi_1^2 - \eta_1^2 = \delta - R.$$

This equation represents a hyperbola having as asymptotes the lines bisecting the odd and even quadrants. The important difference from the elliptical case is that the curve now never shrinks to a point as $R\to\delta$ and then $\mathscr{L}$ will diverge. In order to extract the asymptotic behaviour of $\mathscr{L}$ as $R\to\delta$ we recall that the integral ($A.4$) is evaluated on Σ', a small region containing the origin. We choose Σ' as the region delimited by

$$|\xi| < l_0|A_\delta|^{-1/2} \quad \text{and} \quad |\eta| < l_0|B_\delta|^{-1/2} \tag{A.16}$$

where A_δ and B_δ are obtained from ($A.11$) by taking $R=\delta$ and l_0 is a small positive number. The integral ($A.4$) becomes

$$\mathscr{L}(\mathbf{0}, R) = |\mathscr{H}|^{-1/2} \int_{-\bar{\xi}_0}^{\bar{\xi}_0} \mathrm{d}\xi_1 \int_{-\bar{\eta}_0}^{\bar{\eta}_0} \mathrm{d}\eta_1 \times \delta(\xi_1^2 - \eta_1^2 - \delta + R)\,\bar{l}_r(\xi_1, \eta_1) \tag{A.17a}$$

where

$$\bar{\xi}_0 \equiv l_0|A/A_\delta|^{1/2} \quad \text{and} \quad \bar{\eta}_0 \equiv l_0|B/B_\delta|^{1/2}, \tag{A.17b}$$

and $\bar{l}_r$ is obtained from ($A.5$) by expressing x and y in terms of the rotodilated ξ_1 and η_1. We consider first the case $R\to\delta^-$ and we put $\varepsilon \equiv \delta - R$. Clearly $\varepsilon > 0$. By a well known identity on δ function one has

$$\delta(\xi_1^2 - \eta_1^2 - \varepsilon) = \frac{\delta[\xi_1 - \bar{\xi}_1(\varepsilon, \eta_1)] + \delta[\xi_1 + \bar{\xi}_1(\varepsilon, \eta_1)]}{2\bar{\xi}_1(\varepsilon, \eta_1)} \tag{A.18a}$$

with

$$\bar{\xi}_1(\varepsilon, \eta_1) \equiv (\varepsilon + \eta_1^2)^{1/2}. \tag{A.18b}$$

One finds

$$\mathscr{L}(\mathbf{0}, R) = 2|\mathscr{H}_R(0)|^{-1/2} \int_0^{\bar{\eta}_0} \mathrm{d}\eta_1 \frac{l_s(\bar{\xi}_1, \eta_1)}{(\varepsilon + \eta_1^2)^{1/2}} \tag{A.19}$$

where

$$l_s(\xi_1, \eta_1) \equiv [\bar{l}_r(\xi_1, \eta_1) + \bar{l}_r(-\xi_1, \eta_1) + \bar{l}_r(\xi_1, -\eta_1) + \bar{l}_r(-\xi_1, -\eta_1)]/2 \tag{A.20}$$

is the completely symmetric part of $\bar{l}_r(\xi_1, \eta_1)$. By a partial integration, the integral in (A.19) becomes

$$\begin{aligned} &l_s[\bar{\xi}_1(\varepsilon, \bar{\eta}_0), \bar{\eta}_0] \ln [\bar{\eta}_0 + (\varepsilon + \bar{\eta}_0^2)^{1/2}] \\ &- l_s[\bar{\xi}_1(\varepsilon, 0), 0] \ln (\varepsilon)/2 \\ &- \int_0^{\bar{\eta}_0} \mathrm{d}\eta_1 \ln [\eta_1 + (\varepsilon + \eta_1^2)^{1/2}] \\ &\times l'_{s,\eta_1}[\bar{\xi}_1(\varepsilon, \eta_1), \eta_1] \end{aligned} \quad (A.21)$$

where l'_{s,η_1} denotes the total derivative with respect to η_1 of $l_s[\bar{\xi}_1(\varepsilon, \eta_1), \eta_1]$. As $R \to \delta^-$, $\varepsilon \to 0^+$ and $\bar{\eta}_0 \to l_0$ and owing to their regularity the limits of the first and third terms in (A.21) can easily be evaluated. The second term is logarithmically divergent and its leading behaviour is obtained by expanding $l_s[\xi_1(\varepsilon, 0), 0]$ with respect to ε. Since $l_s(0, 0) = 2\bar{l}_r(0, 0) = 2(\hat{\sigma}_1 . \hat{\sigma}_0)(\hat{\sigma}_2 . \hat{\sigma}_0) = 2(\hat{\sigma}_1 . \hat{\sigma}_2)$, one finds that

$$\begin{aligned} \mathscr{L}(\mathbf{0}, R) \simeq\; & 2|\mathscr{H}_R(0)|^{-1/2} \\ & \times \{-(\hat{\sigma}_1 . \hat{\sigma}_2) \ln (\varepsilon) + c_0 + O[\varepsilon \ln (\varepsilon)]\} \end{aligned} \quad (A.22)$$

with

$$c_0 \equiv l_s(l_0, l_0) \ln (2l_0) - \int_0^{l_0} \mathrm{d}\eta_1 \ln (2\eta_1) l'_{s,\eta_1}(\eta_1, \eta_1). \quad (A.23)$$

Equation (A.22) yields the two leading asymptotic terms of $\mathscr{L}(\mathbf{0}, R)$ as $R \to \delta^-$ in the case $A_\delta > 0$ and $B_\delta < 0$. Let us see the changes required in the case $R \to \delta^+$. In order to have again $\varepsilon > 0$, we have to define the latter as $\varepsilon \equiv R - \delta$. Consequently the δ function present in (A.17) will be written and decomposed as follows:

$$\begin{aligned} &\delta(\eta_1^2 - \xi_1^2 - \varepsilon) \\ &= \frac{\delta(\eta_1 - \bar{\eta}_1(\varepsilon, \xi_1)) + \delta[\eta_1 + \bar{\eta}_1(\varepsilon, \xi_1)]}{2\bar{\eta}_1(\varepsilon, \xi_1)} \end{aligned} \quad (A.24a)$$

with

$$\bar{\eta}_1(\varepsilon, \xi_1) \equiv (\varepsilon + \xi_1^2)^{1/2}. \quad (A.24b)$$

After integrating with respect to η_1 one has

$$\mathscr{L}(\mathbf{0}, R) = 2|\mathscr{H}_R(0)|^{-1/2} \int_0^{\xi_0} \mathrm{d}\xi_1 \frac{l_s(\xi_1, \bar{\eta}_1)}{(\varepsilon + \xi_1^2)^{1/2}}.$$

The asymptotic estimate of this quantity is obtained along the same lines expounded above. Using the symmetry property of $l_s(\xi_1, \eta_1)$ one finds that the final result is again (A.22) with the only modification that now $\varepsilon = R - \delta$. Thus the two cases can be represented by the result.

$$\begin{aligned} \mathscr{L}(\mathbf{0}, R) \simeq\; & 2|\mathscr{H}_R(0)|^{-1/2} \\ & \times [-(\hat{\sigma}_1 . \hat{\sigma}_2) \ln (|R - \delta|) + c_0 + o]. \end{aligned} \quad (A.25)$$

Since in this expression no explicit reference to the condition $A > 0$ and $B < 0$ appears, it is obvious that (A.25) holds true also in the case $A < 0$ and $B > 0$ and thus (A.25) yields the leading asymptotic term of $\mathscr{L}(\mathbf{0}, R)$ near a logarithmic singularity.

APPENDIX *B*

We now evaluate the leading asymptotic term of

$$\mathscr{I} \equiv (2/\pi Q^3) \int_{1-\varepsilon}^{1+\varepsilon} \sin (Qx) \ln (|1 - x|) \,\mathrm{d}x. \quad (B.1)$$

with the change of variable $x = 1 - \varepsilon y$ and from the parity property of the resulting integrand, (B.1) becomes

$$\begin{aligned} \mathscr{I}_1 &\equiv (\pi Q^3/2)\mathscr{I} \\ &= \varepsilon \sin Q \int_0^1 \ln (\varepsilon y) \cos (\varepsilon Q y) \,\mathrm{d}y. \end{aligned} \quad (B.2)$$

With $\bar{Q} \equiv Q\varepsilon$, a simple integration yields

$$\begin{aligned} \mathscr{I}_1 &= [\sin Q \sin (\bar{Q})/Q] \ln \varepsilon \\ &\quad + \varepsilon \sin Q \Re[\mathscr{L}(\bar{Q})] \end{aligned} \quad (B.3)$$

where $\Re$ denotes the operation of taking the real part and we have used the definition

$$\mathscr{L}(\bar{Q}) \equiv \int_0^1 \ln y \exp (i\bar{Q}y) \,\mathrm{d}y.$$

Recalling that the asymptotic expansion of the latter is (Binder & Orszag, 1978)

$$\begin{aligned} \mathscr{L}(\bar{Q}) \simeq\; & -i \ln (\bar{Q})/\bar{Q} - (i\gamma + \pi/2)/\bar{Q} \\ & + i \exp (i\bar{Q}) \sum_{m=1}^{\infty} (-i)^m (m-1)!/\bar{Q}^{m+1} \end{aligned} \quad (B.4)$$

one immediately obtains the sought leading asymptotic term of $\mathscr{I}$, using (B.3) and (B.4), *i.e.*

$$\mathscr{I} \simeq (2/\pi Q^4)[2 \ln \varepsilon \sin Q \sin (Q\delta) - \pi \sin Q] + o. \quad (B.5)$$

This can be immediately converted to the form (35).

References

ABRAMOWITZ, M. & STEGUN, I. A. (1970). *Handbook of Mathematical Functions*, pp. 589-591. New York: Dover.

BALE, H. D. & SCHMIDT, P. W. (1984). *Phys. Rev. Lett.* **53**, 586-599.

BENEDETTI, A., CICCARIELLO, S. & FAGHERAZZI, G. (1988). *Phys. Chem. Glasses*, **29**, 173-178.

BINDER, C. M. & ORSZAG, S. A. (1978). *Advanced Mathematical Methods for Scientists and Engineers*, pp. 381-382. New York: McGraw-Hill.

CICCARIELLO, S. (1985). *Acta Cryst.* **A41**, 560-568.

CICCARIELLO, S. (1989). In preparation.

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.

CICCARIELLO, S., GOODISMAN, J. & BRUMBERGER, H. (1988). *J. Appl. Cryst.* **21**, 117-128.
DEBYE, P., ANDERSON, H. R. & BRUMBERGER, H. (1957). *J. Appl. Phys.* **28**, 679-683.
ERDÉLYI, A. (1956). *Asymptotic Expansions*, ch. II. New York: Dover.
GILLE, W. (1987). *Exp. Tech. Phys.* **35**, 93-98.
GRADSHTEYN, I. S. & RYZHIK, I. M. (1970). *Tables of Integrals, Series and Products*, ch. 8.1. London: Academic Press.
GUINIER, A. (1963). *X-ray Diffraction*, chs. 2 and 10. San Francisco: Freeman.
HILBERT, D. & COHN-VOSSEN, S. (1953). *Geometry and the Imagination.* New York: Chelsea.
JONES, D. S. & KLINE, M. (1958). *J. Math. Phys. (Cambridge, Mass.)*, **37**, 1-28.
MILLER, A. & SCHMIDT, P. W. (1962). *J. Math. Phys. (NY)*, **3**, 92-96.
POROD, G. (1952). *Kolloid Z.* **125**, 51-60.
POROD, G. (1982). *Small-Angle X-ray Scattering*, edited by O. GLATTER & O. KRATKY, ch. I. London: Academic Press.
ROJANSKI, D., HUPPERT, D., BALE, H. D., DACAI, X., SCHMIDT, P. W., FARIN, D., SERI-LEVY, A. & AVNIR, D. (1986). *Phys. Rev. Lett.* **23**, 2505-2508.
SCHMIDT, P. W. (1965). *J. Math. Phys. (NY)*, **6**, 424-431.
SCHMIDT, P. W. (1967). *J. Math. Phys. (NY)*, **8**, 475-477.
SMIRNOV, V. I. (1964). *A Course of Higher Mathematics*, Vol. II, ch. 7. Oxford: Pergamon.
WILLIAMS, J. A., RINDONE, G. E. & MCKINSTRY, H. A. (1981). *J. Am. Ceram. Soc.* **64**, 702-709.
WU, H. & SCHMIDT, P. W. (1974). *J. Appl. Cryst.* **7**, 131-146.

Acta Cryst. (1989). **A45**, 99-104

A Reconsideration of the Role of Two-Phase Seminvariants. V. Basic Results

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Abstract

A basic obstacle to the widespread use of two-phase seminvariants of first rank in direct methods is often the large amount of computing time needed for their probabilistic estimation. A new very fast algorithm for identifying such seminvariants and a modified probabilistic formula for their estimation are described. Contrary to common belief, practical tests show that the amount of information contained in two-phase seminvariants is in general not negligible compared with information provided by triplets.

Symbols

N: number of atoms in the cell.
m: number of symmetry operators of the space group.
$\mathbf{C}_s \equiv (\mathbf{R}_s, \mathbf{T}_s)$: sth symmetry operator: $\mathbf{R}_s$ is its rotational and $\mathbf{T}_s$ its translational part.
$E_{\mathbf{h}}$: normalized structure factor with vectorial index $\mathbf{h}$.
$R_{\mathbf{h}} \equiv |E_{\mathbf{h}}|$.
$\varphi_{\mathbf{h}}$: phase of $E_{\mathbf{h}}$.
$\mathbf{I}$: identity 3×3 matrix.

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1. Introduction

A first attempt at evaluating two-phase seminvariants was described by Grant, Howells & Rogers (1957). The method (the so-called 'coincidence method') was extended to non-centrosymmetric space groups by Debaerdemaeker & Woolfson (1972), according to the following argument. Let

$$\mathbf{u}_1 = \mathbf{h}_1 - \mathbf{h}_2\mathbf{R}_\beta, \qquad (1a)$$

$$\mathbf{u}_2 = \mathbf{h}_2 - \mathbf{h}_1\mathbf{R}_\alpha. \qquad (1b)$$

If $|E_{\mathbf{u}_1}|, |E_{\mathbf{u}_2}|, |E_{\mathbf{h}_1}|, |E_{\mathbf{h}_2}|$ are all sufficiently large then

$$\varphi_{\mathbf{u}_1} \simeq \varphi_{\mathbf{h}_1} - \varphi_{\mathbf{h}_2\mathbf{R}_\beta},$$

$$\varphi_{\mathbf{u}_2} \simeq \varphi_{\mathbf{h}_2} - \varphi_{\mathbf{h}_1\mathbf{R}_\alpha},$$

so that

$$\Phi_2 = \varphi_{\mathbf{u}_1} + \varphi_{\mathbf{u}_2} \simeq 2\pi(\mathbf{h}_1\mathbf{T}_\alpha + \mathbf{h}_2\mathbf{T}_\beta). \qquad (2)$$

Φ_2 is a structure seminvariant and may therefore be estimated by means of (2).