Acta Crystallographica Section A
Foundations of Crystallography
ISSN 0108-7673

Received 19 April 2010
Accepted 9 June 2010

Geometric parameters of isotropic ensembles of right cylinders from the small-angle-scattering correlation function

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The scattered intensity of ensembles of right homogeneous quasi-diluted cylinders with constant oval right section (RS) and volume fraction φ are analyzed using the small-angle-scattering (SAS) correlation function (CF) $\gamma(r) = \gamma(r, \varphi)$ in the isotropic two-phase approximation. A relation between the CF of the cylinder RS, $\beta_0(r)$, and the CF of the single cylinder of height H, $\gamma_0(r, H)$, allows the calculation of the explicit cylinder parameters of height, surface area, RS surface area, RS perimeter and volume. This is accomplished by evaluating the first two derivatives of $\gamma_0(r)$ at $r = 0$. Without the assumption of an oval RS, neither H nor the RS surface area can be uniquely determined.

1. Introduction

The present paper demonstrates that simple, explicit results for specific cylinder parameters (see Fig. 1 for parameter definitions) can be derived in terms of $\gamma(r)$. Using the correlation function for the case of the single cylinder in the dilute limit, $\gamma_0(r)$, the quasi-dilute case is considered. The extension from the dilute to quasi-dilute limit follows as a natural consequence of the fact that the volume fraction, φ, and the volume, V, for any single cylinder can be measured in terms of γ. The case of infinitely long cylinders (Gille, 2010), as well as the transformations describing right cylinders of height H (Ciccariello, 2002, 2010), have been previously investigated. Here, an explicit estimation of H and other derived parameters is presented.

2. Theory

We wish to consider the scattering behavior of right homogeneous cylindrical particles of unique size with right section (RS) embedded in a homogeneous sample matrix. However, our results are general and also hold true for polygonal RSs (*i.e.* pentagonal, hexagonal RSs). In the course of our calculations, intermediate results show that it is useful to assume the RS to be oval.[1] The order range considered, L, is of the order of magnitude of 100 nm. Assuming a quasi-diluted cylinder ensemble of volume fraction φ implies that the minimum distance, $r = r_0$, between any two cylinders is somewhat greater than the diameter of the largest cylinder, L_0.

[1] Furthermore, the assumption of an oval RS automatically restricts our consideration to convex particles.

The density autocorrelation function $\gamma(r) = \gamma(r, \varphi, L)$ of the sample and the small-angle-scattering (SAS) pattern are related by well known integral transformations (Glatter & Kratky, 1982; Feigin & Svergun, 1987).

Using the definitions and assumptions presented in Fig. 1, and restricting the r interval to $0 \le r < r_0 < H < L_0 < \infty$, the generalized Abel transform is used to define the correlation function CF of the cylinder $\gamma_0(r)$,

$$\gamma_0(r) = \frac{1}{r}\int_0^r \left[\frac{x}{(r^2 - x^2)^{1/2}} - \frac{x}{H}\right]\beta_0(x)\,\mathrm{d}x, \qquad 0 \le r < r_0 < H < L_0 < \infty, \tag{1}$$

where $\beta_0(r)$ is the CF of the RS. Equation (1) holds true for any RS shape [see the non-convex butterfly example (Ciccariello, 2009)]. We note that the system of inequalities used to restrict r in equation (1) is valid through to equation (7), and the normalization condition of the density autocorrelation function $\gamma_0(0) = 1$ is satisfied. The information contained near the origin ($r \to 0+$ behavior) of equation (1) will now be considered in the light of previous results (Gille, 2002*a*; Sukiasian & Gille, 2007).

The parametric integral is split into two parts, separating out the contributions from an infinitely long cylinder and a cylinder with finite height, H. The correlation function is given by

$$\gamma_0(r) = \gamma_\infty(r) - \frac{1}{rH}\int_0^r x\beta_0(x)\,\mathrm{d}x, \tag{2}$$

where $\gamma_\infty(r)$ is the CF of the infinitely long cylinder ($H \to \infty$, RS = constant) and the second term of equation (2) reflects

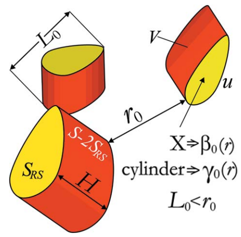

Figure 1
Cylindrical particles with oval right section X: The model comprises the limiting cases lamella and rod. A quasi-diluted, $r_0 < L_0$, ensemble of homogeneous cylinders of order range L is assumed. The length r_0 denotes the shortest distance between any two points, belonging to two different cylinders. The intention is to establish explicit relations that define a first parameter set of six independent geometric quantities: height H, volume V, volume fraction φ, surface area S, right section surface area $S_{\rm RS}$ and the perimeter u of the RS, in terms of the SAS correlation function $\gamma(r, L)$. Other parameters of the model (for example the mean chord length of the RS X, $x_1 = \pi S_{\rm RS}/u$, or the mean chord length l_1 of the cylinder) depend on the first parameter set.

the influence of finite H. The coefficients of the Taylor series expansion of equation (2) lead to the cylinder parameters introduced in Fig. 1. Evaluation of the first term at $r = 0$ leads to the specific properties $\gamma'_\infty(0) = [-S_\infty/(4V_\infty)] = -u/(4S_{\rm RS}) = -1/l_{1\infty}$ and $\gamma''_\infty(r) = 3r/(4l_{1\infty}{}^3) + 5r^3/(16l_{1\infty}{}^5) + \ldots$, where $l_{1\infty}$ denotes the mean chord length of the infinitely long cylinder and u denotes the perimeter of the RS. The derivations of these results have been outlined in detail (Gille, 2002*b*, 2010).

We note for future use that $\beta'_0(0)$ and $\gamma'_\infty(0)$ are interrelated by $\beta'_0(0)/\gamma'_\infty(0) = 4/\pi$. Setting $\gamma''_\infty(0+) = 0$, differentiation of equation (2) with respect to r yields

$$\gamma'_0(r) = \gamma'_\infty(r) - \frac{1}{H}\left(\beta_0(r) - \frac{\int_0^r x\beta_0(x)\,{\rm d}x}{r^2}\right). \tag{3}$$

Consequently,

$$\gamma'_0(0) = \gamma'_\infty(0) - \frac{1}{2H} = -\left(\frac{u}{4S_{\rm RS}} + \frac{1}{2H}\right), \tag{4}$$

where $\gamma'_0(0)$ is expressed in terms of three cylinder parameters: u, $S_{\rm RS}$ and H.

The second derivative of the CF with respect to r, $\gamma''_0(r)$, is

$$\gamma''_0(r) = \gamma''_\infty(r) - \frac{1}{H}\left\{\beta'_0(r) - \left[\frac{\beta_0(r)}{r} - \frac{2\int_0^r x\beta_0(x)\,{\rm d}x}{r^3}\right]\right\}, \tag{5}$$

and as $\gamma''_0(r \to 0+)$ we obtain

$$\gamma''_0(0) = \gamma''_\infty(0) - \frac{2\beta'_0(0)}{3H} = \gamma''_\infty(0) - \frac{2\left[(4/\pi)\gamma'_\infty(0)\right]}{3H}. \tag{6}$$

Using equations (4) and (6), $\gamma''_0(0)$ can be written

$$\gamma''_0(0) = -\frac{8}{3\pi H}\left[\gamma_0{}'(0) + \frac{1}{2H}\right] = \frac{8}{3\pi H}\left(\frac{1}{l_1} - \frac{1}{2H}\right). \tag{7}$$

Generally, equation (7) defines two different H values in terms of $\gamma'_0(0)$ and $\gamma''_0(0)$. These solutions $H_{1,2}$, $0 < H_1 \le H_2 < \infty$, are

$$H_{1,2} = -\frac{1}{T\gamma_0{}'(0)}\left[1 \mp (1-T)^{1/2}\right],$$
$$\text{with } T = \frac{3\pi\gamma''_0(0)}{4\left[\gamma'_0(0)\right]^2} = \frac{3\pi}{4}\Phi(0). \tag{8}$$

The T term involved in equation (8) is related to the so-called puzzle-fitting function $\Phi(r) = \gamma''_0(r)/[\gamma'_0(r)]^2$ as discussed by Gille (2009), where a numerical analysis of T terms is investigated in connection with the limit $\Phi(0+)$.

2.1. Plate-like and rod-like cylinders

The single limiting solution, $H = l_1$, exists if and only if $T \to 1$ (see Fig. 2, left-hand side). We emphasize that $\mp$ signs before the root term in equation (8) have practical consequences. That is, for the $(-)$ sign we have plate-like cylinders of height H, $l_1/2 < H_1 < l_1$, while for the $(+)$ sign, we have rod-like cylinders, $l_1 < H_2 < \infty$ (see Fig. 3 for an analysis of the term $w = H/l_1$). As $\gamma_0(L_0) = 0$ unambiguously defines the maximum particle diameter L_0, when $H_1 \ne H_2$ two different maximum RS diameters result, $L_{{\rm RS}_1} \ne L_{{\rm RS}_2}$. This is discussed first without making the assumption of an oval RS. In §2.1.3, the RS is restricted to the oval case and our findings are revisited. We demonstrate that a restriction to the oval RS case clarifies our final results.

2.1.1. Plate-like cylinders. This is the case in which $H = H_1 \to 0$, and it includes the familiar lamellar shape. The forms of the first and second derivative of the CF are $\gamma'_0(0) \simeq -1/(2H) = 1/l_1$ and $\gamma''_0(0) \to 0$, respectively. The T-term behavior as $T \to 0$ reduces equation (8) to an indeterminate form [0/0],

$$\lim_{T\to 0} H(T) = l_1 \lim_{T\to 0}\frac{1-(1-T)^{1/2}}{T} = \frac{l_1}{2}.$$

Consequently, $H_1 \to 1/(2|\gamma'_0(0)|)$, giving $l_1/2 \le H_1 \le l_1$.

2.1.2. Rod-like cylinders. In the limiting case $H = H_2 \to \infty$, then $\gamma_0(r) \to 1 - r/H_2$, $0 \le r \le H_2$, and the mean chord length l_1 approximately agrees with H, $l_1 \simeq H$. At $r \simeq l_1$ there is a dominant peak in the chord-length distribution density (CLDD), $A(r) = l_1\gamma''_0(r)$, for rod-like cylinders. The larger the value of H_2, the more the CLDD approaches $A(r, H_2) \to \delta(r - H_2)$, where it collapses. This is verified by examining equation (8) and noting that as $\gamma''(0) \to 0$ and $T \to 0$,

$$H(T) = l_1 \lim_{T\to 0, H\to\infty}\frac{1+(1-T)^{1/2}}{T} = \infty.$$

The positive sign in front of the root term is the only difference between this result and that of the plate-like cylinder case.

The equations for fixing cylinder parameters using γ_0 in the infinitely dilute limit are summarized in Table 1. Table 2 summarizes the quasi-diluted case, where the functions $\gamma(r)$ and $\gamma_0(r)$ are connected by the relation $\gamma(r) = [\gamma_0(r) - \varphi]/(1-\varphi)$ (Guinier & Fournét, 1955; Gille, 2002*b*). As $\gamma_0(L_0) = 0$, the value $\gamma(L_0) = -\varphi/(1-\varphi)$ defines the first local minimum of $\gamma(r)$ [Table 2, item (5)]. Of particular

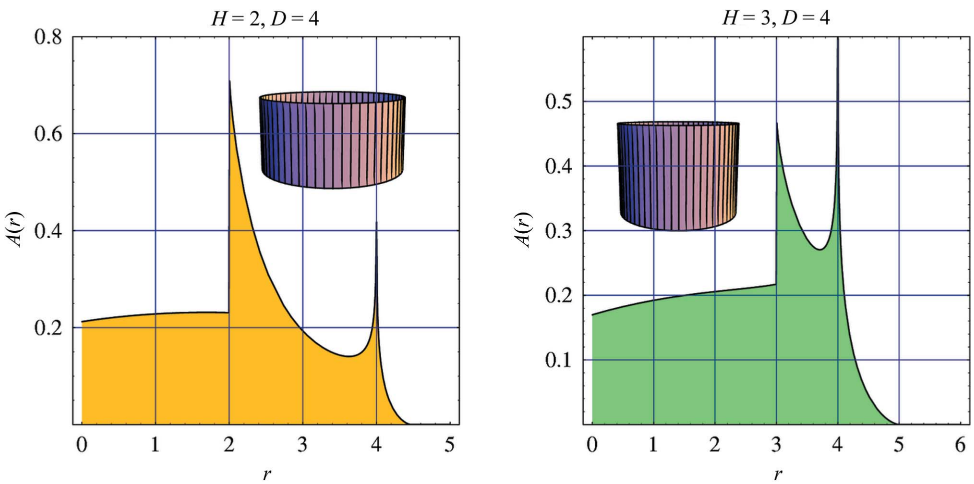

Figure 2
The function $A(r, H, D)$ of circular cylinders [for the second peak (larger r), $\gamma_0''(r) \sim A(r \to D, H, D) \to \infty$, *i.e.* a pole at $r = D$, see Ciccariello (1990)]. The first peak (smaller r) is limited, it is a finite jump. The function $A(r, H, D)$ is not linear in the first interval of representation, $0 \le r \le \min(H, D)$. Cylinder 1: Height $H = 2$ and diameter $D = 4$, $\gamma_0'(0) = -1/2$, $\gamma_0''(0) = 1/(3\pi)$. In this case, $A(0) = 0.212$. The largest particle diameter is $L_0 = 2(5)^{1/2}$ and $V = 8\pi$. Additionally, the parameter $l_1 = 2$ results. Inserting these parameters into equation (8) gives $H_1 = H_2 = H = 2$ [equation (9) involves one solution, as $T = 1$, see Fig. 3]. Cylinder 2: In this case, $H = 3$, $D = 4$. Measuring this using equation (8) requires more effort, as $T < 1$. Here, the largest particle diameter is $L_0 = 5$ and $V = 12\pi$. The values $\gamma_0'(0) = -5/12$ ($l_1 = 12/5$), $\gamma_0''(0) = 0.0707$ and $T = 0.96$ give two different heights, $H_1 = 2$ and $H_2 = 3$, using equation (7). If an oval RS is assumed and the inequalities in equation (9) are applied, the maximum RS diameter is $L_{\mathrm{RS}_{1,2}} = (L_0^2 - H_{1,2}^2)^{1/2}$ and the correct solution $H = H_2$ is found. Equation (9) is fulfilled for $H = H_2$ but not for $H = H_1$. In the latter case, the contradiction 12. < 9. follows from equation (10).

importance is the relation between the characteristic volume, v_c, and $\gamma(r)$, $v_c = \int_0^L 4\pi r^2 \gamma(r)\,\mathrm{d}r = V/(1-\varphi)$ (Gille, 2002*b*). This relation enables the determination of the cylinder volume V, item (4) of Table 2.

2.1.3. Assumption of oval cylinders and identification of *H*. The results summarized in Tables 1 and 2 hold true for right cylinders with any RS. However, this generality has a marked disadvantage. The cylinder height, surface area and maximum diameter of the RS cannot be uniquely determined. Consequently, the mean chord length x_1 of the RS cannot be uniquely determined [note the remark 'two solutions' in Table 1 items (4) and (6), and Table 2, item (7)]. Simply stated, there is not enough of the information necessary to fix these parameters. However, making the assumption that the cylinder has an oval RS simplifies the situation. This is demonstrated using the largest diameter of the RS region L_{RS} and its mean chord length, x_1. Using the results outlined above, the lengths H and the three parameters L_{RS}, x_1 and S_{RS} can be found from L, V, $\gamma_0'(0)$ and $\gamma_0''(0+)$.

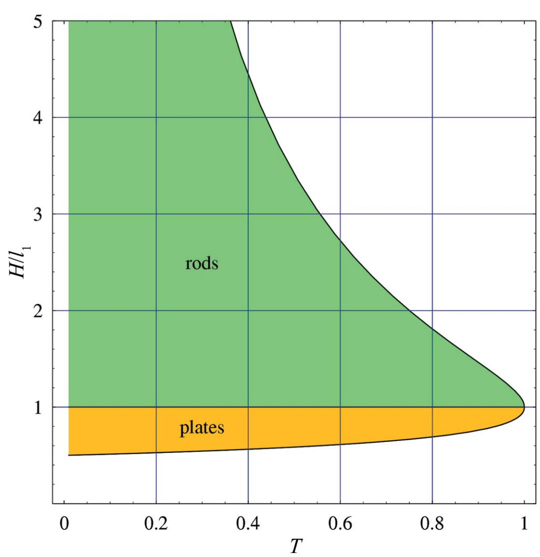

Figure 3
Analysis of $w = H/l_1 = [1 \mp (1-T)^{1/2}]/T$, $0 \le T \le 1$. In both the $\mp$ cases as $T \to 1$, $H = l_1$ results. For each T in the interval $0 \le T \le 1$, the w term is always greater than 1/2. If $T < 1$, two different H exist. The positive sign leads to rod-like cylinders. The negative sign leads to plate-like cylinders, *i.e.* as $T \to 0$, $H/l_1 \to 0$ or $H/l_1 \to \infty$.

If the geometric limiting conditions typical of an oval RS, $S_{\mathrm{RS}} \le \pi {L_{\mathrm{RS}}}^2/4$ and $x_1 \le \pi L_{\mathrm{RS}}/4$, are combined, a unique solution results. Taking $L_{\mathrm{RS}_{1,2}} = (L_0^2 - H_{1,2}^2)^{1/2}$ and summarizing the latter inequalities results in a restricted interval for the mean chord length x_1,

$$S_{\mathrm{RS}}/L_{\mathrm{RS}} \le x_1 \le \pi L_{\mathrm{RS}}/4. \tag{9}$$

Equation (9) simplifies the constellation discussed in the previous sections and fixes one solution of H from $H_{1,2}$. In the infinitely dilute case, equation (9) can be written in terms of L_{RS}, V, $\gamma_0''(0+)$ and H using the right-hand side of equation (7) as

$$\frac{4V}{\pi L_{\mathrm{RS}}} \le \frac{8}{3\pi}\frac{1}{\gamma_0''(0)} \le L_{\mathrm{RS}} H. \tag{10}$$

The case $H_1 \equiv H_2$ is possible, and is illustrated for the first circular cylinder case $H = 2$, $D = 4$ in Fig. 2. For rods $\gamma_0''(0+) \to 0$ and $H \to \infty$, $V \to \infty$, see Gille (2010). For a fixed L, the function γ_0 can be found from γ as described in Table 2, item (5). Thus, equation (10) can be analogously applied to the quasi-diluted case. In summary, owing to the terms $\gamma_0'(0)$ and $\gamma_0''(0)$, the problem of estimating the char-

Table 1
Parameters of a single cylinder in terms of $\gamma_0(r, L_0)$.

Parameter	Symbol	Formula
(1) Height	H	$H_{1,2} = -[1/T\gamma_0'(0)][1 \mp (1-T)^{1/2}]$, $T = (3\pi/4)\Phi(0)$
(2) Volume	V	$V = \int_0^{L_0} 4\pi r^2 \gamma_0(r)\,\mathrm{d}r$
(3) Total surface area	S	$S = -4V\gamma_0'(0)$
(4) RS surface area	S_{RS}	$S_{\mathrm{RS}_{1,2}} = V/H_{1,2}$ (two solutions)
(5) RS perimeter	u	$u = (S - 2S_{\mathrm{RS}_{1,2}})/H_{1,2}$ (one solution)
(6) RS chord length	x_1	$x_1 = \pi S_{\mathrm{RS}_{1,2}}/u$ (two solutions)

Table 2
Recognition of cylinder parameters from the sample CF $\gamma(r)$ in the isotropic, quasi-diluted case.

All parameters are traced back to $\gamma(r, L)$.

Parameter	Symbol	Formula
(1) Characteristic volume	v_{c}	$v_{\mathrm{c}} = \int_0^{\infty, L} 4\pi r^2 \gamma(r)\,\mathrm{d}r$
(2) Mean chord length	l_1	$l_1 = \int_0^{L_0} [r\gamma''(r)/\lvert\gamma'(0)\rvert]\,\mathrm{d}r$
(3) Volume fraction	φ	$1-\varphi = 1/l_1\lvert\gamma'(0)\rvert = 1/\int_0^{L_0} r\gamma''(r)\,\mathrm{d}r$
(4) Cylinder volume	V	$V = (1-\varphi)v_{\mathrm{c}} = \int_0^{\infty} 4\pi r^2 \gamma(r)\,\mathrm{d}r / \int_0^{L_0} r\gamma''(r)\,\mathrm{d}r$
(5) Single cylinder CF	γ_0	$\gamma_0(r) = (1-\varphi)\gamma(r) + \varphi$, $\gamma_0'(r) = (1-\varphi)\gamma'(r)$
(6) Height	H	$H_{1,2} = -[1/T\gamma_0'(0)][1 \mp (1-T)^{1/2}]$, $T = 3\pi\Phi(0)/4$
(7) RS surface area	$S_{\mathrm{RS}_{1,2}}$	$S_{\mathrm{RS}_{1,2}} = V/H_{1,2}$ (two solutions)
(8) Total surface area	S	$S = 4V/l_1 = 4v_{\mathrm{c}}(1-\varphi)^2\lvert\gamma'(0)\rvert = 4v_{\mathrm{c}}l_{\mathrm{p}}/l_1^{\,2}$
(9) RS perimeter	u	$u = 3\pi V\gamma_0''(0)/2$ (one solution)

acteristic parameters of right oval cylinders using the SAS CF can, unexpectedly, be handled quite simply. An application of the relations in Tables 1 and 2 is presented in Fig. 2.

2.2. Aspects of data evaluation

Specialized data-evaluation techniques exist for measuring the parameters $\gamma'(0)$ and $\gamma''(0)$ from the smeared intensity (Ciccariello & Sobry, 1999). On the other hand, for a well selected order range L, the function $\gamma(r, L)$ can still be calculated by using familiar SAS transforms. Care must be taken when working with these transforms due to potential, well documented, truncation errors (Glatter & Kratky, 1982; Feigin & Svergun, 1987; Burger & Ruland, 2001; Hansen, 2003; Gille, 2003). There are many differentiation techniques [*cf.* the approach described by Lanczos (see Groetsch, 1998)] that define $\gamma'(r, L)$ in terms of $\gamma(r, L)$. Numerical estimations for the term $\gamma''(0)$ have been calculated successfully here using the *Mathematica* (Wolfram Research, 2009) function *SequenceLimit*. Details of the procedure are discussed in reference to the puzzle-fitting function $\Phi(r)$ of randomly shaped puzzle fragments in the punch-matrix/particle puzzle case (Gille, 2009).

3. Summary and conclusions

An extensive geometric parameter set (see Tables 1 and 2) describing ensembles of cylinders based on their SAS CF, with practical applications for the evaluation of scattering data, has been discussed. The explicit solutions can be traced back to the terms $\gamma'(0)$ and $\gamma''(0+)$ of the sample CF. Even if $H_1 \neq H_2$, there exists only one solution for the parameters L_0, V, φ, S, l_1 and u. The unique solution for these parameters is independent of whether $H = H_1 \to 0$ or $H = H_2 \to \infty$. By assuming an oval RS and restricting it to the set of inequalities in equations (9)–(10), even S_{RS} and x_1 can be uniquely determined.

For the more general case of a non-oval RS, it was demonstrated that two different parameter sets for the RS surface area and its mean chord length result. The smaller solution for the length H_1 corresponds to a relatively flat cylinder for which $l_1/2 \le H_1 \le l_1$, *i.e.* $H_1 \simeq l_1 \ll L_0$. The greater solution, H_2, corresponds to a more elongated (longer) cylinder, $l_1 \le H_2 \simeq L_0$.

The solutions $H_{1,2}$ correspond to differently shaped right sections X, $X_1 \neq X_2$. Unfortunately, this line of analysis suffers from the disadvantage that it does not allow the unique determination of the shape of X_1 or X_2 unless further assumptions about the RS shape are made. This fact is not surprising, as it agrees with the well known finding of Mallows & Clark (1970*a*,*b*)[2] that two differently shaped convex RSs $X_{1,2}$ correspond to one CLDD. In our context this means that without introducing further assumptions, actually the condition of an oval RS, or adding further independent experimental variables, the cylinder parameters cannot be uniquely determined.

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[2] These authors have demonstrated two non-congruent 12-sided polygons with the same chord-length distribution.

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