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On the autocorrelation functions of right cylindrical particles

S. Ciccariello

Dipartimento di Fisica 'G.Galilei' e unità INFM, via Marzolo 8, I-35131 Padova, Italy. Correspondence e-mail: ciccariello@pd.infn.it

The autocorrelation function of a finite particle with the shape of a right cylinder is determined by the autocorrelation function of the particle right section, whatever the latter's shape, and by the cylinder height. In fact, the first function is an integral transform of the second with a simple kernel depending on the cylinder height. This integral relation is solved to determine the autocorrelation function of the particle section in terms of the autocorrelation function of the full particle.

1. Introduction

In the kinematical approximation, the X-ray or neutron scattering intensity is the Fourier transform (FT) of the so-called autocorrelation function of the scattering density $n(\mathbf{r})$ of the sample (Debye & Bueche, 1949). Confining ourselves to small-angle scattering (SAS), we can assume that $n(\mathbf{r})$ is a two-value function. Furthermore, in the case of statistically isotropic samples formed by a dilute collection of equal particles immersed in a homogeneous solvent, the observed scattering intensity is linearly related to the FT of the isotropic autocorrelation function of the only particle shape (Guinier & Fournet, 1955; Feigin & Svergun, 1987). Many papers that have appeared over the last five decades investigated how the geometrical features of the particle shape are reflected in the autocorrelation function and in the shape of the collected intensity (and *vice versa*). They can easily be traced back starting from two of the most recent papers (Burger & Ruland, 2001; Gille 2002*a*) on this issue. Within this framework, we prove here a general property of the autocorrelation function of a right and finite cylindrical particle of arbitrary cross section. Before we report this property, it is convenient to recall some definitions. The autocorrelation function of a homogeneous particle, which occupies the region $\underline{\mathcal{V}}$ of three-dimensional (3D) space R^3, is defined as (Ciccariello *et al.*, 1981)

$$\gamma_3(r) = \frac{1}{4\pi V}\int_{\underline{\mathcal{V}}} \mathrm{d}v_1 \int_{\underline{\mathcal{V}}} \mathrm{d}v_2 \int \mathrm{d}\hat{\boldsymbol{\omega}}\, \delta(\mathbf{r}_1 + r\hat{\boldsymbol{\omega}} - \mathbf{r}_2), \quad (1)$$

where the first two integrals are performed over the region $\underline{\mathcal{V}}$ (whose volume is denoted by V), the third over all possible directions of the unit vector $\hat{\boldsymbol{\omega}}$, $\delta(\cdot)$ denotes the 3D Dirac function and, finally, the subscript 3 of $\gamma(\cdot)$ is related to the space dimensionality. Clearly, $\gamma_3(r)$ is a non-negative function defined over the range $r \geq 0$. It is equal to zero if $r > L_3$, L_3 denoting the *maximal chord* of the particle, *i.e.* the largest distance between any two points of the particle. Moreover, definition (1) implies that (Ciccariello *et al.*, 1981)

$$\gamma_3(0) = 1, \quad \int_{R^3} \gamma_3(r)\,\mathrm{d}v = V \quad \text{and} \quad \gamma_3'(0^+) = -\Sigma/4V, \quad (2)$$

Σ denoting the area of the particle surface and the prime (or the double prime in the following) denotes the first (second) derivative. The last of these equalities is the core of the Porod law (Porod, 1951; Debye *et al.*, 1957). Assume now that the particle is a right cylinder and denote its right section by $\underline{\mathcal{S}}$. Since $\underline{\mathcal{S}}$ refers to a particle, it must be a connected set bounded by an outer closed curve $\underline{\Lambda}_o$ and by one or more closed curves internal to $\underline{\Lambda}_o$. If the internal closed curves coincide with the void set, the cylindrical particle has no cavity. Similarly to $\gamma_3(r)$, one can define the autocorrelation function of region $\underline{\mathcal{S}}$ according to

$$\gamma_2(r) = \frac{1}{2\pi S}\int_{\underline{\mathcal{S}}} \mathrm{d}S_1 \int_{\underline{\mathcal{S}}} \mathrm{d}S_2 \int \mathrm{d}\hat{\boldsymbol{\omega}}\, \delta(\mathbf{r}_1 + r\hat{\boldsymbol{\omega}} - \mathbf{r}_2), \quad (3)$$

where S denotes the area of $\underline{\mathcal{S}}$, $\hat{\boldsymbol{\omega}}$ is an aribtrary unit vector lying in the plane of set $\underline{\mathcal{S}}$ and $\delta(\cdot)$ is now the 2D Dirac function. It is stressed that the tip of $\hat{\boldsymbol{\omega}}$ spans a unit sphere in equation (1) and a unit circle in equation (3). This explains why equations (1) and (3) involve, respectively, the normalization factors $(4\pi)^{-1}$ and $(2\pi)^{-1}$. Thus, one can write

$$\gamma_n(r)\begin{cases} \geq 0, & \text{if } 0 \leq r \leq L_n \quad \text{and} \quad n = 2, 3, \\ = 0, & \text{if } r > L_n \quad \text{and} \quad n = 2, 3, \end{cases} \quad (4)$$

$$\gamma_n(0) = 1, \quad \int_{R^n} \gamma_n(r)\,\mathrm{d}r^n = \mathcal{V}_n \quad \text{and} \quad \gamma_n'(0^+) = -C_n \quad \text{for} \quad n = 2, 3, \quad (5)$$

where $\mathrm{d}r^n$ is equal to $\mathrm{d}S$ or $\mathrm{d}v$, $\mathcal{V}_n$ to S or V, C_n to $\Lambda/2\pi S$ (Λ denoting the length of the boundary of $\underline{\mathcal{S}}$) or $\Sigma/4V$ for $n = 2$ or 3, respectively. [For $n = 2$, the last equality of (5) is easily obtained by the procedure followed by Ciccariello *et al.* (1981) to prove the corresponding relation for $n = 3$.] As shown in Appendix *A*, both $\gamma_2(r)$ and $\gamma_3(r)$ have a probabilistic meaning.

The property to be proven in this paper is the following statement: *for any right cylindrical particle,* $\gamma_3(r)$ *is simply* *related to $\gamma_2(r)$ by an integral transform and this relation can be inverted to yield $\gamma_2(r)$ as an appropriate integro-differential transform of $\gamma_3(r)$. As will be explained later, this statement generalizes to the case of finite and right cylinders of arbitrary sections the property recently found by Gille (2002a,b) for infinitely long cylinders with convex sections.*

2. Proof of the first part of the statement

To prove the first part of the statement, we proceed as follows. We denote the cylinder height by H and we choose a Cartesian frame having the Z axis parallel to the cylinder axis, the plane $z = 0$ at the mid-point of the cylinder height and the origin at the centre of gravity of the set $\underline{S}$ resulting from the section of the cylinder with the plane $z = 0$. The vector $\mathbf{r}_1 = (x_1, y_1, z_1)$, present in equation (1), can be written as

$$\mathbf{r}_1 = \mathbf{r}_{1,\perp} + z_1\hat{\mathbf{z}}, \tag{6}$$

where $\mathbf{r}_{1,\perp}$ is the component of $\mathbf{r}_1$ along the plane $z = 0$ and $\hat{\mathbf{z}}$ is the unit vector parallel to axis Z. A similar decomposition holds true for $\mathbf{r}_2$. We now introduce polar coordinates (θ, φ) with the polar axis along $\mathbf{Z}$, in order to define the unit vector $\hat{\boldsymbol{\omega}}$. In this way, we have $\hat{\boldsymbol{\omega}} = (\cos\varphi\sin\theta, \sin\varphi\sin\theta, \cos\theta) = \hat{\boldsymbol{\omega}}_\perp\sin\theta + \hat{\mathbf{z}}\cos\theta$, where $\hat{\boldsymbol{\omega}}_\perp = (\cos\varphi, \sin\varphi)$ is a unit vector lying on the plane $z = 0$. Then, the Dirac function present in equation (1) reads

$$\begin{aligned}&\delta(\mathbf{r}_1 + r\hat{\boldsymbol{\omega}} - \mathbf{r}_2)\\ &\quad = \delta(\mathbf{r}_{1,\perp} + r\hat{\boldsymbol{\omega}}_\perp\sin\theta - \mathbf{r}_{2,\perp})\delta(z_1 + r\cos\theta - z_2)\end{aligned}$$

and equation (1) becomes

$$\begin{aligned}\gamma_3(r) &= \frac{1}{4\pi V}\int_{\underline{S}} \mathrm{d}S_1 \int_{-h}^{h} \mathrm{d}z_1 \int_{\underline{S}} \mathrm{d}S_2 \int_{-h}^{h} \mathrm{d}z_2 \int_0^{2\pi} \mathrm{d}\varphi\\ &\quad \times \int_0^{\pi} \delta(\mathbf{r}_{1,\perp} + r\hat{\boldsymbol{\omega}}_\perp\sin\theta - \mathbf{r}_{2,\perp})\delta(z_1 + r\cos\theta - z_2)\sin\theta\,\mathrm{d}\theta\\ &= \frac{S}{2V}\int_0^{\pi}\sin\theta\,\mathrm{d}\theta\int_{-h}^{h}\mathrm{d}z_1\int_{-h}^{h}\mathrm{d}z_2\delta(z_1 + r\cos\theta - z_2)\\ &\quad \times \left\{\frac{1}{2\pi S}\int_{\underline{S}}\mathrm{d}S_1\int_{\underline{S}}\mathrm{d}S_2\int\mathrm{d}\hat{\boldsymbol{\omega}}_\perp\delta(\mathbf{r}_{1,\perp} + r\sin\theta\hat{\boldsymbol{\omega}}_\perp - \mathbf{r}_{2,\perp})\right\},\end{aligned}$$

where we have put $h = H/2$. Comparing the expression inside the curly brackets to equation (3), one realizes that it is equal to the autocorrelation function of $\underline{S}$ evaluated at the point $(r\sin\theta)$. Hence,

$$\begin{aligned}\gamma_3(r) &= (S/2V)\int_0^{\pi}\gamma_2(r\sin\theta)\sin\theta\,\mathrm{d}\theta\\ &\quad \times \int_{-h}^{h}\mathrm{d}z_1\int_{-h}^{h}\delta(z_1 + r\cos\theta - z_2)\,\mathrm{d}z_2.\end{aligned} \tag{7}$$

By the identity $\int_a^b \delta(z - c)\,\mathrm{d}z = \Theta(b - c)\Theta(c - a)$, where $\Theta(\cdot)$ is the Heaviside function, the integrals over z_1 and z_2 yield

$$\begin{aligned}&\int_{-h}^{h}\mathrm{d}z_1\int_{-h}^{h}\delta(z_1 + r\cos\theta - z_2)\,\mathrm{d}z_2\\ &\quad = (H - r|\cos\theta|)\Theta(H - r|\cos\theta|).\end{aligned}$$

After substituting this result in equation (7) and observing that the resulting integral over $[\pi/2, \pi]$ is equal to that over $[0, \pi/2]$, one obtains

$$\gamma_3(r) = \frac{S}{V}\int_0^{\pi/2}\gamma_2(r\sin\theta)(H - r\cos\theta)\Theta(H - r\cos\theta)\sin\theta\,\mathrm{d}\theta.$$

V being equal to HS, after setting $r\sin\theta = x$, the above relation can be written as

$$\gamma_3(r) = \int_{E(r,H)}^{r}\frac{x\gamma_2(x)}{r}\left[\frac{1}{(r^2 - x^2)^{1/2}} - \frac{1}{H}\right]\mathrm{d}x, \tag{8}$$

where $E(r, H)$ is defined as

$$E(r, H) = \begin{cases}0, & \text{if } 0 \le r \le H\\ (r^2 - H^2)^{1/2}, & \text{if } H \le r.\end{cases} \tag{9}$$

Equation (8) represents the general integral transform that allows us to determine the autocorrelation function of a right cylinder of height H from the autocorrelation function $\gamma_2(r)$ of its right section $\underline{S}$, whatever the latter's shape. We make now two remarks. First, according to a general result worked out by Ciccariello (1991), the parallelism between some portions (not necessarily plane) of the particle surface, at a relative and orthogonal distance δ, are responsible for a discontinuous behaviour of $\gamma_3''(r)$ at $r = \delta$. In the case of a right cylinder, the bases are certainly parallel and distant H. Hence, $\gamma_3''(r)$ must show a finite discontinuity proportional to S at $r = H$. This relation is easily verified by evaluating the limits of the second derivative of equation (8) as $r \to H^-$ and $r \to H^+$. Second, in the case of an infinitely long cylinder (*i.e.* $H = \infty$), equation (8) reduces to

$$\gamma_3(r) = \int_0^r \frac{x\gamma_2(x)}{r(r^2 - x^2)^{1/2}}\,\mathrm{d}x, \tag{10}$$

i.e. to the expression reported by Gille (2002*a*). It is stressed that equation (10) has been proven under conditions more general than those reported by Gille. In fact, it applies to an infinite cylinder with a right section not restricted to be a convex and simply connected region.

After putting

$$\xi = r^2, \quad \eta = x^2, \tag{11}$$

$$\Psi(\xi) \equiv \xi^{1/2}\gamma_3(\xi^{1/2}) \quad \text{and} \quad \varphi(\xi) \equiv \gamma_2(\xi^{1/2}), \tag{12}$$

equation (8) takes the form

$$\Psi(\xi) = \tfrac{1}{2}\int_{\mathcal{E}(\xi,H)}^{\xi}\varphi(\eta)\left[\frac{1}{(\xi - \eta)^{1/2}} - \frac{1}{H}\right]\mathrm{d}\eta, \tag{13}$$

where $\mathcal{E}(\xi, H) \equiv \min(0, \xi - H^2)$. Equation (13) is a linear homogeneous integral equation of the Volterra type (though not exaclty a Volterra equation since both integration limits depend on ξ) with a *singular* kernel (see, *e.g.*, Lovitt, 1950). It is remarkable that the limit $H \to \infty$ of equation (13) yields the integral equation

$$\Psi(\xi) = \tfrac{1}{2}\int_0^{\xi}\frac{\varphi(\eta)}{(\xi - \eta)^{1/2}}\,\mathrm{d}\eta \tag{14}$$

which is met in different physical problems. In fact, equation (14) coincides with Abel's integral equation (Bocher, 1909) as well as with the integral equation yielding the scattering intensity collected with an 'infinite' slit (Guinier & Fournet, 1955). In the first case, one considers a material point moving under the action of gravity in the plane (τ, η) along the curve $\tau = \tau(\eta)$ with the vertical axis η upward. Denoting by $\Psi(\xi)$ the time required by the material point to move from the curve's point with ordinate ξ to that with ordinate 0, Abel showed that $\Psi(\xi)$ is given by (14) with $\varphi(\eta) = 2\{1 + [\tau'(\eta)]^2/2g\}^{1/2}$. In the second case, $J(q)$ (the smeared scattering intensity) is related to $I(q)$ (the pin-hole one) by the integral relation

$$J(q) = \int_{-\infty}^{\infty} I([q^2 + t^2]^{1/2})\,\mathrm{d}t = 2\int_0^{\infty} I([q^2 + t^2]^{1/2})\,\mathrm{d}t.$$

With the changes of variables $(t^2 + q^2)^{1/2} = 1/\eta$ and $q = 1/\xi$ and the definitions $\Psi(\xi) \equiv J(1/\xi)/\xi^2$ and $\varphi(\eta) \equiv I(1/\eta)/\eta^3$, it is straightforward to show that the previous integral equation converts into (14).

3. Proof of the second part of the statement

We prove now the second part of our statement, namely that equation (8) can be solved to write $\gamma_2(r)$ as an integro-differential transform of $\gamma_3(r)$. To this aim, we first confine ourselves to those r values such that $0 \le r \le H$. In this case, $E(r, H) = 0$ and equation (8) takes the form

$$r\gamma_3(r) = \int_0^r x\gamma_2(x)\left[\frac{1}{(r^2 - x^2)^{1/2}} - \frac{1}{H}\right]\mathrm{d}x. \qquad (15)$$

We set now

$$\varphi_n(\xi) \equiv \begin{cases} \varphi(\xi), & \text{if } 0 \le \xi \le nH^2, \quad n = 1, 2, \ldots, \\ 0, & \text{elsewhere,} \end{cases} \qquad (16)$$

and

$$\Psi_1(\xi) \equiv \begin{cases} \Psi(\xi), & \text{if } 0 \le \xi \le H^2, \\ 0, & \text{elsewhere.} \end{cases} \qquad (17)$$

In general, functions $\varphi_n(\xi)$ and $\Psi_n(\xi)$ with $n = 1, 2, \ldots$, [$\Psi_n(\xi)$ will be defined later for $n = 2, 3, \ldots$] are defined as being equal to zero if $\xi > nH^2$. Thus, by (16) and (17), (15) becomes

$$\Psi_1(\xi) = \tfrac{1}{2}\int_0^{\xi} \varphi_1(\eta)\left[\frac{1}{(\xi - \eta)^{1/2}} - \frac{1}{H}\right]\mathrm{d}\eta, \quad 0 \le \xi \le H^2, \quad (18)$$

where inequalities $0 \le \xi \le H^2$ are clearly pleonastic. An integration by parts of the first integral on the right-hand side (r.h.s.) of (18) and the property $\gamma_2(0) = \varphi(0) = \varphi_1(0) = 1$ [see equations (5), (12) and (16)] yield

$$\Psi_1(\xi) = \xi^{1/2} + \int_0^{\xi}(\xi - \eta)^{1/2}\varphi_1'(\eta)\,\mathrm{d}\eta - (1/2H)\int_0^{\xi}\varphi(\eta)\,\mathrm{d}\eta, \quad (19)$$

which by derivation gives

$$\varphi_1(\xi) - H\int_0^{\xi}(\xi - \eta)^{-1/2}\varphi_1'(\eta)\,\mathrm{d}\eta = H/\xi^{1/2} - 2H\Psi_1'(\xi). \quad (20)$$

This equation is multiplied by $(\tau - \xi)^{-1/2}$ and integrated with respect to ξ over the range $[0, \tau]$ to get

$$\int_0^{\tau}\varphi_1(\xi)(\tau - \xi)^{-1/2}\,\mathrm{d}\xi - H\int_0^{\tau}\varphi_1'(\eta)\,\mathrm{d}\eta\int_{\eta}^{\tau}[(\xi - \eta)(\tau - \xi)]^{-1/2}\,\mathrm{d}\xi$$
$$= H\int_0^{\tau}[\xi(\tau - \xi)]^{-1/2}\,\mathrm{d}\xi - 2H\int_0^{\tau}\Psi_1'(\xi)(\tau - \xi)^{-1/2}\,\mathrm{d}\xi, \qquad (21)$$

where the integration order has been changed in the second integral. The ξ integrals not involving $\varphi_1(\xi)$ and $\Psi_1'(\xi)$ can be evaluated by the identity $\int_a^b[(x - a)(b - x)]^{-1/2}\,\mathrm{d}x = \pi$ (Gradshteyn & Ryzhik, 1980, equation 2.261). Then, by the condition $\varphi_1(0) = 1$ and by a change of the involved variable names, (21) becomes

$$\tfrac{1}{2}\int_0^{\xi}\varphi_1(\eta)(\xi - \eta)^{-1/2}\,\mathrm{d}\eta - \pi H\varphi_1(\xi)/2$$
$$= -H\int_0^{\xi}\Psi_1'(\eta)(\xi - \eta)^{-1/2}\,\mathrm{d}\eta. \qquad (22)$$

Subtracting (22) from (18), one gets

$$H\pi\varphi_1(\xi) - (1/2H)\int_0^{\xi}\varphi_1(\eta)\,\mathrm{d}\eta$$
$$= \Psi_1(\xi) + H\int_0^{\xi}\Psi_1'(\eta)(\xi - \eta)^{-1/2}\,\mathrm{d}\eta. \qquad (23)$$

The derivative of this equation is

$$\varphi_1'(\xi) - (1/\pi H^2)\varphi_1(\xi) = A_1(\xi), \qquad (24)$$

where

$$A_1(\xi) \equiv \frac{2}{\pi}\frac{\mathrm{d}}{\mathrm{d}\xi}\left\{\frac{\Psi_1(\xi)}{H} + (2/\pi)\int_0^{\xi}\Psi_1'(\eta)(\xi - \eta)^{-1/2}\,\mathrm{d}\eta\right\} \quad (25)$$

is a known functional of $\Psi_1(\xi)$ and, owing to equations (17) and (12), of $\gamma_3(\xi)$. Hence, according to equation (24), the sought for $\varphi_1(\xi)$ obeys to an inhomogeneous linear differential equation of the first order with constant coefficients, the inhomogeneous term being given by equation (25). The general solution of equation (24) is

$$\varphi_1(\xi) = C\exp(\xi/\pi H^2) + \exp(\xi/\pi H^2)\int_0^{\xi}\exp(-\eta/\pi H^2)A_1(\eta)\,\mathrm{d}\eta,$$
$$0 \le \xi \le H^2,$$

where C is an arbitrary constant to be chosen in such a way that the condition $\varphi_1(0) = 1$ be obeyed. Thus, one finds that $C = 1$ and the final expression of $\varphi(\xi)$ within the range $[0, H^2]$ is

$$\varphi(\xi) = \varphi_1(\xi) = \exp(\xi/\pi H^2)\left[1 + \int_0^{\xi}\exp(-\eta/\pi H^2)A_1(\eta)\,\mathrm{d}\eta\right],$$
$$0 \le \xi \le H^2. \qquad (26)$$

The integro-differential expression of $\gamma_2(r)$ in terms of $\gamma_3(r)$ is

$$\gamma_2(r) = \exp(r^2/\pi H^2)\left[1 + \int_0^{r^2}\exp(-\eta/\pi H^2)A_1(\eta)\,\mathrm{d}\eta\right],$$
$$0 \le r \le H. \qquad (27)$$

As stated by equation (4), $\gamma_2(r) = 0$ if r is greater than L_2, the maximal chord of $\underset{\sim}{S}$. Thus, if $H > L_2$, equation (27) fully determines $\gamma_2(r)$. Moreover, since $\gamma_2(r) = 0$ for $r > L_2$, $A_1(\xi)$ is such that

$$1 + \int_0^{r^2} \exp(-\eta/\pi H^2) A_1(\eta)\,\mathrm{d}\eta = 0, \quad \text{if} \quad L_2 < r \le H, \tag{28}$$

which represents an integral constraint obeyed by $\gamma_3(r)$. Thus, in the case of cylinders with length longer than 'diameter', equation (27) solves the problem of inverting equation (8). We now show that (27) coincides with the expression obtained by Gille (2002*b*) for an infinitely long cylinder. In fact, an integration by parts of the integral present in equation (27) yields

$$\begin{aligned} &\frac{2}{\pi}\left\{\exp(-r^2/\pi H^2)\int_0^{r^2}\frac{\Psi_1'(\eta)}{(r^2-\eta)^{1/2}}\,\mathrm{d}\eta - \lim_{r\to 0}\int_0^{r^2}\frac{\Psi_1'(\eta)}{(r^2-\eta)^{1/2}}\,\mathrm{d}\eta\right\} \\ &\quad + \frac{2}{H\pi}\left[\exp(-r^2/\pi H^2)\Psi_1(r^2) - \Psi_1(0^+)\right] \\ &\quad + \frac{1}{\pi^2 H^2}\int_0^{r^2}\exp(-\eta/\pi H^2)\left[\frac{\Psi_1(\eta)}{(r^2-\eta)^{1/2}} + \int_0^{\tau}\frac{\Psi_1'(\tau)}{(r^2-\tau)^{1/2}}\,\mathrm{d}\tau\right]\mathrm{d}\eta. \end{aligned} \tag{29}$$

In the above relation, only the expression inside curly brackets survives in the limit $H \to \infty$. After converting to the new integration variable $x = \eta^{1/2}$ and recalling equations (12) and (17), one finds that

$$\int_0^{r^2}\frac{\Psi_1'(\eta)}{(r^2-\eta)^{1/2}}\,\mathrm{d}\eta = \int_0^r \frac{1}{(r^2-x^2)^{1/2}}\frac{\mathrm{d}}{\mathrm{d}x}[x\gamma_3(x)]\,\mathrm{d}x.$$

The limit of this expression, as $r \to 0$, is easily evaluated by setting $x = rt$ and using equation (12). Its value is $\gamma_3(0)\int_0^1 \mathrm{d}t/(1-t^2)^{1/2} = \pi/2$. By these results, one finds that the limit of (27), as $H \to \infty$, is Gille's expression

$$\gamma_2(r) = \frac{2}{\pi}\int_0^r \frac{1}{(r^2-x^2)^{1/2}}\frac{\mathrm{d}}{\mathrm{d}x}[x\gamma_3(x)].$$

{In passing, we note that this solution is more easily obtained by multiplying both sides of equation (14) by $(\tau-\xi)^{-1/2}$ and using the mathematical identity reported below equation (21) for evaluating the integral with respect to ξ over the range $[0, \tau]$.}

When the cylinder has 'diameter' greater than length (*i.e.* $H < L_2$), we need to find the solution of (8) in the range $[H, L_2]$. In this range, equations (8) and (13) respectively read

$$r\gamma_3(r) = \int_{(r^2-H^2)^{1/2}}^{r} x\gamma_2(x)\left[\frac{1}{(r^2-x^2)^{1/2}} - \frac{1}{H}\right]\mathrm{d}x$$

and

$$\Psi(\xi) = \tfrac{1}{2}\int_{\xi-H^2}^{\xi}\varphi(\eta)\left[\frac{1}{(\xi-\eta)^{1/2}} - \frac{1}{H}\right]\mathrm{d}\eta. \tag{30}$$

This can be written as

$$\begin{aligned}\Psi(\xi) &= \tfrac{1}{2}\int_0^{\xi}\varphi(\eta)\left[\frac{1}{(\xi-\eta)^{1/2}} - \frac{1}{H}\right]\mathrm{d}\eta \\ &\quad - \tfrac{1}{2}\int_0^{\xi-H^2}\varphi(\eta)\left[\frac{1}{(\xi-\eta)^{1/2}} - \frac{1}{H}\right]\mathrm{d}\eta. \end{aligned}\tag{31}$$

At first, we confine ourselves to those r values such that

$$H \le r \le 2^{1/2}H \quad \text{or} \quad H^2 \le \xi \le 2H^2. \tag{32}$$

In these conditions, the integration variable of the second integral on the r.h.s. of equation (31) ranges within $[0, H^2]$ and, owing to equation (26), the integrand is fully known. Hence, after setting

$$\Phi_2(\xi) \equiv \tfrac{1}{2}\int_0^{\xi-H^2}\varphi(\eta)\left[\frac{1}{(\xi-\eta)^{1/2}} - \frac{1}{H}\right]\mathrm{d}\eta, \quad H^2 \le \xi \le 2H^2, \tag{33}$$

which is fully known, equation (31) can be written as

$$\Psi(\xi) + \Phi_2(\xi) = \tfrac{1}{2}\int_0^{\xi}\varphi(\eta)\left[\frac{1}{(\xi-\eta)^{1/2}} - \frac{1}{H}\right]\mathrm{d}\eta, \quad H^2 \le \xi \le 2H^2. \tag{34}$$

We set

$$\Psi_2(\xi) \equiv \begin{cases}\Psi(\xi) + \Phi_2(\xi) & \text{if } H^2 \le \xi \le 2H^2, \\ \Psi_1(\xi), & \text{if } 0 \le \xi \le H^2.\end{cases} \tag{35}$$

This function is continuous with its first derivative at $\xi = H^2$ because the limits of $\Phi_2(\xi)$ and $\Phi_2'(\xi)$, as ξ approaches H^2 from the right, are equal to zero. Combining equations (35), (34) and (16), we find

$$\Psi_2(\xi) = \tfrac{1}{2}\int_0^{\xi}\varphi_2(\eta)\left[\frac{1}{(\xi-\eta)^{1/2}} - \frac{1}{H}\right]\mathrm{d}\eta \quad \text{for} \quad 0 \le \xi \le 2H^2. \tag{36}$$

Equation (36) has the same form as equation (18) and, moreover, $\varphi_2(0) = 1$ owing to equation (16). Thus, it can be solved by the procedure just reported and, after setting

$$A_2(\eta) \equiv \frac{2}{\pi}\left[\frac{\Psi_2(\eta)}{H} + \frac{\mathrm{d}}{\mathrm{d}\eta}\int_0^{\eta}\frac{\Psi_2'(\tau)}{(\eta-\tau)^{1/2}}\,\mathrm{d}\tau\right], \quad 0 \le \eta \le 2H^2, \tag{37}$$

one obtains

$$\varphi_2(\xi) = \varphi(\xi) = \exp(\xi/\pi H^2)\left[1 + \int_0^{\xi}\exp(-\eta/\pi H^2)A_2(\eta)\,\mathrm{d}\eta\right], \quad 0 \le \xi \le 2H^2, \tag{38}$$

and

$$\gamma_2(r) = \exp(r^2/\pi H^2)\left[1 + \int_0^{r^2}\exp(-\eta/\pi H^2)A_2(\eta)\,\mathrm{d}\eta\right], \quad 0 \le \xi \le 2^{1/2}H. \tag{39}$$

It is stressed that equations (37), (38) and (39) respectively coincide with (25), (26) and (27) within the range $0 \le \xi \le H^2$. The aforesaid procedure can be iterated to determine $\gamma_2(r)$ throughout its domain $[0, L_2]$. In fact, assume that

$$(n-1)^{1/2}H \le r \le nH \quad \text{or} \quad (n-1)H^2 \le \xi \le nH^2, \quad \text{with} \quad n \ge 3,$$

and that $\varphi(\xi)$ has been determined throughout the range $0 \le \xi \le (n-1)H^2$, so that we know $\varphi_{n-1}(\xi)$, $\Phi_{n-1}(\xi)$ and $\Psi_{n-1}(\xi)$. Then,

$$\Phi_n(\xi) \equiv \tfrac{1}{2}\int_0^{\xi-H^2} \varphi_{n-1}(\eta)\Big[\frac{1}{(\xi-\eta)^{1/2}} - \frac{1}{H}\Big]\,\mathrm{d}\eta \quad \text{for } (n-1)H^2 \le \xi \le nH^2 \tag{40}$$

is fully known. Since equation (31) is always true, if we set

$$\Psi_n(\xi) \equiv \begin{cases} \Psi(\xi) + \Phi_n(\xi) & \text{if } (n-1)H^2 \le \xi \le nH^2, \\ \Psi_{n-1}(\xi), & \text{if } 0 \le \xi \le (n-1)H^2, \end{cases} \tag{41}$$

throughout the interval $[0, nH^2]$, equation (31) becomes equal to

$$\Psi_n(\xi) = \tfrac{1}{2}\int_0^{\xi} \varphi_n(\eta)\left[\frac{1}{(\xi-\eta)^{1/2}} - \frac{1}{H}\right]\mathrm{d}\eta, \quad 0 \le \xi \le nH^2. \tag{42}$$

Again, the form of equation (42) coincides with that of (18) or (36) and $\varphi_n(0) = 1$ owing to equations (12) and (5). Hence, with the definition

$$A_n(\eta) \equiv \frac{2}{\pi}\left[\frac{\Psi_n(\eta)}{H} + \frac{\mathrm{d}}{\mathrm{d}\eta}\int_0^{\eta} \frac{\Psi_n'(\tau)}{(\eta-\tau)^{1/2}}\,\mathrm{d}\tau\right], \quad 0 \le \eta \le nH^2, \tag{43}$$

we find that

$$\varphi_n(\xi) \equiv \varphi(\xi) = \exp(\xi/\pi H^2)\Big[1 + \int_0^{\xi} \exp(-\eta/\pi H^2) A_n(\eta)\,\mathrm{d}\eta\Big], \quad 0 \le \xi \le nH^2, \tag{44}$$

and

$$\gamma_2(r) = \exp(r^2/\pi H^2)\Big[1 + \int_0^{r^2} \exp(-\eta/\pi H^2) A_n(\eta)\,\mathrm{d}\eta\Big], \quad 0 \le r \le n^{1/2}H. \tag{45}$$

It is clear now that, once n has become sufficiently large for the condition $n^{1/2}H > L_2$ to be obeyed, $\gamma_2(r)$ is fully determined in terms of $\gamma_3(r)$ by equation (45). In other words, equation (8) has been inverted to yield $\gamma_2(r)$ in terms of $\gamma_3(r)$, and our statement is fully proven.

4. Concluding remarks

The main results of this paper are: (*a*) to show that the autocorrelation function $\gamma_3(r)$ of a homogeneous, right and finite cylinder is fully determined by its height H and by the autocorrelation function $\gamma_2(r)$ of its right section $\underline{S}$, and (*b*) to find the integral transform that determines $\gamma_2(r)$ in terms of $\gamma_3(r)$. The first result is not unexpected because a right cylinder is fully determined when we know its right section and its height. One should however recall that the knowledge of $\gamma_2(r)$ neither ensures the exact knowledge of the shape of $\underline{S}$ nor that $\underline{S}$ is unique because a general procedure able to solve the non-linear integral equation (3) is at present unknown. (In fact, we can only use a trial-and-error procedure.) Hence, our result implies that, even if $\gamma_2(r)$ can turn out to be the same for different sets $\underline{S}$, the right cylinders of height H associated with each of these sets certainly have the same autocorrelation function $\gamma_3(r)$, which is given by equation (8). The second result appears to be more interesting. On the one hand, it gives a procedure able to solve the integral equation (13) that can be considered as a generalized Abel equation. On the other hand, the possibility of determining $\gamma_2(r)$ in terms of $\gamma_3(r)$ is, in principle, an interesting result because $\gamma_3(r)$ can be obtained by Fourier transforming the collected intensity $I(q)$ scattered by a sample that, on the basis of further physico-chemical information, is thought to be a dilute, isotropic and monodisperse collection of right cylindrical particles. As already noted, the most important geometrical quantity of a right cylindrical particle is the shape of its right section that can only be determined by a trial-and-error procedure. The right section shape being only related to $\gamma_2(r)$, the trial-and-error procedure carried on $\gamma_2(r)$ is certainly more constrained and, in this sense, more accurate than that carried on $\gamma_3(r)$. In this way, the usefulness of determining $\gamma_2(r)$ from $\gamma_3(r)$ appears evident. It is also remarked that the knowledge of $\gamma_3(r)$ implies that of H. In fact, the volume and the surface area of the particle are determined by the second and the third of equations (2). Moreover, we know that $V = SH$ and $\Sigma = 2S + \Lambda H$ and that Λ (the total length of the cylinder edges) can be obtained by the *angularity* relation [*i.e.* by equation (4.6) of Ciccariello *et al.* (1981)] that, in our case, reads $\gamma_3''(0^+) = \Lambda/3\pi V$. Thus, $\Lambda = 3\pi SH\gamma_3''(0^+)$ and, from the last of equations (2), one obtains the equation $2S + 3\pi H^2 S\gamma_3''(0^+) = -4SH\gamma_3'(0^+)$, which determines H. Our last remark is due to one of the referees and corresponds to the fact that the statement proven above for the case of a homogeneous right cylindrical particle holds true even when the right cylindrical particle is not homogeneous. To prove this generalization, it is first remarked that the cylindrical symmetry implies that the particle scattering density $n_p(\mathbf{r})$ only depends on $\mathbf{r}_\perp$ [see equation (6)], *i.e.*

$$n_p(\mathbf{r}) = n_p(\mathbf{r}_\perp). \tag{46}$$

The two- and three-dimensional autocorrelation functions, defined by equations (3) and (1) in the homogeneous case, respectively become in the inhomogeneous case

$$\gamma_2(r) \equiv \frac{1}{2\pi\langle n_p^2\rangle_2 S}\int \mathrm{d}\hat{\omega}\int_{\mathcal{S}} n_p(\mathbf{r}_1)\,\mathrm{d}S_1 \int_{\mathcal{S}} \mathrm{d}S_2\, n_p(\mathbf{r}_2)\delta(\mathbf{r}_1 + r\hat{\omega} - \mathbf{r}_2) \tag{47}$$

and

$$\gamma_3(r) \equiv \frac{1}{4\pi\langle n_p^2\rangle_3 V}\int \mathrm{d}\hat{\omega}\int_{\mathcal{V}} n_p(\mathbf{r}_1)\,\mathrm{d}v_1 \int_{\mathcal{V}} \mathrm{d}v_2\, n_p(\mathbf{r}_2)\delta(\mathbf{r}_1 + r\hat{\omega} - \mathbf{r}_2). \tag{48}$$

Here $\langle n_p^2\rangle_3$ and $\langle n_p^2\rangle_3$ denote the volume and surface mean values of the squared scattering density and, owing to equation (46), they are equal. In fact,

$$\langle n_p^2\rangle_3 \equiv \frac{1}{V}\int_{\mathcal{V}} n_p^2(\mathbf{r})\,\mathrm{d}v = \frac{1}{SH}\int_{-H/2}^{H/2}\mathrm{d}z\int_{\mathcal{S}} n_p^2(\mathbf{r}_\perp)\,\mathrm{d}^2\mathbf{r}_\perp = \frac{1}{S}\int_{\mathcal{S}} n_p^2(\mathbf{r}_\perp)\,\mathrm{d}^2\mathbf{r}_\perp \equiv \langle n_p^2\rangle_2. \qquad (49)$$

The same property applies to the volume and surface average of the scattering density, so that $\langle n_p\rangle_3 = \langle n_p\rangle_2$. From these definitions and properties, it follows that equations (4) and (5*a*) are also valid for inhomogeneous particles, equation (5*b*) becomes $\int_{R^n}\gamma_n(r)\,\mathrm{d}r^n = \langle n_p\rangle\mathcal{V}_n$. [Equation (5*c*) takes a more involved form never used in our analysis and already reported by Ciccariello *et al.* (1988) in the 3D case.] Applying to equation (48) the same analysis performed in §2, one immediately realizes that equation (8) still holds true. In solving this equation, we used the fact that $\gamma_3(0) = \gamma_2(0) = 1$. But, we already noted that these equalities are also valid for inhomogeneous cylindrical particles. Thus, one concludes that the procedure reported in §3 for solving equation (8) is also valid for inhomogeneous cylindrical particles.

APPENDIX *A*

It is perhaps not useless to recall the probabilistic meaning of the autocorrelation function $\gamma_3(r)$ defined by equation (1). Let us toss at random a stick of length r, where by *random* is meant that one end of the stick has the same probability density of falling within an infinitesimal volume dv, whatever the location of dv in R^3, and that the stick has the same probability density of lying within an infinitesimal solid angle d$\hat{\omega}$ whatever the latter's orientation $\hat{\omega}$. Consider only those tosses where the stick has at least one end within the particle. Then, $\gamma_3(r)/V$ represents the ratio of the number of tosses where the stick lies with *both* ends within the particle over the total number of tosses where one end of the stick falls within the particle. (It is stressed that, in evaluating the first number, all the tosses where only the ends of the stick lie within the particle must be accepted. More explicitly, a toss is acceptable even if some inner portions of the stick lie out of the particle: a case not unlikely when the particle presents some cavities and/or has a non-convex shape.) For this reason, Debye *et al.* (1957) called $\gamma_3(r)/V$ the *stick probability function*. Clearly, *mutatis mutandis*, the same interpretation applies to $\gamma_2(r)$. Ciccariello *et al.* (1981) showed that

$$\gamma_3''(r) = -(1/4\pi V)\int_{\Sigma}(\hat{\mathbf{v}}_1\cdot\hat{\omega})\,\mathrm{d}S_1\int_{\Sigma}(\hat{\mathbf{v}}_2\cdot\hat{\omega})\,\mathrm{d}S_2\int\delta(\mathbf{r}_1 + r\hat{\omega} - \mathbf{r}_2)\,\mathrm{d}\hat{\omega}, \qquad (50)$$

where $\hat{\mathbf{v}}_i$ (for $i = 1, 2$) is the unit vector orthogonal to the infinitesimal surface element dS_i of the particle surface Σ. Applying the same procedure used for deriving equation (50), one easily shows that

$$\gamma_2''(r) = -(1/2\pi S)\int_{\underline{\Lambda}}(\hat{\mathbf{v}}_1\cdot\hat{\omega})\,\mathrm{d}l_1\int_{\underline{\Lambda}}(\hat{\mathbf{v}}_2\cdot\hat{\omega})\,\mathrm{d}l_2\int\delta(\mathbf{r}_1 + r\hat{\omega} - \mathbf{r}_2)\,\mathrm{d}\hat{\omega}, \qquad (51)$$

$\underline{\Lambda}$ and $\delta(\mathbf{r}_1 + r\hat{\omega} - \mathbf{r}_2)$ denoting the set of the closed curves delimiting $\underline{\mathcal{S}}$ and the 2D Dirac function, respectively. The relation considered by Porod (1967) generalizes as

$$\gamma_n(r) = \int_r^\infty (x - r)\gamma_n''(x)\,\mathrm{d}x \quad \text{for} \quad n = 2, 3. \qquad (52)$$

These relations are immediately proven by integrating by parts and using the properties that $\gamma_n(r)$ and $\gamma_n'(r)$ approach zero as $r \to \infty$. Moreover, the relations

$$\int_0^\infty x\gamma_n''(x)\,\mathrm{d}x = 1 \quad \text{and} \quad \int_0^\infty \gamma_n''(x)\,\mathrm{d}x = \Sigma/4V \quad \text{or} \quad \Lambda/2\pi S, \quad \text{for } n = 2, 3, \qquad (53)$$

are also true, owing to the second and third relations reported in equation (5). However, the integral relation (52) and the non-negativeness of $\gamma_n(r)$ do not ensure the non-negativeness of $\gamma_n''(r)$. In fact, according to (50), the non-negativeness of $\gamma_n''(r)$ is only ensured in the cases where $\underline{\mathcal{V}}$ or $\underline{\mathcal{S}}$ are convex sets. In these cases, if vector $\hat{\omega}$ points towards the interior of the 'particle' at dS_1 or dl_1, it will point outward to the 'particle' at dS_2 or dl_2 and the positivity of the quantity $[-(\hat{\mathbf{v}}_1\cdot\hat{\omega})(\hat{\mathbf{v}}_2\cdot\hat{\omega})]$ as well as that of the integrand in equations (50) or (51) is ensured. Conversely, when the particle is not convex, $\gamma_n''(r)$ can be negative within some r intervals. We report here an example. Consider a 2D 'particle' consisting of two tangent and not overlapping circles of radius R. We have $S = 2\pi R^2$. The explicit evaluation of $\gamma_2(r)$ yields

$$\gamma_2(r) = \gamma_{2,p}(r) + \gamma_{2,\mathrm{int}}(r), \qquad (54)$$

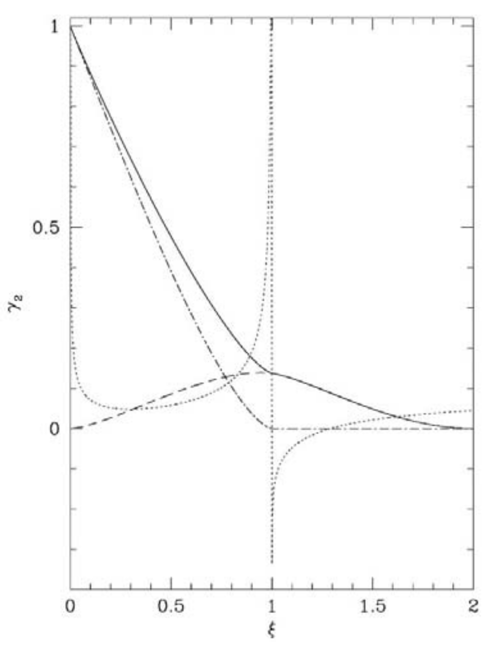

Figure 1
The continuous curve shows the behaviour of the autocorrelation function of a 2D particle that consists of two non-overlapping circles of radius R in contact at a point. The dot-dashed curve shows the sum of the contributions arising from the overlapping of each circle with itself, after the particle has been translated by $\mathbf{r}$. The broken curve, which merges with the continuous one at $\xi = 1$, shows the further 'interference' contribution, *i.e.* the sum of the (angular average of the) overlapping of a circle, translated by $\mathbf{r}$, with the other. Finally, the dotted curve is the plot of $\gamma_2''(r)$ (divided by 10). It shows that $\gamma_2''(r)$ is negative within an interval on the right of the point $\xi \equiv r/2R = 1$.

where

$$\gamma_{2,p}(r) = \frac{2}{\pi}\Theta(1-x)[\arccos(x) - x(1-x^2)^{1/2}], \tag{55}$$

$$\gamma_{2,\rm int}(r) = \frac{2}{\pi^2}\Theta(2-x)\int_0^{\arccos(x/2)} [\arccos(\Delta) - \Delta(1-\Delta^2)^{1/2}]\,{\rm d}\theta, \tag{56}$$

with

$$x \equiv r/2R \quad \text{and} \quad \Delta \equiv [1 - 2x\cos(\theta) + x^2]^{1/2}. \tag{57}$$

Equation (55) is twice the overlapping function (divided by S) of a single circle while equation (56) is the interference contribution, it being equal to twice the angular average of the overlapping of one circle with the other translated by **r**. The continuous, the dot-dashed and the broken curves shown in Fig. 1 represent $\gamma_2(r)$, $\gamma_{2,p}(r)$ and $\gamma_{2,\rm int}(r)$, respectively. The dotted curve plots $\gamma_2''(r)$. The limit of this function, as $r \to 0$, is different from zero because the 'particle' has a contact point (Ciccariello & Benedetti, 1982). The origin of its divergence as $x \to 1^-$ is evident from analytic expression (55). Finally, the negativeness of $\gamma_2''(r)$ within a small interval on the right of $x = 1$ (*i.e.* $r > 2R$) is evident. It is related to the fact that, when the chord length lies within $[2R, 2.58R]$, most of the intersects refer to infinitesimal elements $\mathrm{d}l_1$ and $\mathrm{d}l_2$ of the two circles where the unit normals form, between themselves, an angle smaller than $\pi/2$ so that the integrand of equation (51) is negative.

The intersect distribution $A_3(r)$, defined by Porod (1967) as proportional to the second derivative of the autocorrelation function, can be generalized to the 2D case so as to write

$$A_n(r) = \gamma_n''(r)/C_n \quad \text{for} \quad n = 2, 3, \tag{58}$$

C_n being defined by equation (5). Owing to the first of equations (53), one recovers the normalization condition

$$\int_0^\infty x A_n(x)\,\mathrm{d}x = 1, \quad n = 2, 3. \tag{59}$$

Thus, the integral expression of $A_n(r)$ in terms of the 'particle' boundaries is also given by equations (51) or (50) [times C_n^{-1}]. It is however stressed that: (i) even though the normalization condition (59) always holds true, a probabilistic interpretation of $A_n(r)$ is possible only in the case of a single convex particle; (ii) $A_n(r)$, *via* (50) or (51), requires those chords that have their ends on the particle boundaries to be considered as acceptable, independently from the fact that parts of the chord lie externally to the particle; (iii) only $A_3(r)$ is directly related to the scattering intensity due to equation (52); and (iv) it does not appear possible to express $A_n(r)$ in terms of functions $\varphi(r)$ and $f(r)$ considered by Méring & Tchoubar (1968).

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