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Integral expressions of the small-angle scattering correlation-function derivatives

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Abstract - The integral expression of the n th derivative of the SAS correlation-function ($\gamma(r)$) is reported. It is the average, throughout the sample interface, of the loop integral of a vectorial field $\vec{A}^{(n)}(\mathbf{r}_j(l))$. All the $\vec{A}^{(n)}(\mathbf{r}_j(l))$'s, with $n \geq 3$, are recursively obtained by appropriate differentiation of $\vec{A}^{(2)}(\mathbf{r}_j(l))$, whose explicit expression is given in terms of the parametric equations of the interface. For very smooth interface it results that all the CF even-derivatives are null at the origin.

1. The small-angle intensity ($\equiv I(h)$) scattered from an isotropic system, which can be modelled as a set of homogeneous regions V_i , fully characterized by the electron or scattering-length densities n_i ($i = 1, \dots, N$), is the 3 - D Fourier transform of the so-called correlation function (CF)

$$\gamma(r) = 1 - \sum_{i,j=1}^N \frac{(n_i - n_j)^2}{\langle \eta^2 \rangle} P_{ij}(r) \quad (1)$$

Here $\langle \eta^2 \rangle$ denotes the mean square density fluctuation, while $P_{ij}(r)$ is the *stick probability function* (SPF) relevant to the i th and j th phase. The SPF's depend only on the geometrical configurations of the involved phases since their definition is

$$P_{ij}(r) = (4\pi V)^{-1} \int_{\underline{V}_i} dv_i \int_{\underline{V}_j} dv_j \int_{B^2} d\hat{\omega} \delta(\mathbf{r}_i + r\hat{\omega} - \mathbf{r}_j). \quad (2)$$

Investigating how the geometrical features of the boundaries of sets V_i reflect into the behaviour of the P_{ij} 's and of their derivatives is theoretically interesting and the results[1,2,3] can be of some practical relevance for the noticed relation between $I(h)$ and $\gamma(r)$. Our aim here, is to report the general integral expression of the n th $\gamma(r)$ derivative in terms of the parametric equations of the phase boundaries.

2. By applying twice the mathematical identity

$$\begin{aligned} \frac{d}{dr} \delta(\mathbf{r}_i + r\hat{\omega} - \mathbf{r}_j) &= \hat{\omega} \cdot \nabla \delta(\mathbf{r}_i + \mathbf{r} - \mathbf{r}_j) = \\ \nabla_i \cdot (\hat{\omega} \delta(\mathbf{r}_i + r\hat{\omega} - \mathbf{r}_j)) &= -\nabla_j \cdot (\hat{\omega} \delta(\mathbf{r}_i + r\hat{\omega} - \mathbf{r}_j)) \end{aligned} \quad (3)$$

to eq. (2) and by Gauss' theorem it results[4]

$$4\pi V r^2 P_{ij}''(r) = - \int_{\underline{S}_i} dS_i \int_{\underline{S}_j} dS_j \int_{\underline{S}(\mathbf{r}_i, r)} dS (\hat{\sigma}_i \cdot \hat{\omega})(\hat{\sigma}_j \cdot \hat{\omega}) \delta(\mathbf{r}_i + r\hat{\omega} - \mathbf{r}_j), \quad (4)$$

with $\hat{\sigma}_i$ denoting the unit vector orthogonal to dS_i . The Dirac function requires that the point $\mathbf{r}_i + r\hat{\omega}$ of $\underline{S}(\mathbf{r}_i, r)$ (the boundary of the sphere of radius r centered at $\mathbf{r}_i$) be equal to $\mathbf{r}_j$, a point lying on $\underline{S}_j$. Therefore the two inner integrals on the right hand side (rhs) of (4) amount to a curvilinear integral performed along the curve $\underline{\Gamma}_j(\mathbf{r}_i, r)$ resulting from the intersection of $\underline{S}(\mathbf{r}_i, r)$ with $\underline{S}_j$. It follows that

$$P_{ij}''(r) = -\frac{1}{4\pi V} \int_{\underline{S}_i} dS_i p_{ij}^{(2)}(\mathbf{r}_i, r) \quad (5a)$$

with

$$p_{ij}^{(2)}(\mathbf{r}_i, r) = \oint_{\underline{\Gamma}_j(\mathbf{r}_i, r)} \vec{dl} \cdot \vec{\mathcal{A}}^{(2)}(\mathbf{r}_j(l)), \quad (5b)$$

i.e. $p_{ij}^{(2)}(\mathbf{r}_i, r)$ is the loop integral along $\underline{\Gamma}_j(\mathbf{r}_i, r)$ of the vectorial field

$$\vec{\mathcal{A}}^{(2)}(\mathbf{r}_j(l)) \equiv \frac{[\hat{\sigma}_i \cdot \hat{\omega}(\mathbf{r}_j(l))][\hat{\sigma}_j(\mathbf{r}_j(l)) \cdot \hat{\omega}(\mathbf{r}_j(l))]}{\|\mathbf{r}_j(l) - \mathbf{r}_i\|^2 \sqrt{1 - [\hat{\sigma}_j(\mathbf{r}_j(l)) \cdot \hat{\omega}(\mathbf{r}_j(l))]^2}} \hat{\tau}_j(\mathbf{r}_j(l)). \quad (6)$$

This depends on $\hat{\sigma}_j$ and on $\hat{\tau}_j(\mathbf{r}_j(l))$ (the unit vector tangent to $\underline{\Gamma}_j(\mathbf{r}_i, r)$ at the point $\mathbf{r}_j(l)$) and it is fully determined once the parametric equations of $\underline{S}_j$ are known. The further derivation of (4) yields

$$(4\pi V) P_{ij}^{(3)}(r) = - \int_{B^2} d\hat{\omega} \int_{\underline{S}_i} dS_i \int_{\underline{S}_j} dS_j (\hat{\sigma}_i \cdot \hat{\omega})(\hat{\sigma}_j \cdot \hat{\omega})(\hat{\omega} \cdot \nabla_i) \delta(\mathbf{r}_i + r\hat{\omega} - \mathbf{r}_j). \quad (7)$$

Again, by the same argument used above, the two inner integral amount to a curvilinear integral along $\underline{\Gamma}_j(\mathbf{r}_i, r)$. It has recently been shown that[5]

$$P_{ij}^{(3)}(r) = -\frac{1}{4\pi V} \int_{\underline{S}_i} dS_i p_{ij}^{(3)}(\mathbf{r}_i, r) \quad (8a)$$

with

$$p_{ij}^{(3)}(\mathbf{r}_i, r) \equiv \int_{\underline{\Gamma}_j(\mathbf{r}_i, r)} \vec{dl} \cdot \vec{\mathcal{A}}^{(3)}(\mathbf{r}_j(l)) \quad \forall n \geq 2 \quad (8b)$$

and

$$\tilde{\mathcal{A}}^{(3)}(\mathbf{r}_j) \equiv \frac{\mathbf{r}_{j,u} \cdot \tilde{\mathcal{A}}_{,v}^{(2)}(\mathbf{r}_j) - \mathbf{r}_{j,v} \cdot \tilde{\mathcal{A}}_{,u}^{(2)}(\mathbf{r}_j)}{\|\mathbf{r}_{j,u} \times \mathbf{r}_{j,v}\| \sqrt{1 - (\hat{\sigma}_j \cdot \hat{\omega})^2}} \hat{\tau}_j(\mathbf{r}_j). \quad (8c)$$

Recalling that the knowledge of the parametric equations of $\underline{S}_j$ amounts to knowing $\mathbf{r}_j = \mathbf{r}_j(u, v)$ and since $\tilde{\mathcal{A}}_{,v}^{(2)}(\mathbf{r}_j)$ denotes the partial v -derivative of $\tilde{\mathcal{A}}^{(2)}$, it is clear that the vectorial field $\tilde{\mathcal{A}}^{(3)}$, defined on the variety $\underline{S}_j$, is fully determined. Thus, eq.s (8) represent the sought for integral expression of $P_{ij}^{(3)}(r)$. Provided the relevant derivatives exist, the analysis can be extended to higher order derivatives and one ends up with the following 'iterative' structure

$$P_{ij}^{(n)}(r) = -\frac{1}{4\pi V} \int_{\underline{S}_i} dS_i p_{ij}^{(n)}(\mathbf{r}_i, r) \quad \forall n \geq 2 \quad (9a)$$

with

$$p_{ij}^{(n)}(\mathbf{r}_i, r) \equiv \int_{\Gamma_j(\mathbf{r}_i, r)} d\mathbf{l} \cdot \tilde{\mathcal{A}}^{(n)}(\mathbf{r}_j(l)) \quad \forall n \geq 2 \quad (9b)$$

and

$$\tilde{\mathcal{A}}^{(n)}(\mathbf{r}_j) \equiv \frac{\mathbf{r}_{j,u} \cdot \tilde{\mathcal{A}}_{,v}^{(n-1)}(\mathbf{r}_j) - \mathbf{r}_{j,v} \cdot \tilde{\mathcal{A}}_{,u}^{(n-1)}(\mathbf{r}_j)}{\|\mathbf{r}_{j,u} \times \mathbf{r}_{j,v}\| \sqrt{1 - (\hat{\sigma}_j \cdot \hat{\omega})^2}} \hat{\tau}_j(\mathbf{r}_j), \quad \forall n \geq 3. \quad (9c)$$

3. By these expressions it is possible to analyze the behaviour of the $P_{ij}^{(n)}(r)$'s as $r \rightarrow 0$. It is recalled that these values determine the $\gamma^{(n)}(0)$ -values and, consequently, the coefficients of the asymptotic expansion of $I(h)$ at large h 's. Being $\tilde{\mathcal{A}}^{(n)}(\mathbf{r}_j)$ parallel to $\hat{\tau}_j(\mathbf{r}_j)$, the following decomposition holds true

$$\tilde{\mathcal{A}}^{(n)}(\mathbf{r}_j) = a^{(n)}(r, \varphi) \hat{\omega}_{,\varphi} / \sin \theta + b^{(n)}(r, \varphi) \hat{\omega}_{,\theta} \quad \forall n \geq 2, \quad (10)$$

once the polar-coordinate parameterizations is used. It results

$$p_{ij}^{(n)}(\mathbf{r}_i, r) = \int_0^{2\pi} d\varphi A^{(n)}(r, \varphi) \quad \forall n \geq 3, \quad (11)$$

with $A^{(n)}$ simply related to $a^{(n)}$. When $n(> 1)$ is *even*, the limits of the $A^{(n)}(r, \varphi)$'s, as $r \rightarrow 0$, are antiperiodic functions, in the sense that $A^{(n)}(0, \varphi + \pi) = -A^{(n)}(0, \varphi)$. Thus, from eq. (11) and (9a) it follows that all the even derivatives of $\gamma(r)$ are null at $r = 0$, provided the phase boundaries are sufficiently regular for the r -expansion of $A^{(n)}(r, \varphi)$ to exist. It should be noted that this property had been conjectured by Wu and Schmidt in [3b] on the basis of their findings that $\gamma^{(2)}(0^+) = \gamma^{(4)}(0^+) = 0$.

The explicit evaluation of the odd derivatives at $r = 0$ can be carried through by the same technique. The third derivative yields the Kirste-Porod[2] result. The expression of the fifth derivative is

$$P_{ij}^{(5)}(0^+) = -\frac{S_{ij}}{4V} \left\langle \left[24\mathcal{J}_1 + 12\mathcal{J}_2 - 24\mathcal{J}_3 \right] \right\rangle_{ij} \quad (12)$$

where $\langle \cdot \rangle_{ij}$ denotes the average over the ij -interface of quantities $\mathcal{J}_i$, defined as:

$$\mathcal{J}_1 \equiv \left[5q_{2,0}q_{4,0} + q_{2,0}q_{4,2} + q_{2,0}q_{4,4} + q_{2,2}q_{4,0} + q_{2,2}q_{4,2} + 5q_{2,2}q_{4,4} \right] / 8, \quad (13a)$$

$$\mathcal{J}_2 \equiv \left[5q_{3,0}^2 + 2q_{3,0}q_{3,2} + 2q_{3,1}q_{3,3} + q_{3,1}^2 + q_{3,2}^2 + 5q_{3,3}^2 \right] / 8, \quad (13b)$$

and

$$\mathcal{J}_3 \equiv \left[35(q_{2,0}^4 + q_{2,2}^4) + 20q_{2,0}q_{2,2}(q_{2,0}^2 + q_{2,2}^2) + 18(q_{2,0}q_{2,2})^2 \right] / 64, \quad (13c)$$

with the $q_{m,n}$'s equal to the coefficients of the power-series expansion of the interface equation with respect to a cartesian system having the $X - Y$ plane tangent to the surface and the Z -axis directed along the normal at the tangency point set at the origin, i.e.

$$Z = \sum_{n=2} \sum_{m=0}^n q_{n,m} X^{n-m} Y^m. \quad (14)$$

For spherical interfaces, the $\mathcal{J}_i$'s are easily checked to be null. Finally, it is noted that result (12) was obtained by Wu and Schmidt [3b] (see eq. (13) and the three definitions immediately below) under the more restrictive assumption that the sample is a dilute two-phase system of convex particles.

References

- /1/ Méring J. and Tchoubar D., *J. Appl. Cryst.* **1** (1968) 153; Tchoubar D. and Méring J., *J. Appl. Cryst.* **2** (1969) 128.
- /2/ Kirste R. and Porod G., *Kolloid-Zeit* **184** (1962) 1.
- /3/ a) Schmidt P.W., *J. Math. Phys.*(NY) **6** (1965) 424; b) Wu H. and Schmidt P.W., *J. Appl. Cryst.* **4** (1971) 224; c) Wu H. and Schmidt P.W., *J. Appl. Cryst.* **7** (1974) 131.
- /4/ Ciccariello S., Cocco G., Benedetti A. and Enzo S., *Phys. Rev.* **B23** (1981) 6474.
- /5/ Ciccariello S., preprint DFPD 92/Th/44.