SUPPLEMENTARY MATERIALS
Asymptotic analysis of small-angle scattering intensities of plane columnar layers

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Abstract

The asymptotic behaviour, at large scattering vector $\mathbf{q}$, of the small-angle scattering intensities of isotropic plane samples is similar to that of three-dimensional samples. In fact, its expression, limited to the first two leading terms, is $c_1\gamma^{(1)}(0)/q^3+c_3\gamma^{(3)}(0)/q^5$, where c_1 and c_3 are appropriate numerical constants and $\gamma^{(1)}(0)$ and $\gamma^{(3)}(0)$ the values, at the origin, of the first and third derivatives of the two-dimensional correlation function. These values are proportional to the specific length and to the mean square reciprocal curvature radius of the interface curve. The angularity of the latter can also be determined, while the presence of oscillations in the appropriate Porod plot is related to a parallelism condition obeyed by the interface curve. These results are useful for analysing the small-angle scattering intensities collected under grazing incidence and diffused by film samples that are a collection of homogeneous cylinders of arbitrary right sections.

Appendix A
Algebraic singularities and oscillatory terms

We relax now the continuity assumption on the $\gamma_{\parallel}(r)$ derivatives of order greater than one. Item (c) of §2 stated the geometrical conditions responsible for an algebraic singular behaviour of $\gamma_{\parallel}''(r)$ while the behaviour around the singularity is specified by Eq. (18). This implies that the subsequent derivatives no longer are integrable functions so that the procedure, expounded in §3 to get the asymptotic behaviour of the scattering intensity, requires more care. In fact, it will be shown now that these singularities involve further terms beside the ones already worked out in the asymptotic expansion of the scattering intensity.

Quite generally, let $\delta_0, \ldots, \delta_I$ denote the r values where $\gamma_{\parallel}''(r)$ and its higher order derivatives are singular. Around one of these points (say δ_k, according to Eq.s (28) and (36) of I) the $\gamma_{\parallel}'(r)$ behaviour reads

$$\gamma_{\parallel}'(r) = g_{k,0} + \textstyle\sum_{p=1}^{4} g_{k,p}^{-}(\delta_k - r)^{p/2} + o((\delta_k - r)^2) \qquad \text{if } r < \delta_k, \tag{47}$$

$$\gamma_{\parallel}'(r) = g_{k,0} + \textstyle\sum_{p=1}^{4} g_{k,p}^{+}(r - \delta_k)^{p/2} + o((r - \delta_k)^2) \qquad \text{if } r > \delta_k. \tag{48}$$

Here, superscripts + and − denote that δ_k is approached from the right and left, respectively. From Eq.s (47) and (48) follows that the right (left) second derivative is not singular if $g_{k,1}^{+} = 0$ ($g_{k,1}^{-} = 0$). Similarly, if both $g_{k,1}^{+} = 0$ and $g_{k,3}^{+} = 0$, the right third derivative also is regular about δ_k. Besides, at $\delta_0 = 0$, behaviour (48) only occurs with $g_{0,1}^{+} = g_{0,3}^{+} = 0$ because the third right derivative is regular at $r = 0$. At the end point $\delta_I = \infty$, the assumed exponential decrease of the CF implies that $g_{I+1,0} = g_{I+1,1}^{-} = g_{I+1,2}^{-} = \ldots = 0$ and behaviour (48) does not exist. We shall discuss the simplest case of a single algebraic singularity at $r = \delta_1 = \delta$. Further, by assumption, the singularity is present if δ is approached from the right. Putting

$$g_1(r) \equiv \frac{\mathrm{d}\Big(r\gamma'_{\parallel}(r)\Big)}{\mathrm{d}r}, \quad \text{if} \quad 0 \le r \le \delta, \tag{49}$$

$$g_2(r) \equiv \frac{\mathrm{d}\Big(r\gamma'_{\parallel}(r)\Big)}{\mathrm{d}r}, \quad \text{if} \quad \delta < r, \tag{50}$$

and using Eqs. (47) and (48) one finds that

$$g_1(r) = g_{0,0} + 2g^{+}_{0,2}r + 3g^{+}_{0,4}r^2 + O(r^4), \quad \text{as} \quad r \to 0^+ \tag{51}$$

$$\begin{aligned} g_1(r) &= (g_{1,0} - g^{-}_{1,2}\delta) + 2(g^{-}_{1,2} - g^{-}_{1,4}\delta)(\delta - r) + \\ &\qquad 3(g^{-}_{1,4} - g^{-}_{1,6}\delta)(\delta - r)^2 + O((\delta - r)^3), \quad \text{as} \quad r \to \delta^- \end{aligned} \tag{52}$$

$$\begin{aligned} g_2(r) &= \frac{\delta g^{+}_{1,1}}{2\sqrt{r-\delta}} + (g_{1,0} + \delta g^{+}_{1,2}) + \frac{3}{2}(g^{+}_{1,1} + \delta g^{+}_{1,3})\sqrt{r-\delta} + \\ &\quad 2(g^{+}_{1,2} + \delta g^{+}_{1,4})(r-\delta) + \\ &\quad \frac{5}{2}(g^{+}_{1,3} + \delta g^{+}_{1,5})(r-\delta)^{3/2} + O((r-\delta)^2), \quad r \to \delta^+, \end{aligned} \tag{53}$$

where, as it will be clear later, we only considered the terms that yield asymptotic terms that do not decrease faster than q^{-5}. Setting

$$G_1(q) \equiv \int_0^{\delta} J_0(qr) g_1(r) dr, \tag{54}$$

$$G_2(q) \equiv \int_{\delta}^{\infty} J_0(qr) g_2(r) dr, \tag{55}$$

from Eq. (24) follows that

$$\tilde{\gamma}_{\parallel}(q) = -\frac{2\pi}{q^2}\Big[G_1(q) + G_2(q)\Big]. \tag{56}$$

To determine the asymptotic behaviour of $\tilde{\gamma}_{\parallel}(q)$ we must determine those of $G_1(q)$ and $G_2(q)$ up to the $O(q^{-3})$ terms included. These are obtained using the reported expressions of $g_1(r)$ and $g_2(r)$. In fact, the asymptotic behaviour of $G_1(q)$ is obtained integrating by parts. A first integration gives

$$G_1(q) = -\frac{(g_{1,0} - g^{-}_{1,2}\delta)\mathcal{J}_0(q\delta)}{q} + \frac{g_{0,0}}{q} + \frac{1}{q}\int_0^{\delta} \mathcal{J}_0(r\,q) g'_1(r) dr, \tag{57}$$

where we used Eq.s (25), (27) and (52). An integration by parts of the above integral and Eq.s (33), (34) and (52) give

$$\int_0^\delta \mathcal{J}_0(r\,q)g_1^{'}(r)dr = -\frac{2(g_{1,2}^{-} - g_{1,4}^{-}\delta)\mathcal{J}_1(q\delta)}{q} - \frac{1}{q}\int_0^\delta \mathcal{J}_1(r\,q)g_1^{''}(r)dr. \tag{58}$$

Finally, an integration by parts of the last integral and Eq.s (37), (38) and (52) yield

$$\int_0^\delta \mathcal{J}_1(r\,q)g_1^{''}(r)dr = -\frac{g_1^{''}(\delta^-)\mathcal{J}_2(q\delta)}{q} + \frac{6g_{0,4}}{q} + \frac{1}{q}\int_0^\delta \mathcal{J}_2(r\,q)g_1^{'''}(r)dr \tag{59}$$

with $g_1^{''}(\delta^-) \equiv 6(g_{1,2}^{-} - g_{1,4}^{-}\delta)$. Below Eq. (38) we noted that the leading asymptotic term of $\mathcal{J}_2(x)$ oscillates and decreases as $x^{-1/2}$ [see Eq. (29)]. Then, the last term on the right-hand side of Eq. (59) is $o(q^{-1})$ and the first term is $O(q^{-3/2})$. Collecting these results and recalling that $g_{0,0} = \gamma'_{\parallel}(0^+)$ and $g_{0,4} = \gamma'''_{\parallel}(0^+)/2$, one finds that

$$\begin{aligned} G_1(q) \approx & \frac{\gamma'_{\parallel}(0^+)}{q} - \frac{3\gamma'''_{\parallel}(0^+)}{q^3} - \\ & \frac{2(g_{1,0} - g_{1,2}^{-}\delta)\mathcal{J}_0(q\delta)}{q} - \frac{6(g_{1,2}^{-} - g_{1,4}^{-}\delta)\mathcal{J}_1(q\delta)}{q^2} + o(q^{-3}). \end{aligned} \tag{60}$$

After substituting this expression into Eq. (56) and using Eq.s (15) and (17), the first two terms reproduce the rhs of Eq. (37). The remaining two terms, by Eq.s (29) and (35), give rise to a sum of oscillatory contributions. The first leading ones are $O(q^{7/2})$ and $O(q^{9/2})$. The 'frequency' of the oscillations is equal to $2\pi/\delta$ and is therefore determined by δ the position of the singularity.

To get the asymptotic expansion of $G_2(q)$ we substitute the asymptotic expansions of $J_0(x)$ (see Eq. 8.451 of GR)

$$\begin{aligned} J_0(x) \quad \approx \quad & \sqrt{\frac{2}{\pi x}}\sum_{k=0}^{1}\Big[\frac{(-1)^k\Gamma(2k+\frac{1}{2})}{2^{2k}(2k)!\Gamma(\frac{1}{2}-2k)}\frac{\cos(x-\frac{\pi}{4})}{x^{2k}} - \\ & \frac{(-1)^k\Gamma(2k+\frac{3}{2})}{2^{2k+1}(2k+1)!\Gamma(-\frac{1}{2}-2k)}\frac{\sin(x-\frac{\pi}{4})}{x^{2k+1}}\Big], \end{aligned} \tag{61}$$

into Eq. (55). The sum is truncated at $k=1$ because we are interested in the terms up to $O(q^{-3})$ included. One finds

$$G_2(q) \approx \sum_{k=0}^{1}[a_k A_k(q) + b_k B_k(q)] \tag{62}$$

with

$$a_k A_k(q) \equiv \frac{(-1)^k \sqrt{2}\ \Gamma(2k+\frac{1}{2})}{2^{2k}\sqrt{\pi}\,(2k)!\Gamma(\frac{1}{2}-2k)} \int_\delta^\infty \frac{\cos(qr-\frac{\pi}{4})}{(qr)^{2k+\frac{1}{2}}} g_2(r)dr \tag{63}$$

and

$$b_k B_k(q) \equiv -\frac{(-1)^k \sqrt{2}\ \Gamma(2k+\frac{3}{2})}{2^{2k+1}\sqrt{\pi}\,(2k+1)!\Gamma(-\frac{1}{2}-2k)} \int_\delta^\infty \frac{\sin(qr-\frac{\pi}{4})}{(qr)^{2k+\frac{3}{2}}} g_2(r)dr. \tag{64}$$

Here $A_k(q)$ and $B_k(q)$ denote the integrals and a_k and b_k the numerical coefficients in front of the integrals. Clearly $A_k(q)$ can be written as

$$A_k(q) = \frac{1}{q^{2k+\frac{1}{2}}} \mathrm{Re}\Big(e^{-\frac{i\pi}{4}} \int_\delta^\infty e^{iqr} \frac{g_2(r)}{r^{2k+\frac{1}{2}}} dr \Big) \tag{65}$$

where Re means real part. In the same way, $B_k(q)$ can be expressed as the imaginary part of a similar integral. Now, we rewrite Eq. (53) as

$$g_2(r)/r^{2k+\frac{1}{2}} = \frac{1}{\sqrt{r-\delta}} \frac{\psi_1(r)}{r^{2k+\frac{1}{2}}} + \frac{\psi_2(r)}{r^{2k+\frac{1}{2}}} \tag{66}$$

where $\psi_1(r)$ and $\psi_2(r)$ exponentially decrease as $r \to \infty$ and behave as

$$\psi_1(r) \approx \frac{\delta \overset{+}{g}_{1,1}}{2} + \frac{3}{2}(\overset{+}{g}_{1,1} + \delta \overset{+}{g}_{1,3})(r-\delta) + \frac{5}{2}(\overset{+}{g}_{1,3} + \delta \overset{+}{g}_{1,5})(r-\delta)^2 + \ldots \tag{67}$$

$$\psi_2(r) \approx (g_{1,0} + \delta \overset{+}{g}_{1,2}) + 2(g_{1,2} + \delta \overset{+}{g}_{1,4})(r-\delta) + \ldots \tag{68}$$

as $r \to \delta^+$. $A_k(q)$ becomes the sum of two integrals respectively involving $\psi_1(r)/r^{2k+\frac{1}{2}}$ and $\psi_2(r)/r^{2k+\frac{1}{2}}$. Their asymptotic behaviours are respectively given by Eq.s (4) and (2) of section 2.8 of Erdéley (1957) with the obvious substitutions $(1-\lambda) \to 1/2$ and

$$\varphi(t) \to \varphi_{1,k}(r) \equiv \psi_1(r)/r^{2k+\frac{1}{2}} \tag{69}$$

in the first case, and

$$\varphi(t) \to \varphi_{2,k}(r) \equiv \psi_2(r)/r^{2k+\frac{1}{2}} \tag{70}$$

in the second one (besides $x \to q$, $t \to r$, $\alpha \to \delta$ and $\beta \to \infty$). Hence, the first three leading terms of $A_k(q)$ are

$$A_k(q) = \sum_{n=0}^{2} \Big[\frac{\Gamma(n+1/2)\ {\varphi_{1,k}}^{(n)}(\delta)\ \cos(q\delta+\pi n/2)}{n!\ q^{2k+n+1}} - \frac{{\varphi_{2,k}}^{(n)}(\delta)\ \cos(q\delta+\pi n/2-3\pi/4)}{q^{2k+n+3/2}} \Big]. \tag{71}$$

In a similar way one finds that

$$B_k(q) \quad = \quad \sum_{n=0}^{1} \Big[\tfrac{\Gamma(n+1/2)\ {\varphi_{1,k}}^{(n)}(\delta)\ \sin(q\delta+\pi n/2)}{n!\ q^{2k+n+2}} - \\ \frac{{\varphi_{2,k}}^{(n)}(\delta)\ \sin(q\delta+\pi n/2-3\pi/4)}{q^{2k+n+5/2}} \Big]. \tag{72}$$

Once results (71) and (72) are substituted into Eq. (62), the sums over k and n will be restricted to those values such that the resulting exponents of q do not exceed value 3, *i.e.* $(2k+n+1) \leq 3$, $(2k+n+3/2) \leq 3$, and so on. In this way, $G_2(q)$ will be a sum of known terms that have an oscillatory vanishing behaviour. The frequency of the oscillation is determined by δ. For each term, the amplitude of the oscillation vanishes as a reciprocal power of q with an exponent integers or half-integer (not smaller than one). Actually, powers q^{-1} and $q^{-3/2}$ are present if and only if the second derivative of the CF is singular. In such a case, combining these results with Eq.s (56) and (60), the asymptotic oscillatory leading contribution to $\tilde{\gamma}_{\parallel}(q)$ reads

$$-2\pi\sqrt{\frac{\delta}{2}}\frac{\overset{+}{g}_{1,1}\cos(q\delta)}{q^3}. \tag{73}$$

This is the case of the SqBf illustrated on the left of Fig. 1. In a similar way, if the second derivative of the 2D CF is continuous and the third is not, the amplitudes of the first two oscillatory asymptotic leading terms decrease as q^{-2} and $q^{-5/2}$. This is the T case illustrated on the right of Fig. 1.