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Recommended Citation

Goodisman, Jerry; Delaglio, F.; and Brumberger, H., "Analysis Of Slit-Distorted Small-Angle X-Ray Scattering Intensities Without Desmearing" (1986). *Chemistry - Faculty Scholarship*. 11.
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Analysis of Slit-Distorted Small-Angle X-ray Scattering Intensities Without Desmearing

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(Received 5 November 1985; accepted 25 February 1986)

Abstract

Experimental small-angle X-ray scattering intensities, generated from a primary beam of known intensity profile, are often 'desmeared' to obtain point-collimated intensities. A much simpler way is shown of using the known beam intensity profile to derive, from the experimental scattering intensity, the quantities required for calculation of surface areas.

For an isotropic system formed from two internally homogeneous phases with sharp and smooth interphase boundaries, the interphase surface area can be determined (Brumberger, 1968) from the small-angle X-ray scattering $I(h)$ by the relation

$$S/V = k\pi\varphi_1\varphi_2/Q. \quad (1)$$

Here

$$h = (4\pi/\lambda)\sin\theta, \quad k = \lim_{h \rightarrow \infty} h^4 I(h),$$

$$Q = \int_0^\infty h^2 I(h) dh$$

and φ_1, φ_2 are the volume fractions of the two phases. [For systems for which $h^4 I(h)$ does not approach a constant, see below.] This assumes the incident beam is point-collimated. For an incident beam with 'infinite-slit' collimation, *i.e.* of uniform intensity, 'infinitely' long in one direction, and of negligible width in the other, the scattered intensity $\tilde{I}(h)$ is related to $I(h)$ by

$$\tilde{I}(h) = \int_{-\infty}^{\infty} I[(h^2 + s^2)^{1/2}] ds. \quad (2)$$

The surface-to-volume ratio can be obtained from $\tilde{I}(h)$ according to

$$S/4V = \varphi_1\varphi_2\tilde{k}/\tilde{Q}, \quad (3)$$

where

$$\tilde{k} = \lim_{h \rightarrow \infty} h^3 \tilde{I}(h) = \pi k/2$$

and

$$\tilde{Q} = \int_0^\infty h \tilde{I}(h) dh = 2Q.$$

It is often the case, however, that the incident-beam

intensity is not uniform in one dimension over a sufficient length relative to the extent of the scattered intensity, but follows a known intensity profile. The observed intensity $\bar{I}(h)$ is then

$$\bar{I}(h) = \int_{-\infty}^{\infty} w(s)I[(h^2 + s^2)^{1/2}] ds, \quad (4)$$

where $w(s)$ is known. The question of determining S/V from $\bar{I}(h)$ then arises.

One possibility is inversion or desmearing of (4) to get $I(h)$; this can be done approximately (Hendricks & Schmidt, 1967; Walter & Schmidt, 1981) with some numerical labor, and computer programs have been written which incorporate desmearing for finite beam length. We here show that there often is a much simpler method of determining \tilde{k} and \tilde{Q} given the profile function $w(s)$, so that calculation of the desmeared intensities is avoided. If we assume that $w(s) \simeq 1$ for $|s| < s_1$, the only requirement is that $I(h)$ has taken on its asymptotic form [$I(h)h^4$ is constant] for $h > s_1$. Whether in fact $h^4 I(h)$ is constant for $h > s_1$ can be verified during the treatment. For most samples we have encountered, the condition was fulfilled.

Using the definition of \tilde{k} , we can write

$$I(h) \rightarrow 2\tilde{k}/\pi h^4 \text{ for } h \rightarrow \infty \quad (5)$$

for the point-collimated intensity. Then the slit-smear intensity must obey

$$\bar{I}(h) \rightarrow \int_{-\infty}^{\infty} w(s)(2\tilde{k}/\pi)(h^2 + s^2)^{-2} ds = \bar{I}_d(h)$$

since, for large enough h ,

$$I[(h^2 + s^2)^{1/2}] = (2\tilde{k}/\pi)[(h^2 + s^2)^{1/2}]^{-4}.$$

For known $w(s)$, the integration is easily performed. For example, for the trapezoid

$$w(s) = 1, |s| < s_1; \quad w(s) = (s_2 - s)/(s_2 - s_1), \quad s_1 \leq |s| \leq s_2;$$

$$w(s) = 0, |s| > s_2, \quad (6)$$

we find

$$\bar{I}_d(h)/\tilde{k} = (4/\pi) \int_0^{s_2} w(s)(h^2 + s^2)^{-2} ds$$

$$= [2/\pi h^3 (s_1 - s_2)]$$

$$\times [s_1 \tan^{-1}(s_1/h) - s_2 \tan^{-1}(s_2/h)]. \quad (7)$$

This result is also given by Soler & Baldrian (1972) in their discussion of the effect of finite slit width on the tail of the diffraction curve. By dividing experimental intensities by $\bar{I}_a(h)/\bar{k}$ and verifying that the ratio indeed becomes constant for larger h values, one determines \bar{k} .

To find \bar{Q} , we first obtain Q^1 by numerical integration of the measured intensities $\bar{I}(h)$:

$$Q^1 = \int_0^{s_3} dh h \bar{I}(h), \quad s_3 > s_1.$$

Since $\bar{I}(h) = \bar{k}/h^3$ for $h > s_1$,

$$\begin{aligned} \bar{Q} - Q^1 &= \int_{s_3}^{\infty} dh h \bar{I}(h) + \int_0^{s_3} dh h [\bar{I}(h) - \bar{I}(h)] \\ &= \int_{s_3}^{\infty} dh h (\bar{k}/h^3) + 2 \int_0^{s_3} dh h \\ &\quad \times \int_{s_1}^{\infty} ds [1 - w(s)] 2\bar{k}\pi^{-1} (h^2 + s^2)^{-2}. \end{aligned} \quad (8)$$

The first term is just $\bar{k}s_3^{-1}$ and the second, on inverting the order of integration, is

$$4\bar{k}\pi^{-1} \int_{s_1}^{\infty} ds [1 - w(s)] [s^{-2} - (s_3^2 + s^2)^{-1}],$$

which is easily evaluated for any function $w(s)$. For the trapezoid we find

$$\begin{aligned} \bar{Q} - Q^1 &= [2\bar{k}/\pi(s_1 - s_2)] \{ (s_1/s_3) \tan^{-1}(s_1/s_3) \\ &\quad - (s_2/s_3) \tan^{-1}(s_2/s_3) - \ln(s_2/s_1) \\ &\quad + \frac{1}{2} \ln[(s_3^2 + s_2^2)/(s_3^2 + s_1^2)] \}. \end{aligned} \quad (9)$$

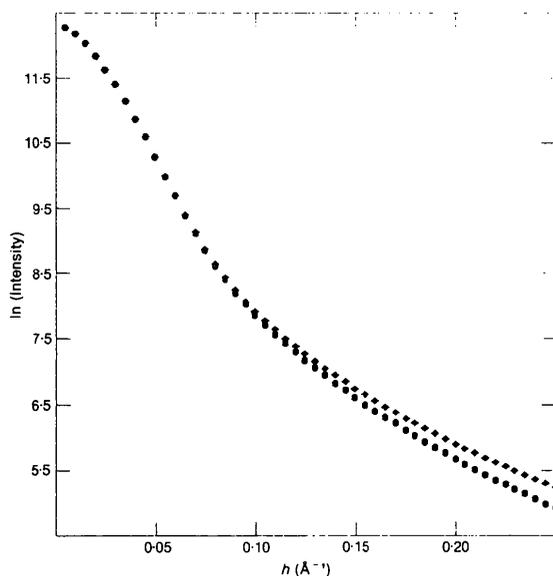


Fig. 1. Logarithm of scattering intensity (numbers of counts) vs h . Circles are experimental data (from trapezoidal beam profile), diamonds are calculated infinite-slit intensities.

As an example of the use of this method, we consider the scattering data of Fig. 1, for a sample of amorphous silica. The slit function $w(s)$ for our instrument is known to be of the form of (6), with $s_1 = 0.1318$, $s_2 = 0.2587 \text{ \AA}^{-1}$. Calculating $\bar{I}_a(h)/\bar{k}$ according to (7) and dividing into the experimental intensities, we obtain the results of Fig. 2. The ratios become constant at sufficiently high angles, with $\bar{k} = 2.94$. Fig. 2 also shows $h^3\bar{I}(h)$, which does not approach a constant limit. Numerical integration of $h\bar{I}(h)$ from 0 to $s_3 = 0.2000$ gives $Q^1 = 148.36$ so that, according to (9), $\bar{Q} = Q^1 + 16.99 = 165.35$. Then $\bar{k}/\bar{Q} = -\gamma'(0) = 0.0178 \text{ \AA}^{-1}$. In fact, these data correspond to a correlation function

$$\begin{aligned} \gamma(r) &= 0.6321 \exp[-(r/34.72)] \\ &\quad + 0.3679 \exp[-(r/55.30)^2] \end{aligned}$$

so that the true value of $\gamma'(0)$ is $-0.6321/34.72 = -0.0182$. The scattering intensities are 4.197 times the transform of the function, so that Q should be $2\pi^2(4.197)$ and \bar{Q} should be 165.7. The agreement between values obtained by our method and those calculated from the known correlation function is very good. The infinite-slit intensities calculated for this correlation function are shown in Fig. 1 (diamonds).

It is of interest, in order to learn about the electron density distribution in a system, to fit theoretical intensity functions to the experimental intensities. The theoretical functions are obtained from models for the correlation function $\gamma(r)$, according to (e.g. Brumberger, 1968)

$$I_t(h) = C \int_0^{\infty} 4\pi r^2 \gamma(r) (\sin hr/hr) dr$$

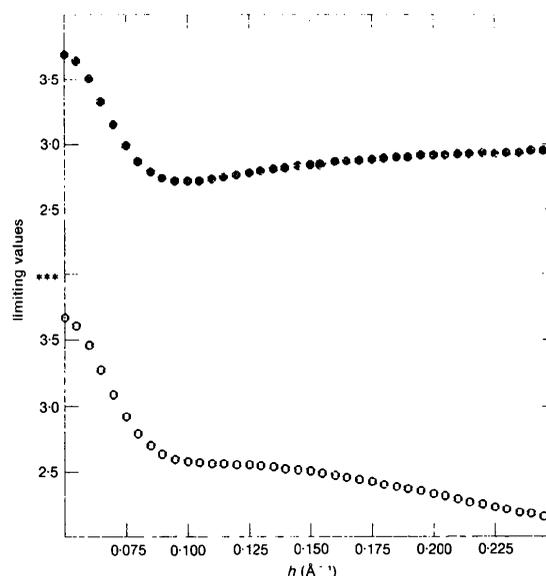


Fig. 2. Filled circles: $\bar{I}(h)/[\bar{I}_a(h)/\bar{k}]$, approaching \bar{k} as h approaches ∞ [see equation (7)]. Open circles: $h^3\bar{I}(h)$, which would approach \bar{k} as h approaches ∞ for infinite-slit conditions.

or

$$\tilde{I}_i(h) = C \int_0^\infty 4\pi^2 r J_0(hr) \gamma(r) dr,$$

where the constant C involves the illuminated volume etc. The initial slope $\gamma'(0)$ is just $-\tilde{k}/\tilde{Q}$. The method of this note can also be applied to the fitting of theoretical intensities to $\bar{I}(h)$. The alternative, smearing $I_i(h)$ according to (4), will involve more complicated calculations.

The relationship between $\bar{I}_i(h)$ and $\tilde{I}_i(h)$ is

$$\begin{aligned} \bar{I}_i(h) &= \tilde{I}_i(h) + 2 \int_0^\infty [w(s) - 1] I[(h^2 + s^2)^{1/2}] ds \\ &= \tilde{I}_i(h) - 8\pi C \int_{s_1}^\infty [w(s) - 1] \gamma'(0) (h^2 + s^2)^{-2} ds \quad (10) \end{aligned}$$

by the previously made assumptions. Thus, the theoretical $\gamma(r)$ should make

$$\tilde{I}_i(h) - 8\pi \gamma'(0) C \int_{s_1}^\infty [w(s) - 1] (h^2 + s^2)^{-2} ds$$

fit the experimental intensities (C is also a fitting parameter if absolute intensities are not measured). For the trapezoidal $w(s)$, the integral is

$$\begin{aligned} &[2h^3(s_1 - s_2)]^{-1} \\ &\times [s_1 \tan^{-1}(s_1/h) - s_2 \tan^{-1}(s_2/h)] - \pi/4h^3, \end{aligned}$$

which is multiplied by $8\pi \gamma'(0)C$ and subtracted from $\tilde{I}_i(h)$.

For some systems, the asymptotic form of $I(h)$ may differ from $2\tilde{k}^2/\pi h^4$. For instance, short-range density fluctuations within the phases or non-sharp phase boundaries can produce scattering intensities $I(h)$ which approach $c_1 h^{-4} + c_2 h^{-2}$ for large h (Ruland,

1971). The interphase surface area is not necessarily calculable from c_1 alone, but one requires values for c_1 and c_2 . To use our method, (7) is replaced by

$$\begin{aligned} \bar{I}_a(h) &= (4\tilde{k}/\pi) \int_0^{s_2} w(s) [c_1(h^2 + s^2)^{-2} \\ &\quad + c_2(h^2 + s^2)^{-1}] ds \quad (11) \end{aligned}$$

and for $w(s)$ of (6), the second integral is

$$\begin{aligned} c_2 \int_0^{s_2} w(s) (h^2 + s^2)^{-1} ds \\ &= [c_2/2(s_1 - s_2)] \ln[(h^2 + s_2^2)/(h^2 + s_1^2)] \\ &\quad + [c_2/(s_1 - s_2)] [(s_1/h) \tan^{-1}(s_1/h) \\ &\quad - (s_2/h) \tan^{-1}(s_2/h)]. \end{aligned}$$

We have thus shown that one can analyze scattering intensities from a non-uniform beam profile without inverting slit-smear data. Simple formulas allow evaluation of parameters of $\tilde{I}(h)$ such as \tilde{k} and \tilde{Q} , and fitting of theoretical models.

This work was supported by the National Science Foundation under grant CPE-7913779.

References

- BRUMBERGER, H. (1968). In *X-ray and Electron Methods of Analysis*, edited by H. VAN OLPHEN & W. PARRISH, ch. IV. New York: Plenum Press.
- HENDRICKS, R. W. & SCHMIDT, P. W. (1967). *Acta Phys. Austriaca*, **26**, 97-122.
- RULAND, W. (1971). *J. Appl. Cryst.* **4**, 70-73.
- SOLER, J. & BALDRIAN, J. (1972). *J. Appl. Cryst.* **5**, 428-429.
- WALTER, G. & SCHMIDT, P. W. (1981). *J. Appl. Cryst.* **14**, 28-32.