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Fourier Transform Methods for the Slit-Height Correction in Small-Angle Scattering

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Fourier transform methods are derived for the correction of collimation errors due to infinite slit-heights in small-angle scattering. The methods are applicable to an arbitrary intensity distribution and have a simple form in the case of a spherically symmetrical distribution. The correction is performed by two successive transforms, the first of which yields a Fourier transform of the 'true' intensity distribution.

The effect of finite slit heights is discussed and an approach to a correction for this error is indicated.

1. Introduction

Primary beams with cross sections which are not point-like are currently used in small-angle scattering in order to increase the intensity yield. The resulting intensity distributions are, in most cases, considerably different from those which would be obtained from a point-like cross section of the primary beam and the recalculation of the 'true' intensity distribution is thus a common task.

From a mathematical point of view the problem can be formulated as a deconvolution (Hosemann, 1951; Kranjc, 1954) which suggests the applicability of Fourier-transform methods. For infinite beam heights, however, direct methods can be used which have been described by Du Mond (1947) and Guinier & Fournet (1947) for a spherically symmetrical intensity distribution and by Syneček (1962) for an arbitrary one. For a spherically symmetrical intensity distribution combined with a finite beam height, a method has been given by Kratky, Porod & Kahovec (1951).

Unfortunately, these methods are rather tedious and not very practical for numerical computation. The present work shows how Fourier-transform methods can be applied to these problems.

2. Arbitrary intensity distribution and infinite beam height

Let $I(\mathbf{s})$ be the intensity distribution near the origin of reciprocal space, $\mathbf{s}$ the reciprocal space vector ($s=2\sin\theta/\lambda$). Let I be normalized so that its three-dimensional Fourier transform ($\mathfrak{F}_3$) yields.

$\mathfrak{F}_3(I(\mathbf{s})) = \varrho^{*2}(\mathbf{r})/\varrho^{*2}(0) = \gamma(\mathbf{r})$

γ 'characteristic function' (Porod, 1951, 1952)

ϱ electron density distribution

$\mathbf{r}$ real space vector

$\varrho^{*2} = \int_v \varrho(\mathbf{y})\varrho(\mathbf{r}+\mathbf{y})dv_y$ (self-convolution of ϱ)

$\mathfrak{F}_3 = \int_v \exp(2\pi i\mathbf{rs})dv_s$ dv_s volume element in reciprocal space

It is permissible in small-angle scattering work to put $\sin\theta \simeq \theta$, so that the Ewald sphere can be replaced by a tangent plane through the origin at right angles to the direction of the primary beam. Let $\mathbf{s}$ be represented in a rectangular system of coordinates by its components $\mathbf{s}_1$, $\mathbf{s}_2$ and $\mathbf{s}_3$ where $\mathbf{s}_1$ and $\mathbf{s}_2$ lie in the tangent plane and are the components of a vector $\mathbf{s}_{12}$. For a given direction of the primary beam the measurable values of I are thus $I(\mathbf{s}_{12})$, which represent a two-dimensional section of $I(\mathbf{s})$ (Fig. 1(*a*)).

The effect of the non-zero dimensions of the cross section of the primary beam together with that of the receiving slit of the counter or, if film techniques are used, the photometer slit, are conveniently represented by a 'measure distribution' $h(\mathbf{s}_{12})$ (Fig. 1(*a*)), which is obtained by convoluting the 'shape function' of the primary beam (h_P) with that of the measuring slit system (h_M).

$$h = h_P * h_M \,.$$

If the method of integrating along lines at right angles to the direction of scanning described by Syneček (1960) is used in order to increase the effective slit height, the path of the receiving slit has to be considered in h_M.

According to Hosemann (1951) and Kranjc (1954), the measured intensity distribution J is given by

$$J(\mathbf{s}_{12}) = I(\mathbf{s}_{12}) * h(\mathbf{s}_{12}) \,.$$

We now assume that the experimental conditions chosen are such that the measure distribution h can be regarded as infinite and constant in the direction of $\mathbf{s}_2$ and infinitely narrow in the direction of $\mathbf{s}_1$ and can therefore be represented by

$$h(\mathbf{s}_{12}) = \delta(\mathbf{s}_1).[1](\mathbf{s}_2)$$

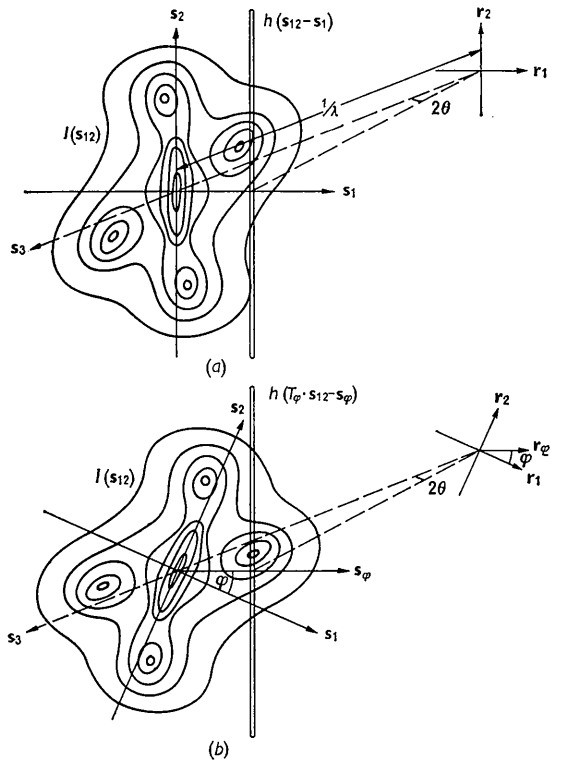

Fig. 1. Positional correlation between the 'true' intensity distribution I and the measure distribution h as function of the direction of scanning $\mathbf{s}_\varphi$.

δ Dirac delta distribution

[1] distribution having the value unity for all values of the argument.

(The term 'distribution' is used in this paper in the sense given by Schwartz, 1950).

If measurements are made in the direction of $\mathbf{s}_1$ only, one finds

$$\begin{aligned} J(\mathbf{s}_1) &= [I(\mathbf{s}_{12}) * (\delta(\mathbf{s}_1) \cdot [1](\mathbf{s}_2))](\mathbf{s}_1) \\ &= \int_{-\infty}^{\infty} I(\mathbf{s}_{12})\, ds_2 \\ &= \{[I(\mathbf{s})]_2\}_1(\mathbf{s}_1) \end{aligned} \tag{1}$$

$[\ ]_2$ two-dimensional section through the origin,

$\{\ \}_1$ one-dimensional projection.

The intensity measured along $\mathbf{s}_1$ is thus the projection of a two-dimensional section of $I(\mathbf{s})$ onto $\mathbf{s}_1$.

Application of the theorems on the Fourier transforms of sections and projections leads to

$$\mathfrak{F}_1(J(\mathbf{s}_1)) = [\{\gamma(\mathbf{r})\}_2]_1(\mathbf{r}_1)$$

$\{\ \}_2$ two-dimensional projection

$[\ ]_1$ one-dimensional section through the origin.

Since $I(\mathbf{s})$ is at least centrosymmetrical, $J(s_1)$ is an even function so that

$$\mathfrak{F}_1(J(s_1)) = 2\int_0^{\infty} J(s_1) \cos 2\pi r_1 s_1\, ds_1 .$$

We now define an arbitrary direction in the two-dimensional section of $I(\mathbf{s})$ by the angle φ relative to $\mathbf{s}_1$ (Fig. 1(*b*)). If the sample is rotated through the angle φ the direction of scanning becomes $\mathbf{s}_\varphi$ and the measure distribution $h(T_\varphi . \mathbf{s}_{12})$, where $\mathbf{T}_\varphi$ is the tensor

$$\mathbf{T}_\varphi = \begin{pmatrix} \cos\varphi & \sin\varphi \\ -\sin\varphi & \cos\varphi \end{pmatrix};$$

then

$$\begin{aligned} J(\mathbf{s}_\varphi) &= \{[I(\mathbf{s})]_2\}_1(\mathbf{s}_\varphi) \\ \mathfrak{F}_1(J(\mathbf{s}_\varphi)) &= [\{\gamma(\mathbf{r})\}_2]_1(\mathbf{r}_\varphi) \end{aligned}$$

By varying φ from 0 to π, all possible one-dimensional projections of $[I(\mathbf{s})]_2$ are obtained. Their corresponding Fourier transforms are one-dimensional sections of $\{\gamma(\mathbf{r})\}_2$ and can therefore be used to reconstruct this function.

In principle, the procedure can be terminated at this point, since all the information contained in $[I(\mathbf{s})]_2$ is present in $\{\gamma(\mathbf{r})\}_2$.

If, however, the 'true' intensity distribution is required, it can be obtained by an inverse Fourier transform:

$$[I(\mathbf{s})]_2 = \mathfrak{F}_2^{-1}\{\gamma(\mathbf{r})\}_2 .$$

Since $\gamma(\mathbf{r})$ is centrosymmetrical,

$$\mathfrak{F}_2^{-1}\{\gamma(\mathbf{r})\}_2 = \int_\sigma \{\gamma(\mathbf{r})\}_2 \cos 2\pi \mathbf{r}_{12}\mathbf{s}_{12}\, d\sigma_{12}$$

$d\sigma_{12}$ surface element in the plane defined by $\mathbf{r}_1$ and $\mathbf{r}_2$.

3. Spherically symmetrical intensity distribution and infinite beam height

If $I(\mathbf{s})$ has spherical symmetry equation (1) becomes

$$J(s) = \{[I(s)]_2\}_1 . \tag{2}$$

There are two possible ways of obtaining $I(s)$ from (2). If one proceeds as in the general case one finds

$$\begin{aligned} \mathfrak{F}_1(J(s)) &= [\{\gamma(r)\}_2]_1 \\ \mathfrak{F}_1(J(s)) &= 2\int_0^{\infty} J(s) \cos 2\pi r s\, ds . \end{aligned} \tag{3}$$

Since $\gamma(r)$ is spherically symmetrical, $\{\gamma(r)\}_2$ has radial symmetry and is thus completely defined by one section through the origin:

$$[\{\gamma(r)\}_2]_1 = \{\gamma(r)\}_2 .$$

The inverse transform yields:

$$\mathfrak{F}_2^{-1}\{\gamma(r)\}_2 = [I(s)]_2 = I(s) . \tag{4}$$

Here again the two-dimensional section defines $I(s)$ completely.

Because of the radial symmetry of $\{\gamma(r)\}_2$, its two-dimensional Fourier transform is given by a Fourier–Bessel transform:

$$\mathfrak{F}_2^{-1}\{\gamma(r)\}_2 = 2\pi\int_0^\infty r\{\gamma(r)\}_2 J_0(2\pi rs)\,dr\,.$$

J_0 Bessel function of the first kind of zero order.

The second way is perhaps of more interest since it leads directly to $\gamma(r)$ in the first step. Reconsidering equation (1), one finds:

$$\begin{aligned}\{[I(\mathbf{s})]_2\}_1 &= \int_{-\infty}^{\infty} I(\mathbf{s}_{12})\,ds_2\\ &= \left(\int_{-\infty}^{\infty} I(\mathbf{s})\,ds_2\right)_{s_3=0}\\ &= [\{I(\mathbf{s})\}_2]_1\end{aligned}$$

which means that the one-dimensional projection of $[I(\mathbf{s})]_2$ equals the one-dimensional section of $\{I(\mathbf{s})\}_2$; this holds in the general case only, when the planes of the section and of the projection are mutually perpendicular.

In the case of a spherically symmetrical intensity distribution $\{I(s)\}_2$ is radially symmetrical and is thus completely defined by one section through the origin; this allows the following development:

$$\begin{aligned}J(s) &= \{I(s)\}_2\\ \mathfrak{F}_2(J(s)) &= [\gamma(r)]_2 = \gamma(r)\\ \mathfrak{F}_2(J(s)) &= 2\pi\int_0^\infty sJ(s)J_0(2\pi rs)\,ds\,. \qquad (5)\end{aligned}$$

A Fourier–Bessel transform of $J(s)$ thus yields $\gamma(r)$ directly. The 'true' intensity distribution is then obtained by

$$\begin{aligned}\mathfrak{F}_3^{-1}(\gamma(r)) &= I(s)\\ \mathfrak{F}_3^{-1}(\gamma(r)) &= \frac{2}{s}\int_0^\infty r\gamma(r)\sin 2\pi rs\,dr\,. \qquad (6)\end{aligned}$$

4. Finite beam height

In this case the measure distribution is defined by

$$h(\mathbf{s}_{12}) = \delta(\mathbf{s}_1).q(\mathbf{s}_2)$$

where $q(\mathbf{s}_2)$ is a symmetrical distribution determining the finite extension of h in the direction $\mathbf{s}_2$.

Equation (1) becomes accordingly

$$\begin{aligned}J(\mathbf{s}_1) &= [[I(\mathbf{s})]_2 * (\delta(\mathbf{s}_1).q(\mathbf{s}_2))]_1\\ &= \{[I(\mathbf{s})]_2.([1](\mathbf{s}_1).q(\mathbf{s}_2))\}_1\,.\end{aligned}$$

Fourier transformation yields

$$\mathfrak{F}_1(J(\mathbf{s}_1)) = [\{\gamma(\mathbf{r})\}_2 * (\delta(\mathbf{r}_1).Q(\mathbf{r}_2))]_1$$

where $Q = \mathfrak{F}_1(q)$.

For a given value of φ one finds

$$\begin{aligned}J(\mathbf{s}_\varphi) &= \{[I(\mathbf{s})]_2.p(T_\varphi\mathbf{s}_{12})\}_1(\mathbf{s}_\varphi)\\ p(\mathbf{s}_{12}) &= [1](\mathbf{s}_1).q(\mathbf{s}_2)\\ \mathfrak{F}_1(J(\mathbf{s}_\varphi)) &= [\{\gamma(\mathbf{r})\}_2 * P(T_\varphi\mathbf{r}_{12})]_1(\mathbf{r}_\varphi)\\ P &= \mathfrak{F}_2(p)\,.\end{aligned}$$

The combination of all sections yields information on $\{\gamma(\mathbf{r})\}_2$ which takes the following form:

$$(\{\gamma\}_2, P) = \int_\sigma \{\gamma\}_2(\mathbf{y})P(T_\varphi(\mathbf{r}_{12}-\mathbf{y}))\,d\sigma_y$$

$\mathbf{y}$ auxiliary variable in the plane defined by $\mathbf{r}_1$ and $\mathbf{r}_2$,

σ_y surface element at the end of vector $\mathbf{y}$.

This function differs from a convolution in that it contains the tensor T_φ. The effect of P on $\{\gamma\}_2$ is a 'smearing' perpendicular to the radius vector. The extent of this 'smearing' is determined by the integral width of Q which according to Fourier transform theory, is reciprocal to the integral width of q

$$\frac{\int_{-\infty}^{\infty} Q(r_2)\,dr_2}{Q(0)} = \frac{q(0)}{\int_{-\infty}^{\infty} q(s_2)\,ds_2}\,.$$

Knowing the width of q one can estimate the effect of the finite beam height on $\{\gamma\}_2$ and decide whether its elimination is worth while.

Because of the presence of the tensor T_φ (which is a function of the direction of $\mathbf{r}_{12}$), a separation of $\{\gamma\}_2$ and P by means of Fourier transformation is impossible. A solution of this problem would be to introduce an auxiliary function G which changes P into a radially symmetrical function and thus eliminates the tensor T_φ.

Taking

$$\mathfrak{F}_1(g) = G$$

one finds

$$\begin{aligned}\mathfrak{F}_1(g(\mathbf{s}_1)J(\mathbf{s}_1)) &= G(\mathbf{r}_1) * \mathfrak{F}_1(J(\mathbf{s}_1))\\ &= G(\mathbf{r}_1) * [\{\gamma(\mathbf{r})\}_2 * (\delta(\mathbf{r}_1).Q(\mathbf{r}_2))]_1\\ &= [\{\gamma(\mathbf{r})\}_2 * (G(\mathbf{r}_1).Q(\mathbf{r}_2))]_1\,.\end{aligned}$$

g should now be chosen such that the product $G.Q$ is independent of φ:

$$G(\mathbf{r}_1).Q(\mathbf{r}_2) = \langle G(\mathbf{r}_1).Q(\mathbf{r}_2)\rangle_\varphi = F(r_{12})$$

where

$$\langle\ \rangle_\varphi = \frac{1}{2\pi}\int_0^{2\pi} d\varphi$$

which means

$$\begin{aligned}g(\mathbf{s}_1).q(\mathbf{s}_2) &= \langle g(\mathbf{s}_1).q(\mathbf{s}_2)\rangle_\varphi = f(s_{12})\\ F &= \mathfrak{F}_2(f)\,.\end{aligned}$$

(Note that the function g defined as above is not identical with that defined by Kratky, Porod & Kahovec, 1951).

This equation has a non-trivial solution only when

$$q(\mathbf{s}_2) = b\exp(-ks_2^2)\,,$$

in which case

$$g(\mathbf{s}_1)=a\exp(-ks_1^2)$$
$$f(s_{12})=ab\exp(-ks_{12}^2)$$
$$s_{12}=|\mathbf{s}_{12}|=\sqrt{(s_1^2+s_2^2)}\,.$$

Since this equation cannot be solved for an arbitrary function q, one can only try to find a good approximation for

$$g(\mathbf{s}_1).q(\mathbf{s}_2)\simeq\langle g(\mathbf{s}_1).q(\mathbf{s}_2)\rangle_\varphi\,.$$

This could be achieved by defining g so that

$$\int_\sigma (g(\mathbf{s}_1).q(\mathbf{s}_2)-\langle g(\mathbf{s}_1)q(\mathbf{s}_2)\rangle_\varphi)^2 d\sigma=\text{Min.}$$

($d\sigma$ surface element) for

$$\int_{-\infty}^{\infty} g(\mathbf{s}_1)\,ds_1=\text{const.}$$

This is a problem which could be solved by the calculus of variations. This definition of the best possible g for a given q seems to be the most correct since, according to Fourier theory,

$$\int_\sigma (g.q-\langle g.q\rangle_\varphi)^2 d\sigma=\int_\sigma (G.Q-\langle G.Q\rangle_\varphi)^2 d\sigma\,.$$

On the other hand, if the experimental conditions are such that the beam height cannot be regarded as infinite one should try to choose the slit system so that q approaches a Gaussian distribution. In this case one finds the best value for k from

$$\int_{-\infty}^{\infty}(q-a\exp[-ks_2^2]^2 ds_2=\text{Min.}$$

since, here again, this approximation is as good in real space as in reciprocal space; in this case k is given by

$$\frac{4k\int_{-\infty}^{\infty} s_2^2 q(s_2)\exp(-ks_2^2)ds_2}{\int_{-\infty}^{\infty} q(s_2)\exp(-ks_2^2)ds_2}=1;$$

thus

$$g\propto\exp(-ks_1^2)$$
$$f\propto\exp(-ks_{12}^2)\,.$$

After a good approximation for g and f has been found the correction for finite beam height proceeds as follows:

$$\mathfrak{F}_1(g(\mathbf{s}_\varphi).J(\mathbf{s}_\varphi))=\lceil\{\gamma\}_2*F\rceil_1(\mathbf{r}_\varphi)\,.$$

The sections are combined to give

$$\{\gamma\}_2*F\,.$$

A two-dimensional Fourier transform of this function yields

$$\mathfrak{F}_2(\{\gamma\}_2*F)=\lceil I\rceil_2.f$$

from which f is eliminated by division.

For radially symmetrical intensity distributions, one finds

$$\mathfrak{F}_1(g(s)J(s))=\{\gamma\}_2*F$$
$$\mathfrak{F}_2(\{\gamma\}_2*F)=I(s).f(s)\qquad(7)$$

or

$$\mathfrak{F}_2(g(s)J(s))=\gamma*F$$
$$\mathfrak{F}_3(\gamma*F)=I(s).f(s)\,.\qquad(8)$$

APPENDIX

The two methods given in § 3 can be verified in the following way:

$$J(s)=2\int_0^\infty I(\sqrt{(s^2+y^2)})\,dy$$

(see Guinier & Fournet, 1955, p. 114).

A combination of equations (3) and (4) postulates

$$4\int_0^\infty\int_0^\infty I(\sqrt{(s^2+y^2)})\,dy\cos 2\pi rs\,ds$$
$$=2\pi\int_0^\infty sI(s)J_0(2\pi rs)\,ds\,.\qquad(9)$$

On the left-hand side, we introduce $z=\sqrt{(s^2+y^2)}$ and interchange the order of integration, which yields:

$$4\int_0^\infty zI(z)\,dz\int_0^z\frac{\cos 2\pi rs}{\sqrt{(z^2-s^2)}}\,ds\,.$$

We now consider the integral in s: the substitution $s=z\cos\varphi$ yields

$$\int_0^{\pi/2}\cos(2\pi rz\cos\varphi)\,d\varphi=\frac{\pi}{2}J_0(2\pi rz)$$

which confirms equation (9).

A combination of equations (5) and (6) postulates:

$$4\pi\int_0^\infty s\int_0^\infty I(\sqrt{(s^2+y^2)})\,dy\,J_0(2\pi rs)\,ds$$
$$=\frac{2}{r}\int_0^\infty sI(s)\sin 2\pi rs.ds\,.\qquad(10)$$

Proceeding as above, we find for the left-hand side:

$$4\pi\int_0^\infty zI(z)\,dz\int_0^z\frac{J_0(2\pi rs)}{\sqrt{(z^2-s^2)}}\,s\,ds$$

and for the integral in s:

$$\int_0^{\pi/2}J_0(2\pi rz\cos\varphi)z\cos\varphi\,d\varphi\,.$$

This is a form of Sonine's first finite integral (see Watson, 1952, p. 373) and yields

$$\sqrt{(z/4r)}J_{\frac{1}{2}}(2\pi rz)=\frac{\sin 2\pi rz}{2\pi r}$$

which confirms equation (10).

The correction for finite slit height and radially

symmetrical intensity distribution (§ 4, equations (7) and (8)) is verified as follows:

$$J(s) = 2\int_0^\infty I(\sqrt{(s^2+y^2)})q(y)\,dy\,.$$

Equation (7) postulates

$$4\int_0^\infty g(s)\int_0^\infty I(\sqrt{(s^2+y^2)})q(y)\,dy\cos 2\pi rs\,ds = 2\pi\int_0^\infty sf(s)I(s)J_0(2\pi rs)\,ds\,. \quad (11)$$

Proceeding as in the case of equation (9) one finds for the left-hand side

$$4\int_0^\infty zI(z)\,dz\int_0^z g(s).q(\sqrt{(z^2-s^2)})\frac{\cos 2\pi rs}{\sqrt{(z^2-s^2)}}\,ds\,.$$

The integral in s yields

$$\int_0^{\pi/2} g(z\cos\varphi)q(z\sin\varphi)\cos(2\pi rz\cos\varphi)\,d\varphi\,.$$

If, as postulated in § 4,

$$g(z\cos\varphi)q(z\sin\varphi)=f(z)$$

this integral yields

$$\tfrac{1}{2}\pi f(z)J_0(2\pi rz)$$

which confirms equation (7).

Equation (8) is easily verified by combining the above procedure with that adopted for equation (10).

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The Effect of Thermal Motion on the Estimation of Bond Lengths from Diffraction Measurements

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Diffraction studies of crystals locate the centroids or maxima of the distributions of atoms undergoing thermal motion, and separations computed from these positions cannot, in general, be interpreted directly as interatomic distances. Methods are presented for calculating the mean separation of two atoms given the isotropic or anisotropic temperature factor coefficients. In order to apply these methods, it is necessary that the joint distribution which describes the motion of the atoms in question be known or assumed.

The atomic coordinates resulting from a crystal structure analysis represent the maximum or the centroid of a distribution of scattering density arising from the combined effects of atomic structure and thermal displacement. It has been common practice to compute an interatomic distance as the distance between a pair of these 'atomic positions'. With improvement in the accuracy of experimental techniques, it has become clear that this estimate is valid only in the limit of negligibly small thermal displacements. For example, a discrepancy between spectroscopic and diffraction estimates of the C–C distance in benzene has been shown by Cox, Cruickshank & Smith (1955, 1958) to arise from the large rotatory oscillation of this molecule about its hexad axis. Cruickshank (1956*a*, 1961) has discussed in detail the effect of the oscillations of a rigid molecule on the positions of maxima in a density distribution, and consequently on the estimation of bond lengths. The present authors (Busing & Levy,

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