Acta Cryst. (1949). **2**, 245

X-Ray Diffraction by Random Layers: Ideal Line Profiles and Determination of Structure Amplitudes from Observed Line Profiles

BY A. J. C. WILSON

Viriamu Jones Laboratory, University College, Cardiff, Wales

(*Received 4 February* 1949)

Warren's calculation of the line profile for diffraction from random layers depends on the use of an approximation function. This can be avoided, and expressions found for (*a*) the ideal line profile for slow variation of the structure amplitude, and (*b*) the variation of the intensity of diffraction as a function of position along the 'rod' of high intensity in reciprocal space, in terms of the layer shape and the observed line profile.

The ideal line profile is, within a trigonometrical factor,

$$I(\sigma)=FF^*S_0^{\frac{1}{2}}\int_{-\infty}^{\infty}A(t)\,|t|^{-\frac{1}{2}}\,(\cos 2\pi\sigma t+\sin 2\pi\sigma\,|t|)\,dt,$$

where $S_0(=2\sin\theta_0/\lambda)$ is the perpendicular distance from the origin of the reciprocal lattice to the centre line of the 'rod', $\sigma=(\sin^2\theta-\sin^2\theta_0)/\lambda\sin\theta_0$, F is the structure amplitude, and $A(t)$ is the area common to a layer and its 'ghost' shifted a distance t parallel to S_0. This expression, evaluated for various layer shapes, gives intensities of diffraction slightly lower than those found by Warren and depending somewhat on the layer shape. In particular, the intensity for large negative volumes of σ is proportional to $|\sigma|^{-\frac{3}{2}}$ multiplied by the maximum breadth of the layer.

If w is measured along the 'rod' from the foot of S_0, $F(w)\,F^*(w)+F(-w)\,F^*(-w)$ can be obtained by 'unfolding' the observed $I(\sigma)$ by means of a double Fourier transformation. Diffraction by random layers can thus give more information than diffraction by a perfect crystal, as the latter gives FF^* only for integral values of the indices.

1. Introduction

Some substances, such as montmorillonite and some varieties of graphite, appear to possess a layer structure in which the layers, although in themselves comparatively perfect and preserving a fairly definite inter-layer spacing, are displaced by random amounts. There is thus no true crystal lattice, and the X-ray diffraction maxima are of two kinds: $00l$, resulting from the inter-layer spacing, and $hk\cdot$, resulting from the comparatively perfect layers. In the reciprocal-lattice representation there are points on the c^* axis, more or less diffuse depending on the size and number of the layers, and rods, more or less diffuse depending on the size of the layers, passing through the points $(ha^*, kb^*, 0)$ parallel to c^*. If the displacements of the layers are entirely random, there will be no concentrations of intensity in these rods corresponding to the hkl diffraction maxima, the only variation of intensity along them being that due to the variation of the structure amplitude of a single layer. The 001 points will give spots on rotation photographs or lines on powder photographs, broadened as usual for small particle size if the number of layers is not large. The rods, on the other hand, will produce peculiar streaks, with a steep rise in intensity at the low-angle end (the 'head'), and a slower decrease toward higher angles (the 'tail'). The rods would be of infinitesimal thickness, and the rise in intensity would be discontinuous if the layers were large, but in general the layers are small, the rods have an appreciable thickness, and the sharpness of the head is reduced. In chrysotile and perhaps some other layer silicates the layers have a finite number (three or six) of possible translations, which occur more or less at random. For these substances the sequence of the layers is effectively random for some diffraction maxima, but for others, for which the possible translations introduce phase changes that are multiples of 2π, the layers are effectively in their proper sequence, and the corresponding regions of high intensity in the reciprocal lattice are no more diffuse than $00l$. There are thus fairly sharp spots for some values of h and k and only streaks for others.

Warren (1941) has calculated the variation of intensity along such streaks, making the approximation that the intensity variation across the rod in reciprocal space is $\exp(-\pi\rho^2L^2)$, where ρ is the distance from the centre of the rod and L is the effective particle dimension of the layers, assumed to be parallelograms. It has, however, been found, for example by Patterson (1939), that this approximation function is unsatisfactory in the related problem of particle-size broadening, and it is therefore of interest to investigate the variation of intensity by a method not involving the use of approximation functions. Such methods have been used for particle-size broadening by Patterson (1939), Waller (1939), Stokes & Wilson (1942, 1944), and Bouman & de Wolff (1942). The essential problem (Fig. 1) is to determine the intensity that in the reciprocal-space representation lies between spheres of radii S and $S+dS$, where $S=2\sin\theta/\lambda$. In discussions of particle-size broadening it suffices to replace these spheres by planes tangent to them and perpendicular to the line joining the point *hkl* to the origin of the reciprocal lattice (Fig. 1 (*a*)), but this approximation is clearly useless in the present problem, and tangent paraboloids are the simplest plausible substitutes for the spheres. For $S<1{\cdot}2S_0$ Warren used paraboloids tangent to the spheres and having the same radius of curvature at the point where the spheres are intersected by a line drawn from the origin of the reciprocal lattice perpendicular to the rod in question (Fig. 1 (*b*)). For larger values of S, when there is an appreciable separation between the spheres and paraboloids in the region Q where the intensity in reciprocal space is greatest, he used two pairs of tangent planes. The necessity for using two different approximations is, however, avoided by taking the paraboloids tangent to the spheres at Q (Fig. 1 (c)). The paraboloids and spheres are then always in coincidence in the important region of high intensity. For small values of $S-S_0$ there is no appreciable difference between the two sets of approximating paraboloids.

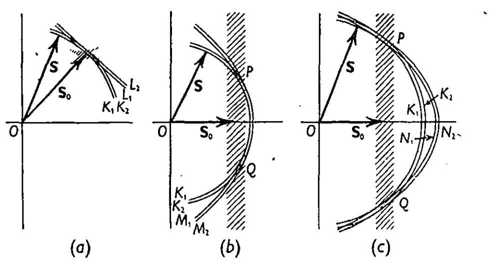

Fig. 1. Spheres in reciprocal space approximated by (*a*) tangent planes (small crystals), (*b*) and (*c*) parabolic cylinders (random layers).

The present more exact investigation leads to two main results. First, if the variations of the structure amplitude with position in reciprocal space is slow (as it would be with graphite), the line profile can be expressed as an integral involving the shape, as well as the size, of the layers, and this integral can be evaluated for various simple layer shapes. For square, triangular and circular layers the intensity of diffraction is a little less than that found by Warren, and the line profile depends to some extent on the shape of the layer. In Fig. 3 the line profiles for square layers 'side-on' and 'corner-on' are shown as a function of $\sigma=(S^2-S_0)/2S_0$, with the profile found by Warren given also for comparison. Other shapes show variations of the same order of magnitude. As already known, the intensity for large positive values of σ is proportional to the area of the layers divided by $\sigma^{\frac{1}{2}}$; a new result is that for large negative values of σ the intensity is proportional to the maximum breadth of the layers divided by $4\pi\sigma^{\frac{3}{2}}$. Secondly, if the variation of the structure amplitude with position in reciprocal space is large, it is possible by an 'unfolding' process (Stokes, 1948) to obtain the variation of $F(w)\,F^*(w)+F(-w)\,F^*(-w)$ as a function of w, where w is measured along the rod of high intensity from the end of S_0.

2. General calculation

The intensity of the X-rays diffracted from a crystal is proportional to

$$I(\mathbf{H})=\Sigma_j\Sigma_{j'}F_jF^*_{j'}\exp\{2\pi i(\mathbf{r}_{j'}-\mathbf{r}_j)\,.\,\mathbf{H}\},\qquad(1)$$

where $\mathbf{H}$ is the position vector in reciprocal space and F_j and $\mathbf{r}_j$ are the structure amplitude and position vector of the jth unit cell. (See, for example, Wilson (1942), where, however, $\mathbf{s}/\lambda$ is written instead of $\mathbf{H}$.) If the phase relation between successive layers is entirely random the intensity (except for $00l$) will be simply N times that of a single layer, where N is the number of layers, and (1) becomes

$$I(\mathbf{H})=NFF^*\,\Sigma_j\Sigma_{j'}\exp\{2\pi i(\mathbf{r}_{j'}-\mathbf{r}_j)\,.\,\mathbf{H}\},\qquad(2)$$

where $\mathbf{r}_j$ is now the position vector within a layer and the summation is over the cells of a single layer. Since the layers are supposed perfect F_j and $F_{j'}$ are the same, and can be taken outside the sum. This will have a greatest value when $(\mathbf{r}_{j'}-\mathbf{r}_j)\,.\,\mathbf{H}$ is integral, that is, when

$$\mathbf{H}=h\mathbf{a}^*+k\mathbf{b}^*+l\mathbf{c}^*,\qquad(3)$$

where h and k are integers and l is arbitrary. This equation determines a line in reciprocal space, and it is convenient to express $\mathbf{H}$ and $\mathbf{r}$ in terms of a set of rectangular axes related to this line as follows. The X axis is taken parallel to $\mathbf{S}_0$, the perpendicular from the origin of the reciprocal lattice on to the line, the Z axis is taken parallel to the line, and the Y axis is taken perpendicular to X and Z. Let

$$\mathbf{H}=\mathbf{S}_0+\boldsymbol{\rho},\qquad(4)$$

and let x, y, z and u, v, w be the components of $\mathbf{r}$ and $\boldsymbol{\rho}$ in the directions just defined. (The value of z is, of course, zero in the application to random layers.) In (2) $\mathbf{r}_j\,.\,\mathbf{S}_0$ $(=hj_1+kj_2)$ is an integer, and may thus be dropped in the exponentials, and for the small values of u and v that are of importance $\mathbf{r}_j\,.\,\boldsymbol{\rho}$ $(=x_ju+y_jv)$ changes only slightly in going from one unit cell to the next, so that the summations may be replaced by integrations over the area of the layer. Then

$$I(u,v,w)=NFF^*c'C^{-1}\int_{A'}\int_{A}\times\exp\{2\pi i[(x'-x)\,u+(y'-y)\,v]\}\,dA\,dA',\qquad(5)$$

where $C=|\,\mathbf{a}\times\mathbf{b}\,|$ is the area of the face of the unit cell containing $\mathbf{a}$ and $\mathbf{b}$, and $c'=\mathbf{a}\times\mathbf{b}\,.\,\mathbf{c}/C$ is the inter-layer spacing. It depends on w only through FF^*. Except for certain constants and geometrical factors, the intensity of the diffracted X-rays as a function of S is got by integrating $I(u,v,w)$ over the space between spheres of radii S and $S+dS$, but, as already discussed, these may be replaced by tangent paraboloids. In the region where the intensity is large u, $v \sim 0$, and the equation of the paraboloid making the closest contact with the sphere

$$S^2 = \mathbf{H}.\mathbf{H} = S_0^2 + 2uS_0 + u^2 + v^2 + w^2 \quad (6)$$

is

$$S^2 = S_0^2 + 2uS_0 + w^2. \quad (7)$$

Let $\sigma = (S^2 - S_0^2)/2S_0$. The intensity of reflexion as a function of σ is given by the integral of $I(u, v, w)\, du dv dw$ over the space between the spheres, or, since the volume element $du dv dw$ corresponds to $d\sigma dv dw$ (Jacobian of the transformation unity), by

$$I(\sigma)\, d\sigma = Nc'C^{-1} \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{A'}\int_{A} FF^* \exp\{2\pi i[(x'-x)\sigma + (y'-y)v - (x'-x)w^2/2S_0]\}\, d\sigma dA\, dA'\, dv dw. \quad (8)$$

The integral with respect to v is singular, being zero unless $y' = y$, when it is infinite in such a way that the double integral over y' and v is unity. Equation (8) therefore becomes

$$I(\sigma) = Nc'C^{-1} \int_{-\infty}^{\infty}\int_{x'}\int_{A} FF^* \exp\{2\pi i[(x'-x)\sigma - (x'-x)w^2/2S_0]\}\, dA\, dx'\, dw, \quad (9)$$

or, with the substitutions $x' - x = t$ and $A(t) = \iint dx dy$ over the area common to the crystal and its 'ghost' shifted a distance t parallel to $\mathbf{S}_0$,

$$I(\sigma) = Nc'C^{-1} \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} FF^* A(t) \times \exp\{2\pi i[\sigma t - w^2 t/2S_0]\}\, dw dt. \quad (10)$$

From this equation two lines of investigation are open. First, one can regard $I(\sigma)$ as an experimentally determined function, and seek to derive from it the variation of FF^* with w in order to gain clues to the crystal structure, or, secondly, one can investigate the variation of $I(\sigma)$ with layer shape, regarding FF^* as a constant or a slowly varying function for the variation of which a correction can be applied. In the latter case the integration with respect to w is of the Fresnel type, giving

$$I(\sigma) = NFF^*c'C^{-1}(\tfrac{1}{2}S_0)^{\frac{1}{2}} \int_{-\infty}^{\infty} A(t)\,|t|^{-\frac{1}{2}} \times \{\cos 2\pi\sigma t + \sin 2\pi\sigma\,|t|\}\, dt. \quad (11)$$

The following section gives a few suggestions with regard to the former problem; the latter, the main subject of this paper, is resumed in § 4.

3. Relation between $I(\sigma)$ and the crystal structure

By (10), $I(\sigma)$ is the Fourier transform of the function $L(t)$ given by

$$L(t) = Nc'C^{-1}A(t) \int_{-\infty}^{\infty} FF^* \exp\left\{-\frac{2\pi i w^2 t}{2S_0}\right\} dw. \quad (12)$$

By the reciprocal relation between such transforms, therefore,

$$L(t) = \int_{-\infty}^{\infty} I(\sigma) \exp\{-2\pi i\sigma t\}\, d\sigma. \quad (13)$$

If $I(\sigma)$ is determined experimentally, $L(t)$ can be found by numerical integration or otherwise. The aim of structure analysis is to find co-ordinates x, y, z for every atom in the unit cell. If the scattering factor for the jth atom is f_j, then

$$F = \Sigma_j f_j \exp\{2\pi i[hx_j/a + ky_j/b + (w + w_0)z_j]\}, \quad (14)$$

where $-w_0$ is the projection of $h\mathbf{a}^* + k\mathbf{b}^*$ on $\mathbf{c}^*$. Substitution in (12) gives

$$\begin{aligned} L(t) &= Nc'C^{-1}A(t)\, \Sigma_j \Sigma_{j'} f_j f_{j'} \exp\{2\pi i[(x_j - x_{j'})h/a + (y_j - y_{j'})k/b + (z_j - z_{j'})w_0]\} \\ &\quad \times \int_{-\infty}^{\infty} \exp\left\{2\pi i\left[(z_j - z_{j'})w - \frac{w^2 t}{2S_0}\right]\right\} dw \\ &= Nc'C^{-1}(S_0/2t)^{\frac{1}{2}} A(t)\, \Sigma_j \Sigma_{j'} f_j f_{j'} \exp\{2\pi i[(x_j - x_{j'})h/a + (y_j - y_{j'})k/b + (z_j - z_{j'})w_0 + (z_j - z_{j'})^2 S_0/2t]\}. \end{aligned} \quad (15)$$

By trial and error or other accepted means of crystal-structure analysis it should be possible to find values of x_j, y_j, z_j satisfying this equation. In principle the values of z_j should be determinable from the $00l$ maxima only, so that only the values of x_j and y_j need be found by a consideration of the tailed reflexions.

Equation (12) may, however, be approached in a different way. Let

$$G(w) = F(w)\,F^*(w) + F(-w)\,F^*(-w), \quad (16)$$

and let $K(t)$, $J(t)$ be the real and imaginary parts of $CL(t)/c'NA(t)$, that is

$$CL(t)/c'NA(t) = K(t) + iJ(t). \quad (17)$$

Then

$$\left.\begin{aligned} K(t) &= \int_0^{\infty} G(w) \cos\frac{2\pi w^2 t}{2S_0}\, dw, \\ J(t) &= \int_0^{\infty} G(w) \sin\frac{2\pi w^2 t}{2S_0}\, dw. \end{aligned}\right\} \quad (18)$$

On making the substitution $\psi = w^2/2S_0$ these become

$$K(t) = (\tfrac{1}{2}S_0)^{\frac{1}{2}} \int_0^{\infty} \psi^{-\frac{1}{2}}\, G\{(2S_0\psi)^{\frac{1}{2}}\} \cos(2\pi t\psi)\, d\psi, \quad (19)$$

$$J(t) = (\tfrac{1}{2}S_0)^{\frac{1}{2}} \int_0^{\infty} \psi^{-\frac{1}{2}}\, G\{(2S_0\psi)^{\frac{1}{2}}\} \sin(2\pi t\psi)\, d\psi, \quad (20)$$

that is, $K(t)$ and $J(t)$ are respectively the cosine and sine transforms of $(S_0/2\psi)^{\frac{1}{2}}\, G\{(2S_0\psi)^{\frac{1}{2}}\}$. Inverting these transforms gives

$$(S_0/2\psi)^{\frac{1}{2}}\, G\{(2S_0\psi)^{\frac{1}{2}}\} = \int_0^{\infty} K(t) \cos(2\pi t\psi)\, dt, \quad (21)$$

$$(S_0/2\psi)^{\frac{1}{2}}\, G\{(2S_0\psi)^{\frac{1}{2}}\} = \int_0^{\infty} J(t) \sin(2\pi t\psi)\, dt, \quad (22)$$

which become, on replacing ψ by $w^2/2S_0$,

$$G(w)=\frac{w}{S_0}\int_0^\infty K(t)\cos\frac{2\pi t w^2}{2S_0}\,dt, \quad (23)$$

$$G(w)=\frac{w}{S_0}\int_0^\infty J(t)\sin\frac{2\pi t w^2}{2S_0}\,dt. \quad (24)$$

It should therefore be possible to determine

$$G(w)=F(w)\,F^*(w)+F(-w)\,F^*(-w)$$

by applying two straightforward, though somewhat tedious, transformations to the observed variation of $I(\sigma)$ with σ; a Fourier transformation to $I(\sigma)$, giving $L(t)$, and a cosine or sine transformation to the real or imaginary part of $L(t)/A(t)$. It is true that $A(t)$ requires a knowledge of the layer shape, but it would probably be sufficient to approximate this either by a circle or by a rectangle.

4. Comparison with particle-size broadening

Equation (11) is analogous to the expression for the line profile of a normal hkl diffraction maximum from a small crystal:

$$I(s)=FF^*U^{-1}\int_{-\infty}^{\infty} V(t)\cos(2\pi s t)\,dt, \quad (25)$$

where $s=S-S_0$, U is the volume of a unit cell, and $V(t)$ is the volume common to the crystal and its 'ghost' shifted a distance t toward the origin of the reciprocal lattice (Stokes & Wilson, 1942; Wilson, 1949, p. 41). The apparent particle size (Jones, 1938) for the normal maximum is easily obtained in the form

$$\epsilon=V^{-1}\int V(t)\,dt, \quad (26)$$

but no corresponding expression can be obtained from (11) since (i) $\int I(\sigma)\,d\sigma$ does not converge, and (ii) the position and height of the maximum of $I(\sigma)$ cannot be expressed in simple form. The nearest analogue is perhaps the ratio of the slope $\partial I/\partial\sigma$ to the actual value of $I(\sigma)$ for $\sigma=0$:

$$\epsilon'=2\pi\int_{-\infty}^{\infty} A(t)\,|\,t\,|^{\frac{1}{2}}\,dt\Big/\int_{-\infty}^{\infty} A(t)\,|\,t\,|^{-\frac{1}{2}}\,dt. \quad (27)$$

This may be evaluated for various simple shapes, but it is unlikely to be of practical importance since the effect of experimental imperfection on $\partial I/\partial\sigma$ may be large and the position on the film corresponding to $\sigma=0$ difficult to locate with certainty. For a square with sides of length p making angles with $\mathbf{S}_0$ whose cosines are $m\geqslant n$ it becomes

$$\epsilon'=2\pi p(7m-3n)/7m(5m-n). \quad (28)$$

The value of this does not vary greatly with m, giving always

$$\epsilon'\doteqdot 1{\cdot}26p. \quad (29)$$

For a circle of diameter D (27) gives (cf. (73) and (76))

$$\epsilon'=\frac{5\pi D}{14}\left[\frac{\Gamma(\frac{5}{4})}{\Gamma(\frac{7}{4})}\right]^2\doteqdot 1{\cdot}09D. \quad (30)$$

The numerical coefficient was wrongly given as $\frac{3}{10}$ instead of $\frac{5}{14}$ in a preliminary account of this work (Wilson, 1948). If the 'true particle size' p is defined as the square root of the area of the layer, (30) becomes

$$\epsilon'\doteqdot 1{\cdot}24p, \quad (31)$$

which is practically the same as that for a square of the same area.

5. Exact and series expressions for $I(\sigma)$

The integral in (11) extends from $-\infty$ to $+\infty$, but this is more or less symbolical, as in reality $A(t)$ vanishes at some finite value τ of t, and is zero for all larger values. Since $A(t)=A(-t)$ the equation may be written

$$I(\sigma)=NFF^*c'C^{-1}(2S_0)^{\frac{1}{2}}\int_0^\tau A(t)\,t^{-\frac{1}{2}}(\cos 2\pi\sigma t+\sin 2\pi\sigma t)\,dt. \quad (32)$$

For σ large only small values of t contribute appreciably to the integral, so that its asymptotic values are obtained on replacing τ by ∞ and $A(t)$ by its value for small t, p^2-bt, where p is the 'true' particle size and b is the maximum breadth of the layer, measured perpendicular to $\mathbf{S}_0$. The integrals in (32) are then known, giving

$$\left.\begin{array}{l} I(\sigma)\sim NFF^*c'C^{-1}p^2(2S_0/\sigma)^{\frac{1}{2}} \\ \text{for } \sigma \text{ large and positive, and} \\ I(\sigma)\sim NFF^*c'C^{-1}b(S_0/2\pi\,|\,\sigma\,|^3)^{\frac{1}{2}} \end{array}\right\} \quad (33)$$

for σ large and negative.

In order to obtain a function suitable for calculation it is convenient to make certain changes in the variables. Let $\xi=2\pi\sigma t$, $x=2\pi\sigma\tau$, and replace the area function $A(t)$ by $p^2a(\xi)$, where p is the 'true' particle size. The function $a(\xi)$ has the properties $a(0)=1$, $a(x)=0$. Equation (32) becomes

$$\left.\begin{array}{l} I(\sigma)=NFF^*c'C^{-1}(2S_0)^{\frac{1}{2}}p^2\tau^{\frac{1}{2}}K(x), \\ \text{where}\quad K(x)=x^{-\frac{1}{2}}\displaystyle\int_0^x a(\xi)\,\xi^{-\frac{1}{2}}(\cos\xi\oplus\sin\xi)\,d\xi. \end{array}\right\} \quad (34)$$

The variables on the right are always to be taken as positive; if, in fact, σ, and consequently ξ and x, is negative, only the encircled sign is to be changed. This function $K(x)$ is suitable for calculation. It differs trivially from Warren's function $F(a)$ in that it is larger by a constant factor $2\pi^{-\frac{1}{2}}\doteqdot 1{\cdot}5$, and that $x=2\pi^{\frac{1}{2}}a$,† but the approximation used by Warren leads to essential differences as well. For theoretical discussion the function

$$\begin{aligned} M(x)&\equiv\frac{K(x)+iK(-x)}{1+i} \\ &=\frac{x^{-\frac{1}{2}}}{1+i}\int_0^x a(\xi)\,\xi^{-\frac{1}{2}}\{(1+i)\cos\xi+(1-i)\sin\xi\}\,d\xi. \\ &=x^{-\frac{1}{2}}\int_0^x a(\xi)\,\xi^{-\frac{1}{2}}\exp(-i\xi)\,d\xi \end{aligned} \quad (35)$$

† More strictly $xs/\sigma=2\pi^{\frac{1}{2}}a$, but the relation in the text extends to Warren's function the benefit of the better-fitting paraboloids.

is easier to manipulate; $K(x)$ is the real part of $(1+i)\,M(x)$ and $K(-x)$ is its imaginary part.

In any practical case $a(\xi)$ can be expressed as a Taylor's series valid over the range 0 to x, or as a finite number of series valid over subranges. The discussion may be limited to cases for which $a(\xi)$ is represented by a single series; no difficulty in principle arises in applying it to particular cases involving more than one series. For several simple layer shapes (triangle, parallelogram, hexagon 'side-on') $a(\xi)$ is simply a quadratic in ξ:

$$a(\xi)=1-(1+\eta)\,\xi/x+\eta\xi^2/x^2, \tag{36}$$

where η is a parameter between 0 and 1 depending on the shape and orientation of the layer. In general it may be expressed

$$a(\xi)=a+a'\xi/x+a''\xi^2/x^2+a'''\xi^3/x^3+\ldots, \tag{37}$$

where $a, a', a'', \ldots$ are constants. Let

$$M_y(x)=x^{-\frac{1}{2}}\int_0^x a(\xi)\,\xi^{-\frac{1}{2}}\exp(-iy\xi)\,d\xi, \tag{38}$$

where ultimately y will be put equal to unity, so that the function reduces to $M(x)$. Inserting $a(\xi)$ from (37) gives

$$\begin{aligned}M_y(x)&=x^{-\frac{1}{2}}\int_0^x\{a+a'\xi/x+a''\xi^2/x^2+\ldots\}\,\xi^{-\frac{1}{2}}\exp(-iy\xi)\,d\xi\\&=\left\{a+\frac{ia'}{x}\frac{\partial}{\partial y}+\frac{i^2a''}{x^2}\frac{\partial^2}{\partial y^2}+\ldots\right\}x^{-\frac{1}{2}}\int_0^x\xi^{-\frac{1}{2}}\exp(-iy\xi)\,d\xi\\&=\left\{a+ia'\frac{\partial}{\partial(xy)}+i^2a''\frac{\partial^2}{\partial(xy)^2}+\ldots\right\}(xy)^{-\frac{1}{2}}\\&\qquad\times\int_0^{xy}(y\xi)^{-\frac{1}{2}}\exp(-iy\xi)\,d(y\xi),\end{aligned}$$

so that

$$M(x)=\left\{a+ia'\frac{d}{dx}+i^2a''\frac{d^2}{dx^2}+\ldots\right\}x^{-\frac{1}{2}}\int_0^x\xi^{-\frac{1}{2}}\exp(-i\xi)\,d\xi. \tag{39}$$

The factors in brackets may be written symbolically as $a(ixd/dx)$, so that

$$M(x)=a\left(ix\frac{d}{dx}\right)x^{-\frac{1}{2}}\int_0^x\xi^{-\frac{1}{2}}\exp(-i\xi)\,d\xi, \tag{40}$$

where $x^{-n}(xd/dx)^n$ is to be interpreted as d^n/dx^n. The integral in (40) is $(2\pi)^{\frac{1}{2}}\{C(x)-iS(x)\}$, where $C(x)$ and $S(x)$ are the Fresnel integrals in the form treated (p. 545) and tabulated (pp. 744–5) by Watson (1922). The line profile is therefore determined explicitly in terms of known functions by the equation

$$M(x)=(2\pi)^{\frac{1}{2}}\,a(ixd/dx)\,x^{-\frac{1}{2}}\{C(x)-iS(x)\}. \tag{41}$$

In the special cases for which $a(\xi)$ is a quadratic

$$a(\xi)=a+\frac{a'}{x}\xi+\frac{a''}{x^2}\xi^2 \tag{42}$$

and

$$a(\xi)=1-\frac{(1+\eta)}{x}\xi+\frac{\eta}{x^2}\xi^2; \tag{43}$$

this gives

$$K(x)=ak_0(x)+a'k_1(x)+a''k_2(x) \tag{44}$$

and

$$K(x)=g_1(x)+\eta g_2(x), \tag{45}$$

where

$$k_0(x)=(2\pi/x)^{\frac{1}{2}}\{C(x)\oplus S(x)\}, \tag{46}$$

$$k_1(x)=(\pi/2x^3)^{\frac{1}{2}}\{\oplus C(x)-S(x)\}+x^{-1}\{\ominus\cos x+\sin x\}, \tag{47}$$

$$k_2(x)=\frac{3}{2}\left(\frac{\pi}{2x^5}\right)^{\frac{1}{2}}\{-C(x)\ominus S(x)\}+x^{-1}\{\ominus\cos x+\sin x\}+\tfrac{3}{2}x^{-2}\{\cos x\oplus\sin x\}, \tag{48}$$

$$g_1(x)=k_0(x)-k_1(x), \tag{49}$$

$$g_2(x)=k_2(x)-k_1(x). \tag{50}$$

The relations between the functions

$$k_1(-x)=\ \partial k_0(x)/\partial x, \tag{51}$$

$$k_2(-x)=\ \partial k_1(x)/\partial x, \tag{52}$$

$$g_2(-x)=-\partial g_1(x)/\partial x, \tag{53}$$

are easily obtained. Substitution of the asymptotic series for $C(x)$ and $S(x)$ (Watson, 1922, p. 545) gives

$$k_0(x)\sim\left(\frac{2\pi}{x}\right)^{\frac{1}{2}}+\frac{1}{x}(-\cos x+\sin x)-\frac{1}{2x^2}(\cos x+\sin x)+\ldots, \tag{54}$$

$$k_0(-x)\sim\frac{1}{x}(\cos x+\sin x)-\frac{1}{2x^2}(\cos x-\sin x)+\ldots, \tag{55}$$

$$k_1(x)\sim\frac{1}{x}(-\cos x+\sin x)+\frac{1}{2x^2}(\cos x+\sin x)+\ldots, \tag{56}$$

$$k_1(-x)\sim-\left(\frac{\pi}{2x^3}\right)^{\frac{1}{2}}+\frac{1}{x}(\cos x+\sin x)+\frac{1}{2x^2}(\cos x-\sin x)+\ldots, \tag{57}$$

$$k_2(x)\sim-\frac{3}{2}\left(\frac{\pi}{2x^5}\right)^{\frac{1}{2}}+\frac{1}{x}(-\cos x+\sin x)+\frac{3}{2x^2}(\cos x+\sin x)+\ldots, \tag{58}$$

$$k_2(-x)\sim\frac{1}{x}(\cos x+\sin x)+\frac{3}{2x^2}(\cos x-\sin x)+\ldots, \tag{59}$$

$$g_1(x)\sim\left(\frac{2\pi}{x}\right)^{\frac{1}{2}}-\frac{1}{x^2}(\cos x+\sin x)+\ldots, \tag{60}$$

$$g_1(-x)\sim\left(\frac{\pi}{2x^3}\right)^{\frac{1}{2}}-\frac{1}{x^2}(\cos x-\sin x)+\ldots, \tag{61}$$

$$g_2(x)\sim-\frac{3}{2}\left(\frac{\pi}{2x^5}\right)^{\frac{1}{2}}+\frac{1}{x^2}(\cos x+\sin x)+\ldots, \tag{62}$$

$$g_2(-x)\sim\left(\frac{\pi}{2x^3}\right)^{\frac{1}{2}}+\frac{1}{x^2}(\cos x-\sin x)+\ldots. \tag{63}$$

The sinusoidal oscillations about the leading term are not shown by Warren's function $F(a)$. The two or three terms written down above give the value of the functions correct within 0·01 for x greater than about four.

Series valid for small x are more conveniently obtained by expanding $\cos\xi \oplus \sin\xi$ in (34) and integrating term by term. The first few terms for the functions required when $a(\xi)$ is a quadratic are

$$k_0(x) = 2+\frac{2}{3}x-\frac{1}{2!}\cdot\frac{2}{5}x^2-\frac{1}{3!}\cdot\frac{2}{7}x^3+\frac{1}{4!}\cdot\frac{2}{9}x^4+\ldots, \quad (64)$$

$$k_1(x) = \frac{2}{3}+\frac{2}{5}x-\frac{1}{2!}\cdot\frac{2}{7}x^2-\frac{1}{3!}\cdot\frac{2}{9}x^3+\frac{1}{4!}\cdot\frac{2}{11}x^4+\ldots, \quad (65)$$

$$k_2(x) = \frac{2}{5}+\frac{2}{7}x-\frac{1}{2!}\cdot\frac{2}{9}x^2-\frac{1}{3!}\cdot\frac{2}{11}x^3+\frac{1}{4!}\cdot\frac{2}{13}x^4+\ldots, \quad (66)$$

$$g_1(x) = 4\left\{\frac{1}{1.3}+\frac{1}{3.5}x-\frac{1}{2!}\frac{1}{5.7}x^2-\frac{1}{3!}\frac{1}{7.9}x^3 +\frac{1}{4!}\frac{1}{9.11}x^4+\ldots\right\}, \quad (67)$$

$$g_2(x) = -4\left\{\frac{1}{3.5}+\frac{1}{5.7}x-\frac{1}{2!}\frac{1}{7.9}x^2-\frac{1}{3!}\frac{1}{9.11}x^3 +\frac{1}{4!}\frac{1}{11.13}x^4+\ldots\right\}, \quad (68)$$

where the signs look after themselves; terms with x to an odd power change sign with x, and terms with x to an even power remain unchanged. The law of formation of further terms is obvious, but convergence is not rapid for x greater than unity. In the general case (34) becomes

$$K(x) = x^{-\frac{1}{2}}\int_0^x a(\xi)\,\xi^{-\frac{1}{2}}\left\{1\oplus\xi-\frac{1}{2!}\xi^2\ominus\frac{1}{3!}\xi^3+\frac{1}{4!}\xi^4\oplus\ldots\right\}d\xi$$

$$= x^{-\frac{1}{2}}\sum_{n=0}^{\infty}\frac{1}{n!}s_n\int_0^x a(\xi)\,\xi^{n-\frac{1}{2}}\,d\xi, \quad (69)$$

where the signs s_n run $++--++--\ldots$ for x positive, and $+--++--+\ldots$ for x negative. For circular layers (and probably for other layers bounded by curved lines) a series with integrals of a different type is more convenient. The integral in (32) is

$$\int_0^\tau A(t)\,t^{-\frac{1}{2}}\{\cos 2\pi\sigma t+\sin 2\pi\sigma t\}\,dt$$

$$= \int_0^\tau A(t)\,t^{-\frac{1}{2}}\left\{1+2\pi\sigma t-\frac{1}{2!}(2\pi\sigma t)^2-\frac{1}{3!}(2\pi\sigma t)^3+\ldots\right\}dt, \quad (70)$$

and thus depends on integrals of the form

$$\int_0^\tau A(t)\,t^{n-\frac{1}{2}}\,dt. \quad (71)$$

In Fig. 2 the layer and its 'ghost' shifted a distance t parallel to $\mathbf{S}_0$ are represented. If T is the width of the layer measured through the point x, y, the area $A(t)$, shaded in the figure, is (compare Wilson, 1949, pp. 37–41)

$$A(t) = \int (T-t)\,dy, \quad (72)$$

so that

$$\int_0^\tau A(t)\,t^{n-\frac{1}{2}}\,dt = \int\left\{T\int t^{n-\frac{1}{2}}\,dt-\int t^{n+\frac{1}{2}}\,dt\right\}dy$$

$$= \frac{1}{(n+\frac{1}{2})(n+\frac{3}{2})}\int T^{n+\frac{3}{2}}\,dy, \quad (73)$$

which becomes, since $T=\int dx$,

$$\frac{1}{(n+\frac{1}{2})(n+\frac{3}{2})}\iint T^{n+\frac{1}{2}}\,dA, \quad (74)$$

where the integration is over the area of the layer. The function $K(x)$ is therefore given by

$$K(x) = \sum_{n=0}^{\infty}\frac{s_n x^n}{(n+\frac{1}{2})(n+\frac{3}{2})\,n!}\cdot\frac{1}{p^2\tau^{n+\frac{1}{2}}}\iint \tau^{n+\frac{1}{2}}\,dA. \quad (75)$$

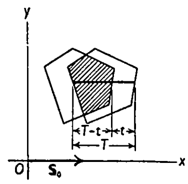

Fig. 2. Layer and its 'ghost' displaced a distance t parallel to $\mathbf{S}_0$.

For a circle of radius R, $T=2(R^2-y^2)^{\frac{1}{2}}$, $\tau=2R$, $p=R\pi^{\frac{1}{2}}$,

$$\frac{1}{p^2\tau^{n+\frac{1}{2}}}\iint T^{n+\frac{1}{2}}\,dA = \frac{2\,.\,2^{n+\frac{3}{2}}}{\pi R^2(2R)^{n+\frac{1}{2}}}\int_0^R (R^2-y^2)^{\frac{1}{2}n+\frac{3}{4}}\,dy,$$

which becomes, on putting $y=R\sin\phi$,

$$\frac{4}{\pi}\int_0^{\frac{1}{2}\pi}\cos^{n+\frac{5}{2}}\phi\,d\phi = 2\pi^{-\frac{1}{2}}\frac{\Gamma(\frac{1}{2}n+\frac{7}{4})}{\Gamma(\frac{1}{2}n+\frac{9}{4})}, \quad (76)$$

so that

$$K(x) = 2\pi^{-\frac{1}{2}}\sum_{n=0}^{\infty}s_n\frac{\Gamma(\frac{1}{2}n+\frac{7}{4})}{(n+\frac{1}{2})(n+\frac{3}{2})\,n!\,\Gamma(\frac{1}{2}n+\frac{9}{4})}\cdot x^n \quad (77)$$

$$= 2\pi^{-\frac{1}{2}}\left\{\frac{4}{1.3}\frac{\Gamma(\frac{7}{4})}{\frac{5}{4}\Gamma(\frac{5}{4})}+\frac{4}{3.5}\frac{\frac{5}{4}\Gamma(\frac{5}{4})}{\frac{7}{4}\Gamma(\frac{7}{4})}x -\frac{4}{5.7.2!}\frac{\frac{7}{4}\Gamma(\frac{7}{4})}{\frac{9}{4}.\frac{5}{4}.\Gamma(\frac{5}{4})}x^2-\frac{4}{7.9.3!}\frac{\frac{9}{4}.\frac{5}{4}\Gamma(\frac{5}{4})}{\frac{11}{4}.\frac{7}{4}\Gamma(\frac{7}{4})}x^3 +\frac{4}{9.11.4!}\frac{\frac{11}{4}.\frac{7}{4}\Gamma(\frac{7}{4})}{\frac{13}{4}.\frac{9}{4}.\frac{5}{4}\Gamma(\frac{5}{4})}x^4+\ldots\right\}, \quad (78)$$

where $\Gamma(\frac{5}{4})=0{\cdot}9064\ldots$, $\Gamma(\frac{7}{4})=0{\cdot}9190\ldots$, and the signs look after themselves. The terms are those of $g_1(x)$ (equation (68)) multiplied by a factor that has the value 0·91 ... for the first term and gradually decreases.

6. Particular layer shapes

The shapes to which the discussion in the previous section is directly applicable are

(i) triangle (any orientation),
(ii) parallelogram (any orientation),
(iii) regular hexagon ('side-on' only), and
(iv) circle (any orientation).

These will be considered in turn.

(i) *Triangle*

Let the sides of the triangle ABC be a, b, c, and its angles α, β, γ. Let the angle between AB and $\mathbf{S}_0$, measured in the same sense as α, be ψ. The sides of the triangle common to the layer and its ghost shifted a distance t parallel to $\mathbf{S}_0$ are reduced by the factor $(1-t/\tau)$, where τ has the following values, depending on the angle ψ:

$$\left.\begin{aligned}&\tau = c\sin\beta/\sin(\beta+\psi)\\ \text{for}\quad &0\leqslant\psi\leqslant\alpha \quad\text{or}\quad \pi\leqslant\psi\leqslant\pi+\alpha,\end{aligned}\right\} \tag{79}$$

$$\left.\begin{aligned}&\tau = b\sin\alpha/\sin\psi\\ \text{for}\quad &\alpha\leqslant\psi\leqslant\pi-\beta \quad\text{or}\quad \pi+\alpha\leqslant\psi\leqslant 2\pi-\beta,\end{aligned}\right\} \tag{80}$$

$$\left.\begin{aligned}&\tau = c\sin\alpha/\sin(\psi-\alpha)\\ \text{for}\quad &\pi-\beta\leqslant\psi\leqslant\pi \quad\text{or}\quad 2\pi-\beta\leqslant\psi\leqslant 2\pi.\end{aligned}\right\} \tag{81}$$

The area of the triangle is reduced by the square of this factor:

$$A(t) = p^2(1-t/\tau)^2, \tag{82}$$

$$a(\xi) = (1-\xi/x)^2 = 1-2\xi/x+\xi^2/x^2, \tag{83}$$

so that η (equation (36)) is unity, and the line profile is

$$K(x) = g_1(x)+g_2(x), \tag{84}$$

where $x = 2\pi\sigma\tau$, and τ is given by (79)–(81). The trigonometric terms in the asymptotic expansion of $K(x)$ cancel in this case, at any rate as far as x^{-2}.

(ii) *Parallelogram*

Let the side AB of the parallelogram $ABCD$ be c, and the side AC be b, and the included angle be α. Let the angle between $\mathbf{S}_0$ and AB, measured in the same sense as α, be ψ. The sides of the parallelogram common to the layer and its ghost are $c-t\,|\sin(\alpha-\psi)|/\sin\alpha$ and $b-t\,|\sin\psi|/\sin\alpha$, so that

$$A(t) = p^2\left\{1-\frac{t\,|\sin(\alpha-\psi)|}{c\sin\alpha}\right\}\left\{1-\frac{t\,|\sin\psi|}{b\sin\alpha}\right\}. \tag{85}$$

The value of τ is the smaller of $c\sin\alpha/|\sin(\alpha-\psi)|$ and $b\sin\alpha/|\sin\psi|$, and the value of η is the ratio $c\,|\sin\psi|/b\,|\sin(\alpha-\psi)|$ if this is less than unity, or its reciprocal if the ratio is greater than unity. The line profile is

$$K(x) = g_1(x)+\eta g_2(x). \tag{86}$$

For a square η is $|\tan\psi|$ or $|\cot\psi|$, whichever is less than unity.

(iii) *Hexagon 'side-on'*

The area common to a regular hexagon and its ghost shifted a distance t perpendicular to one side is

$$A(t) = \frac{3\sqrt{3}\,a^2}{2}\left\{1-\frac{t}{3\sqrt{3}\,a}\right\}\left\{1-\frac{t}{\sqrt{3}\,a}\right\}, \tag{87}$$

where a is the length of one side, so that

$$\tau = \sqrt{3}\,a = \sqrt{2}\,p/\sqrt[4]{3},$$

and

$$a(\xi) = (1-\xi/3x)(1-\xi/x), \tag{88}$$

$$\eta = 1/3. \tag{89}$$

The line profile is therefore

$$K(x) = g_1(x)+\tfrac{1}{3}g_2(x). \tag{90}$$

(iv) *Circle*

Series valid for small x have already been given. They are not simply related to the functions g_1 and g_2.

For comparison it is instructive to plot a quantity proportional to $I(\sigma)$ against σ for a few typical shapes. This is achieved by plotting $\tau^{\frac{1}{2}}K(x)$ with the x scale compressed in the ratio p/τ for the various shapes. Fig. 3 shows $I(\sigma)$ plotted in this way for a square 'side-on' and 'corner-on' with Warren's function also for

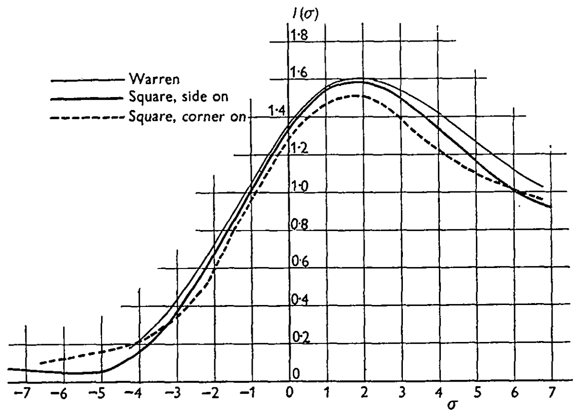

Fig. 3. Line profiles for random square layers.

comparison. It will be seen that for small σ Warren's function is a little too big, and this is confirmed by the other regular shapes so far discussed. All show the same general trend with σ, with variations of the same order of magnitude as the difference between the two orientations of the square. The differences are hardly large enough to be easy to distinguish experimentally.

The author is grateful to Dr G. W. Brindley, Prof. G. H. Livens, and Dr A. R. Stokes for helpful criticism at various stages in the preparation of this paper. It forms part of an investigation of imperfect structures for which an apparatus grant has been received from the Royal Society.

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