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The Effects of Granularity on the Diffracted Intensity in Powders

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The particle size, shape and the geometry of packing may affect the diffracted intensity in a powder. Previous considerations of the statistical aspects of the problem have yielded somewhat conflicting results. The present treatment contributes toward resolving these results by providing a simplified but still exact formulation of the expression for the intensity. It is shown that in addition to the usual expression for the intensity associated with an infinite homogeneous solid there is a corrective term. This term depends in detail on the correlations between a ray's absorbing path in and out of the powder. The correction term vanishes when there are no correlations between these paths. As an example of the effect of correlations, we have obtained the correction term for a simple model of a powder which should be a good approximation in the limit of small porosity. The correction is found to go to zero in the limit of normal incidence in accord with the rigorous results.

Introduction

Recent efforts to measure the absolute diffracted intensity from powders to obtain accurate values of the form factors (Batterman, Chipman & DeMarco, 1961) required reliable estimates of effects of granularity. Although the granularity corrections involved are small, the observed differences between theoretical and experimental form factors are also small. It is therefore important to obtain a rigorous upper limit for such corrections as well as a better understanding of the effects of granularity, if further accurate absolute measurements are to be made.

Various attempts have been made to solve for the effects of particle size, shape and the geometry of packing on the diffracted intensity in a powder. These attempts have yielded differing results for the reflected intensity. Brindley (1945) found an expression for the correction factor which in the absence of extinction effects would reduce to zero in the case of a one-component powder. De Wolff (1947) later gave an elaborate statistical formulation of the problem and pointed out that Brindley's method of averaging was subject to some criticism. De Wolff emphasized that the distribution of absorbing paths between the surface and the point of reflection must be described by a probability distribution which is conditional upon there being a particle at the point of reflection. De Wolff's formulation was mainly directed at the transmission problem previously considered by Schäfer (1933) for a simpler geometry and where one-dimensional considerations are sufficient. His treatment of the reflection problem was less rigorous. Wilchinsky (1951) gave a treatment of the reflection problem based on a simple geometric model of a powder, without attempting a rigorous statistical treatment.

In the present paper, we consider the problem of reflection from an infinitely thick porous sample. We neglect all extinction effects. We assume diffraction from a sample with plane surface, with angles of incidence and reflection equal, and assume the beam wide enough and the sample statistically homogeneous so that results do not depend upon just what portion of the surface of the sample the beam strikes. We neglect beam spreading effects introduced by the diffraction at various depths.

We first derive a simple but general expression for the reflected intensity which exhibits directly the salient features of the problem. We are able to separate the expression into two terms: a term which gives rise to the usual bulk infinite solid absorption factor and an additional term which gives the correction to this term. After discussing some general features of the corrective term, we examine this term for a model which has validity in the limiting case of small porosity.

Formal solution

We consider the case of a porous solid with an impinging beam whose area is wide enough so that its average intensity is equal to the statistical average of the intensity of an infinitesimally narrow beam. In this way we replace statistical averaging by an average over the area of the surface hit by the beam.

Before going into the detailed formulation, it is of value to discuss the problem in terms of a naive model which leads one to expect that an infinite powder might act like an infinite homogeneous solid. For a homogeneous solid, the intensity of the beam is $I_0 \exp(-\mu L)$, at a depth $L \sin\theta$, where L is the distance measured along the ray from the surface to the point of reflection and θ is the angle of incidence = the angle of reflection. If μ is the linear absorption coefficient for the solid, the contribution to the intensity of the emerging beam per increment of path

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length dL is proportional to $\exp(-2\mu L)$ where the paths in and out are of equal length. Integrating over the total path from zero to infinity we find that the total intensity I is proportional to $1/(2\mu)$. (If we had considered transmission through a solid of thickness $D\sin\theta$, the transmitted intensity would have been proportional to $\exp(-\mu D)$.)

If one now calls the absorbing path length L_a as opposed to the geometrical path length L, the absorption factor, between the point of incidence at the surface and the point of reflection, is $\exp(-\mu L_a)$. The intensity is proportional to the incremental length in the material dL_a. *Under the assumption that the absorption path getting out is also* L_a, the integral of the expression $\exp(-2\mu L_a)dL_a$ from zero to infinity yields the total intensity which again is proportional to $1/(2\mu)$. In this calculation the voids have contributed neither to the absorption nor to the reflected intensity. Therefore, the powder has been treated as a homogeneous solid and has obviously yielded the same result as for this case. Actually the only essential assumption necessary for this result is that the absorbing paths in and out are equal. While this assumption is true for a solid and on the average for a powder, it is not identically true for individual paths except for normal incidence. For normal incidence the argument given is rigorous

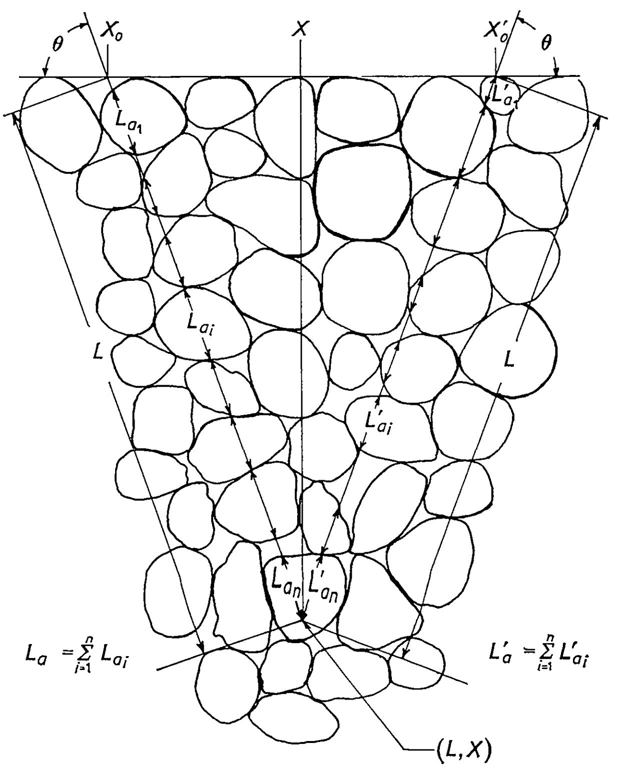

Fig. 1. A schematic representation of L_a and L_a', the absorbing paths in and out, respectively, for a given path length L. X_0 and X_0' are the points of intersection with the surface of the incoming and outgoing rays respectively, and X is the geometric point of reflection.

and the result will prove to be a special case of our more general treatment. In general it is the difference in the absorbing paths in and out which gives rise to the correction over the infinite solid contribution and also to the difficulties in formulating the problem in general.

We denote the absorbing path lengths in and out by L_a and L_a' respectively and the coordinates of the point of reflection L and X where L is the geometric path length as before and X is a coordinate in the plane of incidence, parallel to the surface (Fig. 1). It is apparent that at any given point L, X (in a given plane of incidence), the geometry of particle distribution determines the functions $L_a(L, X)$ and $L_a'(L, X)$. It might be noted that a beam reflected from L, X is incident at the surface at point $X_0 = X - L\cos\theta$. Thus, for a beam incident at some point X_0, the reflected intensity will be given by an integral over all L with X specified by $X_0 + L\cos\theta$. The total intensity of the beam is obtained by integrating over all X_0 within the incident beam width. As previously stated, we assume the beam to be wide enough to give a good statistical average. For convenience the final integrations will be performed over the variables L and X rather than L and X_0. (The Jacobian of the transformation is unity.) Let $P(L, X)dLdX$ be the contribution to intensity of the reflected beam associated with the volume element $dLdX$, and associated with absorbing path lengths $L_a(L, X)$ and $L_a'(L, X)$. $P(L, X)$ will be zero for those cases where there is no particle at (L, X) and otherwise equal to $I_0 \exp[-\mu(L_a + L_a')]$, where I_0 is the normalized intensity, Thus,

$$I = \frac{1}{(X_B - X_A)} \int_0^\infty \int_{X_A + L\cos\theta}^{X_B + L\cos\theta} P(L, X)\, dX\, dL \qquad (1)$$

where the integration of X corresponds to the range of X_0 within the beam, defined by the limits X_A and X_B. We have included a normalization factor $1/(X_B - X_A)$, assuming unit dimensions for the other dimension of the beam, and with the tacit assumption that averaging over this other dimension would not change the result because of the assumed statistical homogeneity of the sample. We may write

$$P(L, X) = I_0 \exp[-\mu(L_a + L_a')]\Delta(L, X)\,, \qquad (2)$$

where $\Delta(L, X)$ is so defined that it is unity when there is a particle at (L, X) and zero when there is no particle there. We now show that it is possible to give an explicit form for $\Delta(L, X)$.

The quantity $(\partial L_a/\partial L)_{X_0}$ represents the change in absorption length with geometric length, for a ray entering at a fixed point X_0. It has the desired property of being unity if there is a particle at (L, X) and zero if there is not. Similarly $(\partial L_a'/\partial L)_{X_0'}$ has the same property, considering a fixed point X_0' of emergence of the ray, where $X_0' = X + L\cos\theta$. But

$$(\partial L_a/\partial L)_{X_0} = (\partial L_a/\partial L)_X + (\partial L_a/\partial X)(\partial X/\partial L)_{X_0}\,,$$

with $(\partial X/\partial L)_{X_0} = \cos\theta$.* Similarly

$$(\partial L_a'/\partial L)_{X'_0} = (\partial L_a'/\partial L)_X + (\partial L_a'/\partial X)(\partial X/\partial L)_{X'_0}\,,$$

with $(\partial X/\partial L)_{X'_0} = -\cos\theta$. We choose to define $\Delta(L, X)$ as the symmetric combination,

$$\Delta(L, X) \equiv \tfrac{1}{2}\{[\partial(L_a+L_a')/\partial L]_X + \cos\theta\,[\partial(L_a-L_a')/\partial X]_L\}\,. \quad (3)$$

With this choice, equation (1) becomes

$$I = I_1 + I_2\,, \quad (4)$$

where

$$I_1 = \frac{I_0}{X_B - X_A}\int_0^\infty dL \int_{X_A+L\cos\theta}^{X_B+L\cos\theta} \times \tfrac{1}{2}[\exp -\mu(L_a+L_a')]\left(\frac{\partial(L_a+L_a')}{\partial L}\right)_X dX\,. \quad (5)$$

$$I_2 = \frac{I_0\cos\theta}{X_B - X_A}\int_0^\infty dL \int_{X_A+L\cos\theta}^{X_B+L\cos\theta} \times \tfrac{1}{2}[\exp -\mu(L_a+L_a')]\left(\frac{\partial(L_a-L_a')}{\partial X}\right)_L dX\,. \quad (6)$$

Examining I_1 we find that

$$\frac{I_1}{I_0} = \frac{1}{X_B - X_A}\int_{X_A}^{X_B} dX \int_0^\infty dL \times \tfrac{1}{2}\exp[-\mu(L_a+L_a')]\left(\frac{\partial(L_a+L_a')}{\partial L}\right)^X + C \quad (7)$$

where C represents a beam spreading correction term. In the Appendix we show that this term is vanishingly small in the limit that the beam is wide compared with the average penetration depth. The integral in equation (7) may now be performed without making any assumptions or restrictions to particular models for the distribution of path lengths in and out yielding the result

$$I_1/I_0 = 1/(2\mu)\,. \quad (8)$$

Since we see that I_1 is in itself just the intensity corresponding to an infinite, non-porous solid, I_2 must contain any correction arising from the granularity. It might be pointed out that this separation into I_1 and I_2 is not a trivial separation, in that it does not simply subtract off from the expression for the intensity the $1/(2\mu)$ factor for the infinite solid. Rather the nature of the separation was such as to produce the I_1 term whose value could be determined independent of the distribution and correlations of the absorbing paths in and out plus an I_2 term which we shall subsequently show does depend on the correlations and distribution of absorbing paths in and out. It is worth emphasizing again that the formulation for I in terms of the infinite continuous solid and a correction is exact and makes no assumptions or restrictions on the distribution of path lengths in and out.

* We assume that all the derivatives of L_a and L'_a are piecewise continuous, in accord with the properties of $(\partial L_a/\partial L)_{X_0}$.

Granularity correction term

General discussion

Before attempting to evaluate I_2, it is of value to look at the various contributions in a qualitative way. We first note that in general, the average (over X) values of $(\partial L_a/\partial X)_L$ and $(\partial L_a'/\partial X)_L$ are zero, as we expect equal positive and negative contributions. The reason that the integral of each of these terms is not zero is that the absorption coefficient gives different weighting to the positive and negative fluctuations. If the paths in and out are completely uncorrelated throughout, we would still expect the two terms to be identical and hence to give zero difference. If the paths in and out were identical, as they would be for $\theta = 90°$, or for a solid with laminations parallel to the surface, I_2 would then again be identically zero. De Wolff (1956) has already pointed out that the granular correction vanishes at normal incidence. With horizontal laminations, the quantities $(\partial L_a/\partial X)_L$ and $(\partial L_a'/\partial X)_L$ will of course individually be identically zero; one may also expect that for geometries consisting of flaky particles with planes roughly parallel to the surface, I_2 will remain small for angles differing appreciably from 90°. Thus, to summarize this qualitative discussion, a non-zero value of I_2 depends on having fluctuations in density in a direction parallel to the surface. Moreover it depends on the difference in the integral over the paths in and out of these density fluctuations. It is worth emphasizing the fact, implicit in the derivation of our equations for the intensity, that the averages that we are discussing are over all points L, X *regardless of whether there is a reflecting particle at this point.* This considerably simplifies any calculation, since one does not have to introduce conditional probabilities for certain events depending on whether a particle is there. Thus, for example, it puts voids and particles on an equal footing in that there are changes in the path length in and out arising both when the end point (L, X) is in a void as well as when it is at a particle. This will become clear in the following example which will serve to give a quantitative estimate of the corrective term.

To facilitate examining the correction term I_2, we write it in the form

$$I_2 = I_0\int_0^\infty dL\,\mathscr{I}_2(L,\theta) \quad (9)$$

where $\mathscr{I}_2$ is given by

$$\mathscr{I}_2(L,\theta) = \frac{\cos\theta}{2(X_B - X_A)}\int_{X_A+L\cos\theta}^{X_B+L\cos\theta} \times \exp[-\mu(L_a+L_a')]\left[\left(\frac{\partial L_a}{\partial X}\right)_L - \left(\frac{\partial L_a'}{\partial X}\right)_L\right] dX\,. \quad (10)$$

It might be noted that the factor $(X_B - X_A)^{-1}$ enters into the definition of $\mathscr{I}_2$. Since we are only interested in $\mathscr{I}_2$ in the limit that $\mu(X_B - X_A)$ is very large, then

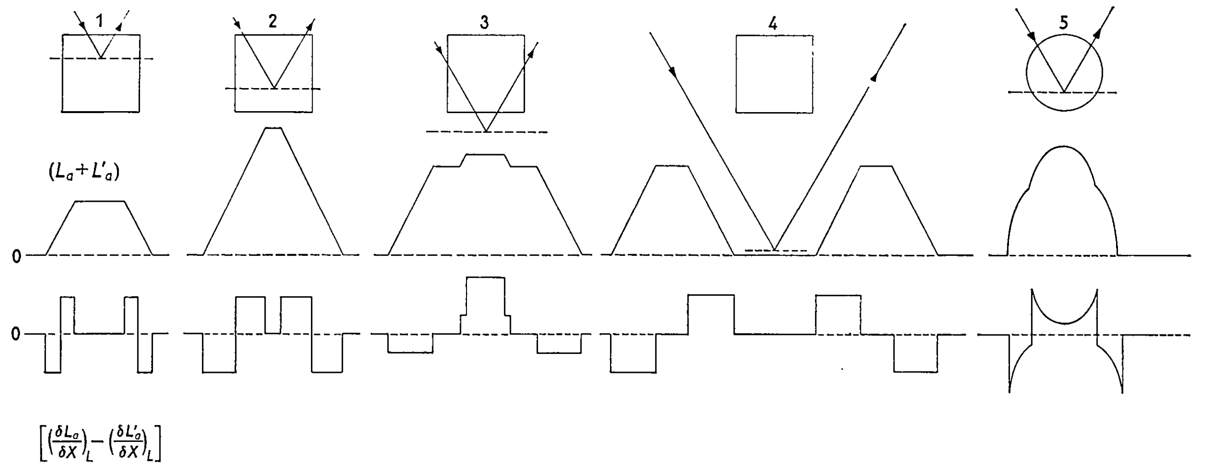

Fig. 2. The absorbing paths L_a and L_a' and their appropriate derivatives as a function of X for a cubic particle and a cylinder. Sections 1–4 give these parameters for the same angle of incidence and different geometric paths of reflection.

we shall regard as zero any term which vanishes in this limit. It might first be noted that $\mathscr{I}_2$ is zero when the absorbing paths in and out are completely uncorrelated. From equation (10) we can write $\mathscr{I}_2$ (uncorrelated)

$$\begin{aligned}\mathscr{I}_2 &\text{ (uncorrelated)}\\ &= \frac{\cos\theta}{2(X_B-X_A)}\Big\{\langle\exp(-\mu L_a')\rangle\int\exp(-\mu L_a)dL_a\\ &\qquad -\langle\exp(-\mu L_a)\rangle\int\exp(-\mu L_a')dL_a'\Big\}\\ &= \frac{\cos\theta}{2\mu(X_B-X_A)}\{\langle\exp(-\mu L_a')\rangle\exp(-\mu L_a)\\ &\qquad -\langle\exp(-\mu L_a)\rangle\exp(-\mu L_a')\}\Big|_{X_A+L\cos\theta}^{X_B+L\cos\theta}\\ &\cong 0 \end{aligned} \tag{11}$$

where in the integral over dL_a we have replaced $\exp(-\mu L_a')$ by its average value and $\exp(-\mu L_a)$ by its average in the integral over dL_a', in accord with the lack of correlation between L_a and L_a'. It should be noted that the separate terms in equation (11) go to zero in the sense defined above. However, this result does not obtain in general when correlations do exist between L_a and L_a'. The correlations of course depend explicitly on the geometry. For a random collection of particles or pores one would expect that the paths would be uncorrelated except where the paths in and out are through the same particle or a closely correlated group of particles. It is therefore useful to consider the correlation arising specifically when the incoming and the outgoing rays are associated with the same particle. For simplicity, the particles are taken to be cubes with planes parallel to the plane of the ray and the surface of the powder. The results, however, are not thought to be sensitive to the geometry. In Fig. 2, we plot the sum of the incoming and outgoing absorbing paths and the derivative of their differences as a function of X. The only non-zero contribution to $\mathscr{I}_2$ will arise when for a given L, there exists a region in X where L_a and L_a' are simultaneously passing through the particle. This corresponds to the region of correlation or overlap. It should be noted that the region of overlap

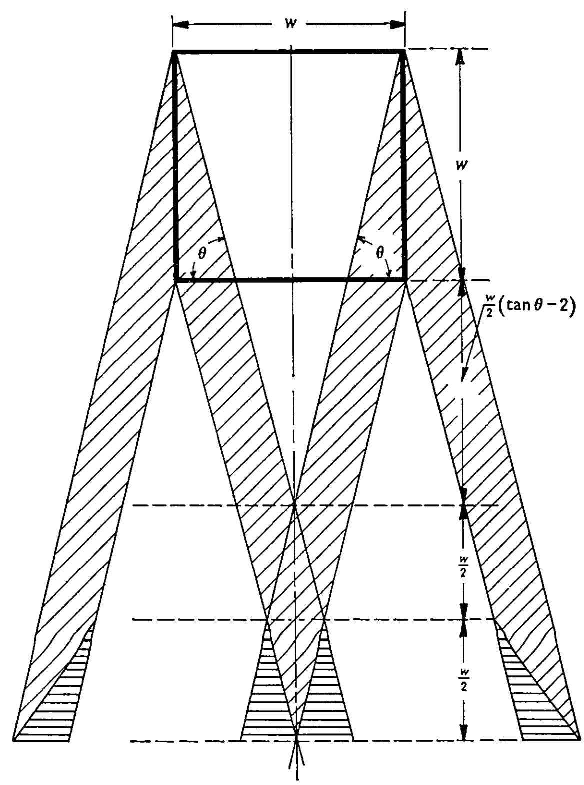

Fig. 3. Region of 'overlap' or 'correlation' about a cubic particle. Contributions to absorption correction arise from shaded portions. Interior unshaded regions give no correction since the two absorbing paths are equal. The heavily shaded regions give mutually cancelling contributions leaving only the diagonally shaded regions as the overlap contribution.

is larger than the particle depth. Fig. 3 depicts the region of overlap around such a particle. In Fig. 2 we also give the absorbing paths for a circular cross-section which shows qualitatively similar results. One can also see the sign of the correction term from these figures, namely, the derivative term is negative where the $L_a+L'_a$ is smallest. Because of the negative sign in the exponent, the negative contribution is therefore larger and the correction is negative. The correction term has the same sign for a pore (for now the derivative term is negative when the absorbing path is smallest and positive when the absorbing path is largest). In the case that there is more than one pore or particle, it is apparent that as long as there are no special correlations between them, and they are not within regions of overlap, the contributions to I_2 are additive.

Estimate for dilutely porous solid

We have therefore considered the corrections for a solid with small well-separated pores, such that $(1-\alpha)$, the fraction of space filled by pores, is small. Our method of computing the contribution from each pore requires that we do a rather extensive set of integrations for each angular region of interest. As the results in the region of normal incidence are of particular interest, we first derive the expression for I_2 valid in the range $\tan\theta \geq 2$. For a cubic pore of dimension w at

$$I_2^0\,(\tan\theta\geq 2) = -\frac{I_0\cos\theta}{(X_B-X_A)2\mu^2} \times [C-(1-\exp[-S])(2-C-2\exp[-C]) - \tfrac{1}{2}\exp[-S]\sinh 2C] \tag{12}$$

where

$$S=\mu w\sec\theta \quad\text{and}\quad C=\mu w\csc\theta\,.$$

In this calculation, I_2^0 is the intensity per pore taken to be located with top at zero depth. (In the following, we will denote the position of the pore by the location of its top surface.) We now examine the effect of having a distribution of pores in depth. If the pore under consideration were the only pore in the solid, its effect at depth $\sin\theta$ would be reduced by the absorption factor $\exp(-2\mu l)$. The effect of having intervening pores between the surface of the solid and position of the pore is to reduce the total absorbing path by the length of pores intercepted. We denote the absorbing paths between the surface and the depth of the pore by l_a and l'_a, so that the absorption factor entering because of the finite depth of the pore is $\exp(-2\mu(l_a+l'_a))$. In principle this factor, which is a function of the variables L, X, should be introduced into the integration over the pore geometry to obtain the contribution to I_2 of the particular pore. However, with the assumption that there is no correlation between the position of the pores, the fluctuations in values of l_a and l'_a from their average values are uncorrelated with the position of the pore, and the average effect of a pore at depth $l\sin\theta$ is just the result for a pore at zero depth multiplied by

$$\langle\exp-\mu(l_a+l'_a)\rangle_{\text{Av}} \simeq \exp(-2\mu\alpha l) \times[1+\tfrac{1}{2}\mu\langle(2\alpha l-l_a-l'_a)^2\rangle_{\text{Av}}]\,.$$

The average number of pores per unit volume is $(1-\alpha)/w^3$, and the total effect is obtained by integrating over depth and the beam with (X_B-X_A) for unit transverse dimension. The resultant expression is

$$\frac{1}{2\mu}\,\frac{(1-\alpha)}{\alpha}\,\frac{(X_B-X_A)I_2^0}{w^2\csc\theta} \tag{13}$$

The fluctuation term has been neglected since it is a factor of order μw smaller than the term retained. Where μw is not small compared with unity a different treatment would have to be used.

One must further add the contribution to the absorption correction arising from pores which are intercepted by the surface and do not appear as full pores. The number of these pores per unit length is $(1-\alpha)/w$. If one assumes that the average correction per pore of these is bI_2^0, then the total absorption correction I_2 is given by

$$I_2=\frac{(1-\alpha)(X_B-X_A)}{2\mu\alpha w^2\csc\theta}[1+2b\alpha\mu w\csc\theta]I_2^0. \tag{14}$$

We have not computed the magnitude of b as a function of angle and μw for our model but instead have taken $b\alpha$ to be one-half. For the region $\tan\theta\geq 2$, and using equations (12) and (14) we obtain for I_2

$$I_2\,(\tan\theta\geq 2) = -\frac{I_0(1-\alpha)}{4\mu SC\alpha} \times[C-(1-\exp[-S])(2-C-2\exp[-C]) - \tfrac{1}{2}\exp[-S]\sinh 2C][1+C] \tag{15}$$

where α is the ratio of the apparent density to the bulk density. To obtain a semi-quantitative estimate of I_2 for the case C and S much less than unity, we expand exponentials in equation (15) to obtain

$$I_2\,(\tan\theta\geq 2)\cong -\frac{I_0}{4\mu}\,\frac{(1-\alpha)}{\alpha}\,C\left(1-\frac{2\cot\theta}{3}\right). \tag{16}$$

We are interested in seeing whether the correction goes to zero smoothly as the angle of incidence approaches 90°. For this case, $S \gg \mu w$ and we return to equation (15) to find

$$I_2\cong -\frac{I_0}{4\mu}\,\frac{(1-\alpha)}{\alpha}\cos\theta\,. \tag{17}$$

Thus, I_2 does go smoothly to zero within a small angular range as θ approaches 90° and there is no abrupt discontinuity in the correction factor, in agreement with intuition and the fluorescence measurements of de Wolff (1956). It should be remembered that the present calculation is for a dilutely porous solid such that the spacing between pores is larger than the overlap or correlation distance. This distance is angular dependent (Fig. 3) and in the region of 90° would be infinite if it were not for the absorption which effectively limits the correlation distance to $1/\mu$. Thus, the dilution requirement is likely to be violated for practical porosities.*

We now give an expression for I_2 valid in the range of smaller angles ($\theta \leq 45°$) in order to obtain the angular dependence of I_2 throughout. Without going into any of the steps (they closely parallel those made in obtaining equation (15)), we find

$$I_2(\theta \leq 45°) = -\frac{I_0(1-\alpha)}{4\mu C\alpha}\left[1-\frac{1}{S}(1-\exp[-S]) - \tfrac{1}{2}\exp[-2C+S]+\frac{1}{2S}\exp[-2C]\sinh S\right](1+C)\,. \quad (18)$$

Expanding functions for S and C much less than unity, we find

$$I_2(\theta \leq 45°) = -\frac{I_0(1-\alpha)}{4\mu\alpha}S(1-\tan\theta/3)\,. \quad (19)$$

In the region close to grazing incidence, the bulk contribution to equation (19) vanishes and one is left with the surface contribution

$$I_2(\theta \to 0) \simeq \frac{I_0(1-\alpha)}{2\mu}\left(\frac{b\mu w}{2}\right)\,. \quad (20)$$

In Fig. 4, we have taken $b\alpha=\frac{1}{2}$, on the assumption that the surface pores contribute half the correction

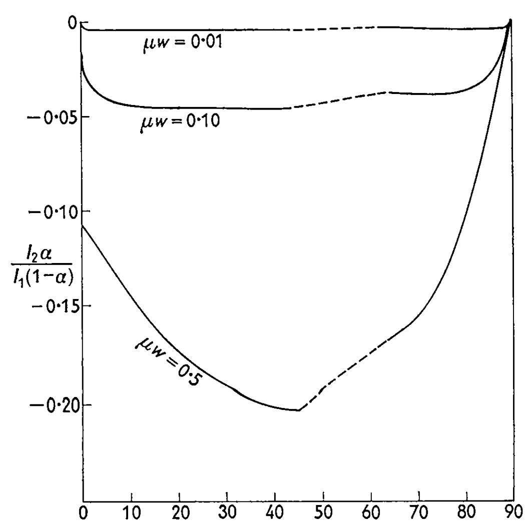

Fig. 4. $(I_2/I_1)\alpha/(1-\alpha)$ *versus* θ for a range of values of $\mu w=$ 0·01 − 0·5 corresponding to the range of effective particle size from fine to coarse, respectively. The dashed line was obtained by interpolation.

* P. M. de Wolff has commented (Private communication) that the way in which the correction term vanishes near 90° is one of the most important problems in this field.

of full pores. In the limit of grazing incidence, we might expect that the surface pores are as effective as the bulk pores and b is close to unity. In Fig. 4 we give the plot of relative correction I_2/I_1 *versus* θ computed according to the above approximation. The central region shown as a dashed line has been obtained by interpolation. It may be noted that for the two smaller absorptions, for which the calculations are more reliable, the correction term is small and fairly independent of angle except quite close to $\theta=90°$. As the angle of incidence goes to zero, surface effects become dominant and the apparent decrease in the correction term is not to be taken seriously because of the crude approximations made in estimating this term.

Conclusions

The present exact formulation of the granularity correction has made it possible to gain physical insight into the sources of this correction as well as to obtain a quantitative estimate of the correction. We find that the correlations between a ray's incoming and outgoing absorption lengths determine the magnitude of the correction term. In the special case where the correlated incoming and outgoing absorbing paths are identical, the correction vanishes. A zero correction also arises when there are no correlations; however, correlations of a more general nature will result in a non-zero correction. Correlations that do arise come almost entirely from particles or pores that are at or near the geometric point of reflection. We have estimated the magnitude of the correction term for a single pore utilizing cubic geometry for the pore shape. We have shown that this result can be used to obtain the correction term in a dilutely porous material, provided that the pores are more widely separated than the correlation or overlap distances. The neglect of extinction effects also mplies the assumption that the crystallites are irandomly oriented and small compared with any characteristic dimension involved in the description of porosity. Although the quantitative estimate of the correction term is given here for only a simple geometry, we think the present exact formulation will serve as a good starting point when more details of the geometry and statistics of particle distributions are introduced. Our present result is that the relative correction is of the order $(1-\alpha)\mu w/\alpha$. As the porosity increases, $(1-\alpha)$ would be replaced by α and the average pore size w by the average particle size since the role of pore and particle become interchanged as the average particle size becomes smaller than the average pore size. We would be rather surprised if more exact treatments should yield results significantly different from our present estimate.

It is difficult to make quantitative comparisons of the present theory with experiment. While the formulation of the problem is fairly exact, the quantitative estimate of the correction term is only valid for small porosity and small values of μw. In the measurements of Wilchinsky (1951), a point at small μw was normalized to his theoretical value and thus quantitative comparison is not possible. De Wolff (1956) used fluorescence to check theory. This technique is directly applicable to present theory provided that the absorption coefficients for the incident and fluorescent X-rays are equal, as they were in de Wolff's experiment. It also has the advantage that extinction and preferred orientation corrections are absent. De Wolff's fine particle data are closest to fitting the assumptions of our theory, and show a slowly varying correction at high angles, curving over towards zero for normal incidence in qualitative accord with theory. In the region of low angles the de Wolff data indicate an increasing porosity correction with decreasing angle whereas our calculation yields a decreasing correction with decreasing angle. In this region, our quantitative estimate is certainly less valid since detailed surface roughness corrections have not been made, while their importance is enhanced at low angles. It might be noted, however, that de Wolff's solid sample also shows some intensity decrease in the low-angle region, suggesting that at least part of the effect in this region for the particle samples also may not be due to porosity. Batterman, Chipman & DeMarco (1961) report that the fluorescence intensity from their porous and solid samples agreed within their experimental error (less than 2%). Since the bulk porosities of the Fe and Cu briquettes were 0·39 and 0·55, respectively (Chipman and DeMarco, private communications), we would expect the corrections to be about 5% for Fe and 10% for Cu. Although we have extended the theory to larger porosities than those for which the quantitative result is strictly applicable, nevertheless, we do believe a discrepancy exists. It is suggested that their pressing technique may have reduced the porosity close to the surface. As the diffracted intensity in their measurements arose mostly in the first 25 microns of the surface, the porosity correction could be considerably reduced. It becomes apparent that there is further need for a series of carefully controlled experiments on effect of porosity on intensity.

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APPENDIX

Reversing the order of integration in equation (5) and letting $L_a+L'_a \equiv \mathscr{L}[L, X]$ leads to

$$
\begin{aligned}
I_1 = {} & \frac{I_0}{2(X_B-X_A)} \\
& \times \int_{X_A}^{X_B} dX \int_0^{(X-X_A)\sec\theta} dL \exp\{-\mu\mathscr{L}[L, X]\} \left(\frac{\partial\mathscr{L}}{\partial L}\right)_X \\
& + \frac{I_0}{2(X_B-X_A)} \\
& \times \int_{X_B}^{\infty} \int_{(X-X_B)\sec\theta}^{(X-X_A)\sec\theta} dL \exp\{-\mu\mathscr{L}[L, X]\} \left(\frac{\partial\mathscr{L}}{\partial L}\right)_X .
\end{aligned}
$$

We can perform the integration over L, obtaining

$$
\begin{aligned}
I_1 = {} & \frac{I_0}{2\mu(X_B-X_A)} \left\{ \int_{X_A}^{X_B} dX \right. \\
& \left. + \int_{X_B}^{\infty} dX \exp[-\mu\mathscr{L}[(X-X_B)\sec\theta, X]] \right\} \\
& - \int_{X_A}^{\infty} dX \exp\{[-\mu\mathscr{L}[(X-X_A)\sec\theta, X]\} .
\end{aligned}
$$

Finally,

$$\frac{I_1}{I_0} = \frac{1}{2\mu} + C ,$$

where

$$
\begin{aligned}
C = {} & \frac{1}{2\mu(X_B-X_A)} \int_0^{\infty} dX' \\
& \times \{\exp(-\mu\mathscr{L}[X'\sec\theta, X'+X_B]) \\
& - \exp(-\mu\mathscr{L}[X'\sec\theta, X'+X_A])\} .
\end{aligned}
$$

C will not be identically zero in general. However its expectation value will be zero if X_B-X_A is large enough that there is no correlation between $\mathscr{L}(L, X)$ and $\mathscr{L}[L, X+X_B-X_A]$. This is usually the case, unless there is long range order in the granule geometry. For the complete correlation that exists for a non-porous solid, C will obviously be identically zero. Even if correlation exists, C will at most be of order

$$\frac{1}{2\mu}\,\frac{1}{\alpha\mu(X_B-X_A)\sec\theta} ,$$

where α is the ratio of average density to that of the non-porous solid. Therefore for wide enough beams, C can always be neglected.

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