

Microabsorption of X-ray Intensity in Randomly Packed Powder Specimens

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Abstract

The microabsorption of X-rays diffracted from planar granular powder specimens is caused by bulk porosity and surface roughness of the material. Methods of stochastic geometry are used to describe the geometrical characteristics of powder by volume fraction, mean chord length of powder particles, and density-density correlation function (covariance). Towards the surface of the specimen, the volume fraction of powder particles decays continuously from the bulk value to zero. Within the framework of the kinematic theory, analytical expressions are derived for both bulk and surface contributions to the microabsorption of symmetrically diffracted X-rays in randomly packed powder specimens with particles of irregular shape. Previous theoretical estimates and empirical formulae are discussed as limiting cases of the present more general results.

Introduction

The granular structure of powder specimens causes an angle-dependent contribution to the absorption of the incident and diffracted beams. This effect has been studied experimentally by de Wolff (1956) and by Suortti (1972; referred to as S) who measured the reduction of specimen fluorescence radiation due to granularity. Trucano & Batterman (1970) investigated the effect of porosity of amorphous powders, analysing diffuse scattering. Though the experimental results differ in some details, the intensity reduction due to granularity is described by a constant term proportional to volume fraction of pores, linear absorption coefficient, and mean chord length of particles, whereas the contribution of surface roughness is a smooth function of scattering angle. To our knowledge, the paper of S essentially represents the actual level of understanding of the effect of microabsorption.

Previous theoretical work on X-ray absorption in powder specimens suffers from a fragmentary description of porosity and surface roughness. Harrison & Paskin (1964) analysed the case of an isolated cubic pore and estimated correction terms for a dilutely porous solid. Otto (1984) calculated numerically the absorption of a special two-dimensional

computer model, in which the grains of the powder are simulated by circles of equal diameter. He was able to reproduce the experimental results of S qualitatively. On the other hand, a quantitative correction of X-ray scattering from granular specimens is desirable in certain cases (e.g. Valvoda & Čapcová, 1984). For these reasons, a refined analytical treatment of porosity and surface roughness seems to be useful.

In the present paper, we calculate the kinematical X-ray power reflected from a plane powder sample. The powder sample is described by the very general and variable three-dimensional Boolean model that has been developed within the framework of stochastic geometry (Stoyan, 1979; Stoyan, Kendall & Mecke, 1986). Contrary to the models of Harrison & Paskin (1964) and Otto (1984), our theory is not restricted to powder particles of certain regular shape. We derive analytical expressions for the contribution of both bulk porosity and surface roughness to the absorption of X-ray power. The relation of our formulae to previous estimates is discussed. Numerical results are given for various values of parameters and are compared to the experimental curves after S.

Structure model for powder

We consider statistically isotropic irregularly packed powder specimens. Corresponding to the lines of the Boolean model, the structure of such types of specimens is characterized in the following way: points $P_i = (x_i, y_i, z_i)$ are distributed randomly in the three-dimensional space. They are called germs. The number $N(G)$ of germs in an arbitrary region G obeys a Poisson distribution. Further, a sequence of isotropic independent identically distributed bounded random close sets A_1, A_2, \dots is generated. The A_n are called primary grains. Now, at each germ P_i one sample A_i of the primary grains is placed. The union of all primary grains A_i situated at P_i , or, in other words, that part of the space which is covered by one or by several primary grains, represents a random set A . In the present case, we use Poisson polyhedra as primary grains. A Poisson polyhedron is a typical mosaic stone of a random tessellation of space by random planes characterized by its mean width b . We use the complement A^c of the random set A as a structure model

for irregularly packed powder specimens (see Fig. 1). The mean chord length of A^c is known (Stoyan, Kendall & Mecke, 1986); it will be related to the mean chord length of powder particles. This means that the pores of the specimens are described by the union of randomly distributed Poisson polyhedra.

For the calculation of the absorption length of a ray reflected from the powder, an expression for the probability P of finding two points Q, Q' with distance r both belonging to A^c will be necessary. This probability is given by the covariance $C(r)$.

Obviously, $C(r \rightarrow 0) = \alpha$ and $C(r \rightarrow \infty) = \alpha^2$ where α is the volume fraction of powder particles. For a Boolean model with Poisson polyhedra we have (Sonntag, Stoyan & Hermann, 1981)

$$C(r) = \alpha^2 \exp[-(\ln \alpha) \exp(-r/\beta)], \quad \beta = 2b/3. \quad (1)$$

If α is sufficiently high ($0.7 \leq \alpha < 1$), (1) can be expanded in terms of $(1 - \alpha)$ and we obtain

$$C(r) = \alpha^2 + \alpha(1 - \alpha) \exp(-r/\beta), \quad (2)$$

a simple type of correlation function that has been discussed already by Debye & Bueche (1949), but without a geometrical interpretation of β . Whereas the bulk properties of the powder specimens are characterized by α, β and the covariance $C(r)$, we describe the surface structure of the specimen by

$$\alpha = \alpha(z) = \begin{cases} \alpha_0 [1 - \exp(-z)], & z \geq 0 \\ 0, & \text{otherwise} \end{cases} \quad (3)$$

with $z = t/t_0$, t is the coordinate perpendicular to the surface of the specimen (see Fig. 1). Parameter t_0 characterizes the surface roughness and α_0 is the packing fraction of the bulk material.

Absorption correction

The absorption path length of a ray reflected from point Q depends on the scattering angle θ and the

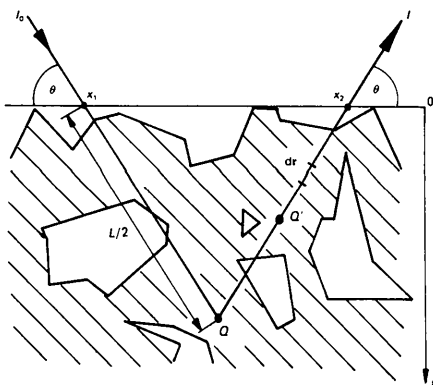


Fig. 1. Absorption length L_A in a powder specimen for the symmetrical case. L is the geometrical path length of the ray in the specimen. L_A is determined by the integral over all increments dr lying in powder particles.

distance t of Q from the surface (Fig. 1). Since the point of reflection Q is, of course, always situated in A^c the probability of finding another point Q' in A^c on the incident or reflected ray with distance r from Q is equal to $C(r)/\alpha$. Therefore, the absorption length L_A of the ray depicted in Fig. 1 is

$$L_A = \int_{x_1}^Q C(r)/\alpha \, dr + \int_Q^{x_2} C(r)/\alpha \, dr \\ = 2 \int_0^{L/2} C(r)/\alpha \, dr, \quad (4)$$

where L is the geometrical length of the beam in the specimen. For simplicity, the integrals are evaluated for symmetrically diffracted beams. In (4) a statistical average over a sufficiently large number of powder particles is carried out. Inserting (2) and (3) into (4) we obtain

$$\mu L_A / \varepsilon = \tau z / \sin \theta + (1 - \alpha_0) [1 - \exp(-\tau z / \sin \theta)] / \alpha_0 \\ - (\tau / \sin \theta) [1 - \exp(-z)] \\ + \{1 - \exp[-(\tau + \sin \theta)z / \sin \theta]\} \\ \times \tau / (\tau + \sin \theta); \\ \varepsilon = 2\mu\beta\alpha_0, \quad \tau = t_0/\beta. \quad (5)$$

Of course, the special cases $L_A = L$ (for $\alpha_0 \rightarrow 1$) and $L_A = \alpha_0 L$ (for $\beta/L \rightarrow 0$) follow from (5) for vanishing surface roughness ($t_0 = 0$).

According to Harrison & Paskin (1964) and S we write

$$I = I_0(1 - P)/2\mu = I_0 J \quad (6)$$

where P is the term resulting from both bulk granularity and surface roughness ($I_0 =$ normalized intensity). Now the problem is reduced to the evaluation of the integral

$$J = \int_{V_s} \exp(-\mu L_A) \, dV / Q_0 \\ = \int_0^\infty \alpha(z) \exp[-\mu L_A(z)] \beta \tau / \sin \theta \, dz \quad (7)$$

($Q_0 =$ cross section of incident beam, $V_s =$ volume of the sample). We insert (3) and (5) into (7). Terms of the type $\exp[c' \exp(-c''t)]$ with $c' = \varepsilon(1 - \alpha_0)/\alpha_0$ or $c' = \varepsilon\tau/(\tau + \sin \theta)$ are replaced by $1 + c' \exp(-c''t)$ with $c'' > 0$. The mean chord length \bar{l} of the powder particles is, within the present model, given by the mean chord length of the complement of the random set A : $\bar{l} = -\beta/\ln \alpha_0$ (Stoyan, Kendall & Mecke, 1986). Consequently, the condition for the validity of the approximation mentioned above reads as follows

$$\mu \bar{l} \ll [-2(1 - \alpha_0) \ln \alpha_0]^{-1}. \quad (8)$$

For example, we have $\mu \bar{l} \ll 1.5$ and $\mu \bar{l} \ll 5$ for $\alpha_0 = 0.5$ and 0.7 , respectively.

As a final result, we obtain

$$\begin{aligned}
 P &= 1 - \exp[-\varepsilon(1 - \alpha_0)/\alpha_0 + g - f] \\
 &\quad \times \sum_{n=0}^{\infty} (-1)^n g^{n+1} c_n/n!, \\
 c_n &= 1/(g+n)(g+n+1) \\
 &\quad + [\varepsilon(1 - \alpha_0)/\alpha_0]/(h+n)(h+n+1) \\
 &\quad + f/(h+n+1)(h+n+2) \\
 f &= \varepsilon\tau/(\tau + \sin \theta), \quad g = \varepsilon\tau/\sin \theta, \\
 h &= (1 + \varepsilon)\tau/\sin \theta. \quad (9)
 \end{aligned}$$

Discussion

(a) Vanishing surface roughness

Parameter $\tau = t_0/\beta = -t_0/\bar{l} \ln \alpha_0$ describes the degree of surface roughness. It is essentially the ratio of the thickness t_0 of the surface defined in (3) and the mean chord length \bar{l} of powder particles. The limiting case $\tau \rightarrow 0$ of vanishing surface roughness is realized by a planar cut through an infinitely extended porous material. From (9) we obtain for $\tau \rightarrow 0$

$$\begin{aligned}
 P_0 &= 1 - [1 + (1 - \alpha_0)\varepsilon^2/\alpha_0(1 + \varepsilon)] \\
 &\quad \times \exp[-(1 - \alpha_0)\varepsilon/\alpha_0]. \quad (10)
 \end{aligned}$$

This means:

(i) In the case of vanishing surface roughness the absorption correction does not depend on angle θ . The fictitious increase of P_0 for $\theta \rightarrow 90^\circ$ suggested by Harrison & Paskin (1964) is not found.

(ii) For the case $\varepsilon = 2\mu\beta\alpha_0 \ll 1$, which is generally realized in experiments,

$$P_0 = 2\mu\beta(1 - \alpha_0) = 2\mu\bar{l}(1 - \alpha_0) \ln \alpha_0^{-1} \quad (11a)$$

results from (10). For high volume fraction α_0 of powder particles we have

$$P_0 = 2\mu\bar{l}(1 - \alpha_0)^2. \quad (11b)$$

(b) Weak surface roughness

We expand (9) up to terms of order ε and $\tau^2/\sin^2 \theta$ and obtain

$$\begin{aligned}
 P(\theta) &= P_0 + P_s(\theta) \\
 P_s &= 2\mu\beta\alpha_0(\tau/\sin \theta)(1 - \tau/\sin \theta) \quad (12)
 \end{aligned}$$

where P_0 [see (11)] and P_s describe the absorption correction due to bulk porosity and surface roughness, respectively. The separation of P into a constant bulk term P_0 and the angle-dependent term P_s derived theoretically from our structure model for irregularly packed powder specimens is in accordance with the corresponding experimental results of S. In this paper, S discussed a surface roughness model and the corresponding formula $P_s = c_1[1 - \exp(-c_2/\sin \theta)]$ containing two adjustable

parameters c_1 and c_2 . If we expand this formula into a power series and compare the coefficients with our results (12) the empirical parameters c_1 and c_2 can be determined. We obtain $c_1 = \varepsilon/2$ and $c_2 = 2\tau$. Thus c_1 is given by the linear absorption coefficient μ , the mean chord length \bar{l} of powder particles, and the packing fraction α_0 whereas c_2 describes the degree of surface roughness τ .

(c) Extension to lower volume fraction of powder particles

One of the most important points of the present study is the application of an analytical expression for the covariance $C(r)$ derived from a well defined structure model for powder specimens. The covariance presented in (1) is valid for arbitrary volume fraction ($0 \leq \alpha \leq 1$) of powder particles. For simplicity, we calculated the absorption correction term P using the first-order approximation (2) which is correct for high volume fraction α of powder particles. Expanding (1) in a power series and taking into account second-order terms, we have for lower α values

$$\begin{aligned}
 C(r) &= \alpha^2 + \alpha(1 - \alpha) \exp(-r/\beta) \\
 &\quad - \frac{1}{2}\alpha(1 - \alpha)^2 \exp(-r/\beta)[1 - \exp(-r/\beta)].
 \end{aligned}$$

We consider the case of vanishing surface roughness $\tau = 0$ and $\mu\beta \ll 1$ and obtain for the bulk contribution to the absorption correction

$$P_0 = 2\mu\beta(1 - \alpha_0)[1 - (1 - \alpha_0)/4]. \quad (13)$$

According to (11), the absorption term P_0 for $\tau = 0$, $\mu\beta \ll 1$ calculated with covariance (2) is $P_0 = 2\mu\beta(1 - \alpha_0)$. This means that expression (11) for the bulk contribution to microabsorption calculated within the limit of high α is, in cases of low volume fraction α of powder particles, an upper limit for P_0 .

(d) Numerical results

In Fig. 2 the typical behaviour of the microabsorption dependence on the scattering angle is illustrated. The absorption is nearly constant at high scattering angles but increases rapidly at low θ . Experimental data after S are compared with the theoretical results. We assume the experimental values for α_0 to be most reliable, whereas \bar{l} is affected by some uncertainties arising, for example, from the finite resolution of micrographs from which the mean chord lengths of the powder specimens are determined. Variation of $\mu\bar{l}$ and τ with fixed α_0 leads to a good fit of the experimental points by the theoretical curves 1 ($\alpha_0 = 0.69$) and 4 ($\alpha_0 = 0.60$), respectively. The theoretical values for $\mu\bar{l}$ are smaller than the experimental ones which may be caused by the experimental uncertainties mentioned above.

The low values for the surface roughness parameter (0.05 and 0.08, respectively) are reasonable, since the samples had been prepared under high pressure against a polished steel plate. According to the definition in (5) the thickness of the surface region, where the structure deviates markedly from that of the bulk material, is $t_0 = \tau\beta$. For $\alpha_0 \approx 0.6$ to 1, β is of the order of the diameter of pores. Hence t_0 for the experimental cases discussed is about 1/10 to 1/20 of the mean pore diameter. The influence of surface roughness on the absorption is shown separately in Fig. 3.

For growing degree τ of surface roughness, the absorption increases. The range at $\theta \leq 90^\circ$ where P_s is nearly constant becomes smaller with increasing τ . The simple expression given by S represents, with parameters adjusted to the present model, a good approximation for very weak surface roughness but fails for $\tau > 0.1$ at low θ .

The dependence of P_s on $\mu\bar{l}$ is similar to that of τ [cf. (12)]. Since the penetration depth of a ray in comparison with t_0 diminishes with growing $\mu\bar{l}$, the influence of the surface region $0 \leq t \leq t_0$ increases compared with the bulk effect. For this reason, it is plausible that increasing τ and $\mu\bar{l}$ leads to similar changes of the $P_s(\theta)$ curves.

In Fig. 4 the bulk contribution P_0 to the absorption correction is plotted versus volume fraction of pores. P_0 increases with $1 - \alpha_0$ for all values of $\mu\bar{l}$ according to (10). The increase of P_0 with $1 - \alpha_0$ is essentially nonlinear and shows, for $\alpha_0 \leq 1$, a parabolic behaviour [see (11b)]. A linear behaviour of $P_0 = P_0(1 - \alpha_0)$ had been suggested by S who separated P_0 from the experimental values for the absorption by subtracting a simple model function [see part (b) of this section] describing the surface contribution P_s .

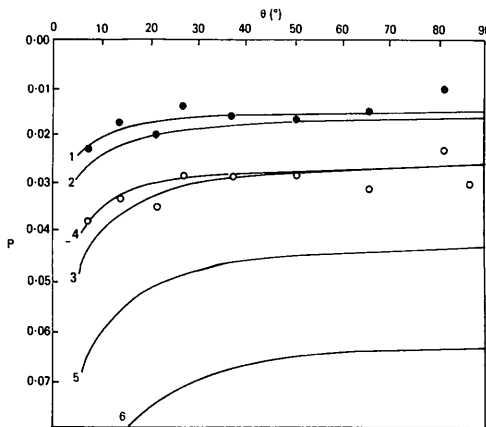


Fig. 2. Dependence of microabsorption P on scattering angle θ . Parameters ($\alpha_0, \mu\bar{l}, \tau$) of theoretical curves are 1: (0.69, 0.06, 0.05); 2: (0.69, 0.06, 0.10); 3: (0.69, 0.10, 0.10); 4: (0.60, 0.06, 0.08); 5: (0.60, 0.10, 0.10); 6: (0.60, 0.15, 0.10). Parameters of the experimental points after Suortti (1972): filled circles $\alpha_0 = 0.69, \mu\bar{l} = 0.10$; open circles $\alpha_0 = 0.60, \mu\bar{l} = 0.15$.

from the experimental P . An unambiguous experimental determination of the bulk contribution should be carried out using samples without surface roughness which may be prepared by a planar cut through a rigid porous material.

Concluding remarks

The present stochastic model describes the X-ray microabsorption of three-dimensional randomly packed flat specimens prepared from powder particles of irregular shape. Both bulk (P_0) and surface (P_s) contributions to the microabsorption are treated simultaneously and are presented in a concise analytic form. The microabsorption $P = P_0(\alpha_0, \mu\bar{l}) + P_s(\alpha_0, \mu\bar{l}, \theta)$ is a function of volume

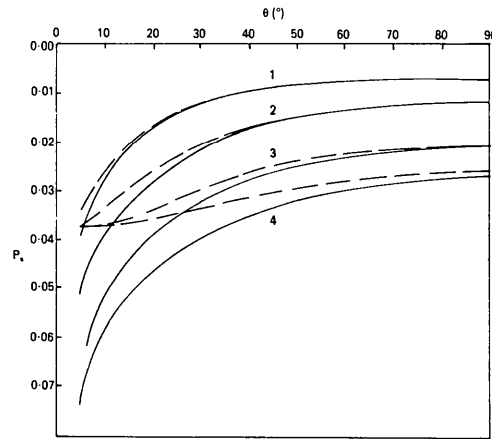


Fig. 3. Dependence of the surface contribution $P_s(\theta)$ on the degree τ of surface roughness ($\mu\bar{l} = 0.15, \alpha_0 = 0.70$). 1: $\tau = 0.1$; 2: $\tau = 0.2$; 3: $\tau = 0.4$; 4: $\tau = 0.6$; full curves present model, broken curves formula of Suortti (1972) with parameters adjusted to the present model.

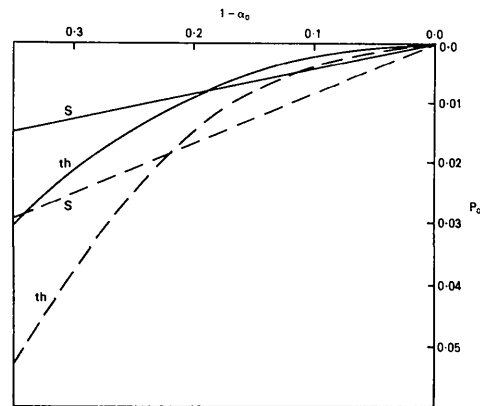


Fig. 4. Dependence of bulk contribution P_0 to absorption correction on volume fraction $1 - \alpha_0$ of pores for different values $\mu\bar{l}$ (full curves $\mu\bar{l} = 0.1$; broken curves $\mu\bar{l} = 0.2$); th = theoretical curves calculated from (10); S = estimate after Suortti (1972) given by the difference between experimental data and P_s calculated from a simple surface roughness model.

fraction α_0 of powder particles, linear absorption coefficient μ , mean chord length \bar{l} of powder particles and scattering angle θ . There are no dramatic effects of microabsorption if the packing fraction of powder particles and the scattering angle are not too small.

The theoretical results agree well with the experimental data after Suortti (1972) especially with respect to the dependence of the microabsorption on the scattering angle. For practical use, the approximate formulae (11), (12) should be sufficient in most cases.

The present method is applicable not only to powders but also to other heterogeneous specimens such as sinter materials. In forthcoming papers, the following related problems will be analysed: (i) microabsorption in quantitative phase analysis; (ii) influence of regularity of packing of powder particles on microabsorption.

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Deduction and Systematic Classification of Spatial Motifs of the Antiparallel β Structure in Globular Proteins

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Abstract

A systematic classification of complex topological types for polypeptide-chain folding in the antiparallel β form is proposed. Three well known simple topological types, β , m , g , were chosen as the basic ones: single β strand, hairpin of two strands and simple Greek key type of four strands. The new topologically allowed motifs are formed of a combination of the three basic motifs. All spatial motif types possible with this basis were considered for more complicated double Greek key motifs. This was done on the basis of a complete set of 14 basic spatial motifs of simple Greek key topology. Analysis of about 20 globular proteins shows that some spatial motifs appear to be realized as the main part of the chain fold of the molecule. This suggests that chain folds of antiparallel β proteins are necessarily conditioned by simple topological requirements.

1. Introduction

Polypeptide-chain folding in a globular protein molecule is evidently governed by general regularities. In particular, it depends on topological

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References

- DEBYE, P. & BUECHE, A. M. (1949). *J. Appl. Phys.* **20**, 518–525.
 HARRISON, R. J. & PASKIN, A. (1964). *Acta Cryst.* **17**, 325–331.
 OTTO, J. (1984). *Z. Kristallogr.* **167**, 55–64.
 SONNTAG, U., STOYAN, D. & HERMANN, H. (1981). *Phys. Status Solidi A*, **68**, 281–288.
 STOYAN, D. (1979). *Biom. Z.* **21**, 693–715.
 STOYAN, D., KENDALL, W. S. & MECKE, J. (1986). *Stochastic Geometry and its Applications*. Chichester: Wiley & Sons.
 SUORTTI, P. (1972). *J. Appl. Cryst.* **5**, 325–331.
 TRUCANO, P. & BATTERMAN, B. W. (1970). *J. Appl. Phys.* **41**, 3949–3953.
 VALVODA, V. & ČAPCOVÁ, P. (1984). *Phys. Status Solidi A*, **81**, 203–208.
 WOLFF, P. M. DE (1956). *Acta Cryst.* **9**, 682–683.

requirements for the main-chain fold and the packing symmetry of the repeated motifs (Ptitsyn & Finkelstein, 1980; McLachlan, 1980; Richardson, 1981). In recent years a number of new three-dimensional protein structures have been determined, and for many known protein structures the data have been considerably improved at higher resolution. This promotes a more successful study of the principles of protein structure. Two general topological motifs of the up-and-down and simple 'Greek key' types were shown to exist in globular β proteins (Richardson, 1977). A chain fold for such proteins or domains was shown to have a highly limited number of topological variants (Ptitsyn, Finkelstein & Falk, 1979; Finkelstein, Ptitsyn & Bendsko, 1979). Some of the possible spatial patterns for the simple 'Greek key' topology were shown to be part of the molecular architecture in β proteins (Efimov, 1982). Therefore, the next step in studying spatial motifs for the antiparallel β structure in proteins became possible. This consists of the deduction and classification of all topologically allowed spatial motifs. A preliminary communication on this topic has recently been published (Chirgadze, 1985). The practical significance of this study is a complete summary of spatial motifs of the antiparallel