

# Submicroscopic voids in glassy carbon

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Small angle X-ray scattering by glassy carbon was used to establish the characteristic of submicroscopic porosity. A monochromatized linear beam was used and corrections were made to obtain the scattering curve free of aberration. From analysis of the scattering curve, the voids were deduced to be oblate ellipsoids of revolution. Using the two-density theory, the geometrical parameters and concentration of the voids were determined. Fluctuations of atomic density in the carbon matrix were detected and their magnitude evaluated.

## 1. Introduction

Glassy carbon is a monolithic form of carbon produced by degradation of an organic polymer. The production of this material starts from an organic resin which is put in the desired form and continues with a pyrolysis heat-treatment at temperatures ranging from 500 to 3000°C. The properties of the glass-like carbon obtained depend mainly on the final heat-treatment temperature. The structure of glassy carbon shows interesting features. It consists of tetrahedrally bonded carbon atoms in an amorphous part which links graphite-like layers in a random way [1]. It has been observed that, with increased temperature of heat-treatment, the spacing between the layers of graphite decreases and the size of the crystals increases. With temperatures between 500 and 600°C the amorphous part amounts to 80% but it decreases with rising temperature so that at 3000°C it amounts to only 10%. X-ray patterns show diffraction lines belonging to graphite crystals whose size increase from about 10 Å at 500°C to 90 Å at 3000°C and superposed on these lines are diffuse rings from the amorphous part.

The density of pure graphite is 2.15 g cm<sup>-3</sup> while that of glassy carbon is less than 1.50 g cm<sup>-3</sup>. This great difference in density (larger than 30%) cannot be accounted for by the general observation that density decreases when materials pass from crystalline to amorphous state. Detection of an appreciable small-angle X-ray scattering from this material, indicative of the presence of inhomogeneities in the electron concentration, suggests the possibility of explain-

ing this great density difference by the presence of voids [2]. These must be very small as no substructure can be observed with an optical microscope.

A study of the small-angle X-ray scattering of glassy carbon was carried out [2] using a "linear and infinite collimation" mounting. From the scattering curves which were obtained, the presence of approximately  $3.6 \times 10^{18}$  voids cm<sup>-3</sup> was calculated. These voids may be assumed to have the shape of somewhat oblate ellipsoids of revolution, with minor half-axes varying between 10.6 and 25 Å for different types of samples produced by different heat-treatments, and the ratio of the major to minor axis varied between 1.07 and 1.35. The curves obtained by this author [2] conformed to Porod's law in all cases, supporting the hypothetical model with two electronic densities (uniform matrix and voids) and a step discontinuity at the interface between the two. This work was criticized by Perret and Ruland [3], who objected to the determination of the size of the voids from the values of the scattering angle at which Porod's law begins to be obeyed.

In view of the difficulty of obtaining a constant beam with the method of linear and infinite collimation, we decided to study a sample of glassy carbon by means of a beam with gaussian profile along the length of the slit. This profile allows us to correct the scattering curves and obtain the normalized scattering intensity free from aberrations, which is called the diffusion power  $i(h)$  [4], by a numerical calculation developed by Schmidt [5]. We point

out the convenience of this method, particularly for glassy carbon where the domain of scattering is very large. The use of linear and infinite collimation requires a beam of uniform intensity in an extension which is very difficult to obtain experimentally. We also used a monochromatic X-ray beam obtained by reflection from a quartz crystal, which represents an improvement over the conventional filtering used in the above-mentioned work.

## 2. Theory

To present the theory, we consider the small-angle scattering produced by a set of particles of uniform electronic density immersed in a medium also of uniform density but different from the particles (two-density system). Let us suppose these particles, in our case voids, to be sufficiently separated so that interference between the amplitudes scattered by different particles may be neglected.

Let us suppose the particles to be identical and oriented at random. Under these conditions, Guinier [4] gives the following formula for the diffusion power  $i(h)$  which is applicable to very small angles:

$$i(h) = i(0) \exp(-R_g^2 h^2/3) \quad (1)$$

where  $h = 4\pi (\sin \theta)/\lambda$ ;  $2\theta$  being the scattering angle,  $\lambda$  the wave length of the X-ray radiation, and  $R_g$  the radius of gyration of the particles with respect to their mass centres

$$R_g^2 = \frac{\int_V r^2 dV}{V}$$

where  $V$  is the volume of the particles. The intensity at the origin  $i(0)$  is related to the structure according to

$$i(0) = N \frac{(\rho - \rho_0)^2}{\bar{\rho}} V^2 \quad (2)$$

where  $N$  is the number of particles per unit volume,  $\rho_0$  the electronic density of the particles,  $\rho$  the electronic density of the matrix and  $\bar{\rho}$  the mean density. The value of  $i(0)$  is obtained by extrapolation of the experimental curve. If the intensity is isotropic, as in the case under consideration, we have an integral property [4]

$$\int_0^\infty h^2 i(h) dh = 2\pi^2 \frac{(\rho - \rho_0)^2}{\bar{\rho}} N V. \quad (3)$$

After obtaining the value of  $i(0)$  we can calculate  $N$  if we know the densities and the volume of the voids. The volume can be obtained by combining Equations 2 and 3

$$V = \frac{2\pi^2 i(0)}{\int_0^\infty h^2 i(h) dh}. \quad (4)$$

The limit of the large-angle scattering produced by a two-density system is given by Porod's law

$$i(h) = 2\pi \frac{(\rho - \rho_0)^2 S}{\bar{\rho} h^4} \quad (5)$$

where  $S$  is the surface of the interface per unit volume. Porod has shown that Equation 5 is valid for particles of uniform electronic density of any shape and for any number of particles per unit volume, provided the particles are oriented at random and none of their dimensions is "zero" (needle or plate-shaped). Equation 5 is not limited to low concentrations of particles because interparticle interference has very little effect at large scattering angles. For identical particles we have

$$h^4 i(h) = 2\pi \frac{(\rho - \rho_0)^2}{\bar{\rho}} N s \quad (6)$$

where  $s$  is the surface area of the particles.

Systematic deviations from Porod's law can occur when there are density fluctuations in the phases or when the interface is not well defined. In the first case, the deviation is positive, in the second negative. (Plotting  $h^4 i(h)$  versus  $h$  we have a positive deviation when the slope is positive at large angles and negative deviation when it is negative.) In the case of voids, it is evident that a fluctuation in density can exist only in the matrix. Assuming that there is a step discontinuity of the electron concentration at the interface, we have [6] for one-dimensional fluctuations

$$i(h) = \frac{b_0}{h^4} + \frac{b_1}{h^2}, \quad (7)$$

for two-dimensional fluctuations

$$i(h) = \frac{b_0}{h^4} + \frac{b_2}{h}, \quad (8)$$

and for three-dimensional fluctuations

$$i(h) = \frac{b_0}{h^4} + b_3 \quad (9)$$

where  $b_0$  is the limiting value of  $h^4 i(h)$  if Porod's law is satisfied and  $b_1$ ,  $b_2$  and  $b_3$  are parameters associated with the fluctuations. In the case of graphite, the one-dimensional fluctuations have an appreciable value in the direction perpendicular to the hexagonal planes and according to [7] we obtain

$$b_1 = \frac{F a_3}{K P} \int_0^\infty h^2 i(h) dh \quad (10)$$

where  $a_3$  is the mean spacing between the graphite layers,  $P$  is the fraction of the volume occupied by the voids,  $K$  is a term depending upon the distribution of the orientation of the hexagonal planes and  $F$ , the magnitude of the fluctuations, is given by

$$F = \frac{\bar{N}^2 - \bar{N}^2}{\bar{N}}$$

where  $\bar{N}$  indicates the mean value and  $\bar{N}^2$  the mean square value of the number of atoms. In the case of isotropy, as in glassy carbon,  $K=2/\pi$ , so that  $F$  is given by

$$F = \frac{2b_1 P}{a_3 \pi \int_0^\infty h^2 i(h) dh} \quad (11)$$

### 3. Experimental techniques

The sample we used corresponds to specification Lockheed LMSC 2000 (final heat-treatment at 2000°C). X-ray scattering was studied in the following way: a linear type beam produced by  $\text{CuK}\alpha$  radiation was monochromatized by a quartz crystal. Slits were used in order to reduce parasitic scattering. Measurement of the incident intensity, necessary for the determination of the diffusion power  $i(h)$ , was done by means of a set of calibrated filters.

The profile of the beam from top to bottom was approximated to a Gaussian by including, at the output of the monochromator, aluminium sheets of variable thickness. Fig. 1 shows the intensity as a function of angle  $\phi$  (with the same units as  $h$ ) obtained by vertical displacement of the Geiger counter, the beam being attenuated by filters at the input of the counter. A monitor permitted control of stability of the incident beam during the measurement of a scattering curve.

The scattering curve was obtained by means of a horizontal goniometer and a proportional detector. Parasitic scattering was determined by counting without sample and subtracted from the total intensity.

The normalized experimental intensity function,  $F(h)$ , is related to the diffusion power  $i(h)$  by

$$F(h) = \int_0^\infty W(\phi) i[(\phi^2 + h^2)^{\frac{1}{2}}] d\phi \quad (12)$$

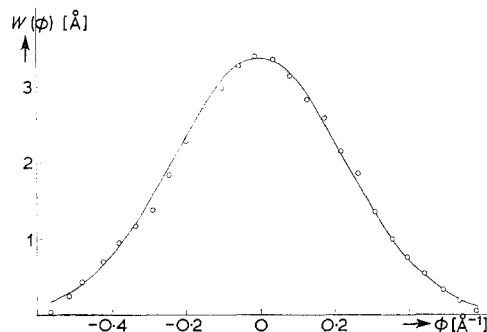


Figure 1 Vertical normalized profile of incident beam obtained from the measured intensities and Gaussian curve used in the correction of experimental scattering.

with the condition

$$\int_0^\infty W(\phi) d\phi = 1.$$

$W(\phi)$  is the weight function of the distribution of intensities in the beam profile.

In our case

$$W(\phi) = 2p\pi^{-\frac{1}{2}} \exp(-p^2\phi^2) \quad (13)$$

and  $i(h)$  can be deduced by a numerical method proposed by Schmidt [5]. An IBM 1130 computer was programmed to carry out the numerical computations. The diffusion power  $i(h)$  obtained in this way is the ratio between the intensity scattered by a sample with a point-like collimated beam and the intensity that would be scattered under the same conditions if all the electrons were free.

### 4. Results

Fig. 2 shows the small-angle X-ray scattering from our sample of glassy carbon normalized and corrected for the collimation effect. It is plotted in electrons/electron units. To show that these results follow Guinier's law, expressed by Equation 1, we plotted  $\log i(h)$  against  $h^2$  in Fig. 3. The fact that the points approximate a straight line over a large range of  $h^2$  values indicates that Guinier's law is obeyed.

At very small angles, there is a noticeable negative deviation which we attribute to the interference between the amplitudes diffused by the voids. Fig. 2 shows another effect at very low angles, near the rim of the measured area. This sharp rise of intensity was associated with multiple scattering [8]. Both of these effects influence the scattering curve fundamentally at very small angles. For this reason, we shall not

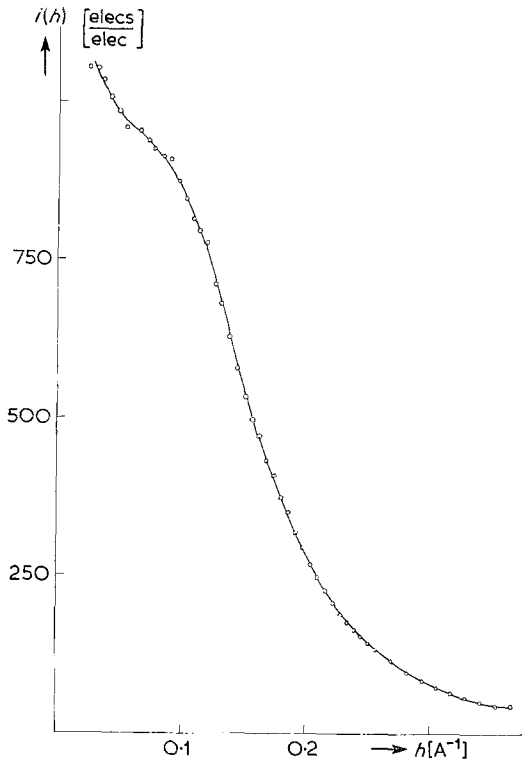


Figure 2 Normalized and free of aberrations scattering curve.

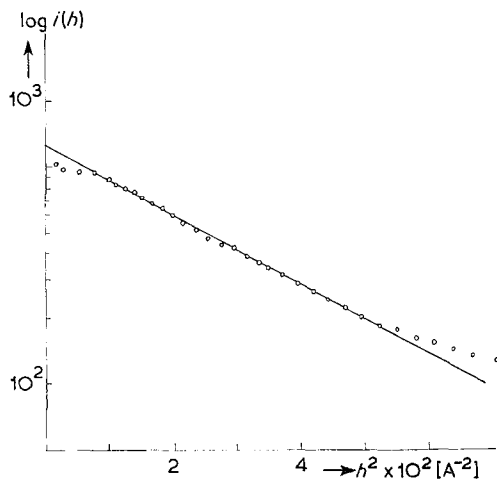


Figure 3 Guinier's plot showing the linear behaviour and some deviation at very small angles.

use the experimental results at such small angles but rather estimate the intensity in this region by extrapolating the straight part of Fig. 3. Applying Guinier's law to the plot of Fig. 3, we obtain the radius of gyration  $R_g$  of the voids from the slope of the straight line. From the

fact that Guinier's law is obeyed over a wide range of  $h^2$ , we deduce that the voids have approximately equal sizes, with  $R_g = 10.4 \text{ \AA}$ .

In Fig. 4 we plotted  $h^4 i(h)$  against  $h^2$ , with the data obtained in our experiments. From the plot, we see that Porod's law is not obeyed; the curve fluctuates for  $h > h_1$  about a straight line

$$h^4 i(h) = b_0 + b_1 h^2$$

instead of approaching a constant value

$$h^4 i(h) = b_0 \quad h \rightarrow \infty$$

This deviation from Porod's law, according to Equation 7, indicates the presence of one-dimensional density fluctuations in the matrix.

The previously developed theory is valid for a two-density systems. To apply this theory to our experiment, we have to subtract the fluctuation contribution  $i_f(h)$  from the total intensity  $i_t(h)$ . We found (Fig. 4) that  $i_f(h)$  at large angles is

$$i_f(h) = \frac{b_1}{h^2}, \quad (14)$$

If this term is subtracted from  $i_t(h)$  we have the "two-density system" intensity  $i(h)$  at large angles

$$i(h) = \frac{b_0}{h^4} \quad h > h_1 \quad (15)$$

Extrapolating the straight line to  $h^2 = 0$  (Fig. 4) we obtain  $b_0$ .

From our data, we have not been able to obtain the fluctuation contribution at small angles. However, because the two-density system intensity values were very great, we neglected  $i_f(h)$  for  $h < h_1$ . Therefore, we considered that the  $R_g$  value calculated from Guinier's law was still valid.

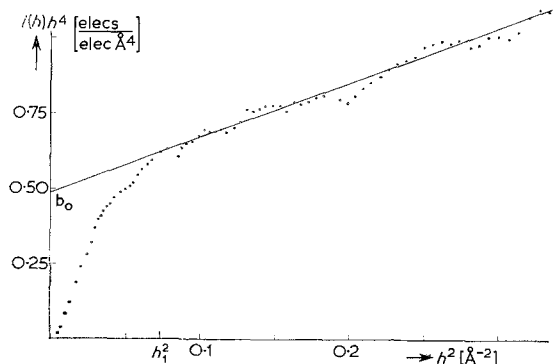


Figure 4 Variation of  $h^4 i(h)$  versus  $h^2$  showing the positive deviation from Porod's law.

To determine the shape of the voids, which all have approximately the same size, we must know their volume and surface area. The volume can be obtained from Equation 4 and the surface area by combining Equations 2 and 6 to give

$$s = \frac{V^2 [i(h) h^4]_{h \rightarrow \infty}}{2\pi i(0)}, \quad (16)$$

To calculate  $V$  and  $s$  we must obtain from our experimental data the  $\lim_{h \rightarrow \infty} h^4 i(h)$ ,  $i(0)$  and  $I =$

$\int_0^\infty h^2 i(h) dh$ . We saw that, deducting the fluctuation contribution, we have

$$\lim_{h \rightarrow \infty} h^4 i(h) = b_0$$

and neglecting the fluctuation contribution at small angles,

$$i(0) = i_t(0).$$

To obtain an approximate value of the integral  $I$ , we must calculate

$$I = \int_0^{h_1} h^2 i(h) dh + \int_{h_1}^\infty h^2 \left[ \frac{b_0}{h^4} \right] dh. \quad (17)$$

Neglecting  $i_t(h)$  for  $h < h_1$  we can approximate

$$i_t(h) \simeq i(h), \quad h < h_1$$

then an approximate value of  $I$  is given by

$$I = \int_0^{h_1} h^2 i_t(h) dh + \frac{b_0}{h_1} \quad (18)$$

(the first term was calculated in numerical form). The  $V$  and  $s$  values obtained via Equations 4 and 16 are given in Table I.

If the voids had been spherical we would have

$$V = \frac{4\pi}{3} \left( \frac{5}{3} \right)^{3/2} R_g^3 \quad (19)$$

$$s = \frac{20}{3} \pi R_g^2, \quad (20)$$

but as our  $R_g$ ,  $V$  and  $s$  values did not obey these equations, we suppose that the void shape is that of ellipsoids of revolution. This shape is characterized by two parameters: the radius of gyration  $R_g$  and the ratio  $\nu$  between the axis of revolution and the perpendicular axis. Values of  $\nu$  smaller than unity correspond to oblate ellipsoids and greater than unity to prolate ellipsoids.

By means of the following formula

$$V = \frac{4}{3} \pi \nu R_g^3 \left( \frac{2 + \nu^2}{5} \right)^{-3/2} \quad (21)$$

we calculate the values of  $V$  associated with

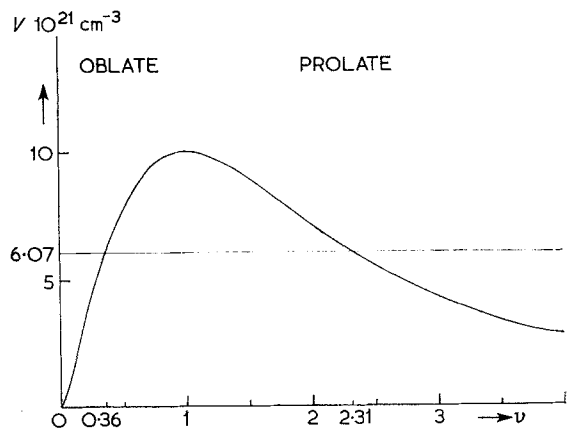


Figure 5 Volume associated to ellipsoids of revolution with  $R_g = 10.4 \text{ \AA}$ .

ellipsoids of  $R_g = 10.4 \text{ \AA}$ . In Fig. 5, where  $V$  is plotted against  $\nu$ , we see that the volumes of ellipsoids of  $\nu_0 = 0.36$  and  $\nu_p = 2.31$  correspond to the value calculated independently from Equation 4, i.e.,  $V = 6.07 \times 10^{-21} \text{ cm}^3$ .

Concerning the surface associated with the ellipsoids of  $\nu = \nu_0$  and  $\nu = \nu_p$  we found that  $s_0 = 1.96 \times 10^{-13} \text{ cm}^2$  and  $s_p = 1.79 \times 10^{-13} \text{ cm}^2$ . Comparing these values with those obtained from Equation 16 we see the oblate ellipsoid surface area  $s_0$  is in better agreement than the prolate surface area  $s_p$ . The value  $s_0$  is approximately 15% smaller than that found using Porod's law; this might be because the surfaces of the voids are not smooth, but they may have a special shape which can be approached by an ellipsoid. We conclude, therefore, that our results agree better with the oblate ellipsoid-shaped void hypothesis, with  $R_g = 10.4 \text{ \AA}$  and  $\nu = 0.36$ .

The number of voids per unit volume  $N$  and the porosity  $P = NV$  can be calculated from Equation 2. We took  $\rho_0 = 0$  (voids) and  $\rho$  was calculated by the equation

$$\rho = \rho_M \frac{AZ}{M} \quad (22)$$

where  $M$  is the atomic weight of carbon,  $A$  is Avogadro's number,  $Z$  the atomic number and  $\rho_M$  the graphite density ( $\rho_M = 2.15 \text{ g cm}^{-3}$ ). With the same formula we calculate the mean electronic density  $\bar{\rho}$ , here  $\rho_M$  is the macroscopic density of our sample ( $\rho_M = 1.45 \text{ g cm}^{-3}$ ). The results obtained are given in Table I.

The value of the density fluctuation,  $F$ , was calculated by taking  $b_1$  from the slope of the

TABLE I Values of voids and fluctuations parameters obtained in this work.

$R_g$ (Å)	$V$ ( $10^{-21}$ cm <sup>3</sup> )	$s$ ( $10^{-13}$ cm <sup>2</sup> )
10.4	6.07	2.26
$N$ (voids cm <sup>-3</sup> )	$P$	$F$
$3.45 \times 10^{19}$	0.21	0.028

straight line in Fig. 4 and  $a_3 = 3.4$  Å. From Equation 11 we obtained  $F = 0.028$ . This result is similar to those obtained by other authors [7] for carbon fibres heat-treated at 2000°C.

## 5. Discussion and conclusions

Our results support the hypothesis that glassy carbon contains voids of approximately uniform size with the shape of oblate ellipsoids of revolution. This conclusion is in agreement with the work of Rothwell previously mentioned although the eccentricity of the ellipsoids which we have found is much greater than Rothwell's. Research on carbon fibres [9] and other non-graphitizable carbons leads us to suppose that the voids are between graphite layers. Thus, we see the structure of glassy carbon as composed of amorphous carbon and graphite layers with voids in the form of oblate ellipsoids of revolution between these layers. The voids are probably irregular polyhedrons, the ellipsoids of revolution being an approximation to their real shape. The fact that Porod's law yields a surface 15% larger than the surface calculated from the oblate ellipsoid shape is consistent with this interpretation.

In previous work [2], it was found that Porod's law is satisfied over an ample range of  $h$  for samples heat-treated at 1000, 2000 and

3000°C. However, we observe a clear deviation from Porod's law for our glassy carbon which was heat-treated at 2000°C. Concerning other materials prepared in similar way, Perret [7] observed that in carbon fibres, the deviation from Porod's law becomes smaller as the heat-treatment temperature is increased, and vanishes for fibres heated at 3000°C. Another recent study [9] of glassy carbon heat-treated at 3000°C showed that it also obeys Porod's law. The results of these studies together with the present work show a marked similarity in the behaviour of the fluctuation terms found in glassy carbon and carbon fibres.

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