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## Structural studies of activated carbons by pulsed neutron diffraction

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**Abstract.** Pulsed neutron diffraction results are presented for a series of activated carbons with a variable microporosity. The results cover a wide  $Q$ -range extending up to  $50 \text{ \AA}^{-1}$  and enable the pair correlation function to be evaluated with good spatial resolution. The diffraction pattern shows a broad oscillatory behaviour representative of a highly defective crystal structure and differs considerably from graphite. Detailed investigation shows that the local atomic structure is similar to that of graphite and exhibits the expected hexagonal network but that the first peak arising from the carbon–carbon bond has two components, indicating a quinooidal distortion of the network. The correlation length within the graphene sheet is short ranged and the inter-layer spacing also displays some disorder with an increased spacing compared with graphite. The data provide a good basis for the detailed modelling of the structure and exhibit characteristics that could not have been easily observed by other techniques.

### 1. Introduction

One of the main features of the LAD instrument has been the possibility of using the epithermal neutron flux to extend the range of the diffraction measurements to high values of the scattering vector,  $Q$ . There are several reasons why the use of short wavelength neutrons in an energy-dispersive mode has advantages in the investigation of structural features for liquids and disordered materials; these characteristics have been detailed in several earlier papers. A summary of the comparative characteristics between pulsed neutron and reactor techniques is given in the appendix. It has probably not been fully appreciated that the wide  $Q$ -range has useful applications in the investigation of defective solids which are primarily crystalline in their local atomic environment. One such group of materials is the activated carbons which have been used in the present measurements.

Activated carbons are produced by controlled pyrolysis of organic precursors to produce a material that consists almost entirely of carbon in a graphitic form. The resulting structures have a high surface area due to the micro- and meso-porosity. It is these features that make them useful for a wide range of commercial applications. The bulk supply of activated carbons has been based on the use of natural products such as wood, olive stones etc but more recently a higher-quality product has been produced from the use of polymer resins where control of specific characteristics is more readily achieved. In the present study the precursor is a phenol resin and has been prepared at the Universidad de Alicante, Spain.

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## 2. Theoretical background

### 2.1. Scattering formalism

For the activated carbons, the diffraction pattern arises from the coherent interference of scattered waves from the distribution of identical scattering centres. The structure factor,  $S(Q)$ , can therefore be written as

$$S(Q) = \int \rho(r) \exp(iQ \cdot r) d^3r \quad (1)$$

where  $\rho(r)$  is the nuclear distribution function. In the case of a powdered sample with random orientation of crystallites, it is possible to take an orientational average as for liquids and amorphous solids and to use the inverse Fourier–Bessel transform to express the pair correlation function,  $g(r)$ , as

$$d(r) = 4\pi r \rho_N [g(r) - 1] = \frac{2}{\pi} \int_0^\infty Q I(Q) \sin(Qr) dQ \quad (2)$$

where  $I(Q)$  is the interference function

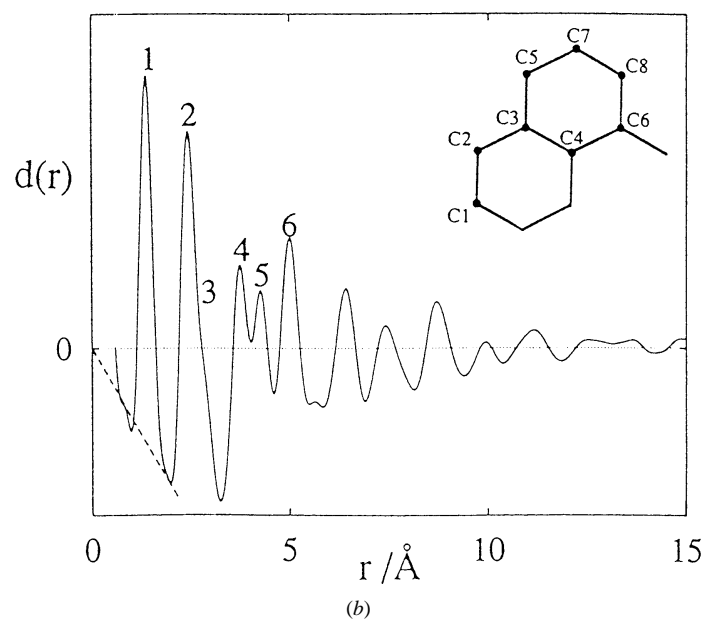
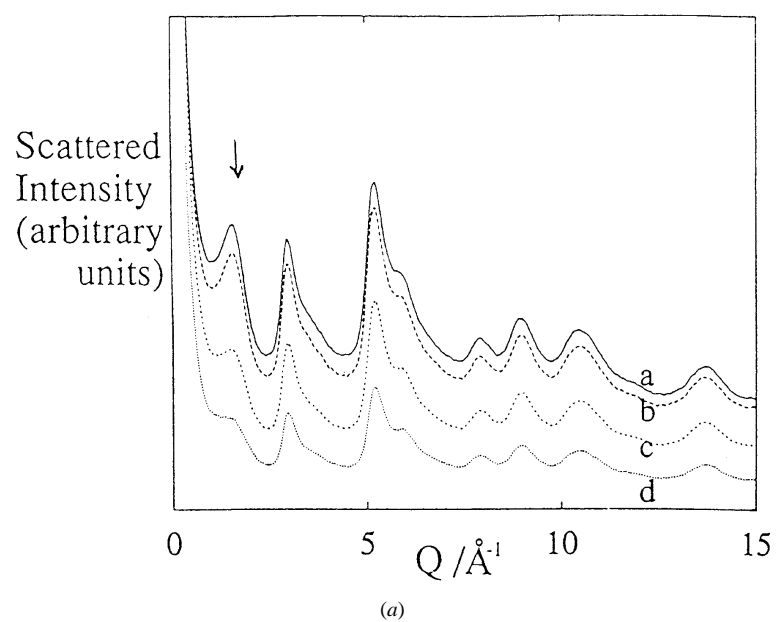
$$I(Q) = S(Q) - 1 \quad (3)$$

and  $\rho_N$  is the number density for the bulk material. This expression is more familiar in the context of scattering from disordered materials but is equally applicable to powdered crystalline samples. It is not normally used for these systems because the Bragg scattering from the crystalline planes can be written as  $S(hkl)$  where  $h, k, l$  are the Miller indices. In most cases the structural characteristics can be described by measurements over the first few peak positions and the higher  $Q$ -value data, which usually contains many overlapping peaks, are largely redundant unless very precise information is required about the displacement from equilibrium sites. The situation for the activated carbons is different since it is found that the peaks of the diffraction pattern are very broad and have an asymmetric distortion. In fact, the diffraction pattern appears to have an oscillatory behaviour which resembles that of a disordered material and might initially be considered to arise from an amorphous solid. The diffraction pattern for neutron scattering from an activated carbon sample [1] is shown in figure 1 to illustrate this effect. The increase in intensity at low  $Q$ -values arises from the microporosity of the sample material and can be studied in detail by extending the measurements to cover a much lower range ( $\sim 10^{-4} \text{ \AA}^{-1}$ ) using either SANS or SAXS techniques.

### 2.2. The Warren profile

Defective crystals can have a number of different structural characteristics leading to the loss of long range order in the periodic lattice arrangement. One particular version arises from the faceting effects in crystal structure and was originally developed by Warren [2] for the analysis of diffraction data from carbon blacks. The most common form of carbon is graphite which consists of sheets of carbon atoms arranged in a hexagonal network which is stacked in an 'abab' sequence. The spatial correlations for the in-plane arrangement is generally better developed than that perpendicular to the plane. As a result, the crystallites making up the activated carbon may have different correlation lengths along different axes.

The sharpness of the Bragg peaks is representative of the extent to which the periodicity is maintained over long distances. In some cases the range may be quite short, leading to broadening of the peaks, but it is also influenced by crystal shape arising from two correlation lengths in different directions. The averaging over crystal orientations leads to an asymmetric broadening of the diffraction peaks. This feature is termed the Warren profile and, in some



**Figure 1.** Reactor measurements of the neutron diffraction pattern for a microporous activated carbon [1].

cases, the broadening effect may be sufficiently large to cause the pattern to resemble that of an amorphous solid. This behaviour has already been noted in the data obtained from a set of treated materials originating from the Alicante group [3] and also in the more varied range of activated carbons available commercially [4].

### 3. Experimental procedure

#### 3.1. Samples

Three samples of activated carbon were prepared with variable burn-off at the University of Alicante using standard procedures. The first, termed carbon A, was prepared from a phenolformaldehyde polymer resin which was carbonized by heating to 1000 °C for two hours in a nitrogen gas flow. The resulting material has high carbon purity with an ash content of only 0.01%.

The other two samples, termed carbon AC14 and carbon AC32 were produced by carbon burn-off for the carbon A sample in a CO<sub>2</sub> atmosphere at 800 °C. The numbers indicate the percentage weight loss in each case; i.e. there is a 14% weight loss to produce the carbon AC14 sample and this corresponds to an increase of both the micro- and meso-porosity in the material. The BET surface area increases from 580 m<sup>2</sup> g<sup>-1</sup> for carbon A to 1000 m<sup>2</sup> g<sup>-1</sup> for carbon AC32.

#### 3.2. Measurements

The samples were heated to 200 °C to ensure that all water was removed and they were then mounted in a 15 mm diameter thin walled vanadium cell. The cells were installed on the LAD instrument and the usual procedure followed for recording the scattered intensity, including the use of a standard vanadium sample to provide a normalization to the incident spectrum.

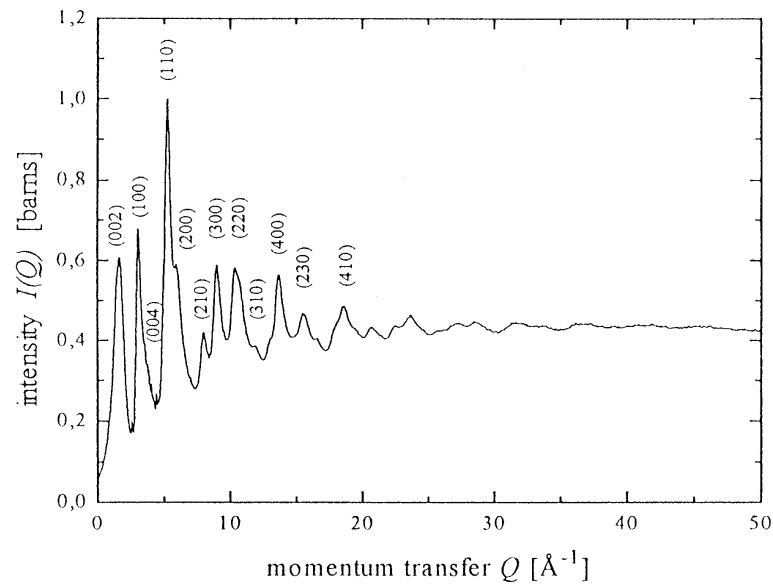
#### 3.3. Data analysis

The usual experimental corrections were applied to the recorded datasets for each of the samples including cell scattering, attenuation factors, multiple scattering and spectral profile. The total scattering distribution was evaluated by the combination of the datasets for the separate detectors and the intensity profile evaluated in each case. An example of the data is given in figure 2 for the carbon A sample. The peaks are broad, as expected, but it is still possible to associate the main characteristics with the pattern given by graphite and the appropriate Miller indices for the graphite reflections are indicated on the figure.

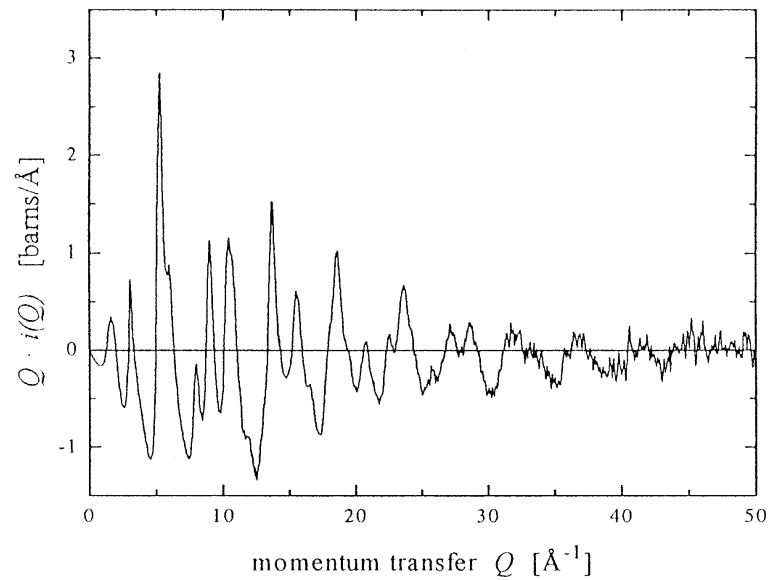
### 4. Data interpretation

The low  $Q$  behaviour follows the expected pattern and displays a range of broad asymmetric peaks as seen in the earlier reactor measurements. However, the extended  $Q$ -range of the measurements shows significant oscillatory structure at higher  $Q$ -values, extending beyond 40 Å<sup>-1</sup>. This profile shows little variation between the samples and is characteristic of the short range features in the graphene sheet. A plot of the  $QI(Q)$  function is given in figure 3; the SANS contribution at low  $Q$ -values has been subtracted before the treatment and it has little effect on the short range atomic features. The use of a  $QI(Q)$  plot shows more clearly the characteristics at high  $Q$ -values and defines the function used directly in the transform equation. The statistical accuracy is indicated by the 'noise' in the points defining the pattern and it is clear that this level of precision can only be obtained by the use of pulsed neutron methods.

The datasets can be transformed to a real-space representation and the resulting  $d(r)$  curve for carbon AC14 is given in figure 4. Well defined peaks are shown in the 1–5 Å region corresponding to the local arrangement of the atoms in the graphene sheet. The way the different peaks are created is shown schematically in a separate diagram, figure 5, which is based on a representation first produced by Wilk [5]. These results provide an excellent



**Figure 2.** The intensity profile for pulsed neutron scattering from the carbon A sample obtained with the LAD instrument.



**Figure 3.** The derived  $QI(Q)$  function for the data shown in figure 2.

basis for the detailed modelling of the structural relations and the fact that the system is homonuclear means that the  $d(r)$  curve provides a complete picture of the angle-averaged spatial correlations. The derived functions are found to be very similar for the three samples emphasizing that the structural relations are not strongly affected by the relatively high burn-off factor. The main changes are restricted to the SANS region (not shown in these plots) and the first diffraction peak. This behaviour is puzzling because it is known from the gas adsorption

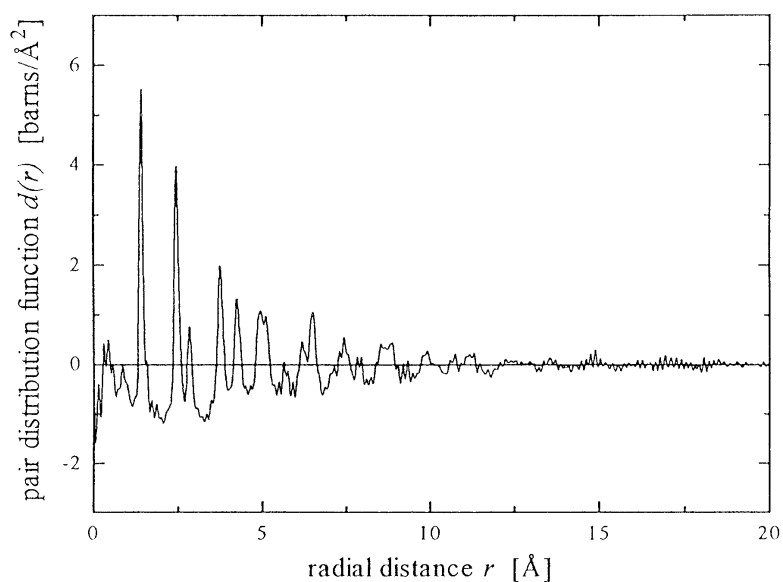


Figure 4. The real-space distribution function  $d(r)$  for carbon AC14.

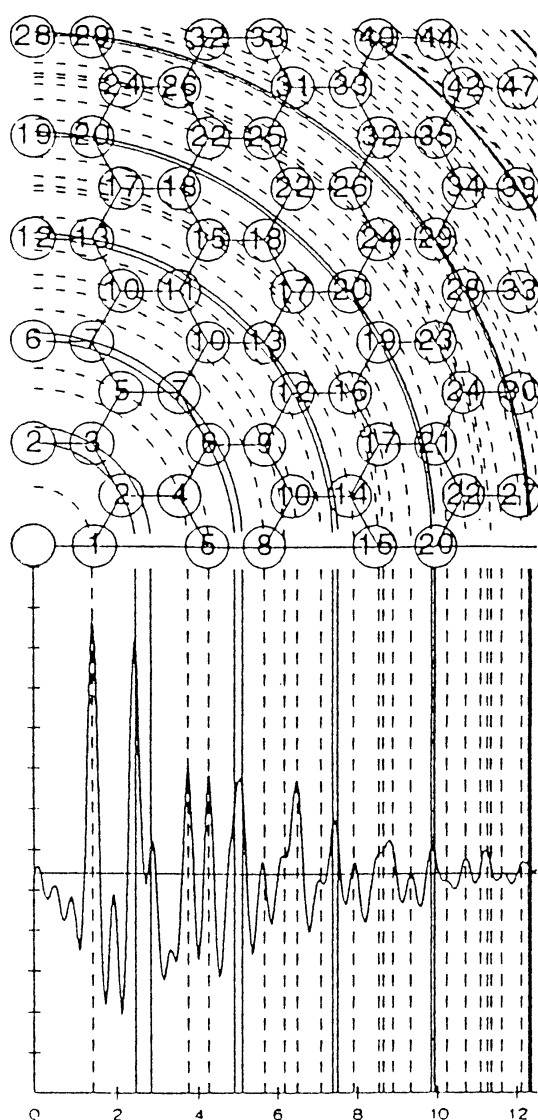
measurements that the microporosity is much increased and it would be expected that this would be reflected in the local correlation function. This feature is subject to continuing study through the modelling of the network.

A close examination of the first peak, corresponding to the C–C bondlength, is also of interest. A plot on an extended scale is given in figure 6 for carbon AC32. It can be seen that there is a subsidiary peak on the high  $r$  side of the main peak. Decomposition into two peaks with distances of 1.395 and 1.542 Å gives a good fit to the data. These peaks are also shown in the datasets for the other samples and the integrated peak areas are in the approximate ratio of 6:1. This unexpected discovery has led to a closer investigation of the local network structure and is discussed in the following section. It is clear that this feature could only be observed due to the high resolution obtained in the  $d(r)$  function, resulting from the wide  $Q$ -range of the diffraction measurements. In this respect, the use of a pulsed neutron technique has enabled a new feature to be seen in the results.

## 5. Modelling of activated carbons

A comparison of the data for the activated carbons with that of graphite emphasizes different features in the  $I(Q)$  and  $d(r)$  curves. The sharp peaks in the diffraction pattern for graphite define the long-range order associated with the regular crystal lattice. In contrast, the broad peaks of the  $I(Q)$  curve for the activated carbons indicate the limited extent of these spatial correlations.

The behaviour of the  $d(r)$  curves shows the similarity in the local arrangement of carbon atoms for both cases indicating that the main difference between the sample arises from the mesoscopic features rather than the short range behaviour. The commonly held view is that the activated carbons have a basic graphitic structure based on a planar hexagonal network but there is a complete loss of correlation between planes: the resultant structure is frequently termed turbostratic graphite.



**Figure 5.** A schematic representation of the spatial correlation functions arising from a planar hexagonal lattice; this representation is due to Wilk [5].

The present results can be used as a basis for detailed modelling either in  $Q$ -space or  $r$ -space. The simplest approach is to consider the inter-planar spacing to be defined by the first diffraction peak (002) at approximately  $1.6 \text{ \AA}^{-1}$ . The sharpness of this peak relates either to the extent or regularity of the spacing of the layer planes. The peak position is not precisely defined as it is broad and is situated on top of the continuous SANS distribution arising from the porosity. However, it is clear that the peak is displaced to a lower  $Q$ -value than for graphite, indicating a general increase in the layer spacing. This increase corresponds to a change of a few per cent over the normal graphite spacing of  $3.354 \text{ \AA}$ . The increased width of the peak suggests that there are only a few layers (four to six) which remain strongly correlated in the



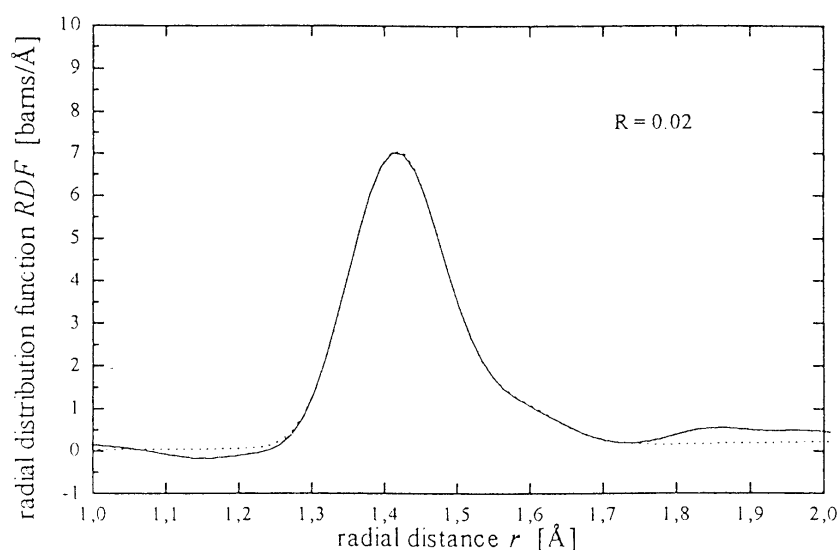


Figure 6. The expanded first peak in  $d(r)$  corresponding to the C–C bondlength.

micro-crystalline stacking and that they are presumably influenced by the pore structure. In this special case it is not really possible to separate the diffraction and SANS regions as the length scales are of a similar magnitude. These features are readily studied using reactor data and therefore do not require the use of pulsed neutrons. The system is quite complex and work is proceeding on the interpretation [6].

The  $d(r)$  plots relate to the orientationally averaged pair-correlation functions and primarily give direct information about the atomic arrangement within the graphene sheet. The first few peaks correspond to the expected positions of the regular hexagonal lattice but the agreement with the graphite structure is lost in a surprisingly short distance of less than 10 Å. This feature shows that there is disorder in the planar array of the hexagonal network and consequently there is disorder in the plane as well as perpendicular to it. The picture which emerges from this qualitative analysis is that although there remain essential elements of the graphitic structure over a limited range, there are considerable variations. The material is best described as being a highly defective crystal with spatial correlations extending over a restricted range in both directions, perpendicular and parallel to the graphene sheet.

Another surprising feature is also revealed in the  $d(r)$  curves as the first peak is found to have a small subsidiary peak on the high  $r$  side. This peak is consistent across all the activated carbon samples studied and has been the subject of a detailed analysis using peak-fitting routines [7]. The main peak is at  $1.395 \pm 0.002$  Å corresponding to the main C–C bondlength and the subsidiary peak is at  $1.53 \pm 0.01$  Å. The quoted bondlength for graphite is 1.421 Å which is close to the weighted mean of the two peaks. It is normally assumed that all C–C bonds are equivalent in the hexagonal lattice but Pauling had suggested that a quinoidal distortion could arise due to an effective distribution of single and double bond character within the network. This phenomenon appears to provide a satisfactory explanation of the observation. It is also noticeable that there is even a small feature at this distance in the data for a graphite sample run in a separate study [8] and this may indicate that natural graphite also contains some distortion of the network arising from quinoidal effects. The picture emerging from this study indicates that the graphitic carbons may be much more varied than had previously been realized. It also

seems likely the structure of the activated carbons is quite complex due to the additional effects of the mesoscopic structure which has not yet been precisely defined.

One approach to the modelling is to utilize the paracrystalline formalism and to incorporate the quinoidal effect into the separate layers. A detailed investigation has been conducted by Szczygielska [9] and preliminary results have already been published in a paper by Burian *et al* [10]. However, it is likely that the microporosity of the materials has a direct influence on the loss of order between the graphene sheets and a complete modelling of the local structure will require a more sophisticated treatment, possibly using individual atom locations.

## 6. Conclusions and future work

The present results have demonstrated the importance of pulsed neutron techniques in the study of activated carbons. The data have revealed several features about the atomic arrangement that were previously unknown. Furthermore, it is clear that these features could not have been easily obtained from other observational methods. The main advantage of the use of pulsed neutrons has been the ability to measure the  $I(Q)$  function over a wide  $Q$ -range and consequently to obtain a good spatial resolution in the resulting  $d(r)$  function. The complexity of these structures has been demonstrated and now awaits a detailed interpretation; further work is in progress.

The interest in these materials has now extended to other samples and reactor measurements have recently been made for a series of heat-treated carbons made from saccharose and anthracene precursors [11]. These samples exhibit structural change when heated above 1600 °C and it is hoped that the results will give some indication of the behaviour associated with graphitizing and non-graphitizing carbons. It seems likely that the answer to this long standing paradox rests with a precise understanding of the local structure and the network connectivity. Consequently, it will be necessary to use pulsed neutrons to give the required improvement in the spatial resolution for these samples. It is hoped that this work can be done on the new GEM diffractometer that will replace LAD and to continue to structural investigation of these fascinating materials.

Other techniques can be used to investigate structural characteristics. The use of nmr will be important in verifying the variation in the C–C bondlength and this work is just starting [12]. Furthermore, x-ray diffraction is an important complementary method for structural studies of defective and disordered systems, particularly using third generation synchrotron radiation sources. The disadvantage of x-rays is that measurements of  $I(Q)$  at large  $Q$ -values are difficult due to the intensity fall-off arising from the atomic form-factor and the contribution of Compton scattering. Although x-ray studies will never be able to reach the high  $Q$ -values attained in pulsed neutron experiments, recent measurements [13] for the saccharose and anthracene samples using a high energy diffraction technique with a 116 keV x-ray beam have extended the range up to 30 Å<sup>-1</sup>. Data analysis is in progress and it seems likely that this new technique will provide an important complementary method which can give information on the electron distribution in these carbons. Smaller quantities of sample material are needed and therefore a wider range of materials can be investigated.

There are significant topical developments in other areas of carbon science based on fullerene structures and particularly on carbon nanotubes. Neutron diffraction studies [14] on several different forms of multi-walled nanotubes prepared by different routines have already shown that significant differences exist but detailed structural characteristics of the cylindrical graphene sheet have yet to be determined. It can be anticipated that pulsed neutron studies will be needed to fully characterize these materials. A further extension of this research area concerns the materials that can be encapsulated inside the nanotubes and this is currently

an unexplored area where metal and semiconductor properties are strongly influenced by the confined geometry. The main method of current investigation is through electron microscopy [15] but it seems inevitable that neutron and x-ray studies will be required for complementary studies and structural characterization.

In conclusion it is apparent that the present studies represent an initial phase of a research topic that has not yet developed its full potential. The data that can be obtained are well capable of providing a firm basis for computer modelling although new analytic methods will probably be required to represent the defective nature of the material if quantitative information is to be extracted from the measurements.

### **Acknowledgments**

The experimental work was carried out at the ISIS facility using the LAD instrument and one of us (DC) wishes to acknowledge support from the EU in the form of a travel grant through the Large Facilities Programme which allowed participation in the experiment. Another one of us (MS) wishes to acknowledge receipt of a Tempus grant for an exchange year at the University of Kent during which the measurements were made; the work subsequently formed the basis of a master's thesis at the University of Silesia, Katowice and was the first one submitted to the Physics Department in English. The work on carbons now forms a major part of a collaborative project between the University of Kent (JCD) and the University of Silesia (AB).

### **Appendix. A comparative summary of the differences between reactor and pulsed neutron diffraction techniques**

#### *A.1. Fundamental principles*

The experimental techniques used in diffraction studies effectively produce the total differential scattering cross-section for the sample as a function of scattering angle and neutron energy (or wavelength). The reactor method is based on an angle-dispersive method with a fixed input energy whereas the pulsed neutron method uses time of flight to define an energy-dispersive method with several fixed angle detectors. The observed count-rates must then be converted to an effective structure factor based on the coherent elastic scattering from the sample at a fixed  $Q$ -value.

The conversion to a normalized structure factor involves both experimental and analytic corrections and satisfactory routines have now been developed for the data treatment. However, the corrections for inelastic scattering events are fundamentally different for the reactor and pulsed neutron studies. Any error in the application of the so-called Placzek corrections may lead to systematic errors in the derived functions. Although established procedures are now in common usage, it is important to realize that a complete solution of this problem has not been achieved and some care must be exercised in the interpretation of the final results, particularly for the scattering from light nuclei such as deuterium and/or hydrogen. The following subsections briefly review the basic differences between the two methods and address some of the practical aspects of the remaining problems.

#### *A.2. Self-scattering corrections*

A formalism for the application of corrections to the self-scattering contribution has been developed by a number of people in the context of molecular systems. For the reactor case, the cross-section shows a monotonic decrease with increasing  $Q$ -value and gives the characteristic

'Placzek fall-off' in the intensity profile. For the pulsed neutron case, the conditions are such that the self-scattering is closer to the free atom cross-section and there is no fall-off in the high  $Q$  region. This feature has frequently been cited as one of the important advantages of the pulsed neutron technique but it is important to put this comment into a proper context. The structural information is obtained from the interference function after the self-scattering contribution has been subtracted from the observed total scattering distribution. In practice, there are few problems in handling the Placzek corrections for reactor measurements except possibly in the extreme case of hydrogen and empirical methods are found to work well even for this case [16]. It is pertinent to note that in electron diffraction studies of gases, where it is impossible to evaluate the self-scattering from first principles, there is no concern about systematic errors arising from the use of a smooth fitted function. Furthermore, there are several consistency checks that can be made to check the extrapolation to low  $Q$ -values.

The inelasticity effects for the self-scattering component in pulsed neutron measurements arise from the spectral shape and the finite secondary flight path; the main departure from a constant level occurs at low  $Q$ -values due to the use of longer wavelength neutrons. This feature is not frequently discussed in the combination of datasets from the different detector banks but the overlap region from adjacent detectors gives a useful indication of any differences. In principle there are a number of consistency checks that can be made, depending on the range of wavelengths used in the data analysis. In practice, this is rarely done and the effects are assumed to be negligible even for scattering from light nuclei. As the required precision improves, it may be necessary to examine this region in more detail, particularly where H/D isotopic substitution is used.

### A.3. Interference effects

The structural information is derived from the interference function,  $I(Q)$ . The intensity profile may be of an oscillatory nature as for liquids and glasses or consist of sharp Bragg peaks as for a crystalline solid with long range order. The present case of a defective crystal represents an intermediate situation that has not been frequently investigated. The analytic corrections will be negligible for solid materials as the scattering is essentially elastic but for other systems, such as molecular liquids, there can be significant effects due to inelasticity arising from movement of the scattering centres. The full expressions involve the dynamic structure factor  $S(Q, \omega)$  and are complicated by the different nature of the scattering assembly. For molecular systems some approximations can be used and these show that there is an effective recoil which may affect the periodicity of the high  $Q$  oscillations if the atoms are light. If the correct bondlengths are to be extracted, these corrections must be carefully applied and there is no definitive method of doing this, although several satisfactory approximations have been proposed and used. The recoil corrections are generally reduced for higher energy neutrons giving an implicit advantage to the use of pulsed neutron techniques. It was this principle that led to the original proposal to construct a 'small-angle diffractometer' which subsequently became SANDALS. However, the vibrational features also affect the corrections and the situation is still not fully resolved. There are a number of cases, including that of heavy water,  $D_2O$ , where the derived  $I(Q)$  functions from reactor and pulsed neutron experiments are not in sufficiently good agreement but a detailed discussion goes beyond this brief comparative summary.

### A.4. Calibration, stability and reproducibility

The accuracy of the  $Q$ -scale depends on the effective determination of the scattering angle and neutron wavelength from a standard crystalline solid. For reactor techniques, the  $Q$ -value for

elastic scattering can be defined to better than 1 in  $10^3$ , although the  $Q$ -resolution is usually only at the 1–2% level. The  $Q$ -scale calibration for pulsed neutron studies depends on the time-of flight system which defines the neutron wavelength. The calibration is complicated by the thermalization process in the moderator such that the fast neutrons may have a different 'zero' time and pulse width to the thermal neutrons. These effects have been studied for specific arrangements and suitable calibration procedures established; the effects occur mainly in the short flight-time region which might affect the large  $Q$ -values.

The accuracy and reproducibility of any measurement is influenced by the stability of the cell elements in the recording system and the period of the observation. Great improvements have been made in the detector and electronic technology and for reactor systems it is possible to achieve a stability of better than 1 in  $10^4$  over a period of several days. Reactor power is well controlled so that the neutron flux remains stable during the measurements. In comparison, accelerator-driven sources are inevitably less stable and may have significant changes in primary beam current during a measurement. Although first order fluctuations can easily be handled, any change in the operating temperature of the moderator can potentially lead to changes in the emitted spectral distribution of the neutrons. It is, consequently, necessary to make more regular calibration checks when using pulsed neutrons and to check the reproducibility of the individual measurements.

#### A.5. General conclusions

It is clear from the above critique that there are significant differences in the two techniques and there are additional issues related to data processing which cannot be considered here. In the past, proponents of each technique have tended to claim superiority by addressing only some of the criteria listed above. However, it should be apparent that each method has its advantages for specific types of investigation. The comments above are intended to focus on the complementarity of the two techniques and the over-riding importance of retaining facilities which can be used in the next development phase of these research investigations. Each method has a clearly defined category where it is beneficial or even essential to use the one rather than the other. In broad terms, pulsed neutrons are required where a wide  $Q$ -range is needed, as in the present case of the activated carbons. In other cases where small differences are to be measured and the low  $Q$ -value region is of prime importance, the reactor method may be preferable.

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