Modelling studies of carbon nanotubes—Comparison of simulations and X-ray diffraction data

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Abstract

Computer simulations of the powder diffraction profiles for multi-wall carbon nanotubes were performed using the Debye equation including a generalized Debye–Waller factor. The X-ray diffraction data were recorded using high-energy synchrotron radiation and an image plate as a detector for the carbon nanotubes produced by a template chemical vapour deposition (CVD) process. The computed and experimental structure factors were converted to real-space via the Fourier transform. The results of computation, obtained in the form of the structure factor and the pair correlation function, are compared with the X-ray experimental data in both reciprocal and real-space. The nanotube model consisting of five layers with the length of 12 Å has proved to account very well for the experimental data.
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1. Introduction

Electronic and mechanical properties of carbon nanotubes (CNTs) depend on their geometrical parameters as diameter, length, chirality and the number of layers [1]. The structural dependence of the physical and chemical properties of the CNTs made them attractive materials for a wide range of applications [1]. That is why efforts are directed towards development and/or improvement of fabrication methods which would make it possible to control easily the size and the structure of the CNTs. One of the applied production method, which meets these requirements, is preparation of the CNTs by a chemical vapour deposition (CVD) of carbon from polypropylene inside the channels of an anodic aluminium oxide membrane [2]. Structural characterisation of such nanotubes has been performed using electron microscopy and electron diffraction [2]. Although these techniques have pro-

vided valuable information about the local atomic arrangement in the investigated CNTs, it is desirable to study their structure as a whole in a more global sense.

In the present work, the X-ray diffraction data collected for the multi-wall carbon nanotubes produced in the microchannels of the alumina template [2] are compared with simulated diffraction profiles, calculated for computer-generated models of the nanotubes. The results of such simulations are also compared in real-space. The experimental data have been collected on the ID15B high-energy beam line at the European Synchrotron Radiation Facility (Grenoble, France) using the image plate technique. The 'Fit2D' program was employed to convert the 2D diffraction patterns to the 1D intensity profiles. The detailed description of the X-ray experiment is reported in Ref. [3].

2. Theoretical background

X-ray diffraction is an effective technique for obtaining the structural information for disordered and polycrystalline

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materials, also for the CNTs. Analysis of the X-ray diffraction data for the CNTs yields average information about the structural characteristics as spatial correlations between atoms within a single layer, the nature of inter-layer correlations, the number of layers, diameter, length and chirality of the nanotubes [4–7]. For powder samples, the diffraction pattern arises from interference of coherently scattered waves from a system of scattering centres, which are the carbon atoms in the case of the CNTs. In three-dimensional space, the intensity scattered by N atoms can be written as:

$$I(\mathbf{K}) = f^2(K) \sum_{i=1}^{N} \sum_{j=1}^{N} \exp(-\mathbf{K} \cdot r_{ij}), \tag{1}$$

where $\mathbf{K}$ is the scattering vector, f the atomic scattering factor and $\mathbf{r}_{ij}$ is the inter-atomic vector defined as the difference between the position of ith and jth atoms. The magnitude of the scattering vector $\mathbf{K}$ is related to the scattering angle 2θ as

$$K = |\mathbf{K}| = \frac{4\pi \sin \theta}{\lambda}, \tag{2}$$

where λ is the wavelength. The intensity averaged over all orientations in three-dimensional space and divided by the number of the atoms N and square of the atomic scattering factor f^2 gives the structure factor $S(K)$ expressed by the so called Debye equation [8–10]. Allowing for atomic displacements from their equilibrium positions due to static disorder and thermal vibrations, one obtains:

$$S(K) = \frac{1}{N} \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{\sin(Kr_{ij})}{Kr_{ij}} \exp\left(-\frac{K^2\sigma^2}{2}\right), \tag{3}$$

where σ indicates the standard deviation of the inter-atomic distances.

The diffraction data can be transformed to real-space by the Fourier sine transform, yielding the pair correlation function $d(r)$ expressed as

$$\begin{aligned} d(r) &= 4\pi r[\rho(r) - \rho_0] \\ &= \frac{2}{\pi} \int_{K_{min}}^{K_{max}} K[S(K) - 1] \frac{\sin(\pi K/K_{max})}{\pi K/K_{min}} \sin(Kr) \, dK, \end{aligned} \tag{4}$$

where ρ_0 is the number density (i.e. the average number of atoms per Å^3), K_{min} and K_{max} indicate the lower and upper limits of the scattering vector available in the experiment. The present experimental data were smoothly extrapolated to the zero K value [8–10]. The convergence term $\sin(\pi K/K_{max})/(\pi K/K_{min})$ was used in Eq. (4), according to Lorch [11].

3. Models of nanotubes

The models of the multi-wall CNTs were constructed from the individual single-wall CNTs and then joined together. The single-wall CNTs were generated by rolling up a fragment of a graphene sheet, defined by two perpendicular vectors: the chiral vector $\mathbf{C}_h$ and the translation vector $\mathbf{T}$, into a seamless cylinder. Both vectors determine the size of the unit cell of the nanotube and can be expressed by the linear combination of the Bravais lattice vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ of the single graphene sheet as follows:

$$\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2 = (n, m) \tag{5}$$

$$\mathbf{T} = t_1\mathbf{a}_1 + t_2\mathbf{a}_2 = \frac{n + 2m, -2n - m}{W}, \tag{6}$$

where W is the greatest common divisor of the expressions $n + 2m$ and $2n + m$. In the present work, the base vectors forming angle $60°$ are used [1]. The pair of integers (n, m) describes all possible rolling ways of the graphene sheet and also characterises the type of the nanotubes: $(n, 0)$ zig zag type, (n, n) armchair and $(n, m \neq n)$ chiral nanotubes [1]. The magnitude of the vector $\mathbf{C}_h$ gives the radius of the nanotube $R = C_h/2\pi$. The coordinates of the atoms on the graphene sheet can be transformed into a new system in which the vector $\mathbf{T}$ is directed along the y-axis and the graphene atomic coordinates (x, y) are converted by the cylindrical transformation to the final form. This procedure has been described in our previous paper [4].

4. Results and discussion

The CNTs investigated in the present work have about 30 nm outer diameter as found by the electron microscopy studies [2]. Therefore, this parameter was kept constant in the present simulations. In order to construct the model of the multi-wall CNTs, a series of individual nanotubes with diameters in the range 26.3–29.9 nm were taken. The following nanotubes satisfy this constraint: (238, 202), (239, 190), (240, 178), (241, 166), (246, 149) and (243, 141). The distances between layers are in the range of 3.47–3.58 Å. At this stage, it is essential to point out that the structure factors and the pair correlation functions of the nanotubes with diameter from about 7 nm and greater are practically identical and do not depend on chirality as it has been shown in our previous paper [7]. For the CNTs of a small diameter ($\sim$0.7 nm), the contribution of a pair of atoms occupying positions on the opposite sides of the tubule circumference to the total structure factor has a much higher weight (proportional to $1/r_{ij}$, according to Eq. (3)) than that of wider CNTs. Thus, for the CNTs of greater diameters, the resulting structure factors look more like those of flat graphene layers [4] and information about chirality is lost. In this context, the pairs of the integers (n, m) specified above cannot be regarded as unique. Their choice is related only to the diameters. As each nanotube constituting the model has different chirality, there are no spatial correlations between atoms occupying positions in adjacent layers. In other words, the structure is turbostratic. Attempts made to rotate individual cylinders or to translate them along the tube axis lead to the same structure factors within the line