Journal of Alloys and Compounds 479 (2009) 484–488

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Simulated XRD profiles of carbon nanotubes (CNTs): An efficient algorithm and a recurrence relation for characterising CNTs

Bosco Emmanuel*, Sebastian Thomas[1], G. Raghuvaran, Daniel Sherwood

Modelling & Simulation Group, Central Electrochemical Research Institute, Karaikudi 630006, India

ARTICLE INFO

Article history:
Received 31 July 2008
Received in revised form
23 December 2008
Accepted 23 December 2008
Available online 4 January 2009

Keywords:
Carbon nanotube
Debye function
XRD
Algorithm
Recurrence relation

ABSTRACT

We develop an efficient algorithm and a novel recurrence relation for computing the Debye function of carbon nanotubes. This allows the computation of the XRD profile of CNTs for arbitrary lengths in times which scales linearly with the tube length. Using the recurrence relation, we further show that the XRD peak intensities are proportional to the tube length. The slopes and intercepts of the peak intensity versus tube length plots are characteristic of the CNT type. This work will help to create a database for CNTs akin to the ICDD data for 3-D crystals. Methods are also sketched to deduce tube properties from the XRD data.

1. Introduction

Besides electron microscopy, X-ray diffraction is a valuable tool to elucidate the structure of carbon nanotubes (CNTs). Compared to three-dimensional crystals with Bravais lattices periodic in all the three directions, CNTs have the periodicity only in one direction, i.e. along the tube axis. Consequently, the XRD profiles of CNTs are characteristically different from those of the conventional X-ray crystallography. While the analysis of the XRD data of 3-D crystals (both powder and single crystal) is presently supported by quite advanced theories, algorithms and softwares, the analysis of the XRD data of CNTs is in its infancy. Further, one is yet to build a database of XRD for CNTs, similar to the ICDD Reference Library. Burian, Koloczek and their co-workers [1–3] have made the first attempts towards the eventual goal of putting CNTs on par with three-dimensional crystal structures. The work of Hall and co-workers [4] on 3-D crystal shapes and structures is also worthy of mention here as their research foreshadowed the corresponding developments in the area of CNTs. Two of us (B.E. and D.S.), in related work, have advanced a mathematical algorithm to compute the 3-D shapes of nano-crystals [5]. In the present paper, we report further progress in the same direction.

In Section 2, we review the Debye function based analysis of the XRD of arbitrary structures and Section 3 describes the method of computing the atomic co-ordinates of CNTs which enter as inputs to the Debye function. Taking advantage of the one-dimensional periodicity in CNTs, we develop in Section 4 an efficient computational algorithm for computing the Debye function of CNTs of arbitrary lengths. This is made possible by an interesting recurrence relation that we discovered for the XRD intensity as a function of the CNT length and an asymptotic linear regime resulting from this recurrence relation. Based on this asymptotic linearity, we propose in Section 5 methods of analyzing the XRD data of CNTs. In Section 6, we present XRD data of two types of CNTs simulated using the present algorithm, verify the presence of the asymptotic linear regime, indicate the generality and possible extensions of the method and propose it as a versatile tool for building a simulated reference library of XRD data for a wide range of CNTs.

2. Debye function

Debye function gives the diffraction intensity as a function of the scattering angle θ or equivalently the scattering parameter s defined as

$$s = \frac{2\sin(\theta)}{\lambda} \tag{1}$$

where λ is the wave-length of the radiation.

For systems containing only one type of atom, like pristine carbon nanotubes, the Debye function can be written as [4,1]

$$I_N(s) = I_0 N f^2(s)\left(1 + \frac{D}{N}\sum_{i\neq j}\frac{\sin(2\pi s r_{ij})}{(2\pi s r_{ij})}\right) \tag{2}$$

* Corresponding author. Tel.: +91 4565 227550; fax: +91 4565 227779.
E-mail address: boscok@rediffmail.com (B. Emmanuel).
[1] Cognizant Technology Solutions India, Chennai 96, India.

0925-8388/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2008.12.109

where I_0 is the incident intensity, N the number of atoms in the system (e.g. CNT), $f(s)$ the scattering factor (available for most elements) and r_{ij} is the distance between atom i and j. D is the Debye–Waller factor which reflects the attenuation of the interference due to thermal vibrations and static random defects. In this article, we set $D=1$. For aggregates containing several types of atoms, generalization of the Debye function is available [6] and CNTs loaded with hetero-atoms or molecules may be studied with its help.

3. Atomic co-ordinates of CNTs

The method by which carbon nanotubes can be generated from the graphene sheet and computing the atomic co-ordinates are well documented in the literature [1,7,8]. In order to make the presentation self-contained, we summarize the method in this section.

CNTs are rolled-up versions of the graphene sheet [7]. Using a pair of integers (k,l) and the Bravais lattice vectors $\vec{a_1}$ and $\vec{a_2}$ of the graphene monolayer, construct the following two vectors:

$$\vec{C_h} = k\vec{a_1} + l\vec{a_2} = (k, l)$$

and

$$\vec{T} = t_1\vec{a_1} + t_2\vec{a_2} = \frac{k+2l,\ 2k+l}{w}$$

where $\vec{C_h}$ is called the chiral vector and $\vec{T}$ the translation vector. w is the greatest common divisor of $k+2l$ and $2k+l$. The chiral vector and the translation vector are perpendicular to one another ($\vec{C_h} \cdot \vec{T} = 0$). The radius of the CNT is given by $R = C_h/2\pi$. The CNT is generated by cutting the graphene sheet using the chiral and translation vectors and folding the resulting graphene segment. The three major types of CNTs are: zig-zag $(k,0)$, armchair (k,k) and chiral $(k,l \neq k)$.

For computing the CNT's atomic co-ordinates, we first generate the Cartesian co-ordinates of the atoms of the graphene segment for the chosen pair of indices (k,l). These co-ordinates are then transformed to a cylindrical co-ordinate system in which the vector $\vec{T}$ is pointing along the y-axis. Now, the atomic co-ordinates (x, y) of the graphene are related to the atomic co-ordinates (X, Y, Z) of the nanotube by

$$(X, Y, Z) = \left[R\cos\left(\frac{x}{R}\right), R\sin\left(\frac{x}{R}\right), y\right].$$

4. An efficient algorithm for computing the Debye function of CNTs of arbitrary length

Take a CNT of n unit cells, one stacked over the other along the tube axis. The Debye function contains a sum over all distinct pairs of atoms in the CNT. Let us start counting the number of intra-cell, inter-cell and the total pairs of atoms:

$$\text{Number of intra-cell pairs of atoms} = nm\frac{m-1}{2} \quad (3)$$

$$\text{Number of inter-cell pairs of atoms} = nC_2m^2 \quad (4)$$

$$\text{Number of total pairs of atoms} = \left(\frac{m^2}{2}\right)n^2 - \left(\frac{m}{2}\right)n \quad (5)$$

where m is the number of atoms in the unit cell.

Clearly, the total number of pairs of atoms in the CNT and hence the computational time grows as n^2. Though this is a polynomial time problem, the times required may be excessive for large n and m.

We can make the algorithm more efficient if we note that the nC_2 inter-cell combinations are not all distinct, thanks to the one-dimensional periodicity of the CNT along the tube axis.

Table 1
Illustrating the grouping together of identical inter-cell combinations when the number of cells in the CNT is six ($n=6$).

Inter-cell distance u (in units of the c parameter)	Identical inter-cell combinations	Number of identical inter-cell combinations ($n-u$)
1	(1,2), (2,3), (3,4), (4,5), (5,6)	5
2	(1,3), (2,4), (3,5), (4,6)	4
3	(1,4), (2,5), (3,6)	3
4	(1,5), (2,6)	2
5	(1,6)	1

In fact, one can enumerate and group identical inter-cell combinations together according to the inter-cell distance in a table. Table 1 illustrates this idea for a CNT with 6 unit cells.

In Table 1, the inter-cell combination (i, j) stands for all the inter-cell pair interactions between the ith cell and the jth cell in the CNT. Clearly, it follows from Table 1 that only one unit of computations (for the m^2 carbon-atom pairs, where m is the number of carbon atoms in the unit cell) is required for each inter-cell distance u. For $n=6$, there are five inter-cell distances. Therefore the total number of computational units required is $n-1$, where n is the number of unit cells in the CNT. To this we must add the intra-cell computations, $m(m-1)/2$ in number, which needs to be performed only once.

$\therefore$ The total number of pair-interactions to be computed

$$= m^2(n-1) + \frac{m(m-1)}{2} \quad (6)$$

Compare this with the number of pair-interactions that should be computed in the brute-force method:

$$\frac{(n-1)n}{2}m^2 + \frac{nm(m-1)}{2} = \frac{nm}{2}\{(n-1)m + (m-1)\}$$

$$= \frac{nm}{2}(nm-1) \quad (5)$$

By equation (6), the computational time required grows linearly in n, whereas it grows parabolically with n in the brute-force algorithm. Hence we used the linear-in-n algorithm. Fig. 1 confirms that the CPU time varies linearly with the length of the CNT if we use this fast algorithm.

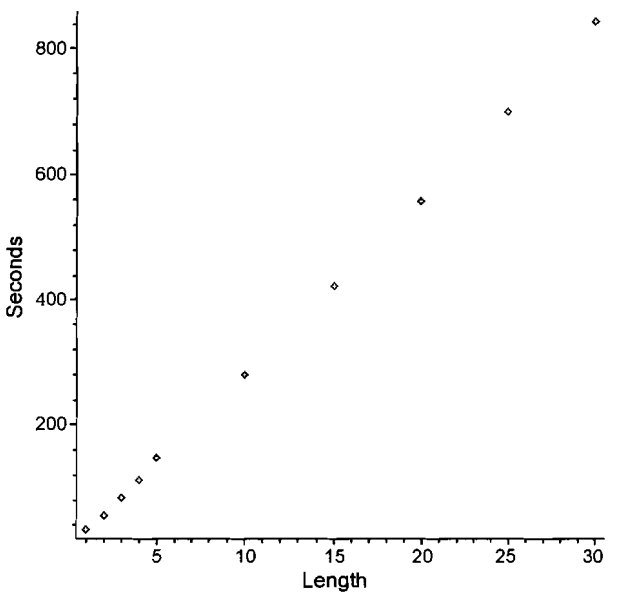

Fig. 1. CPU time vs. tube length for (5,5) CNT. The length is normalized using the unit cell length of the CNT.

A recurrence relation for the intensity $I_N(s)$:

$$I_N(s) = I_0 f^2(s)\left(N + D\sum_{i\neq j}\frac{\sin(2\pi s r_{ij})}{(2\pi s r_{ij})}\right) \quad (7)$$

where N is the total number of carbon atoms in the CNT. $N = n$m.

Write the Debye function using n:

$$I_n(s) = I_0 \times f^2(s)\left(n \times m + \sum_{i\neq j}\frac{\sin(2\pi s r_{ij})}{(2\pi s r_{ij})}\right) \quad (8)$$

The summation in this equation can be resolved into a total of n terms using the periodicity of the CNT and the ideas which were developed above.

$$\sum_{i\neq j}\frac{\sin(2\pi s r_{ij})}{(2\pi s r_{ij})} = \sum_{u=0}^{n-1}(n-u)S_u \quad (9)$$

where S_u represents all the terms, in the summation, which connects two unit cells separated by an inter-cell distance u (See Table 1). S_0 stands for the contribution of intra-cell interactions, n in number.

Now, taking the difference between $I_{n+1}(s)$ and $I_n(s)$,

$$I_{n+1}(s) - I_n(s) = I_0 f^2(s)\left\{(n+1)m + \sum_{u=0}^{n}(n+1-u)S_u - nm - \sum_{u=0}^{n-1}(n-u)S_u\right\} \quad (10)$$

$$I_{n+1}(s) - I_n(s) = I_0 f^2(s)\left\{m + \sum_{u=0}^{n}S_u\right\} \quad (11)$$

$$I_{n+1}(s) = I_n(s) + I_0 f^2(s)\cdot m + I_0 f^2(s)\sum_{u=0}^{n}S_u \quad (12)$$

The sum $\sum_{u=0}^{n}S_u$ converges fast and hence for sufficiently large n, $I_n(s)$ versus n plot will be linear for any given scattering parameter. The advantage of this asymptotic linearity is that, knowing the slope and the intercept of this asymptote, the diffracted X-ray intensity for any length of the CNT follows easily without any additional computation. Interestingly, this linear regime is reached within a few unit cells.

Table 2
Slopes and intercepts (by the method of Least Squares).

	5,5 CNT		8,0 CNT	
	Slope	Intercept	Slope	Intercept
First peak	1137.411	−424.248	1689.229	−140.801
Second peak	346.176	−28.796	492.725	4.528
Third peak	245.122	−128.512	339.522	−8.716
Fourth peak	103.768	1.669	113.650	0.062701
Fifth peak	48.886	−2.598	210.023	−68.120

5. Analysis of XRD-data of CNTs

Any given CNT sample may consist of (I) only one type of CNT but with a distribution of lengths and (II) a mixture of several types of CNTs with a distribution of their lengths. We need separate strategies to cull out information from the XRD's corresponding to these two cases. In this section we outline methods of analyzing the XRD using the developments in the two previous sections.

5.1. Case I

In section 4, we showed that, for sufficiently long CNTs, the XRD intensity for any given scattering parameter s is linearly related to the tube length n.

$$I_n(s) = \mu(s)n + \lambda(s) \quad (13)$$

If there are w_n CNTs of length n in the sample, the total observed intensity will be

$$I(s) = \sum w_n I_n(s) \quad (14)$$

$$I(s) = \mu(s)\sum w_n n + \lambda(s)\sum_n w_n \quad (15)$$

where $\sum_n w_n$ is the total number of CNTs and $\sum_n w_n n/\sum_n w_n$ the average length of the CNTs in the sample. Clearly, to find these two unknowns, the observed XRD intensities at two values of s, corresponding to two different XRD peaks, will suffice. The slope and intercept parameters $\mu(s)$ and $\lambda(s)$ are theoretically known for each XRD peak. They are presented in Table 2 for (5,5) and (8,0) CNTs.

5.2. Case II

This case applies to a CNT sample where there are several tube types labeled by a parameter t which runs from 1 to T. Further, the length n_t of a CNT of type t may have a distribution.

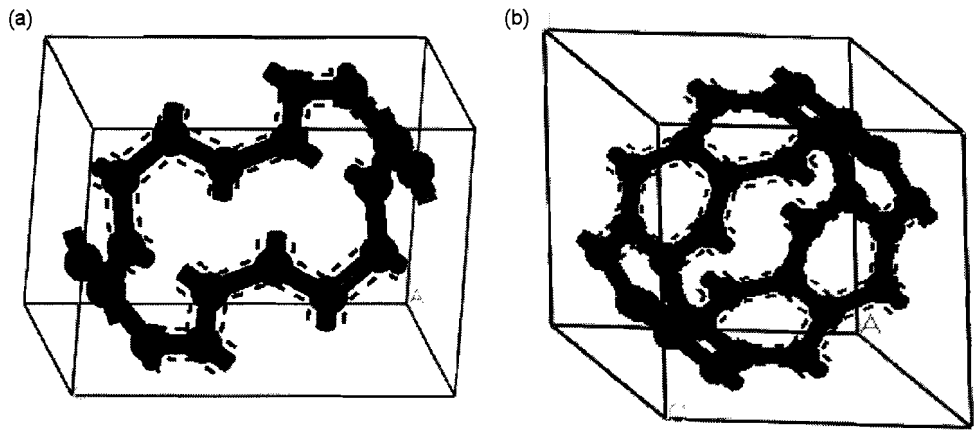

Fig. 2. (a) SWCNT of type (5,5), (b) SWCNT of type (8,0).

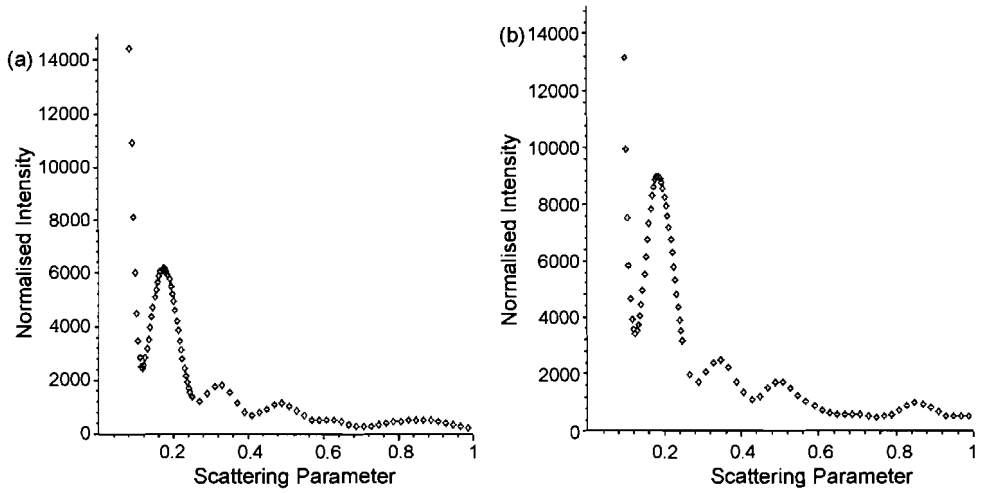

Fig. 3. (a) Simulated XRD for SWCNT of type (5,5). Normalized intensity is plotted against the scattering parameter ($Å^{-1}$). (b) Simulated XRD for SWCNT of type (8,0). Normalized intensity is plotted against the scattering parameter ($Å^{-1}$).

Now, equations analogous to Eqs. (13)–(15) can be written down:

$$I_{n_t}(s) = \mu_t(s) n_t + \lambda_t(s)$$

$$I(s) = \sum_{n_t} \sum_{t} w_{n_t} I_{n_t}(s)$$

$$I(s) = \sum_{t=1}^{T} \mu_t(s) \left\{ \sum_{n_t} w_{n_t} n_t \right\} + \sum_{t=1}^{T} \lambda_t(s) \left\{ \sum_{n_t} w_{n_t} \right\} + C$$

Including the over-all constant C, which may be used for making any background correction, we have $2T+1$ unknowns for the mixture of T number of types of CNTs. Obviously, we require the intensities of the XRD at that many peaks and the corresponding theoretical slopes and intercepts $\mu_t(s)$ and $\lambda_t(s)$.

We would have liked to illustrate the usefulness of this method on XRD data collected from real CNT samples. We tried hard to obtain, from several sources, suitable experimental XRD data for this purpose. However, we faced two major hurdles: paucity of XRD data on pure CNT samples to which one may apply the method advanced in case I above. Analysis of mixed or polydisperse CNT samples can be made using the method outlined in case II. However, this analysis will require a library of simulated XRD data on a host of CNT types. As we have just started building this library in the present work, we hope to apply these methods to real systems once we have equipped ourselves with a library of simulated XRD's for carbon nanotubes. (The authors thank an anonymous reviewer for suggestions in this regard.)

6. Results and discussion

In this paper, we have restricted ourselves to single-walled CNT (SWCNT), though the method equally applies to multi-walled CNTs too. Two types of SWCNTs were selected [Fig. 2(a) and (b)] and their XRDs simulated using the Debye function [Fig. 3(a) and (b)]. The XRD intensity $I_n(s)$ versus the tube length n was plotted for the first 5 peaks of these two SWCNTs [Figs. 4 and 5]. Note the asymptotic linear region theoretically anticipated in Section 4 above. The slope and intercept parameters are collected together in Table 2.

The main goal of the present work has been to standardize a method based on the Debye function for computing the XRD profiles of carbon nanotubes. Using this method one can build a database analogous to the ICDD database for 3-D crystals. While the peak positions are characteristic of the CNT type, the peak

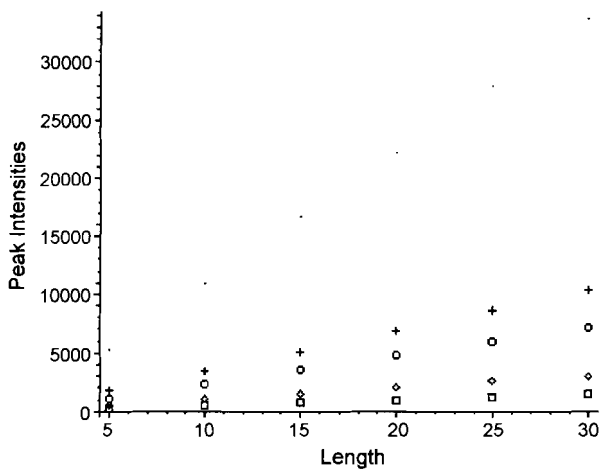

Fig. 4. Peak intensities vs. Tube length for (5,5) CNT. The length is normalized using the unit cell length of the CNT. Point (first peak); cross (second peak); circle (third peak); diamond (fourth peak); box (fifth peak).

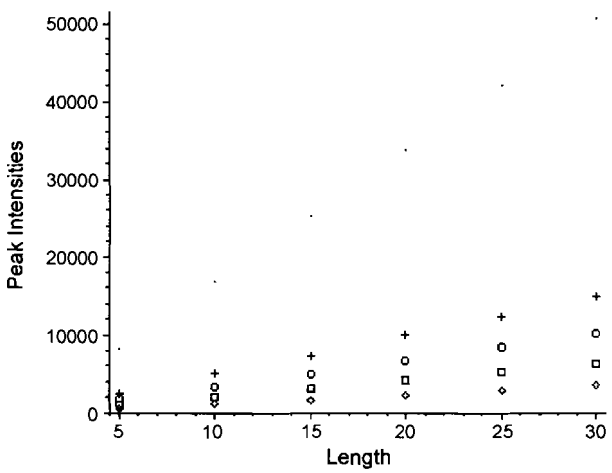

Fig. 5. Peak intensities vs. tube length for (8,0) CNT. The length is normalized using the unit cell length of the CNT. Point (first peak); cross (second peak); circle (third peak); diamond (fourth peak); box (fifth peak).

intensities measure the length of the CNT. Equipped with the peak positions and the intensities data, the computational schemes outlined in Section 5 can provide information on the types of CNTs and the average length of each type of CNT present in the sample.

7. Conclusion

The algorithm advanced in the present study is equally applicable to multi-walled carbon nanotubes and also to CNTs modified by incorporating guest atoms or molecules [9]. The needed generalization of the Debye formula is already known [6]. The effect of high temperatures or pressures on the CNT structures may also be probed.

References

[1] J. Koloczek, Y.-K. Kwon, A. Burian, J. Alloys Compd. 328 (2001) 222–225.
[2] J. Koloczek, A. Burian, J. Alloys Compd. 382 (2004) 123–127.
[3] J. Koloczek, L. Hawelek, A. Burian, J.C. Dore, V. Honkimaki, T. Kyotani, J. Alloys Compd. 401 (2005) 46–50.
[4] B.D. Hall, J. Appl. Phys. 87 (2000) 1666–1675.
[5] D. Sherwood, B. Emmanuel, Cryst. Growth Des. 6 (2006) 1415–1419.
[6] D.T. Cromer, J.B. Mann, Acta Crystallogr. A24 (1968) 321–324.
[7] M.S. Dresslhaus, G. Dresslhaus, P.C. Eklund, Science of Fullerenes and Carbon Nanotubes, Academic Press, New York, 1996.
[8] R. Saito, G. Dresselhaus, M.S. Dresselhaus, Physical Properties of Carbon Nanotubes, Imperial College Press, London, 1998.
[9] S. Kawasaki, K. Komatsu, F. Okino, H. Touhara, H. Kataura, Phys. Chem. Chem. Phys 6 (2004) (1769).