A method for diffraction-based identification of amorphous sp^2 carbon materials

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ABSTRACT

A method is suggested for estimation of structural properties of amorphous sp^2 carbon and applied to amorphous fullerene and its derivatives produced by vacuum annealing. The method is based on the fitting of the neutron or x-ray powder diffraction patterns for scattering wave vector's modulus in the range from few units to several tens of inverse nanometers. The respective inverse problem assumes that the nanostructure of a sample is representable by a limited number, N_{str}, of candidate structures (e.g. fullerenes, carbon flakes with graphene-like atom arrangement) of a limited number of atoms, N_{atom}. These structures are packed heterogeneously, in the domains with various average densities of atoms and various total potential energy, using the rigid body molecular dynamics with variable parameter of pair interaction of atoms in the neighboring nanostructures. The method is applied to interpreting the data of neutron diffraction by an amorphous C_{60} fullerene annealed at 600, 800, 850, 900 and 1000 °C. The results for $N_{str} = 36$ and $N_{atom} = 14 \div 285$ enabled us to quantify structural properties of the samples in terms of the average size and curvature of the sp^2 carbon structures, and analyze sensitivity of results to the layout of these structures in the domains.

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1. Introduction

Identification of structural contents of amorphous materials in the nanometer length scales from an analysis of powder diffraction patterns (x-ray, neutron, etc.) is known to be a complicated task: the lack of spatial ordering typical to crystalline media leaves much freedom in the reconstruction of structural content [1]. In the case of a single or few structural blocks and spatial homogeneity of the blocks in the sample one can use the method of the Reverse Monte Carlo (RMC) modeling (cf., e.g., [2]). The RMC reconstruction is based on the fitting of the experimental pair distribution function of relative atomic positions with that calculated for variable (unknown) layout of atoms in the structural block(s) and known chemical composition of the sample. In this approach the variation procedure is applied to positions of separate atoms. If there is no preliminary data on the structural content, the initial atomic ensemble should be taken random and the possible presence of chemical bonds between atoms may be recognized only on the final step of the algorithm (cf., e.g., identification of fullerenes in [3]). The RMC method applied to the structure refinement of the annealed C_{60} fullerenes (similar material to that analyzed in this paper) enabled the authors of [4] to quantify the structure of the amorphous samples in terms of the number of angles in carbon rings. The characterization of

the structure on the space scale larger than the distances between neighboring atoms was impossible because the structure, recovered by the RMC modeling, was fully chaotic on that space scale.

There is an alternative to the RMC approach, which is based on the variation within a set of many predefined structural blocks (of course, of limited total number) of the nanoscale size. Here the variety of possible chemical bonds is introduced on the first step of algorithm. The remaining freedom of packing these structural blocks in the sample requires additional numerical modeling which may generate various samples as various snapshots of an ensemble of blocks during the rigid-body dynamics of blocks subject to inter-atomic forces between them. In this approach, both the chemical bonds and the atomic positions within certain block are fully conserved.

A part of the outlined method (namely, identification of structural content in the case of "manual" packing of structural blocks, without rigid-body dynamics simulation of packing for various parameters of packing) has been used in the interpretation [5] of measurements of the synchrotron XRD by hydrocarbon films deposited in the vacuum vessel of tokamak T-10 in Kurchatov Institute. This enabled us to recover the structural content of carbon nanostructures of various topology and size in these films. To solve the problem [5] we developed the following software and methods: (i) software package XaNSoNS (X-ray and Neutron Scattering on Nanoscale Structures) for calculating the diffraction patterns of the ensembles of nanostructures, (ii) method [6] of an approximate description of positions of carbon atoms in a curved

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graphene sheet, (iii) optimization procedure and the respective web-services [7] created in the Mathcloud distributed environment [8] for fitting the experimental x-ray and/or neutron diffraction patterns with a set of numerically simulated ones. In this work we use the tools of items (i) and (iii).

Here we develop a method of diffraction-based identification of structural content of amorphous sp^2 carbon materials and apply it to amorphous fullerene and its derivatives produced by vacuum annealing, which are of interest for various applications. The respective inverse problem assumes that the nanostructure of the samples can be described with a limited number, N_{str}, of candidate sp^2 carbon structures (e.g. fullerenes, flat and curved flakes with graphene-like atom arrangement) of a limited number of atoms, N_{atom}. Note, that the classification of the fullerene as well as the curved carbon flakes as the sp^2 carbon is an approximate one. As known, hybridization of atoms in these structures falls between sp^2 and sp^3 but is closer to sp^2. These structures are packed heterogeneously, in the domains with various average density and mutual orientation. We use the rigid body molecular dynamics (RBMD) with variable parameter of pair interaction of atoms in the neighboring rigid-body nanostructures. The RBMD technique was applied in [9] to packing of various sp^2 and sp^3 carbon structures, to analyze the impact of packing on the x-ray diffraction data analysis. The model developed here is applied to interpreting the experimental data of Section 3 of neutron diffraction by an amorphous C_{60} fullerene annealed in a vacuum at 600, 800, 850, 900 and 1000 °C [10]. To interpret experimental results (Section 4) we apply the model for $N_{str} = 36$ and N_{atom} in the range from 14 to 285. This enabled us to quantify the structural properties of the sample in terms of the average size and curvature of the sp^2 carbon structures, and analyze sensitivity of results to the layout of these structures in the domains (ensemble of domains, where each domain is a mixture of various nanostructures, vs. ensemble of domains, where each domain is composed of identical nanostructures).

2. Main features of the method

The method is aimed at estimation of structural properties of amorphous sp^2 carbon materials. The method may be represented as the following sequence of actions.

(A) Definition of the structural blocks that we choose for quantitative description of a carbon component in the sample. Particular conditions of the production of the sample and the data from other diagnostics (chemical composition of the sample is supposed to be known) may help to limit the set of possible structural blocks, e.g., to a set of a limited number, N_{str}, of the sp^2 carbon structures.

(B) Numerical modeling of the possible layout of structural blocks within a sample. As far as packing of structural blocks in an amorphous sample gives much freedom (as compared to crystalline samples) the numerical modeling may generate various samples as various snapshots of an ensemble of blocks during the rigid-body dynamics of blocks subject to inter-atomic forces between the blocks (the principles of numerical modeling are described below). The diversity of these samples is described by continuous parameters like the average density of atoms in the sample and the blocks' mutual orientation, e.g. random or ordered. The variation of possible packing may be described by a set (a grid) of the values of these parameters and, for *arbitrary* composition of structural blocks from the predefined set, gives a number of variants which is too large even for supercomputer simulations. We restrict our analysis to the following two limiting cases and one intermediate case.

(B1) First, we consider the case of a packing in the form of domains (an ensemble of nanostructures from a few dozens to several thousands in number) that contain only identical structural blocks and possess quasi-homogeneous density of atoms on the space scale of the entire domain. Such a sample appears to be a heterogeneous material in which the variation of structural content is limited to a variation of the composition of domains composed of identical blocks (we call these domains as mono-structural ones). The linear size of domains has a lower limit of 10 nm to avoid the impact of the finite size of the domain on the diffraction patterns in the range of scattering wave vector's modulus under consideration (from few units to several tens of inverse nanometers). For such domains the effects of interference of atoms, located closely to the boundaries of domains, are small, and the diffraction pattern is merely a sum of those for separate domains. The total number of the mono-structural domains is equal to the product $N_{str} \cdot N_p$, where N_p is a number of variants with different density and mutual orientation of blocks in each mono-structural domain. The case of composing a sample from mono-structural domains enables one to start solving a general problem with a computationally feasible task and to find the fraction of each structural block in the total number of carbon atoms in the sample, which may be used as a test (initial) distribution for other partial cases of a general inverse problem.

(B2) Second, we consider the case of a mixture of different structural blocks within domains (we call these domains as multi-structural ones) with the fractions of these blocks in the total number of atoms in the multi-structural domain taken from the above-mentioned solution in the case of mono-structural domains. Suppose, e.g., that in the case *B1*, we found that the sample contains N_{C_x} ($N_{C_x} \le N_p$) mono-structural domains of the structural block with the name C_x, and the ratio of carbon atoms' number in all these N_{C_x} domains to the total number of carbon atoms in the sample is equal to X_{C_x}. This means that the fraction of the C_x structural blocks in the total number of atoms in the multi-structural domains will be taken equal to X_{C_x}. The average density of atoms and the mutual orientation of the blocks in the domains are varied similarly to the case of mono-structural domains. The total number of the domains in this case is equal to N_p.

If the simulated scattering intensity in the case of multi-structural domains may fit the experimental diffraction pattern as well as it does in the case of mono-structural domains, one can claim that the diffraction pattern is not sensitive to the type of domains (mono- or multi-structural ones) and the mono-structural domains may or may not be present in the sample. One can stop on this and characterize the sample in terms of averaged values of major parameters, e.g., average size and average curvature of the sp^2 carbon structures (these parameters will be the same in the cases of mono- and multi-structural domains). The parameters that are determined by the packing of structural blocks (e.g. density of the sample), may take different values in the cases of mono- and multi-structural domains, even despite the closeness of theoretical diffraction patterns in these cases.

If various combinations of multi-structural domains with given domain's structural content fail to fit the experiment, it will be a sign that the mono-structural domains of certain structural blocks may be present in the sample. In this case one has to try the cases that are close to the case of mono-structural domains. The choice of the test distributions may be suggested by particular features of the sample and its production. In this paper we consider such a case, an intermediate one between *B1* and *B2*, for the C_{60} fullerene samples annealed at low temperatures to show that the mono-structural domains of the C_{60} are very likely present in the samples.

To complete the description of the algorithm we briefly describe the rigid body molecular dynamics (RBMD) simulations of packing and formulate an inverse problem.

We use the RBMD approach [11] to model the packing of the carbon structural blocks in the domains. In this approach, blocks are considered