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cif2tube – Algorithm for constructing nanotube and nanoscroll models from crystallographic information files

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ABSTRACT

This study developed a user-friendly program, cif2tube, to facilitate the construction of a nanotube or a nanoscroll model using an input crystallographic information file (*.cif file). This program makes it possible for users to determine several parameters used in the construction of the nanotube/nanoscroll model, including the chirality, the directions in which it will roll-up, and the interlayer spacing of the nanoscroll. The ability to vary these parameters enables the customization of the resulting models. The capability of the cif2tube program was demonstrated by constructing models of existing as well as hypothetical nanotube/nanoscroll materials. The as-generated models from cif2tube were then compared with models obtained from commercial molecular simulation packages and as-generated models that were subjected to geometric optimization and molecular dynamics simulations. We also demonstrated the capability of cif2tube in the creation of models comprising hypothetical nanotubes of perovskite, zeolite, and metal organic frameworks (MOFs). cif2tube enables the creation of a large variety of existing and novel nanotube models to facilitate the computational study of nanotube materials.

1. Introduction

Since the discovery of single-walled carbon nanotubes (SWCNTs) in 1992 [1], nanotubes have been the subject of considerable interest, due to their one-dimensional microstructure and unique mechanical [2–7], thermal [8–10], electrical [11–17], and mass transport properties [18,19]. Over the past two decades, SWCNTs have been implemented in a variety of applications, including sensors [20–22], power generation systems, nanocomposite materials [23,24], and molecular separation [19,25]. In the last decade, a new class of one-dimensional materials referred to as metal oxide nanotubes or nanoscrolls has been the focus of many studies. Unlike SWCNTs, inorganic nanotubes ("non-carbon" nanotubes) come in a wide variety and can be synthesized using scalable hydrothermal and solvothermal reactions. Hydrothermally synthesized titanate nanotubes and nanoscrolls are an excellent photocatalyst, widely regarded as a benchmark anode material in electrochemistry [26–29]. Hydrothermally synthesized imogolite (aluminosilicate) nanotubes with pores of just 1 nm have been applied in applications involving molecular storage [30,31], separation [31–39], and catalysis [35,40–44]. Zinc oxide nanotubes, which are also synthesized in a hydrothermal reaction [9,45–49], possess unique optical [46] and piezoelectric properties [47]. Chrysotile possesses a nanoscroll structure of magnesium silicate [50,51] or nickel silicate [52,53], which gives it excellent electronic and mechanical properties.

The scale of nanotubes imposes numerous challenges in the experimental [54–58] characterization of individual nanotubes. Thus, computational tools play a critical role in the investigation of nanotube materials [59,60]. For example, calculations based on density functional theory (DFT) and force fields have been performed to discover the probable dimensions and electrical properties of aluminosilicate and aluminogermanate nanotubes [33,61–66]. Molecular dynamics (MD) and grand canonical Monte Carlo (GCMC) simulations have been employed to investigate the diffusion and adsorption properties of various molecules in nanotubes [32,36,37]. Nanoscale continuum modeling has also been applied in the study of their mechanical properties [67].

Theoretically, these computational tools are applicable to the study of any nanotube system; however, a nanotube model based on its actual atomic structure must be constructed prior to conducting any computational study. One critical limitation of any computational investigation of nanotubes (new or existing) is the lack of a reliable tool for the construction of the nanotube model. Furthermore, existing crystallographic databases, such as the International Crystal Structure Database (ICSD) [68] and the Cambridge Crystallographic Data Centre (CCDC) [69–74], do not include the structure of nanotubes or nanoscrolls. One commercial software package, Biovia Materials Studio® (formerly Accelry's Materials

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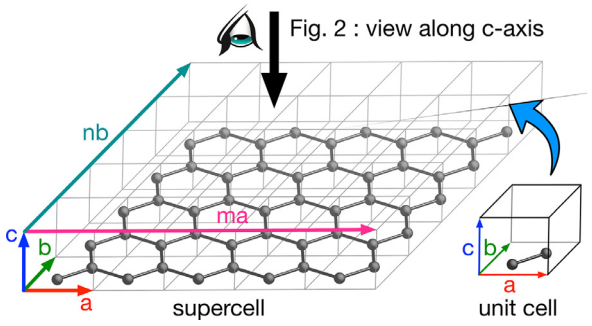

Fig. 1. Schematic illustration of supercell created by a primitive unit cell.

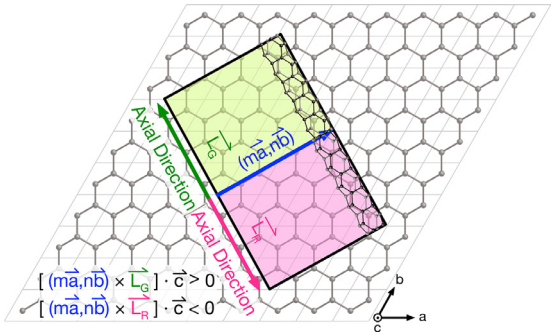

Fig. 2. Schematic illustration of vector $(\vec{ma}, \vec{nb})$ and $\vec{L}$ used in construction of a nanotube or a nanoscroll model ($\vec{L_R}$ and $\vec{L_G}$ here is only for distinguish different cases for $[(\vec{ma}, \vec{nb}) \times \vec{L}] \cdot \vec{c} > 0$ and $[(\vec{ma}, \vec{nb}) \times \vec{L}] \cdot \vec{c} < 0$, respectively).

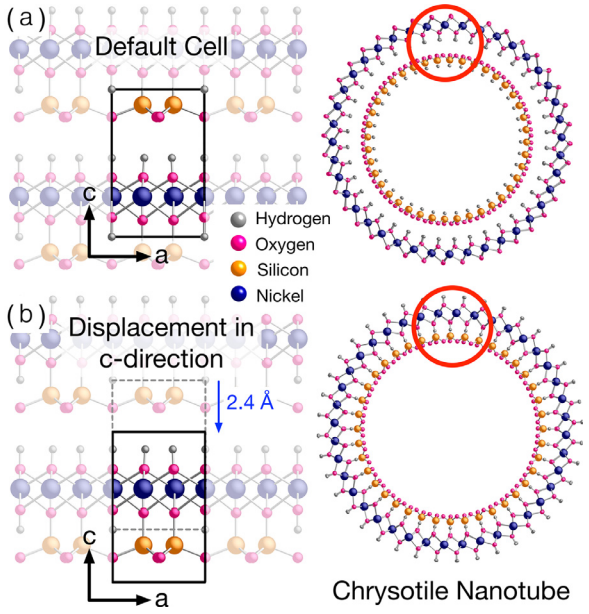

Fig. 3. Schematic illustration showing displacement in the *c*-direction, which may be required for formation of nanotubes: (a) absence of offset could lead to an unrealistic double-walled nanotube; (b) realistic single-walled nanotube model formed using an offset of -2.4 Å.

Studio®), enables users to generate two types of nanotube model: carbon nanotubes and boron nitride nanotubes. Other commercial packages, such as JCrystalSoft Nanotube Modeler® [75,76], and free software, such as Avogadro® [77], are limited to the construction of carbon nanotube models; *i.e.*, they are inapplicable to the construction of nanoscroll models. CrystalMaker® (version 9) is the only existing package capable of converting a user-input crystallographic information file [78,79] (CIF file) into a nanotube model; however, it requires that the user enters the chirality and diameter of the nanotubes independently. Furthermore, any mismatch in the values of chirality and diameter result in a faulty nanotube model. The absence of practical tools for the construction of such models is a serious impediment to the advancement of computational studies on emerging and hypothetical nanotube/nanoscroll materials.

Herein, we proposed a novel software package, cif2tube, for the construction of nanotube and nanoscroll models using any crystallographic information file (*.cif file). The ultimate purpose of present work is providing a program for generating models of nanotubes and nanoscrolls from any given *.cif file. Then the output nanotube or nanoscroll models can be used for molecular simulations. cif2tube users are free to customize several construction parameters, including the chirality, diameter, and length, as well as the direction in which the 2D nanotube or nanoscroll is to "roll up". Following construction of the nanotube/nanoscroll, cif2tube generates an output file in *.xyz format, which is compatible with most existing computational packages. We demonstrate the capability of cif2tube by constructing models of existing materials, including carbon nanotubes, aluminosilicate nanotubes, and crysotille nanoscrolls. The as-constructed models are then compared with the models that have undergone geometric optimization. Finally, we illustrate the practicality of cif2tube in the construction of hypothetical nanotube models through the generation of three non-existent nanotubes of perovskite, zeolite, and a metal organic framework (MOF).

2. Method

2.1. From primitive unit cell to nanosheet supercell

The first step in converting a primitive unit cell into that of a nanotube or a nanoscroll involves the construction of a nanosheet supercell from the primitive unit cell with lattice constants *a*, *b*, and *c*. As long as the nanosheet supercell grows along the plane parallel to the *a*- and *b*-axes, the user would input two integers, *m* and *n*, to define the direction in which the nanosheet is meant to "roll up" into a nanotube or nanoscroll (Fig. 1). The "roll up" direction is described using the vector $(\vec{ma}, \vec{nb})$. The absolute value of vector $(\vec{ma}, \vec{nb})$ is equal to the circumference of the nanotube or the edge-to-edge distance of an unfolded nanoscroll (Fig. 2). The radius (R) of the nanotube is equal to $\frac{|\vec{ma}+\vec{nb}|}{2\pi}$. In the case of a nanoscroll, two additional parameters, interior radius (r_0) and the spiral constant (s), must be specified in order to describe its dimensions. The nanoscroll is formed by rolling up a nanosheet along an Archimedean spiral, in which the spiral constant, *s*, is used to define the layer-to-layer distance and the direction of the spiral. When $s > 0$, the nanoscroll forms a counterclockwise spiral, and *vice versa*. The vector $\vec{L}$, which is perpendicular to $(\vec{ma}, \vec{nb})$, is also specified by the user. The absolute value of $\vec{L}$ is equal to the length of a nanotube or nanoscroll. The user is allowed to determine the direction of the vector $\vec{L}$ *via* determining the sign of $[(\vec{ma}, \vec{nb}) \times \vec{L}] \cdot \vec{c}$ (Fig. 2). Vector $(\vec{ma}, \vec{nb})$ and $\vec{L}$ define two long sides of the nanosheet supercell, as shown in Fig. 2. The short side of the nanosheet supercell is the absolute value of vector $\vec{c}$ in the primitive unit cell. Depending on how a primitive unit cell is defined, an offset of the nanosheet in the *c*-direction may be required. A failure to do so would lead to the creation of a double-walled nanotube, an example of which is presented in Fig. 3. In this case, an offset of 2.4 Å in the negative *c*-direction is necessary to create the desired single-walled nanotube (Fig. 3b). An appropriate value for this offset is based on the input crystallographic file

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