

## STRUCTURAL MODELING OF SOME NANOMETRIC ARCHITECTURES

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The atomic configurations possible in various solid materials at the nanometric scale are investigated. Closed clusters based on As-Se composition, silicon wires and carbon nano-configurations are modeled starting from hand-built models and followed by Monte-Carlo – Metropolis energy relaxation in order to reach the structures of minimum free energy.

*Keywords:* Nano-wire, Nano-tube, Fullerene, Nano-pie, Chalcogenide, As<sub>2</sub>S<sub>3</sub>, Nano-technology

### 1. Introduction

The rapid development of the field of nano- technology and nano-devices stimulated the nano-science and, also, the study of primary structures of the atomic configurations. To reach the maximum of device miniaturization means to go into the intimate life of the lattices and networks of atoms, including clusters of atoms or molecules. How small could be the devices? At the limits of several nanometers the material science is completely different. The practical applications of the new science lead to completely different devices.

The first problem of the nano-physics and technology is the creation of the assembling elements, as bricks for the construction of various devices. One important step in this direction is the discovery of the carbon nano-objects by Kroto, Curl and Smalley in 1985 (Nobel Prize for Chemistry in 1996) [1].

In this paper we present the results obtained during simulation of several nanometric configurations based on the most attractive atomic architectures, which are considered as the most probable objects to be used in the near or far future in the nano-device technology. The modeling aims not only to suggest specific configurations for nano-technology, but also has the power to discard those configurations that are highly improbable, due to the impossibility to maintain the values of the crystallo-chemical parameters known from the study of the packing of atoms in the bulk of a specific material [2-6].

### 2. Silicon nano-wires

Silicon nanowires are long and narrow objects made of silicon atoms, with tetrahedral bonding. We have simulated the atomic-scale configurations of three nano-wires based on silicon. The first two models have open ends, while the third one is completely closed. In each of these structures, the fourth bond on every silicon atom is considered to be passivated by hydrogen.

The narrowest wire, has been built from 54 silicon atoms linked as 6-fold rings of atoms. The wire has a diameter of 0.38 nm. Figure 1 shows the model of minimum diameter and its structural properties. It is remarkable the exact tetrahedral angle on the silicon atoms, identical to that of bulk silicon. The pair distance distribution in the model fits well with the distribution of the first distances in bulk crystal or amorphous solid. This model is fully compatible with the crystallo-chemistry of tetrahedral silicon. The diffraction pattern of the configuration shows particularities

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well related to tetrahedral silicon, especially for the first diffraction peaks. The total free energy/atom of the model is  $E = 0.00567 \times 10^{-16}$  nJ.

The second silicon wire of larger diameter is shown in Fig. 2. The silicon configuration comprises 72 atoms and its diameter is 0.52 nm. The total free energy/atom of the model is large:  $E = 51707 \times 10^{-16}$  nJ this demonstrating the incompatibility of the structural configuration with the crystallo-chemistry of silicon. If one regards the bond angle distribution, one remarks that the distribution is very narrow, but its centre is situated significantly away of the tetrahedral angle (at  $\sim 114^\circ$ ).

Fig. 3 shows the wire model of largest diameter simulated by us. The model contains 100 atoms and has the diameter, after relaxation, of 0.72 nm. The total free energy of the model is again high,  $E = 169.53 \times 10^{-16}$  nJ. This enough large value is given by the distortion of the ideal angle between bonds, which, due to steric hindrances, prevents the reaching of the true tetrahedral angle of silicon bonds in crystal.

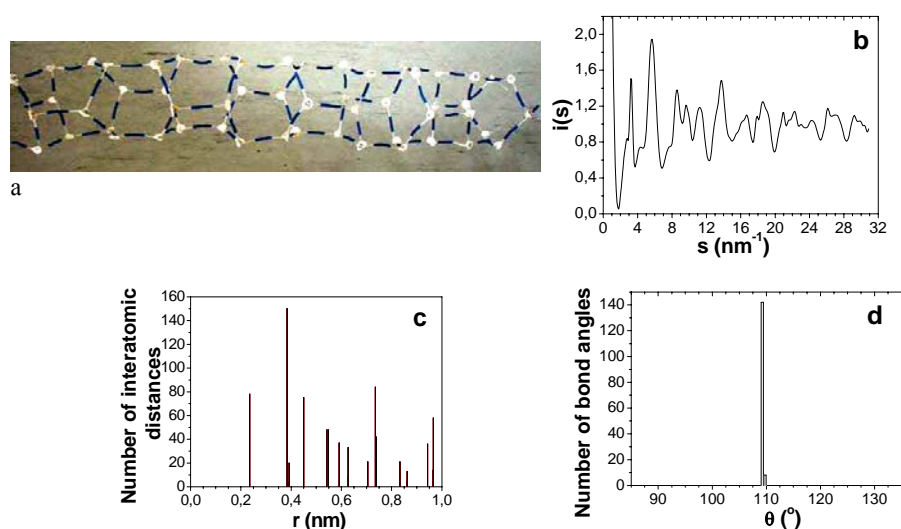


Fig. 1. A silicon wire of minimum diameter, having a tubular shape (54 atoms). a. model; b. the structure factor (X-ray diffraction pattern); c. pair distance distribution; d. bond angle distribution.

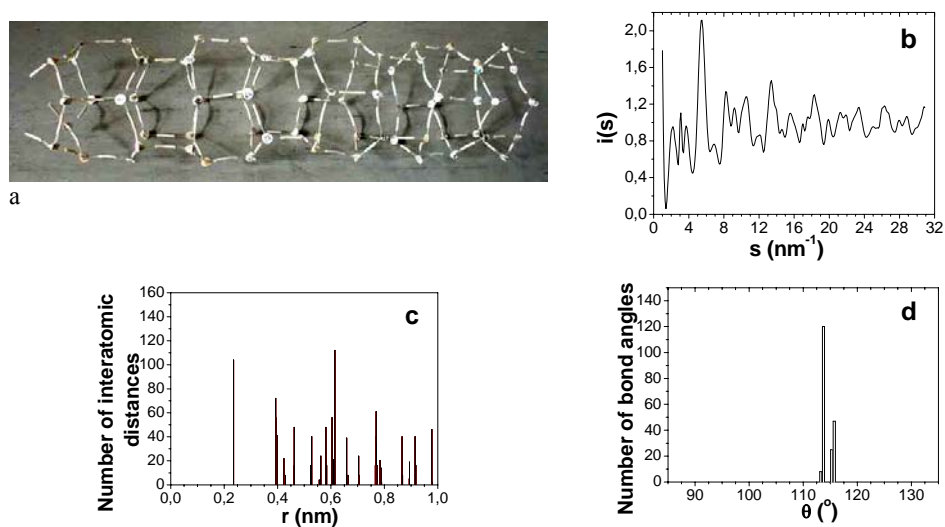


Fig. 2. The nano-structural configuration for a medium-large diameter silicon nano-wire a. model; b. the structure factor; c. pair distance distribution; d. bond-angle distribution.

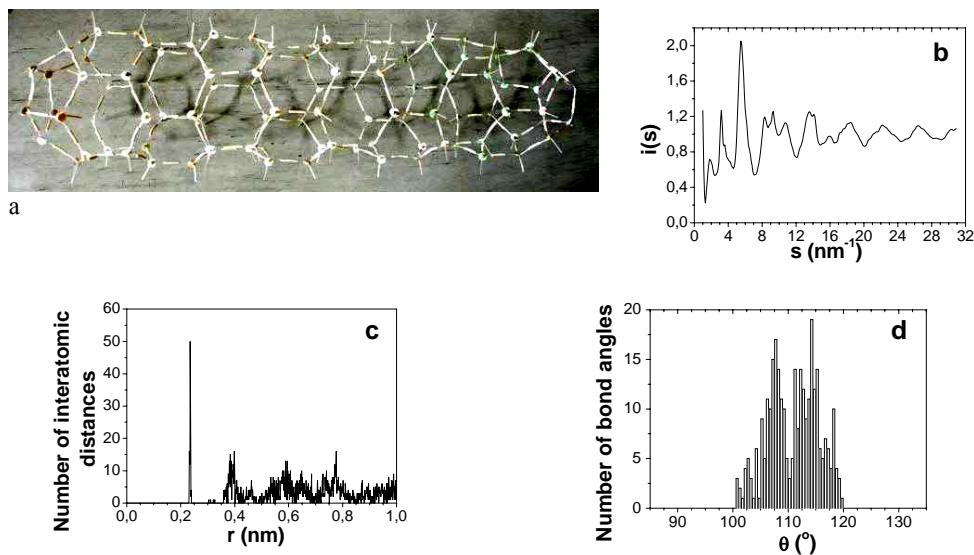


Fig. 3. The silicon wire of largest diameter simulated in this paper (a) b. the structure factor; c. pair distance distribution; d. bond angle distribution.

### 3. The carbon nano-tubes and combination with fullerene

The world of nano-carbon configurations is rich and a continuous diversification is produced. Nano-tubes [7], single and multi-wall-tubules [8, 9], nano-horns, simple and onion-like fullerenes [10, 11], etc... are known and largely studied.

Of high interest in nano-electronics are the nano-connectors, i.e. wires or tubules, which can change the direction at the desired position, in order to connect the devices after will, i.e. to be extended in space in various directions.

With the aim to demonstrate the possibility to build different nano-tube connections for building networks of connectors, we have modeled the bonding configuration between two carbon nano-tubes at right angle (Fig. 4). The total number of the atoms in the model is 246 atoms. The tubule diameter is 0.655 nm. It is remarkable that the distortion of the bonding between carbon atoms, at the joining portion is enough low (after relaxation) and this speaks in favour of the stability of the tube-tube connections in these nano-configurations.

The total free energy/atoms in the relaxed model is:  $E = 11044 \times 10^{-16}$  nJ.

Another configuration of interest is that between a fullerene molecule and a carbon nano-tube. We have simulated this atomic scale connection in a frame of a model with 214 atoms (Fig. 5). The total free energy/atoms of the combination ( $74426 \times 10^{-16}$  nJ) is significantly larger than that of the connection tube-tube. This is due to a higher distortion of the carbon bonds in the connection region.

The connection of fullerene with nanotube is important because a fullerene cage could be filled by quantum dots or single atoms that make fullerene luminescent or superconducting or both, thus ensuring special properties to an optoelectronic circuit, where the connectors are essential for the detailed function of the circuit.

It is interesting to note that the bonding angle distribution in the complex model is split in two narrow distributions centered on  $108^\circ$  and on  $118^\circ$ .

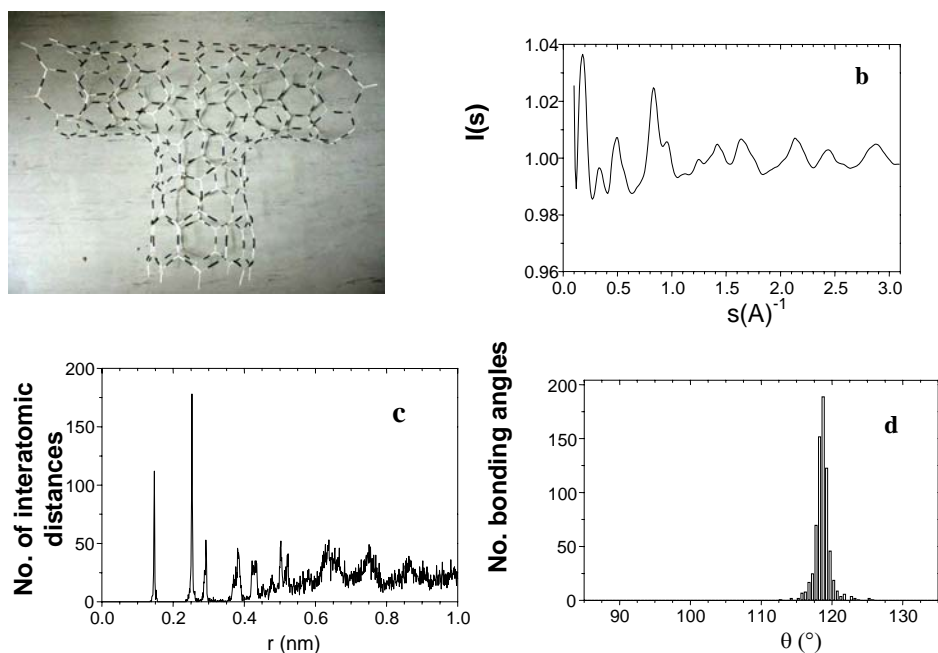


Fig. 4. The atomic scale connection of two carbon nanotubes at right angle (246 atoms) (a) b. structure factor; c. pair distance distribution; d. bond angle distribution.

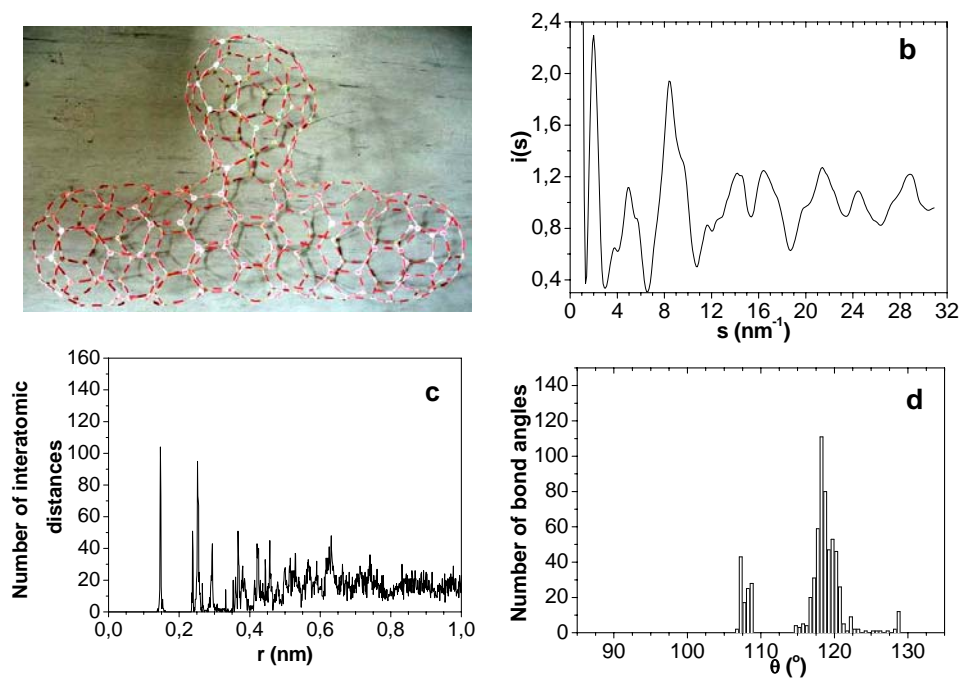


Fig. 5. The complex configuration fullerene + nanotube (214 atoms) a. model; b. structure factor; c. pair distribution histogram; d. bond angle distribution.

#### 4. The chalcogen-Pnictogen nano-configurations

The chalcogens are the elements of the 6-th group of the periodic table: sulphur, selenium and tellurium. The pnictogens are element of the 5-th group of the periodic table. Due to specific peculiarities of these atoms, in particular the formation of only two or three covalent bonds, and the

maintaining of a lone pair of electrons not involved in the chemical bonds, the atomic scale configuration is quite special. Layered structures and, also, closed clusters are possible without significant distortion of the covalent bonds. Large varieties of planar clusters made of sulfur (chalcogen) and arsenic (pnictogen) have been modeled by us in order to demonstrate the possibility to build technologically new structures based on chalcogens.

Fig. 6 shows a large round cluster based on  $As_2S_3$  chemical composition, well known both in crystalline and amorphous form. The relaxed model show structural particularities of interest. The angles on arsenic and sulfur respect the angles considered in simulation. The first distances in the radial distribution function agree with that known from the experimental data on amorphous and crystalline  $As_2S_3$ .

This means that the structure is highly compatible with the crystallo-chemistry of the  $As_2S_3$ .

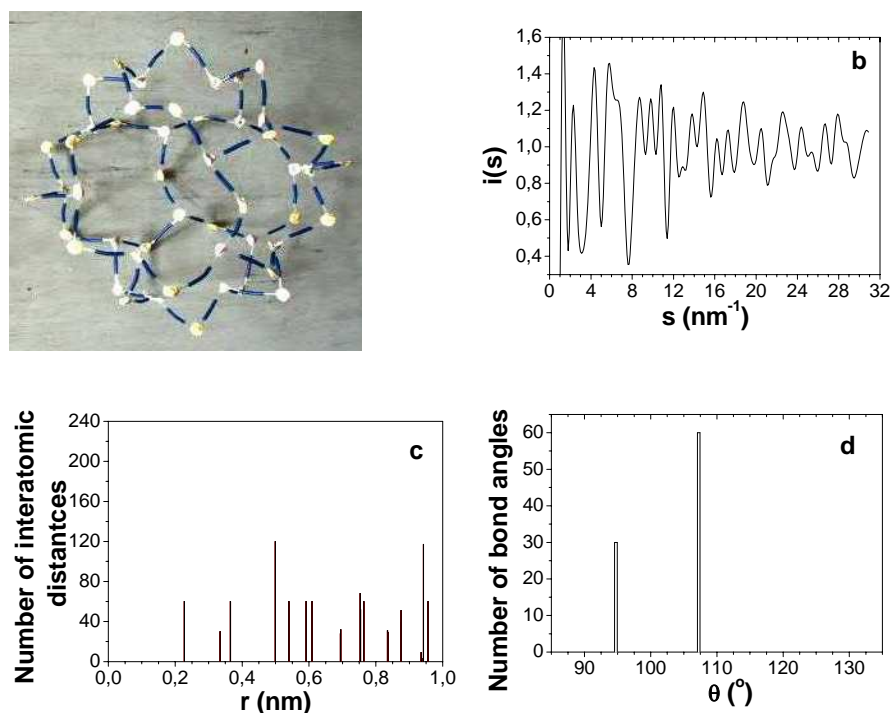


Fig. 6. The model of a big cluster of composition  $As_{20}S_{30}$  a. the model (50 atoms); b. the structure factor; c. the pair distribution function; d. the bonding angle distribution

An other configuration tried by modeling was that of a long nano-tube with or without closed ends. One of the successes of our modeling was the demonstration that, in the chalcogen-pnictide networks it is possible to find nano-tube configurations!

Fig. 7 shows such configuration. One remarks that both pair distribution histogram and bond angle distribution in the model exhibit, after relaxation, narrow peaks, that demonstrate the exact fit with the true network of covalently bonded atoms, with the same crystallo-chemical parameters as in the case of the crystalline compound of  $As_2S_3$ . The free energy/atoms of the cluster with open ends is  $7.14 \times 10^{-16}$  nJ, a very small value, which speaks in favour of the high stability of the cluster. The cluster with closed ends has a free energy/atoms of  $268.62 \times 10^{-16}$  nJ a value that allows for the stability of the cluster against thermal perturbations.

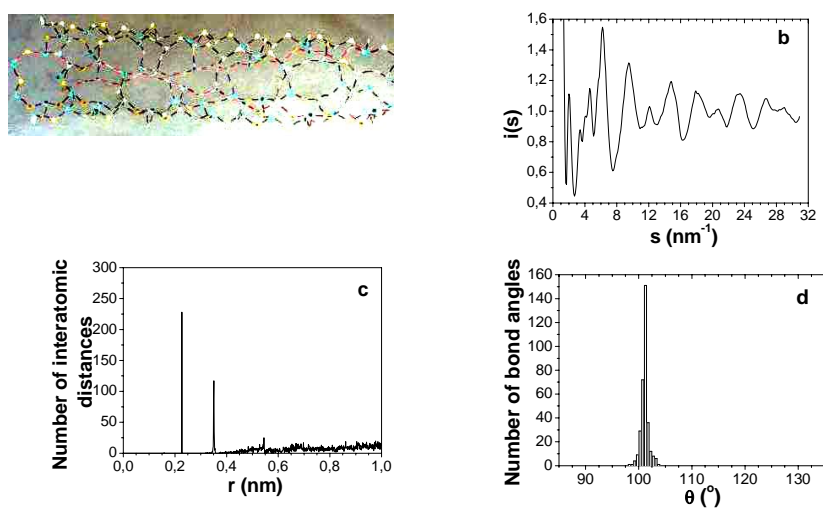


Fig. 7. The model of a nano-tube configuration based on  $\text{As}_2\text{S}_3$  composition  
 a. model; b. structure factor; c. pair distribution function; d. bond angle distribution

An other configuration that could be continued into a series of nano-objects based on double planar clusters, is the so-called nano-pie cluster. The nano-pie model has 180 atoms. Fig. 8 shows the model and its structural characteristics. The bond angle distribution is narrow and speaks in favour of the stability of such extended clusters. The free energy/atoms of the cluster is  $0.1235 \times 10^{-16}$  nJ.

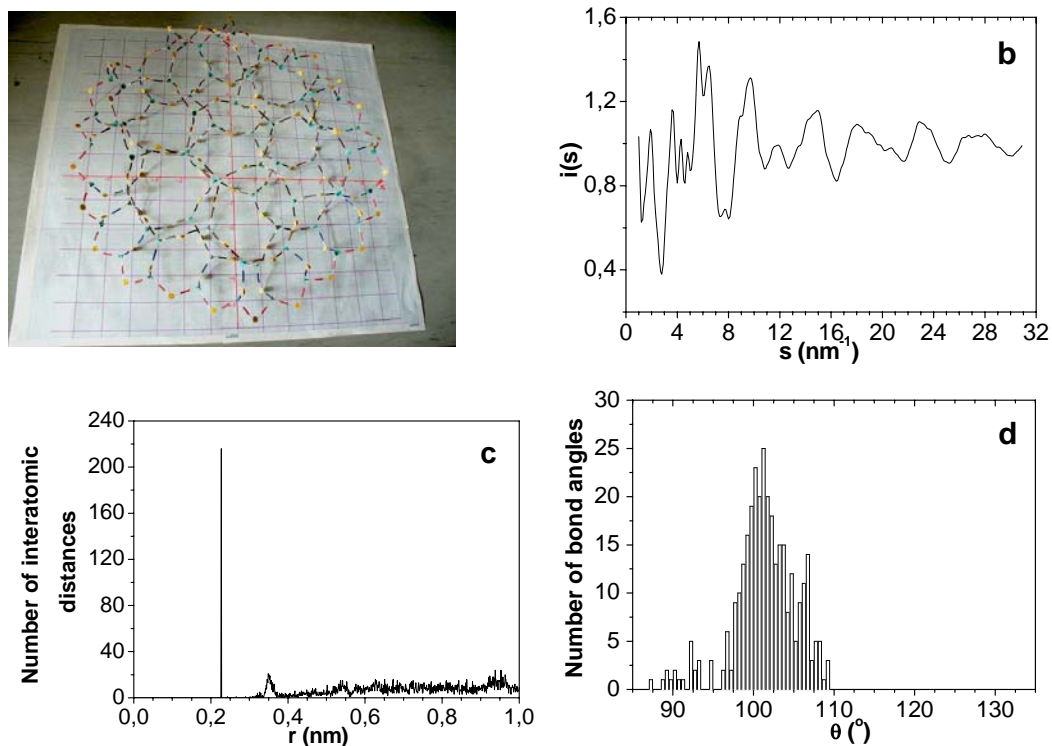


Fig. 8. The nano-pie model and its structural characteristics a. nano-pie model;  
 b. structure factor; c. pair distribution function; d. bond angle distribution.

## 5. Conclusions

The simulations of several architectures at the nanometric scale have been performed.

From the assembly of nano-objects simulated in this work only part of them are compatible with the crystallo-chemistry of the atoms that constitute the bulk crystalline lattices. The wires, the tubules, the interconnections fullerene-tubule, the various cluster configurations in  $\text{As}_2\text{S}_3$  composition, could be produced because their atomic properties are akin to those of the atoms in crystals. It is the task of the advanced technology to build nano-configurations and to find the right way to connect these configurations one to another.

The new technological methods will involve new tools for manipulation of the atoms (e.g., self assembly and atomic force microscopy).

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