Structure and thermal conductivity of carbon multilayered “onion” fullerenes

Yu P Zarichnyak 1,2, VA Ivanov 3, A A Marova 1, and N V Pilipenko 1

1 National Research University of Information Technologies, Mechanics and Optics (ITMO University), 49 Kronverksky Pr., St. Petersburg, 197101, Russia.
2 Corresponding author.
3 Institute of Physical and Technical Problems of the North, SB RAS, Yakutsk, Russia

Abstract. Using the proposed model of the structure of carbon multilayer “onion” fullerenes, approximate quantitative estimates of the effective thermal conductivity of multilayer onion fullerenes are obtained using the methods of generalized conductivity theory.

1. Introduction.
The onion form of carbon (figure 1 a) was discovered in 1980 by the Japanese scientist Sumio Iijima [1]. This takes place, when fullerene molecules of different sizes are concentrically embedded into each other like onion layers [2,3] (figure 1).

Figure 1. Electron microscopy images and polyhedral models of the structure of carbon multilayer “onion” fullerenes: a) electron microscopic image of a carbon Nano sphere (onion) [1]; b) three-layer “onion” fullerene C60-C240-C540 [3]; c) - multilayer polyhedral model [4].

Onion forms of carbon are formed along with the synthesis of fullerenes and nanotubes (in small quantities) in high-temperature processes with evaporation of carbon. During the condensation of atoms or carbon clusters generated in an electric arc discharge during laser or electronic processing of
a carbon material, single-layer (fullerenes, nanotubes) and multilayer (onion) nanostructures are formed simultaneously.

Onion fullerenes are the most stable carbon structures if the number of atoms in a cluster is 106-107. The inner fullerene is fullerene C60 with an outer diameter of 1.1 nm, followed by a shell-C240, etc. up to giant molecules with a diameter of 30-70 Å [2-4].

Although onion carbon nanostructures were discovered in 1985, even earlier than carbon monofullerenes C60 and carbon nanotubes, they are the much less studied spatial forms of carbon. Due to the lack of experimental methods for measuring the thermal conductivity of objects with a size of several nanometers, even for the most studied to date fullerene C60, data on fullerite samples obtained by sintering compressed fullerene backfills can be found by thermal conductivity for different fullerite samples from previous publications: high-pressure samples (HSP) made by first applying high pressure and then the high temperature HSP1 with $\lambda=0.4 - 0.5$ W/(m K) [5], high-pressure sample made by heating the sample up to a high temperature, then applying in high pressure HSP2 with $\lambda=0.8$ W/(m K), and latest data of hard carbon HC2 with $\lambda=2$ W/(m K) [6], hard carbon HC1 with $\lambda=6$ W/(m K) [6].

However, such structures have great potential for practical application, for example, in the development of technologies for the production of synthetic diamonds with higher physical and mechanical parameters than natural diamonds and antifriction fillers in polymer composite materials, electrodes for supercapacitors. Synthesis technologies at high temperatures and pressures require knowledge of the thermophysical properties of the initial components: multilayer fullerenes. Knowledge of thermophysical properties of fillers is also necessary for certification of polymer composite materials.

The thermal conductivity of onion fullerenes is estimated using generalized conductivity methods. Let us present a model of the structure of onion fullerenes.

2. The model used and mathematical formulation.

For figure 1 it can be seen that carbon shells and their models are not actually spherical, but polyhedral. The shape of polyhedron can be significantly different (from almost tetrahedral or cubic shapes to the shapes of convex polyhedral close to spherical). Since the cube is one of the simplest intermediate forms for approximate estimation, we replace (figure 2) the spherical shape of the fullerene onion by a cubic shape of equal volume $V$ (1):

\[
\Delta = \frac{\delta V}{2}
\]

\[
\delta = \frac{\Delta}{L}
\]

**Figure 2.** Replacing a Spherical Model with an Equal-Volume Cube.
V = \frac{4}{3} \pi R^3 = L^3, \hspace{1cm} (1)

where \( R = \frac{D}{2} \) is the radius of the nano-fullerene, \( L \) is the size of the side of the cube-model of the fullerene sphere.

Let us express the size of the side of the cube:

\[ L = R \sqrt[4]{4 \pi / 3} \hspace{1cm} (2) \]

The radius of the first inner sphere C60 is 0.505 nm, and the length of the side of the cube of the equal volume will be \( L = 0.83 \) nm.

Relative wall thickness of the model is:

\[ \delta = \frac{\Delta}{L} \equiv 0.4. \hspace{1cm} (3) \]

Estimates of the thermal conductivity even by the most studied C60 fullerene are very few and differ significantly (up to two orders of magnitude: 0.2-0.4 W/(m*K) [5], 0.4 [6], 2.5 W/(m*K) [7], up to 120 W/(m*K) [8]).

The thermal conductivity along the wall of the cubic model of the molecule is different from the thermal conductivity across the wall. We estimate these values using Knudsen's (number) criterion \( Kn = \frac{\Lambda}{p_{th}}. \)

Thermal conductivity along the wall of the cubic model is:

\[ \lambda_{wal} = \frac{\lambda_{gral}}{Kn} = \lambda_{gral} \frac{L}{\Lambda_{phal}}, \hspace{1cm} (4) \]

where \( \lambda_{wal} \) is the thermal conductivity along the wall (\( wal \)) of the cube, which we assume to be equal to the thermal conductivity of graphene along the layer; \( \Lambda_{phal} = 645 \) nm is the length of the free path of phonons along the graphene layer (\( phal \)).

The thermal conductivity across the wall of the model is:

\[ \lambda_{wac} = 0.8 \cdot \lambda_{gr2ac} \frac{\Delta}{\Lambda_{gr2ac}}, \hspace{1cm} (5) \]

where \( \lambda_{gr2ac} = 475 \) W/(m*K) is the transverse thermal conductivity of a single crystal of graphite; \( \Lambda_{gr2ac} = 140 \) nm is the length of the free path of phonons across the layers of single-crystal graphite.
It is also necessary to take into account the molecular $\lambda_{mol}$ and $\lambda_{rad}$ radiation components of the thermal conductivity of the air $\lambda_3$ inside the cube

$$\lambda_3 = \lambda_{mol} + \lambda_{rad},$$

$$\lambda_{mol} = \lambda_0 / (1 + \frac{B}{H(L-2\Delta)}),$$

$$\lambda_{rad} = 0,227 \cdot \varepsilon \cdot (L-2\Delta) \cdot \left(\frac{T}{100}\right)^3,$$

where $\lambda_0$ is the thermal conductivity of air at atmospheric pressure $H=760$ mm Hg. $B=1.75 \cdot 10^{-4}$ [7], $\varepsilon=1$ is wall black degree; $T=300$ K is average temperature.

Next, following the recommendations of [5], we use the Rayleigh method and estimate the equivalent thermal conductivity of the model using the partition of the cubic model by adiabatic planes parallel to the heat flow:

$$\lambda_{ad} = 4\delta(1-\delta)\lambda_{wal} + \frac{\lambda_{wac} \cdot \lambda_3 (1-2\delta)^2}{2 \cdot \delta \cdot \lambda_3 + \lambda_{wac} (1-2\delta)},$$

Then we estimate the equivalent thermal conductivity of the model by breaking it up with isothermal planes perpendicular to the heat flux:

$$\lambda_{iz} = \frac{1}{2\delta} \left[ \frac{1}{\lambda_{walz}} + \frac{1-2\delta}{4\delta(1-\delta)\lambda_{walz} + (1-2\delta)^2 \cdot \lambda_3} \right],$$

where,

$$\lambda_{walz} = \lambda_{gral} \frac{L_{iz}}{\Lambda_{phal}},$$

$$L_{iz} = L - 2\Delta.$$

As an approximate estimate of the equivalent thermal conductivity of the molecule model, we assume the arithmetic mean between the values of the equivalent thermal conductivity when divided by adiabatic and isothermal planes.
\[ \lambda_{eq} = \frac{\lambda_{ad} + \lambda_{iz}}{2}. \] (10)

Similarly, we will determine the thermal conductivity of the subsequent layers of the fullerene onion with the difference that before the calculation it is necessary to calculate the average thickness of the corresponding layer. And for the thermal conductivity of the volume "inside the cube" we will take the effective thermal conductivity obtained for the previous layer.

3. Results of calculations.
Figure 3 shows the results of thermal conductivity calculation for the group of "small fullerene onions" with the number of layers from 3 to 20 at different values of thermal conductivity of graphene along the layers $3500 \ll 6500$ W/(m K).

4. Conclusion.
It can be seen that the results of calculations for the limiting case (single-layer fullerene C60) are completely within the field of experimental data of independent studies [5,6]. This confirms the possibility of using the results of our calculations, at least, as a first approximation for predicting the thermal conductivity of multilayer fullerene "nano-onions".

**Figure 3.** The results of thermal conductivity calculation for the group of "small fullerene multilayered onions". N – number of layers in fullerene nano-onions.

**References**

[1] Iijima S 1980 Direct observation of the tetrahedral bonding in graphitized carbon black by high resolution electron microscopy *J. Cryst. Growth* **50** 675-83.

[2] Rakov E 2006 *Nanotubes and fullerenes* University book publishing house 260.

[3] Katz E 2004 Leonard Euler and modern views on the molecular structure of fullerenes *Energy: Economics, technology, ecology* **2** 51-57.
[4] Glukhova O, Druzhinin A, Zhbanov A and Rezkov A 2005 Structure of fullerenes of high symmetry groups *Journal of structural chemistry* **46** 514-20.

[5] Liang C, Xiaojia W and Satish K 2015 Thermal transport in fullerene derivatives using molecular dynamics simulations *Scientific Reports* **5** (2015)2763.

[6] Lasjaunias J C, Saint-Paul M, Bilišić A, Smontara A, Gradečak S, Tonejc A M, Tonejc A and Kitamura N 2002 Acoustic and thermal transport properties of hard carbon formed from C$_{60}$ fullerene *Physical Review B* **66** 014302

[7] Dul’nev G and Zarichnyak Yu 1974 *Thermal Conductivity of mixtures and composite materials* (Leningrad: Energy) p 284.

[8] Zarichnyak Yu and Chaplygin V Investigation of longitudinal and transverse thermal conductivity of defect-free carbon single-wall nanotubes. 2nd International Scientific and Engineering Conference” Modern methods and means of research of thermophysical properties of substances (St. Petersburg: ITMO University).