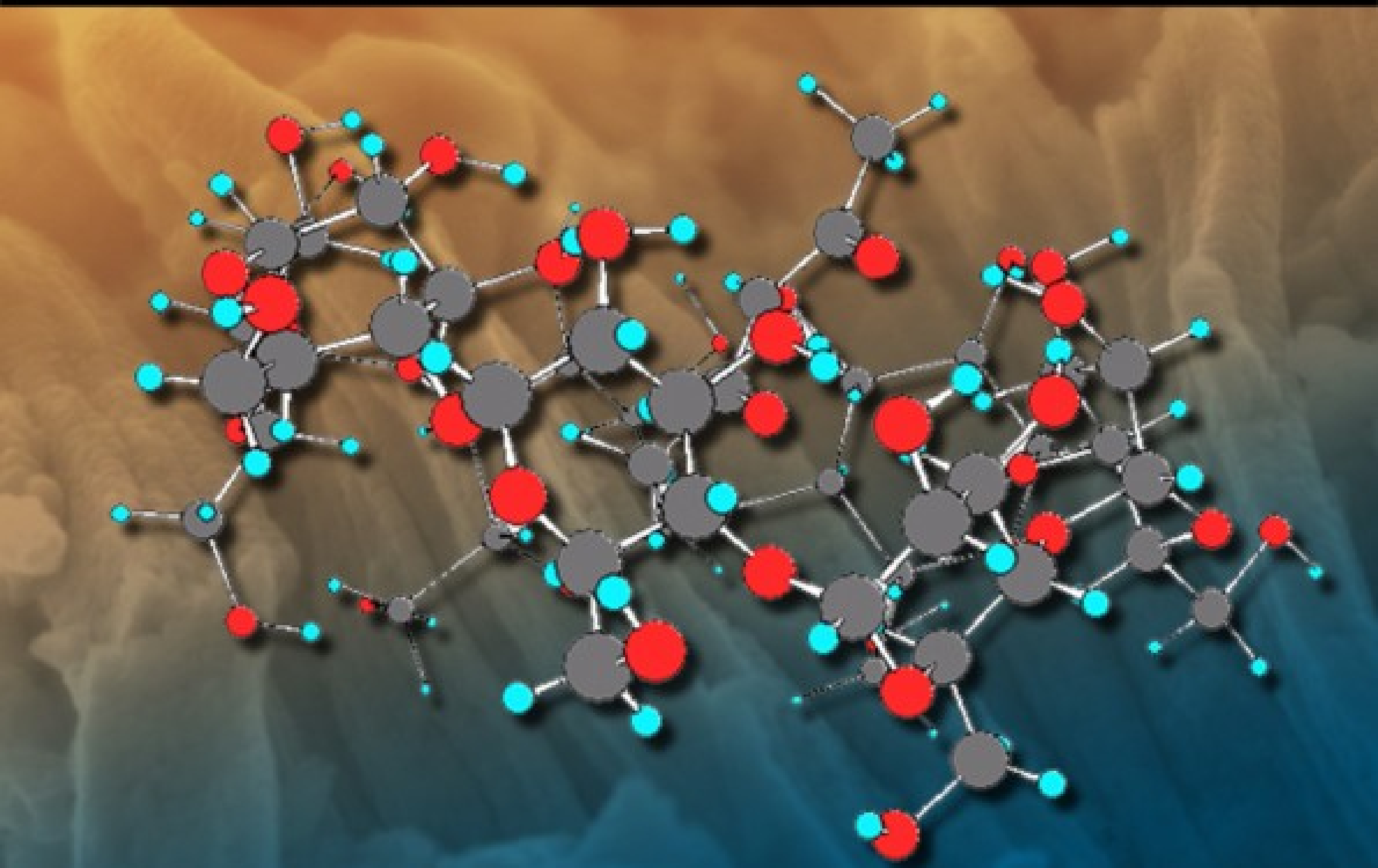
ISSN 1726-5479

Sensors & Transducers

11/12 vol. 146



Nanosensors and Nanodevices

International Frequency Sensor Association Publishing

Sensors & Transducers

Volume 146, Issue 11 **www.sensorsportal.com** **ISSN 1726-5479**
November 2012

Sensors & Transducers Journal (ISSN 1726-5479) is a peer review international journal published monthly online by International Frequency Sensor Association (IFSA).
Available in electronic and on CD.

Sensors & Transducers Journal

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Volume 146
Issue 11
November 2012

www.sensorsportal.com

ISSN 1726-5479

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Sensors & Transducers Journal, Vol. 146, Issue 11, November 2012, pp. 1-7

Sensors & Transducers

ISSN 1726-5479

http://www.sensorsportal.com

Diffusion in Carbon Nanotubes: Details, Characteristics, Comparisons at Nanolevel

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Received: 26 October 2012 /Accepted: 23 November 2012 /Published: 30 November 2012

Abstract: The theoretical modelling improves the knowledge of matter at nanoscale and utilizing the results of experimental research brings continuously new details to be experimentally verified. It has been recently appeared a new "time-domain" Drude-Lorentz-like model for classical and quantum transport in nanosystems, which demonstrates high generality and good fitting with experimental data of literature. It allows interesting applications in the field of nanostructured materials, for biological and medical applications, as well as in nano-bio-sensoristics. I use this model considering interesting details of Carbon Nanotubes, in relation to variations of parameters, like temperature and effective mass of electrons and in comparison with other important nanomaterials of current scientific and technological use. *Copyright © 2012 IFSA.*

Keywords: Carbon nanotubes, Diffusion, Nano-bio-sensors, Nano-bio-materials, Theoretical modeling.

1. Introduction

The growing global needs of energy at technological and social levels require at present scientific efforts for the development of nanodevices and nanosystems of critical importance for implantable, ultrasensitive, chemical and molecular bio-sensoristics, so as for medical science, nano-robotics, micro-(nano)-opto-electro-mechanical systems (M(N)OEMS), remote and mobile environmental sensors, portable and resistant personal electronics, defense technologies. It is also required and highly desirable that the implantable biomedical devices are self-powered, i.e. batteries-free. Therefore it became crucial the exploration of innovative nanotechnologies for the conversion of mechanical energy (body movements, muscle stretching), vibrational energy (acoustic and ultrasonic waves), hydraulic energy (flow of body fluids), chemical energy (for example from glucose) into electrical energy, to be used for such batteries-free devices [1]. Considering also the global pollution, the research of “green” and renewable energetic resources is one of the most urgent challenges to the sustainable development of the human civilization. At great scale, near the known energetic resources of the actual world, as oil, coal, hydroelectric energy, natural gas, nuclear energy, alternatives energetic resources are in great development, as solar energy, geothermal energy, biomasses, eolic energy, hydrogen. For all these reasons, one of the challenges of actual nanotechnology is the study and development of ultra small, ultrasensitive, multifunctional, low-consumption systems [2, 3]. At today, among the most commonly studied, promising and used materials at nanoscale we find zinc oxide (ZnO), titanium dioxide (TiO_2), gallium arsenide (GaAs), silicon (Si) and carbon nanotubes (CNTs). About nanotubes, these cylindrical carbon molecules have interesting properties and increasing use for nano-bio-technology, electronics, optics and other materials science fields. The strength and flexibility of carbon nanotubes makes them of potential use in controlling other structures at nanoscale, particularly in nano-bio-technology engineering sector, as nanoelectronic devices, field emitters, gas sensors, high-strength composites, for hydrogen storage. It is so crucial the theoretical detailed understanding and the previsions that the existing and the new models can offer for an always deeper knowledge of this nanomaterials [4, 5].

2. Characteristics of Carbon Nanotubes

The word “nanotube” derives from its size, being the diameter of a nanotube of order of a few nanometers and it can be up to several micrometers in length. The nanotube is a member of the fullerene structural family. Carbon nanotubes are cylindrical carbon molecules with particular mechanical, electrical, thermal, and chemical properties; they are 10^2 times stronger than steel, among the best field emission emitters, can maintain a current density of order or more than 10^{-9} A/cm² and have a thermal conductivity comparable to that of diamond. These characteristics make them potentially useful in a wide range of applications, from optics to nanoelectronics, from composite materials to conductive polymers, in the sensoristics. CNTs are of two types, the “single-walled carbon nanotubes” (SWCNTs) and the “multi-walled carbon nanotubes” (MWCNTs). Discovered in 1993, SWCNTs have normally a diameter of order of 1 nm and a tube length from 10^3 nm to the order of cm [6]. The form of a SWCNT consists in a wrapping of a one-atom-thick layer of graphite (or graphene) into a cylinder, with possible representation by a pair of indices (n, m) called the chiral vector. SWCNTs exhibit interesting electrical properties not showing by MWCNTs. The most basic building block of these systems is the electric wire, an excellent conductor.

MWCNTs consist of multiple layers of graphite rolled up on themselves forming a tube. The outer diameter of a MWCNT is normally in the range 1-50 nm, while the inner diameter is usually of some nm. CNTs carry high currents with negligible heating, act as sensing materials in pressure, flow, thermal, gas, optical, mass, position, stress, strain, chemical, and biological sensors.

Important sectors of CNTs utilization are:

a) Biomedical industry: as examples we remember the glucose sensing application, the monitoring of the exposure to hazardous radiation like in nuclear plants/reactors or in chemical laboratories or industries, as implantable sensors, for tracking glucose levels in the blood, for detecting DNA sequences in the human body;
b) Food industry: sensors and biosensors for providing safety and quality control, for meat freshness monitoring [7]. CNT-based chemical sensors can be used also to detect undesired chemical residues resulting from food additives, animal drugs, pesticides, herbicides, and other environmental contaminants;

c) Agriculture and fishing industry: MWCNT-coated quartz crystal microbalance humidity sensors used for monitoring relative humidity, CNT based CO_2 sensors to monitor the CO_2 concentration, CNT-based pressure sensors for uniform spraying of liquid fertilizer, insecticides, pesticides, herbicides. CNT-based pH sensors are highly useful for maintaining proper pH balance of water quality for fishing industries [8];
d) Manufacturing industry: CNT based strain and pressure sensors for making strain and pressure measurements in manufacturing industries, CNT-based hydrogen gas sensors in hydrogen monitoring and control for petroleum transformation, rocket engines, welding;
e) Security: CNT-based sensors in defense and security, in unmanned defense systems like unmanned aerial vehicles, CNT-based chemical sensors as electronic noses to detect hidden bombs, chemical weapons in luggage, vehicles, aircraft.

Therefore the exceptional properties of these compounds make them relevant to a very growing quantity of potential interesting and useful applications.

3. Interesting Features from a New Drude-Lorentz-like Model

The sensitivity is one of the most important feature of a nano-bio-sensor and nano-bio-device in general, resulting in the ability to detect in very high modality, feature in connection with the charge transport. Recently it has been appeared a new generalization of the Drude-Lorentz model, based on the complete Fourier transform of the frequency-dependent complex conductivity $\sigma(\omega)$ of a system, able to offer analytical expressions of the velocities correlation function $<\vec{v}(t)\cdot\vec{v}(0)>_T$ at the temperature *T*, the mean squared displacement $R^2(t)=\left\langle[\vec{R}(t)-\vec{R}(0)]^2\right\rangle$ and the diffusion coefficient *D* [3,9,10]. One of the most interesting peculiarities of the model is the "time domain" approach used, not previously found in such contest, contrarily to the existing theoretical approaches, which are "frequency domain" treatments. Using literature data, it is possible to fit and confirm experimental results, so as to find new characteristics and details to offer for confirmation at experimentalists.

4. Results and Discussion

The diffusion coefficient *D* related to the new model has the following classical analytical expression [9]:

$$D=\left(\frac{KT}{m^*}\right)(\tau)\left(\frac{1}{\alpha_I}\right)\left(-\exp\left(-\frac{1+\alpha_I}{2}\frac{t}{\tau}\right)+\exp\left(-\frac{1-\alpha_I}{2}\frac{t}{\tau}\right)\right), \tag{1}$$

where K is the Boltzmann's constant, T is the temperature, m^* is the effective mass and τ is the relaxation time. The parameter α_I of the model is defined in this way:

$$\alpha_I^2=1-4\tau^2\omega_0^2 \tag{2}$$

It has been considered the *D* behaviour of CTNs at three different temperatures T_1=100 K, T_2=200 K, T_3=300 K, considering $m^*=0.5m_e$ [11] (m_e is the electron mass), $\tau=0.17\cdot10^{-12}\,s$ [12] and $\alpha_I=0.5$ ($\alpha_I\in[0,1]$ is a real number). The diffusion coefficient *D* is directly proportional to the temperature *T*, so the increase of *T* promotes the diffusion, interesting characteristics to keep into account in particular in the case of the utilization at nanosensoristic level. We note from Fig. 1 how the values of *D*, relatively to the chosen parameters, span the range from 4 cm^2/s to 12 cm^2/s, of considerable interest at technological industrial level.

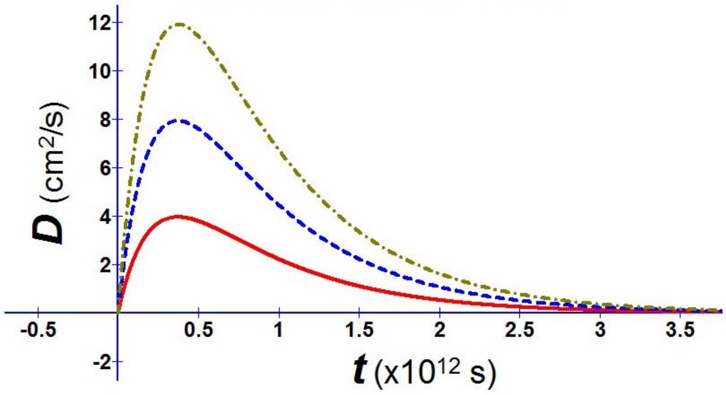

Fig. 1. D vs. t for CNT at three different temperatures (red solid line: T_1=100 K; blue dashed line: T_2=200 K; green dot-dashed line: T_3=300 K) ($\alpha_I = 0.5$, $\tau = 0.17 \cdot 10^{-12}\ s$).

In Fig. 2 it has been compared the D value of CNTs (violet dots line) with respect to Si (red solid line), TiO_2 (blue dashed line), ZnO (green dot-dashed line) and GaAs (light blue dashed line), with values of parameters resumed in Table 1.

Table 1. Values of effective mass m^* and relaxation time τ for the five studied nanomaterials.

Nanomaterial	***m****	**τ (s)**
CTN [11, 12]	0.5 m_e	$0.17 \cdot 10^{-12}$
Si [13]	1.08 m_e	$0.5 \cdot 10^{-13}$
TiO_2 [14]	6 m_e	$0.1 \cdot 10^{-13}$
ZnO [15]	0.24 m_e	$0.84 \cdot 10^{-13}$
GaAs [16, 17]	0.067 m_e	10^{-12}

Except the case of GaAs (deliberately left out of scale in Fig. 2), CTN present for short times a high diffusivity with respect to the other tested nanomaterials, feature of great importance at nano-bio-sensoristic and nano-technological level [3].

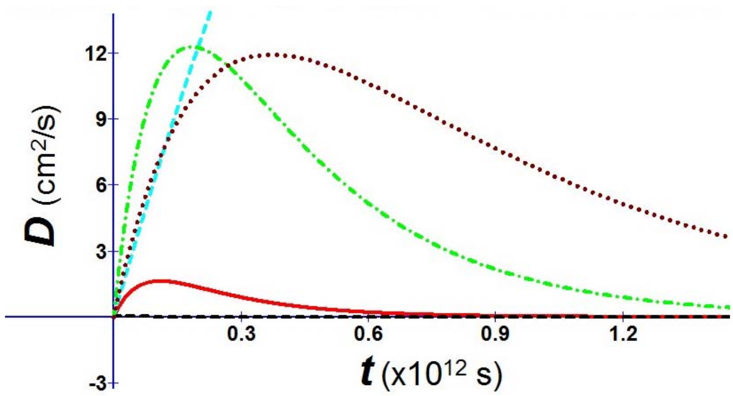

Fig. 2. Comparison in diffusion for the five studied nanomaterials (for details see text and Table 1) ($\alpha_I = 0.5$, $T = 300\,K$).

In Fig. 3 it is presented a detail of Fig. 2, i.e. considering long times; only GaAs demonstrates to have the best response in diffusion, but with a peak in diffusion at bigger time with respect to CNT. This feature could be not good if we need of a device with high fast initial diffusivity.

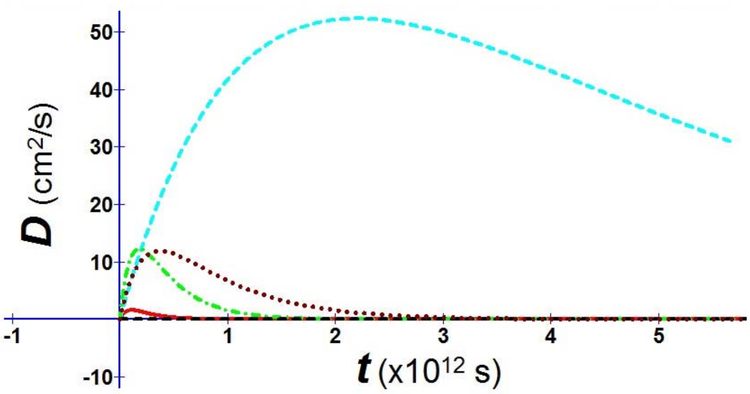

Fig. 3. Detail of Fig. 2 considering long times.

Subsequently it has focused the attention on the diffusion behaviour of CNTs, in particular changing their effective mass, which vary with the chiral vector inscribed in (n, m) indices. Fig. 4 illustrates the variation of D in relation to three different CNT, two giving the greatest difference in mass and an intermediate value, i.e. the CNT with (n, m) indices equal to (3,1) (green dot-dashed line), (4,2) (blue dashed line) and (9,2) (red solid line). We note that the decrease of the effective mass involves a raise of the diffusion of the CNT; the particular needs at practical and technological level will imply the choice of the CNT with the right requested features [11].

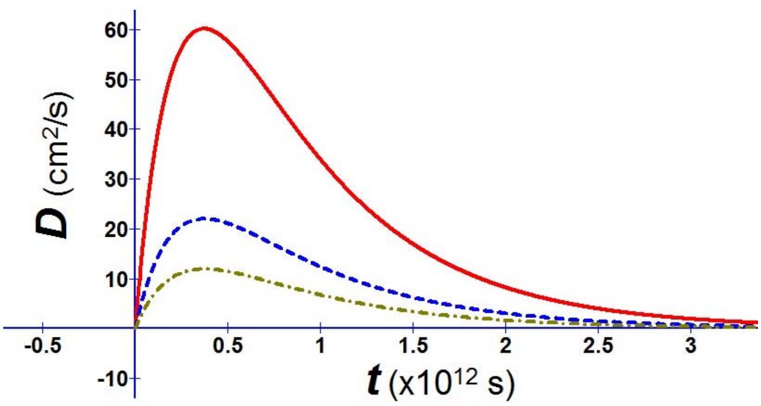

Fig. 4. Variation of D for CNT with (n, m) indices equal to (3,1) (green dot-dashed line), (4,2) (blue dashed line) and (9,2) (red solid line) ($\alpha_I = 0.5$, $T = 300\,K$).

Finally it has tested the variation of diffusivity of CNTs varying the relaxation time τ . Fig. 5 represents the behaviour of D in relation to the values $\tau_1 = 10^{-13}\,s$ (red solid line), $\tau_2 = 0.17 \cdot 10^{-12}\,s$ (green dot-dashed line) and $\tau_3 = 10^{-12}\,s$ (blue dashed line). We note that, changing τ , not only changes the value of D, but also the width of the curves, since the change involves also the arguments of the exponentials of Eq. (1).

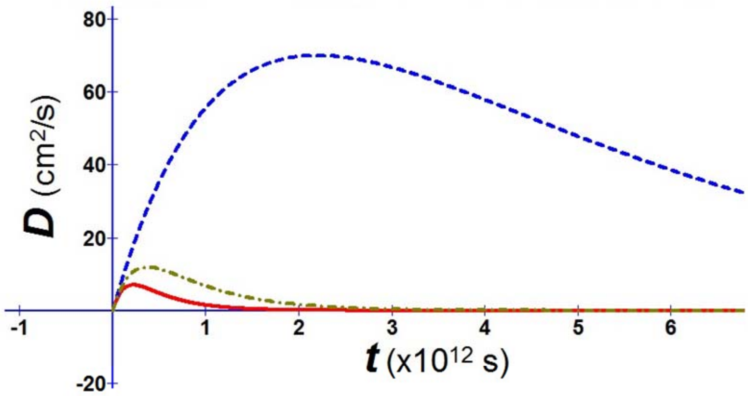

Fig. 5. Variation of D for CNT with three different values of τ ($\tau_1 = 10^{-13}\,s$ (red solid line), $\tau_2 = 0.17 \cdot 10^{-12}\,s$ (green dot-dashed line) and $\tau_3 = 10^{-12}\,s$ (blue dashed line)) ($\alpha_I = 0.5$, $T = 300\,K$).

5. Conclusions

In this work I have considered an application of the classical version of a new recently appeared theoretical model [3, 9, 10] for testing the efficiency of CNTs in comparison to other important materials actually utilized at nano-bio-level [3].

The carried analysis showed that CNT represent a very versatile and interesting nanomaterial, with high values of diffusivity and able to meet, through appropriate combinations of the parameters, a large spectrum of practical and technological needs, especially in the nano-bio-devices sector and at nano-bio-sensoristic level. The possibility of a rapid answer for the carriers transport is a very important peculiarity concerning nano-bio-devices, also in the nano-energy systems and nano-technologies sector. The enhanced transport times for nanostructured systems may be also the basis for the creation of new single nanotube nano-bio-sensors.

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Guide for Contributors

Aims and Scope

Sensors & Transducers Journal (ISSN 1726-5479) provides an advanced forum for the science and technology of physical, chemical sensors and biosensors. It publishes state-of-the-art reviews, regular research and application specific papers, short notes, letters to Editor and sensors related books reviews as well as academic, practical and commercial information of interest to its readership. Because of it is a peer reviewed international journal, papers rapidly published in *Sensors & Transducers Journal* will receive a very high publicity. The journal is published monthly as twelve issues per year by International Frequency Sensor Association (IFSA). In additional, some special sponsored and conference issues published annually. *Sensors & Transducers Journal* is indexed and abstracted very quickly by Chemical Abstracts, IndexCopernicus Journals Master List, Open J-Gate, Google Scholar, etc. Since 2011 the journal is covered and indexed (including a Scopus, Embase, Engineering Village and Reaxys) in Elsevier products.

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- Theory, principles, effects, design, standardization and modeling;
- Smart sensors and systems;
- Sensor instrumentation;
- Virtual instruments;
- Sensors interfaces, buses and networks;
- Signal processing;
- Frequency (period, duty-cycle)-to-digital converters, ADC;
- Technologies and materials;
- Nanosensors;
- Microsystems;
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