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Parametric Modeling of Conductivity in Percolating Nanotube Network

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***Abstract* — The work is devoted to three-dimensional computer simulations of nanotube network formed in non-conductive volume and studies the electrical properties of the model network considering various types of conductivity mechanisms. Results of the simulation for nanotube networks with different geometrical parameters are presented.**

Keywords — conductivity; nanotubes; simulations

I. INTRODUCTION

Nanotubes are essentially tubes with diameters shrunk down to nanometers and ranging in length from tens to hundreds of nanometers. Depending on material and specific structural parameters nanotubes can exhibit different type of electrical conductivity being metallic, semiconductor or insulating.

Of growing interest are recently networks formed by nanotubes inside (or on the surface) of a given material, usually dielectric. This type of composite structures has a significant potential for flexible microelectronics as it is capable to provide unique combination of electric and mechanical features [1]–[5].

Experimental studies of complex networks of nanotubes in dielectric media are time and resource consuming. They require numerous adjustment of parameters such as, for example, volume fraction of the nanotubes in the host material and careful sample preparation (often involving sophisticated dispersion techniques) [6], [7]. This is where computer simulation can be of particular importance as it allows to mimic the electrical behavior of such system with a reasonable degree of accuracy and investigate the crucial phenomena in the system as a function of different parameters.

II. NANOTUBE NETWORKS MODELING METHOD

A. Model of nanotube network

Nanotube network can be described as a set of conductive nanotubes (CNT) placed inside 3D volume box also known as representative volume element (RVE). CNTs can potentially create connections between each other and, therefore, form long chains of connected tubes between the opposite sides of RVE [8], [9]. The key feature of the system of nanotubes is that the electrical properties of the system can dramatically change at some point: the total conductivity of the system "jumps", when the amount of nanotubes in RVE reaches a specific critical value. It has been proved that in the case of a large system with a huge number of nanotubes the concentration of the nanotubes (amount per unit volume) needed to achieve the mentioned "jump" effect approaches some stable value. To explore the system thoroughly, one need to define the principal significant parameters of such a system. There are two kinds of them: geometrical parameters of individual CNTs (length, diameter, aspect ratio) and global system parameters (RVE dimensions, volume fraction of CNTs inside RVE, connection types, collisions).

In this work, we consider a model of nanotube network which comprises a large number of fixed size tubes with a high aspect ratio, randomly positioned and directed. These CNTs are considered to be solid, that means they cannot overlap each other by volume. There can be two types of contacts between CNTs: direct (or, in other words, touch) contact and contact when tubes are put at a very close distance but still not touching each other. This type of contact is a representation of tunneling effect which exists between nanoscale objects. Moreover, a number of papers conclude [10], [11] that this type of conductivity is dominant in the systems composed of nanoscale objects.

B. Nanotubes network generation process

In our simulation model CNT is approximated as a cylinder with spherical endings. The axis of this cylinder starts at point A with coordinates (x_1, y_1, z_1) and ends at point B (x_2, y_2, z_2). The process of generating and placing nanotube in RVE consists of several phases. Randomly selected inside RVE point A with coordinates (x_1, y_1, z_1) stands for start point of cylinder axis [12]:

$$x_1 = rand \times L_x \quad (1)$$

$$y_1 = rand \times L_y \quad (2)$$

$$z_1 = rand \times L_z \quad (3)$$

Where $rand$ is a random floating point value from [0,1] range. Then the random direction in space is described by two angles α and β:

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$$\alpha = 2\pi \times rand_1 \quad (4)$$

$$\beta = 2\pi \times rand_2 \quad (5)$$

Based on this, two direction angles the position of the end point *B* is defined as:

$$x_2 = x_1 + l_{CNT} \times cos(\alpha)cos(\beta) \quad (6)$$

$$y_2 = y_1 + l_{CNT} \times \sin(\alpha)cos(\beta) \quad (7)$$

$$z_2 = z_1 + l_{CNT} \times \sin(\beta) \quad (8)$$

If the ending point of CNT appears to be located outside RVE then the part of CNT which exceeds the RVE boundary is cut off in a way that makes the ending point of CNT to be located at the side of RVE.

Also, we should enforce the following restriction on placing CNTs in RVE: they should not overlap each other. In order to achieve this, we need to establish an additional verification process which must be performed when new CNT is generated and is going to be placed in RVE. This verification process is based on checking the distances between the last generated tube and all the other tubes already contained in RVE. If the distance between a pair of CNTs is less than CNT diameter d it means that the nanotubes are penetrating each other. In this case the newly generated CNT is rejected and we proceed to generating the next one. The process continues until volume fraction of CNTs inside RVE reaches the desired value.

After the process of generating CNTs is finished the connections between CNTs need to be found. It is worth noting that a number of mutually connected nanotubes can form a cluster. If such a cluster contains CNTs connected to both electrodes it is called conductive (or percolative) cluster. The notion of a conductive cluster is extremely important because its existence allows RVE to be the part of electric circuit. One should take into account that in the same RVE we can have several independent conductive clusters. The weighted union find algorithm with the path compression can be utilized in order to find conductive clusters in RVE.

C. Equivalent random resistor network

We use random resistor network approach to simulate the equivalent conductivity of the CNTs network. To illustrate the technique that we utilize, the example of possible connection pattern is shown on Fig 1. Each contact area between two CNTs is represented as a pair of contact points: one on the axis of the first CNT and the other one on the axis of the second CNT. At the same time a pair of "contact" points located at the same nanotube defines the part of this nanotube as the segment with length l_s (see Fig 1), which the electric current will be run through.

For finding distances between CNTs we use the procedure which calculates both the shortest distance between CNTs and the actual coordinates of these "contact" points. The coordinates of the point situated on the CNT axis is described as:

$$p + \alpha \cdot \vec{d}, \quad (9)$$

where p is the starting point of the CNT, $\vec{d}$ is the directional vector of the CNT and α is a coefficient ($\alpha \in [0,1]$), whose concrete values define the points located on the CNT axis.

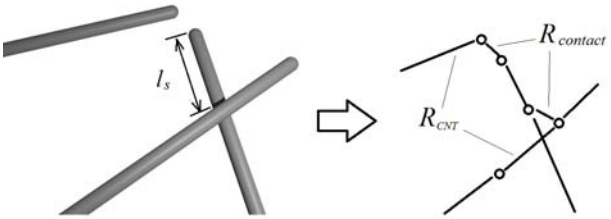

Fig. 1. Relation between CNTs connections and representative resistors.

Then $(p_1 + \alpha \cdot \vec{d}_1) - (p_2 + \beta \cdot \vec{d}_2)$ is the vector, which connects this two connection points. The minimal distance between CNTs is obtained as the norm of this vector:

$$D = \| (p_1 + \alpha \cdot \vec{d}_1) - (p_2 + \beta \cdot \vec{d}_2) \|^2 . \quad (10)$$

Using equation (9) and the found values of α and β coefficients we can find the actual position of contact points on both CNTs.

Here we are considering two types of conductivity: the one between CNTs and CNT intrinsic conductivity. Two CNTs are treated as the connected ones, when the shortest distance between them is shorter than some preset value of the cut-off distance d_{cutoff}.

Let us define a part of CNT by a pair of points located on its axis. Suppose, the length of this segment is l_s (see Fig 1). Then the intrinsic resistance of this part of CNT can be calculated according to the formula [11], [12]:

$$R_{intrinsic} = \frac{4l_s}{\pi \sigma_{CNT} d^2}, \quad (11)$$

where σ_{CNT} is the intrinsic electrical conductivity of the CNT and d is the diameter of the CNT.

The contact resistance between a pair of nanotubes is caused by a tunneling effect at the "contact" points.

After finding all "contact" points between CNTs and local resistances between them the random resistor network is formed. The example structure of such network is shown on Fig. 2. Here we have our RVE placed in electric circuit. Our random resistor network now becomes a part of this electric circuit, so it is important to calculate its total conductivity. In order to achieve it we utilize combination of Kirchhoff's current law (KCL) and Ohm's law.

Let's consider some element E (which connects nodes i and j on Fig. 2) in resistor network. Using Ohm's law the current which enters and leaves this resistor element is defined as:

$$\begin{Bmatrix} I_i^e \\ I_j^e \end{Bmatrix} = \left[K_{ij}^e \right] \begin{Bmatrix} V_i \\ V_j \end{Bmatrix} \quad (12)$$

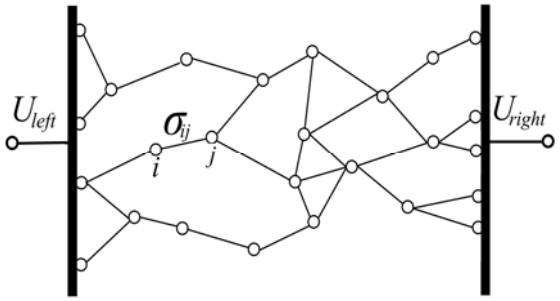

Fig. 2. Example structure of random resistor network

where V_i and V_j is electric potential value at nodes i and j (see Fig. 2), I_i and I_j represent current flowing through i and j points respectively. The matrix of local conductivity K_{ij}^e is defined as follows:

$$\left[K_{ij}^e \right] = \sigma_{ij} \begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix} \quad (13)$$

For the entire resistor network, according to KCL, the following system of linear algebraic equations must be held true:

$$\begin{pmatrix} K_{11} & \dots & K_{1N} \\ \dots & \dots & \dots \\ K_{i1} & \dots & K_{iN} \\ \dots & \dots & \dots \\ K_{N1} & \dots & K_{NN} \end{pmatrix} \times \begin{pmatrix} V_1 \\ \dots \\ V_i \\ \dots \\ V_N \end{pmatrix} = \begin{pmatrix} I_1 \\ 0 \\ \dots \\ 0 \\ I_N \end{pmatrix} \quad (14)$$

Here K represents the global conductivity matrix of the resistor network. V_i is unknown electrical potential at each node, I_1 and I_N are the currents entering and leaving the system respectively.

Now we will show how to build this matrix K using element-wise conductivity matrices K_{ij}^e. We start with zero-valued matrix K and iterate through a set of resistors accumulating K_{ij}^e into K in a following way:

$$K = \begin{pmatrix} \dots & \dots & \dots & \dots & \dots \\ \dots & K_{ii} += \sigma_{ij} & \dots & K_{ij} -= \sigma_{ij} & \dots \\ \dots & \dots & \dots & \dots & \dots \\ \dots & K_{ji} -= \sigma_{ij} & \dots & K_{jj} += \sigma_{ij} & \dots \\ \dots & \dots & \dots & \dots & \dots \end{pmatrix} \quad (15)$$

However, in most practical applications the values of I_1 and I_N are unknown. Instead, the voltage difference applied to the RVE is preset:

$$V_1 = U_{left}, V_N = U_{right}. \quad (16)$$

So, we can just drop first and last equations from the system (14) and obtain a new system of linear equations of dimensions $(N-2)\times(N-2)$.

The specifics of the nanotubes network model is so that the equivalent resistor network consists of small amount of resistors connected to each node. So, it results in matrix K being sparse and symmetric. The system of equations (14) is stored in compressed column format and we use a specific solver contained in SuperLU [14,15] library, which is optimized for handling sparse matrices.

After solving the system and obtaining the values of V_i vector we can calculate all currents flowing through resistor elements as:

$$I^e = \sigma_{ij}(V_i - V_j), \quad (17)$$

where σ_{ij} is conductivity of the resistor element between i and j nodes and V_i, V_j are electrical potentials in those nodes (see Fig 2.). All I_i values can be used for highlighting conductive path between electrodes and showing distribution of current flow through CNTs network.

To calculate the total current, the currents through all resistor elements which are directly connected to the one of the electrodes are summed up:

$$I_{total} = \sum_{j=1}^{m} I_j^e \quad (18)$$

Here m is the number of resistors directly connected to the electrode.

Finally, the total equivalent electrical conductivity of random resistor network is calculated using Ohm's law as follows:

$$\sigma_{total} = \frac{1}{R_{total}} = \frac{I_{total}}{U_{left} - U_{right}} \quad (19)$$

The calculated value of σ_{total} is then used for estimation of a specific conductivity of RVEs with different dimensions.

III. Results and Discussion

We have developed software for modeling electrical conductivity of carbon nanotubes network. The main goal of our computer simulations was to explore how geometrical parameters of individual CNTs influence the total conductivity of nanotubes network.

To validate our numerical model, we consider a simple model problem which consists of small amounts of CNTs with predefined positions and geometrical parameters. It is used for verification of simulation accuracy and testing the performance of the implemented computer system under different problem sizes.

Our second numerical experiment is dedicated to simulating a real nanotube composite, which consists of dielectric polymer matrix filled with conductive carbon nanotubes. The parameters of the system during this numerical experiment are described below. RVE dimensions along X, Y and Z axes are 1000 nm, 1000 nm and 100 nm respectively. The CNT diameter is fixed to 2 nm and by varying the length of the CNT between 160nm and 320 nm we achieve the change of CNT aspect ratio from 80 to 160. CNT intrinsic conductivity is 10^4 S/m, while resistance of the direct contact between CNT is 10^5 Ohm. The maximum possible distance between contacting tubes surfaces (tunnel cut-off distance) is set to 1.8 nm.

The conductivity values obtained during computer simulations of nanotubes network with above discussed parameters for various CNTs volume fractions are shown on Fig 2. It is important to take a series of simulation of the system with exactly the same parameters in order to reduce the influence of stochastic processes on simulation results. As one can see from Fig. 2 the CNTs of higher aspect ratio show better conductivity for the same volume fraction.

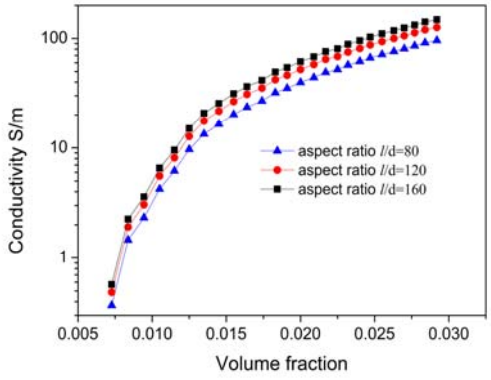

Fig. 3. Dependence of nanotubes system conductivity as a function of aspec ratio of individual CNTs

CONCLUSION

Computer simulations of conductive network of nanotubes in three-dimensional model are reported. Model is based on experimental evidences of different types of conductivity mechanism in such network and utilizes general electrical theory approach to matrix calculations of resistor grids systems. Validation of the model consistency was performed and numerical experiment reproducing electrical behavior of nanotube conductive network in dielectric medium depending of geometrical parameters was carried out.

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