3D self-consistent percolative model for networks of randomly aligned carbon nanotubes

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Abstract. A numerical percolative model for simulations of random networks of carbon nanotubes is presented. This algorithm takes into account the real 3D nature of these networks, allowing for a better understanding of their electrical properties. The nanotubes are modeled as non-rigid bendable cylinders with geometrical properties derived according to some statistical distributions inferred from the experiments. For the transport mechanisms we refer to the theory of one-dimensional ballistic channels which is based on the computation of the density of states. The behavior of the entire network is then simulated by coupling a SPICE program with an iterative algorithm that calculates self-consistently the electrostatic potential and the current flow in each node of the network. We performed several simulations on the resistivity of networks with different thicknesses and over different simulation domains. Our results confirm the percolative nature of the electrical transport, which are more pronounced in films close to their percolation threshold.

1. Introduction
Random carbon nanotube (CNT) networks are nowadays very attractive thanks to the combination of interesting electrical properties, low cost fabrication processes and the possibility to deposit them over flexible substrates. Among the possible applications, these networks are studied as transparent electrodes, thin-film transistors and several types of sensors [1]. Despite this great interest, the main transport mechanisms are still not fully understood. The presented model is based on a stochastic algorithm that can generate non-rigid solid objects in a three-dimensional space, emulating with high fidelity the typical fabrication processes involved (i.e. spray-coating). This represents a crucial step, since with the available two-dimensional models all the nanotubes are projected into one plane, making the number of junctions between different CNTs highly overestimated. An appropriate formalism for the electrical transport in one-dimensional channel has been introduced, together with an iterative algorithm that calculates self-consistently all the electrical quantities in every node of the network. Our work is intended to overcome some of the flaws regarding the modeling of these networks and provide a tool for the controlled design of devices based on this technology.

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2. Computational models
The software is composed of two main programs, one for the generation of the structure and one for the actual simulation, plus a tool for the visualization of the results. The electrical simulation is carried on by a SPICE software which executes at each call a netlist generated by our program. Everything is embedded in a self-consistent framework, which will update at each iteration the netlist to simulate.

2.1. Network generation
For the generation of the structure we referred to our previously developed simulation tool [2]. Every nanotube is represented as a bendable cylinder with radius and length that are randomly chosen according to a certain statistical distribution, which is inferred from AFM images of the investigated samples [3]. During this step also the electronic properties will be determined by randomly choosing the two indexes of the chiral vector. The number of nanotubes to be generated is determined by a specific density of CNTs/μm² that is chosen accordingly to the used experimental setup [4].

![Figure 1. 3D view (left) and side view (right) of a CNT network generated over a 10x10 μm² area. The density of nanotubes is around 18 CNTs/μm².](image)

In our approach, CNTs are placed sequentially, controlling each time if there are any intersections between the incoming nanotube and the already existing network; if an intersection occurs, the new nanotube will be bent of an angle usually smaller than 10 degrees; if the angle is greater than the maximum allowed, the nanotube will slide until it finds a resting point over the substrate or over another nanotube. The result is a film in a three-dimensional space, which is depicted in figure 1. The values of thickness and surface coverage are in good agreement with the measurements, as we already reported elsewhere [3].

2.2. Network simulation
The resulting set of tube segments and tube junctions must be then converted into a netlist and the overall electrical behavior is computed by coupling our program with a SPICE software. Each segment is represented by a voltage-dependent resistor, whose value is dynamically calculated within a self-consistent algorithm. After a first guess on the value of the resistor, the netlist is solved and the potential at each node of the entire network is calculated. The value of every resistor will be then updated according to the new applied potential and the process will be iterated until the difference between two consecutive steps is less than a previously set tolerance. The expression of the resistance follows equation (1).

\[
R(V) = R_0(V) \left( 1 + \frac{L}{\lambda_{EFF}} \right)
\]

where \(R_0\) represents the so-called quantum resistance, \(L\) is the length of the tube segment and \(\lambda_{EFF}\) is the effective mean free path, which contains the effects due to phonon scattering events [5]. The quantum resistance is calculated as the ratio between the applied voltage and the current that flows through the nanotube. The latter is solved according to the theory of one-dimensional conducting channels [6] and follows the equation
\[ I(V) = \frac{q}{\hbar} \int_{-\infty}^{\infty} dE D_\varepsilon(E) \frac{\gamma_1 \gamma_2}{\gamma_1 + \gamma_2} [f_1(E, V) - f_2(E, V)] \]

where \( q \) is the electronic charge, \( \hbar \) is the reduced Planck constant, \( D_\varepsilon(E) \) is the density of states per unit of energy, \( \gamma_1 \) and \( \gamma_2 \) are the broadening functions at the contacts. From (2) we can see that the current is a function of the electrostatic potentials imposed at the two contacts of the nanotube (this dependence is implicit in the Fermi functions \( f_1(E, V) \) and \( f_2(E, V) \) at the two nodes), which is the reason why an iterative approach for the solution of the system is needed. In equation (2) the variable that discriminates the different properties of the nanotubes (i.e. the chirality) is the DOS, which is computed according to the numerical model developed in [7].

3. Results and discussion

We performed different studies on the resistivity of different networks in terms of film thickness, showing the percolative nature of the transport. In figure 2 we report the current flow through a network of a certain area, and the same plot for two subsets obtained by cutting half of the network along its width.

![Figure 2](image)

**Figure 2.** Plot of the current flow through a film of 12 CNTs/\( \mu \text{m}^2 \) (top) and a film of 24 CNTs/\( \mu \text{m}^2 \) (bottom). From left to right, the entire network, the network with the bottom half cut out and the network with the top half cut out. While for the dense film the density of current is almost constant in the three different cases, for the sparse network it instead changes considerably.

As it stands out, the percolative behavior is much more evident in films with a low density of nanotubes. When the density increases, the network tends to become more uniform, and the film approaches a behavior similar to the one of a bulk material. In figure 3a we show the value of the normalized resistivity versus the aspect ratio of the network. When the film is close to its percolation threshold, it is very likely that a cut could eliminate fundamental percolation paths, increasing dramatically the resistivity of the network. On the other hand, if the width is greater than its initial value, more paths will be formed, causing a serious drop of the resistivity. These effects are much less influential on more dense networks, where the resistivity seems to be less affected by the variations of the aspect ratio of the film.

A similar analysis has been done on the resistivity of films with different densities, as is shown in figure 3b. Consistently with our previous findings, we observed two different behaviors on the resistivity, depending on the density of the nanotubes. After a certain threshold, an increase of the density does not affect anymore the resistivity of the film, which tends to saturate to a certain value. As we previously mentioned, CNT networks could be employed as transparent electrodes. Since in this particular application a trade-off exists between the resistivity and transparency of the film, this analysis could be useful for a proper design of the electrode. When such a threshold is actually reached, an
increase of the film thickness will not bring any appreciable benefit to the conductivity of the network, but will drastically reduce the transparency of the film.

![Figure 3](image-url)

**Figure 3.** (a) Normalized resistivity versus the aspect ratio of the simulated area for three different densities. (b) Normalized resistivity versus the density of the nanotubes.

### 4. Conclusion

In conclusion, we report the implementation of a simulation tool based on a percolative model. Accurate morphologies have been generated in a three dimensional space, reducing the gap between the real structures and the one resulting from 2D models previously presented in the literature. We implemented an accurate model for the transport through the single nanotubes and we included it in a self-consistent framework for the simulation of the entire network. The results obtained by our simulations are in agreement with the percolation theory. We observed that the percolative behavior is much more evident for low densities of nanotubes, and it tends to vanish when the networks are far from their percolation threshold.

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### References

[1] Hu L, Hecht D S and Grüner G 2010 Carbon nanotube thin films: fabrication, properties, and applications. *Chem. Rev.* **110** 5790–844

[2] Colasanti S, Deep Bhatt V and Lugli P 2014 3D Modeling of CNT Networks for Sensing Applications *2014 10th Conference on Ph. D. Research in Microelectronics and Electronics (PRIME)* pp 3–6

[3] Colasanti S, Robbiano V, Loghin F C, Deep Bhatt V, Abdellah A, Cacialli F, and Lugli P 2015 Experimental and Computational Study on the Temperature Behavior of CNT Networks *2015 15th IEEE Int. Conf. Nanotechnol.*, in press.

[4] Abdellah A, Abdelhalim A, Horn M, Scarpa G, and Lugli P 2013 Scalable spray deposition process for high-performance carbon nanotube gas sensors *IEEE Trans. Nanotechnol.* **12** (2) 174–181

[5] Pennington G and Goldsman N 2005 Low-field semiclassical carrier transport in semiconducting carbon nanotubes *Phys. Rev. B* **71** 205318

[6] Datta S 2005 *Quantum Transport Atom to Transistor* (New York: Cambridge University Press)

[7] Mintmire J and White C 1998 Universal Density of States for Carbon Nanotubes *Phys. Rev. Lett.* **81** 2506–9