Modelling and simulation of CNTs- and GNRs-based nanocomposites for nanosensor devices

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Abstract

The main objective of the current study is to demonstrate the implementation of advanced simulation models providing a proper description of the electronic properties, electrical conductivity, electromagnetic and electromechanical phenomena of functionalized CNT- and GNR-based nanostructures of different morphologies and their interconnects for nanosensor and nanomemory systems. The sensitivity of the local electronic density of states to external influences (mechanical, chemical, magnetic, etc) on the fundamental electromagnetic properties of CNTs, GNRs and their metal interconnects have been analyzed from the point of view of nanosensor applications. Nanoporous systems are considered as complicated ensembles of basic nanocarbon interconnected elements (e.g., CNTs or GNRs with possible defects and dangling boundary bonds) within the effective media type environment. The model of nanocomposite materials based on carbon nanocluster suspension (CNTs and GNRs) in dielectric polymer environments (e.g., epoxy resins) is regarded as a disordered system of fragments of nanocarbon inclusions with different morphologies (chirality and geometry) in relation to a high electrical conductivity in a continuous dielectric environment. The electrical conductivity of a nanocomposite material depends on the concentration of nanocarbon inclusions (in fact, carbon macromolecules). Various nanocomposite morphologies are considered and computer simulation results are discussed.

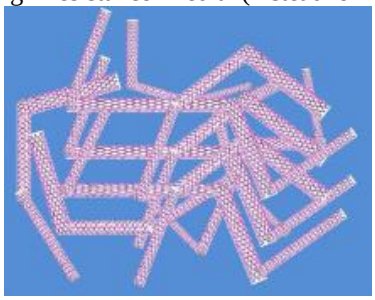
Keywords: carbon-based nanocomposites pressure nanosensors hopping conductivity

1 Introduction

We develop a set of prospective models of nanocarbon-based nanomaterials and nanodevices based on the various interconnects and interfaces (see Figure 1). In particular, nanoporous systems are considered as complicated ensembles of basic nanocarbon interconnected elements (e.g., CNTs or GNRs with possible defects and dangling boundary bonds) within the effective media type environment (Figure 1a,1b). Interconnects are essentially local quantum objects and are evaluated in the framework of the developed cluster approach based on the multiple scattering theory formalism as well as effective medium approximation [1-3].

In cases when nanocarbon clusters are embedded in high resistance media (instead of vacuum) we come to nanocomposite material. Talking about carbon based nanocomposites, the formation of direct nanocarbon interconnects may not be mandatory (see, Figure 1e).

The utilization of polymeric composite materials (e.g., epoxy resins) supplemented with various morphological nanocarbon groups of carbon nanotube-type (CNTs) and graphene nanoribbons (GNRs) allows us to create effective pressure and temperature sensors. Application of such nanocomposites as coatings can provide continuous monitoring of the mechanical strains in piping systems (for example, in aircraft or automotive applications), when the critical pressure values can indicate malfunctions of the engine. Such an ongoing monitoring is essential for the development of intelligent engine management and cooling systems.



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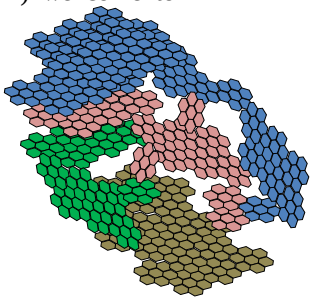

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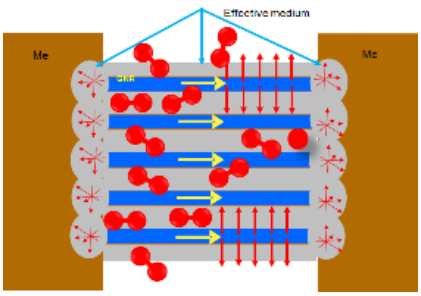

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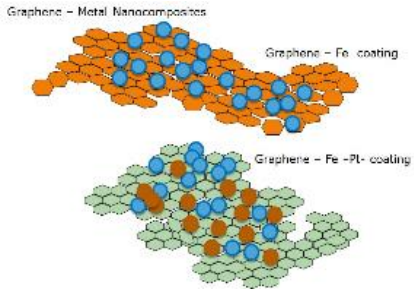

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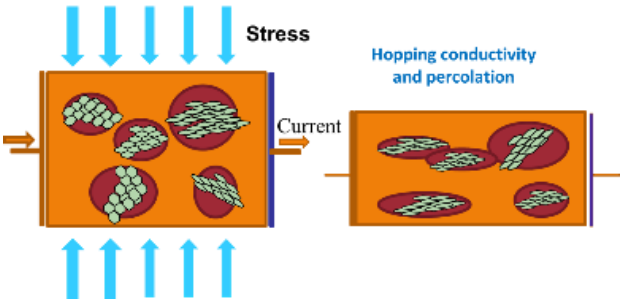

e)

FIGURE 1 A set of simulation models: a) Structural model of CNTBA; b) Structural model of GBA; c) GNRs-based gas nanosensor device; d) Graphene-metal nanocomposites- Fe and Fe-Pt coatings; e) model of nanocomposite based pressure and temperature sensor

The interest in the CNTs and GNRs based polymer nanocomposites as prospective pressure nanosensor materials is based on the observed electric percolation phenomena via the nanocarbon inclusions concentration. In particular, the electrical conductivity of a nanocomposite increases with the increasing CNT loading till a critical filler concentration, where a dramatic increase in conductivity is observed. This critical filler concentration is called electrical percolation threshold concentration. [4, 5]. At percolation threshold concentration, a filler forms a three-dimensional conductive network within the matrix, hence electron can tunnel from one filler to another, and in doing so it overcomes the high resistance offered by insulating polymer matrix.

It is worth mentioning some experience in the creation of CNTs-based experimental prototypes of pressure nanosensors [6-8].

External stresses applied to nanocarbon based nanocomposites lead to a relative volume decrease and, as a result, to nanocarbon concentration increase. This process explains the trends in conductivity increase under the stress growth for improving percolation conditions.

2 Models CNTs- and GNRs-based nanocomposites

Consider the model of composite material with carbon nanocluster inclusions of CNTs- and GNRs- types. The host material – is a flexible dielectric medium of epoxy resin-type with high resistance [3, 9]. However, low concentration of nanocarbon inclusions cannot change the mechanical properties of the host material. At the same time, high electrical conductivity of CNTs- and GNRs incorporated in the host material can significantly affect the total conductivity of the nanocomposite material. According to our model, the mechanism of these changes is related to the effects of percolation through the hopping conductivity.

Thus, the model of nanocomposite materials based on carbon nanocluster suspension (CNTs and GNRs) in dielectric polymer environments (e.g., epoxy resins) is considered as a disordered system of fragments of nanocarbon inclusions with different morphology (chirality and geometry) in relation to a high electrical conductivity in a continuous dielectric environment. Presumably, the electrical conductivity of a nanocomposite material will depend on the concentration of nanocarbon inclusions (in fact, carbon macromolecules). Isolated nanocarbon inclusions will provide conductivity due to the hopping conductivity mechanism through dangling bonds up to the percolation threshold, when at high concentrations (some mass %) a sustainable ballistic regime appears, which is characteristic of pure carbon systems. The hopping mechanism is regulated by the hopping of electron between 'nanocarbon macromolecules' [10]:

$$\sigma_{IC} = \sigma_0 \cdot \exp\left(-\frac{4}{3}\left(\frac{4\alpha r_{IC}}{a}\right)^{3/4}\left(\frac{W_0}{kT}\right)^{1/4}\right), \quad (1)$$

where r_{IC} is the length of the tunnel 'jump' of the electron equal to the distance between 'nanocarbon' clusters, σ_0 - normalization constant, which means the conductivity of monolithic dielectric medium [10]. Added to this is the effect of intrinsic nanocarbon cluster conductivity, which is dependent on its morphology. The electric conductivity will also depend on the spatial orientation of nanocarbon inclusions. It will be greater for the longitudinal electric field orientations and lower for the transverse ones. Of course, any spatial orientations are technologically possible.

If we introduce the volume part as an indicator of the nanocarbon inclusions concentaration:

$$\eta = \left(\frac{R_0}{R_0 + R}\right)^3,$$

where R_0 is the average nanocarbon macromolecule radius, R is, as earlier, the width of the potential barrier between the nearest nanoclusters, which is responsible for percolation ability of the model nanocomposite. We should also diminish the hopping phenomena and percolation probability taking into account the nanocarbon macromolecule orientation within a hypothetical sphere embedded into high resistance dielectric medium.

Based on this definition, we can obtain a contribution of potential nanocarbon clusers to nanocomposite conductivity as follows (see also Figures 2, 3):

$$\ln\left(\frac{\sigma_{IC}}{\sigma_0}\right) = -\frac{4}{3}\left(\frac{4\alpha}{a} R_0 (\eta^{-1/3} - 1)\right)^{3/4}\left(\frac{W}{kT}\right)^{1/4} \quad (2)$$

The overall conductivity of nanocomposite material is [9, 11]:

$$\Sigma \approx \Sigma_D + \Sigma_{NC}, \quad (3)$$

where $\Sigma_{NC} = \sum_i^N (\mathrm{R}_i)^{-1}$,

$$R_i = A\sum_{k=1}^{N_i}(\sigma_{nano,i.k}^{-1} + \sum_{k=0}^{N_i}(\mathrm{N}_{eff,i,k}\,\sigma_{IC,i,k})^{-1}),$$

where N - is the number of conductivity channels, N_i – is the number of nanocarbon clusters in the conductivity channel, N_{eff} is the number of effective bonds of tunneling bonds including the contact region, $\sum_D = (R_D)^{-1}$ is the conductance of dielectric medium, σ_{nano} is the conductivity nanocluster, σ_{IC} - is the hopping conductivity of the effective bond, which creates interconnect for large nanocarbon inclusion concentrations.

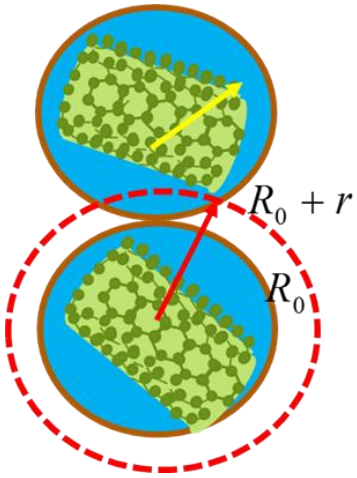

FIGURE 2 Nanocomposite conductivity via volume concentration of nanocarbon inclusions [3]

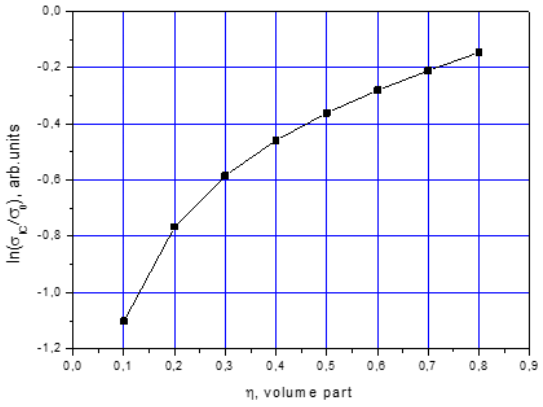

FIGURE 3 The hopping conductivity correlation via the average nanocarbon macromolecules volume part within continuous dielectric medium

3 Simulation of stress-induced resistance of carbon-based nanocomposite sensors

The overall configuration of the sample for the model calculations is presented in Figure 4. The basic dimensions of nanocarbon clusters (CNTs and GNRs) are as follows: the diameter of the CNT - 5 nm, the height - 10 nm, the width of the expanded CNT, ie, the width of the GNR = $\pi \cdot 5 \approx 15,6nm$.

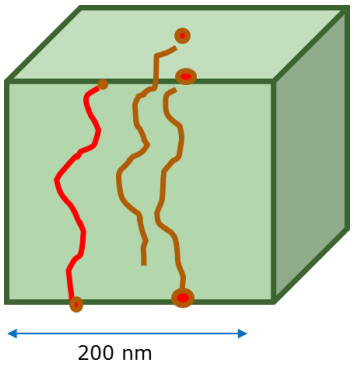

FIGURE 4 Nanocomposite sample with a probabilistic percolation way of the electric current

The average statistical distance between nanocarbon clusters is - 5 nm. This is the key distance for the mechanism of hopping conductivity (see Figure 5). Nanocarbon cluster is considered as a potential well with a typical size 2a. Neighboring potential wells are separated by a distance r_{IC} . These two parameters are ultimately determine the morphology of the nanocomposite material.

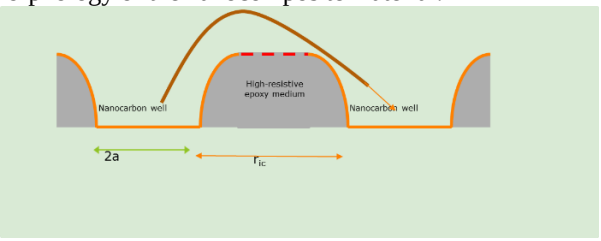

FIGURE 5 Jumping between neighboring nanocarbon potential wells

The proposed model of hopping conductivity for current percolation in carbon-based epoxy-resin nanocomposite [4] takes into account basically the percolations along the nanocluster sets which are located along the stress direction. Interactions between the neighbouring sets are not considered for a low general concentration of nanocarbon inclusions [11].

Figure 6 demonstrates resistances correlations via static stresses for ideal morphologies of a nanocomposite when CNTs and GNRs are oriented pure longitudinally or pure transversely.

From the technological point of view, it is not so simple to provide such ideal orientations for host polymer materials similar to epoxy resins. The first problem of the nanocomposite morphology is the selection of CNTs and GNRs with identical parameters. The second problem is the polymer-nanocarbon mixture creation when we evidently should expect a homogenous random distribution of nanocarbon orientations.

Figure 7 demonstrates the marginal rotational disordering of CNTs inclusions from 'ideal' longtitudinal orientation. Deviations of orientations give the characterictic intercluster distances of 3.82 and 7.02 nm taking into account basic 5 nm in the ideal case.

Figure 8 presents the full-scale simulation of CNTs orientation deviations within a host material. The results show various sensitivity of the model nanocomposite as a potential pressure nanosensor in dependence of its morphology. Configurations of the 4th type (see Figure 8) are more sensitive and, evidently, more practically preferable.

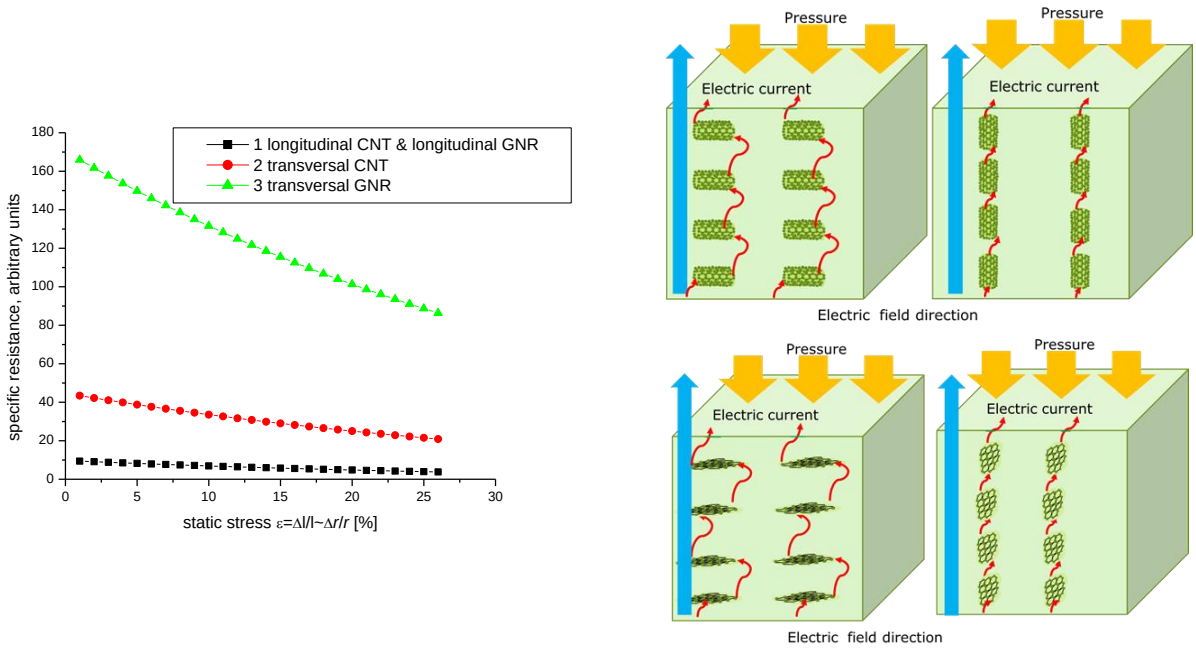

FIGURE 6 Specific resistance of CNTs and GNRs based nanocomposite (epoxy resin) via static stress. To the right – variants of morphological orientations of nanocarbon inclusions

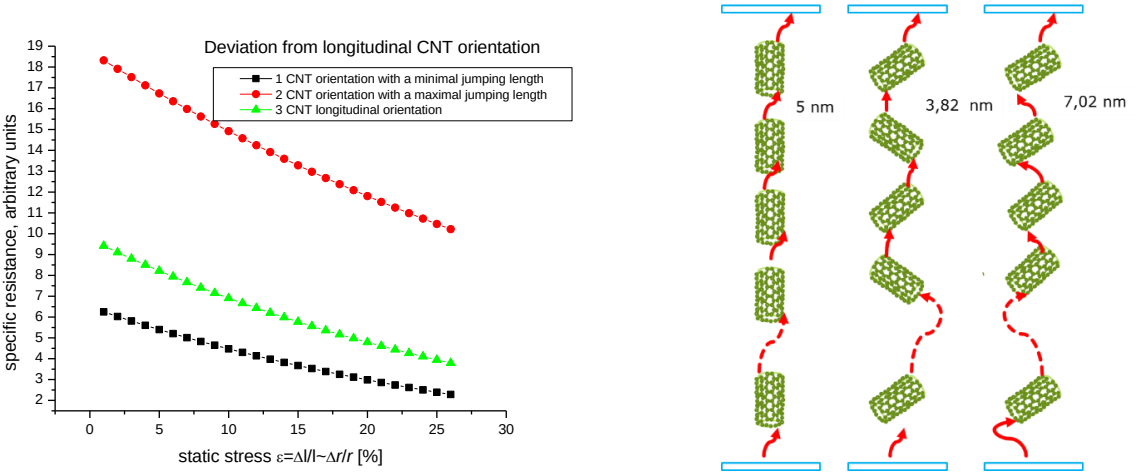

FIGURE 7 Rotational disordering of nanocarbon inclusions: longitudinal case. To the right – morphological variants of CNTs orientations

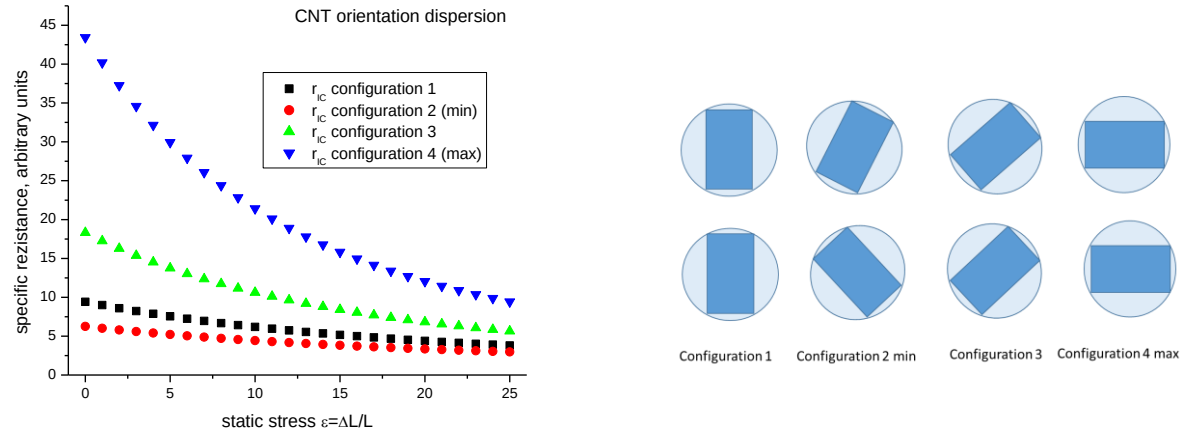

FIGURE 8 Resistances of CNTs based nanocomposites via static stress for various marginal morphologies

The model uses morphologically compatible carbon nano configurations with the same number of carbon atoms, the same surface area of model CNTs and GNRs, and the same chirality. In this way, the model CNTs and GNRs are interconnected by a simple topological transformation from a cylinder to a rectangular fragment. Monte-Carlo simulations of orientation deviations for CNTs and GNRs morphologies are presented on Figures 9 and 10.

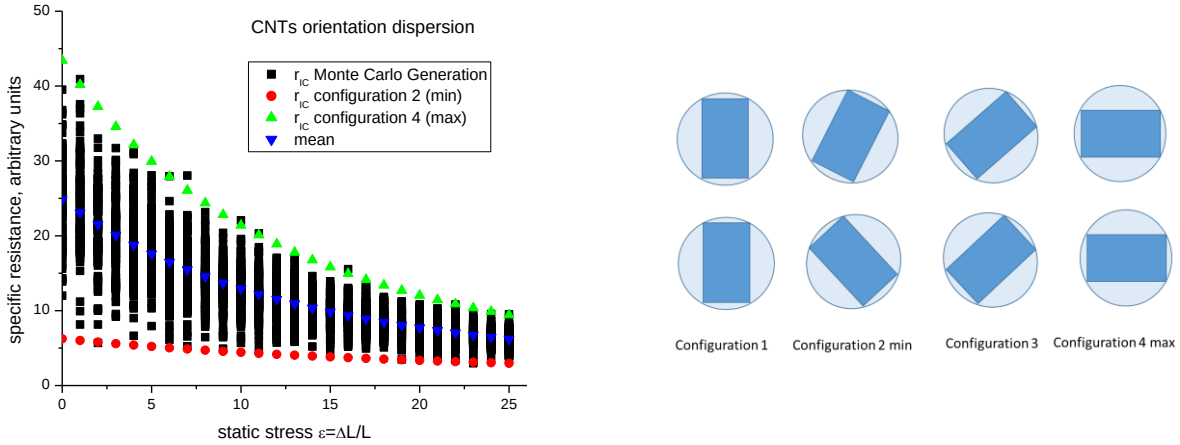

FIGURE 9 Resistances of CNTs based nanocomposites via static stress for Monte-Carlo varied morphologies. To the right – marginal orientations of CNTs within a host polymer material

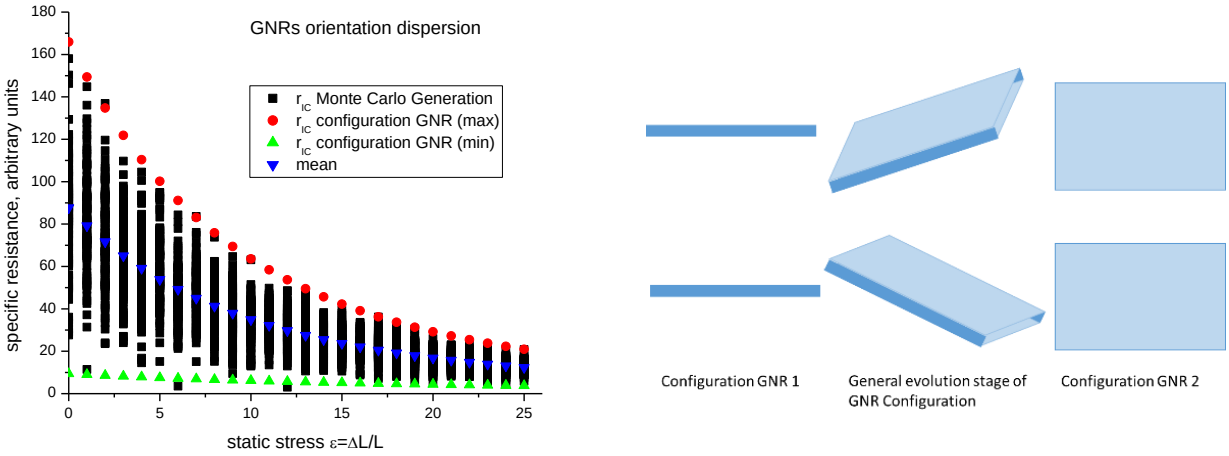

FIGURE 10 Resistances of GNRs based nanocomposites via static stress for Monte-Carlo varied morphologies. To the right – marginal orientations of GNRs within host polymer material

The middle curves of resistances via the static stress (Fig. 9, 10) characterize the main phenomenon trend for the expected pressure CNTs and GNRs-based nanosensor prototypes.

4 Conclusions

A nanocomposite pressure nanosensor prototype has been simulated. The hopping conductivity mechanism gives the adequate description of possible nanosensor qualitities.

An important problem of manufacturing sensors based on CNTs is nanotube orientation, which determines the electrical properties of the future sensor.

A temperature nanosensor prototype needs a host medium with a high heat conductivity and low electrical conductivity. Epoxy resin parameters do not answer these requirements.

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