Model-Assisted Study for Deeper Analysis of Conductivity and Piezoresistivity of Nanocomposites and Films with Graphene Nanoplatelets for Smart Structure Application

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Abstract

The use of two-dimensional graphene, with its inherent low thickness and weight, provides high potential for large-area application and building smart structures without changing their properties. Nanocomposites and films with graphene nanoplatelets promote the formation of electrical conductive networks with piezoresistive sensing capabilities for potential sensor-structure fusion. A computational percolation model with hardcore-softshell discs was implemented to calculate the conductivity and the strain-induced piezoresistivity based on the network in a parametric study. The simulations are carried out for homogenous, random or agglomerated distributions by considering the number of particles, the potential barrier and the tunneling distance in form of tunneling vectors in representative two-dimensional unit. The individual current paths with their corresponding current density inside the network have been generated and visualized by the model for initial and deformed state. Moreover, the model provides the main parameters to find an optimum of sensitivity and reproducibility. A more reproducible piezoresistivity without prevalent disadvantage for the gauge factor is predicted by random distribution. A symmetric arrangement of particles inside the network predicts the best result, but poses problem in practical realization. The current work provides a simplified numerical two-dimensional model for designing smart materials in form of nanocomposites and strain sensitive films based on graphene nanoplatelets. The results offer insights which may upon up new design directions.

1. Introduction

The combination of extraordinary mechanical [1,2] and electrical properties [3,4], and its ability to be dispersed in aqueous solution [5] and polymer matrix [6], promises a broad application of graphene in the field of bulk nanocomposites (e.g., reinforced [7] and conductive polymer [8]) and layered functional films (e.g. strain gauges [9–12], pressure sensors [13,14], shielding [15]). By embedding graphene nanoplatelets (GNP) inside an insulator, pathways for electron transfer are created, which enables a transition from insulator to conductor at the percolation threshold [16,17]. Many theoretical and experimental investigations focus on the percolation threshold of composites with GNP fillers and the power-law describing the conductivity behavior by considering the filler geometry and volume fraction [18–21]. Most of the theoretical studies have been carried out for random distribution. Besides that, Gong et Wang et al. considered also the significance of spherical shaped agglomeration to the conductivity and the percolation
threshold in nanocomposites [18,22]. Particularly with regard to smart materials application and self-sensing activities of mechanical structures the piezoresistive effect (PRE) becomes important [23]. Investigations in the literature demonstrated the piezoresistivity for GNP nanocomposite assisted by theoretical investigations with 3D numerical model. Oskouyi et al. found out that the piezoresistive behavior of nanocomposites mainly depends from the conductive filler density which is represented by the volume fraction inside a representative volume element [19]. The theoretical study of Hempel et al. considers the change of contact area of overlapped GNP and the density of GNP inside a strain sensitive film without deeper details of the modeling procedure [12]. The experimental study of Chen et al. revealed that the gauge factor can be increased by increasing the tunneling junction distance in out-of-plane direction and reducing the flake diameter [10]. However, a non-linear and complex network exist, which has high degrees of freedom and tailoring properties on the one hand, but on the other hand the prediction of the PRE behavior can be difficult.

In the following sections, a theoretical analysis will be presented to model the piezoresistive effect of GNP networks in order to determine the effective parameters and optimize the overall performance since most of the studies are described schematically derived from experimental observations [10,17,24–26]. Theoretical studies in percolative GNP networks shall be considered by using a two-dimensional charge tunneling model with hardcore-softshells which is derived from a 3D resistor network. New insights should be obtained by visualization of the conductive paths and calculation of the sensitivity by considering the established theory of tunneling effect by Simmon’s formula [27]. A crucial point in sensor application of percolative GNP films is the reproducible sensor behavior, which is always underestimated and has not been considered by recent investigations. The sensor performance shall be considered for different GNP distributions. Computational studies are carried out for symmetric GNP arrangements inside the two-dimensional area, which can only be realized with highly energy consuming CVD process [28]. Therefore the perfect symmetry is slightly disordered, quantified with a disorder degree. Besides the random distribution, agglomerated arrangements, which form micro- and macro-cluster (see Section 2.2.3), are investigated considering the PRE. The outcome of the simulations should provide a further guideline for design and application of smart sensor technologies in the context of GNP films and nanocomposites for strain sensing application.

2. Modeling Procedure

2.1 Flow chart of modeling procedure

In this section, we will first outline our modeling procedure which is divided into three steps (see Figure 1). Based on the model assumption and parameter definition (e.g., settings of distribution, number of GNP, connection criterion) we calculate clusters of connected GNP, similar to the approach of Oskouyi et al [19]. By this way a percolated network is formed between two parallel faces, which represent the electrodes (Figure 1b). In the second step the current paths are calculated and visualized, considering the resistivity between connected GNP. In the third step the piezoresistive effect is described by the gauge factor. Each simulation will be repeated 30 times in order to ensure statistical validation for the obtained results.
2.2 Computational model

2.2.1 Model abstraction of GNP network
As seen in the morphology of two different spray deposited graphene films in Figure 2, the particle distributions have a random distribution characteristic. Nevertheless, there is still a significant difference in the structure. While the morphology of a spray deposited graphene dispersion by Paton et al. [29] show a surface layered structure (see Figure 2a right), the film of graphene ink by Secor et al. [30] have a random orientation of GNP (see Figure 2a left). A model abstraction of GNP networks by introducing a three dimensional tunneling vector $t_{3D}$, which corresponds to quantum tunneling for different orientation and distance of adjacent GNP (see Figure 2b), is derived from the aforementioned morphology. The model assumption of the tunneling vectors $t_{3D}$ in GNP networks enables the description of PRE by projecting tunneling vectors $t_{xy}$ in two-dimensional strain fields, exemplified in Figure 2b. This simplifying assumption does not holistically describe the arrangement of PRE inside the network – especially the change of intrinsic resistance of GNP or the contact area between GNP. However, as shown by Li et al. the order of magnitude of resistivity due to a tunneling distance is significantly higher than the intrinsic resistance and the contact area resistance in nanocomposites [31].

In the two-dimensional model the tunneling mechanism is investigated by using a hardcore-softshell model. The hardcore is assumed as an impenetrable core which represents the physically extent of GNP. The hardcore is surrounded with its softshell
which represents the penetrable boundary in order to describe interaction between adjacent GNP's [20].

![Figure 2](image-url)  
**Figure 2.** a) Morphology of two spray deposited graphene films [29,30], b) two-dimensional tunneling-percolation model for analysing the PRE in two-dimensional strain field \((\varepsilon_x, \varepsilon_y)\) by projecting tunneling vector \(t_{ij}\) between adjacent GNP

### 2.2.2 Simulation parameters
Monte Carlo simulations are seen as an effective tool for analyzing randomly distributed GNP networks [19,32]. The dimension of the hardcore-softshell is selected by the thickness of GNP and quantum tunneling mechanism. Hicks et al. assumed a thickness of 1 nm due to the crumbled and wrinkled nature of GNP, which shall be considered for the hardcore diameter of 1 nm in the simulations [20]. The surrounding softshell has a diameter of 3 nm and corresponds to a maximum cutoff-distance of 2 nm, where an interaction of GNP shall be considered. Further increase of the soft-shell diameter has no significant contribution to the network behaviour as shown by Oskouyi et al. [19]. The number of particles is determined by the area fraction of a square, which is given by

\[
AF = n \frac{\pi \cdot r_{HC}^2}{L^2},
\]

where \(r_{HC}\) is the radius of the hardcore and \(n\) corresponds to the number of deposited GNP's. The simulations are carried out for approximately 4000 tunneling vectors which correspond to the same size of GNP.

### 2.2.3 Formation of cluster
Once the position of GNP is determined, the distance between the \(i\)-th and \(j\)-th GNP is determined by

\[
d(i, j) = \|r_i - r_j\|_2,
\]
where $d(i,j)$ describes the minimum distance and $r_i, r_j$ the origin of the corresponding GNP. The softshell of each deposited GNP determines the interaction between adjacent GNPs. Once a penetration inside a softshell is given, the particles are linked together and form a cluster [19]. The criterion of percolation must fulfill the formation of a cluster from left to the right electrode.

In order to investigate the influence of distribution systematically, three different settings of particle arrangement shall be investigated. Firstly, the GNPs are serially deposited for the given representative unit, using a pseudorandom generator (see Figure 3a). Secondly, irregularities in form of agglomeration are investigated in a qualitative manner. In the present work the simulations of “pseudo”-agglomeration includes micro- and macro-clusters by two different criteria of GNPs arrangements. The simplified model does not describe the physics of agglomeration. Nevertheless, a mathematical-stochastic approach of “pseudo”-agglomeration for percolated networks shall be considered in order to assess the influence to the PRE. In the following, a brief introduction in modelling of “pseudo”-agglomeration is given: Once a GNP is deposited in the square unit, the minimum distances $d_{0i}$ to adjacent GNP inside a virtual circle with a radius of $R$ from the centre point is calculated. The distribution inside the circle determines the micro-cluster and is generated by considering all adjacent GNP with two different constraints:

\[
1^{\text{st}} \text{ constraint: } \text{rand}(l) > \frac{1}{R^n} \prod_{i=1}^{n} d_{0i},
\]

\[
2^{\text{nd}} \text{ constraint: } \text{rand}(l) < \frac{1}{R^n} \prod_{i=1}^{n} d_{0i},
\]

where $n$ is the number of particles inside the virtual radius and $\text{rand}(1)$ is a pseudorandom number between 0 and 1. Once no GNP particle exist inside the virtual circle, a new seed to form a macro-cluster exist, given by the 3rd constraint

\[
d_{0i} > R + C,
\]

where $C$ describes the minimum distance of adjacent GNP to the circle. By using the aforementioned “pseudo”-agglomeration, the GNP network tends to form different micro- and clusters. The influence of agglomeration is considered in a parametrical study by changing $R$ and $C$, considering the constraints. The fractal dimension of agglomerated distribution for different parameters is given in Figure 3b/c. It is interesting to note, that $R$ as well as $C$ affect the pattern of distribution. The higher $R$ and $C$, the more spread the GNP-cluster out. Moreover, the network is packed more densely for the 1st constraint. Finally, by introducing a degree of disorder (DOD), representing a pseudorandom position shift within a circle radius from the centre point of the GNP, the perfect particles arrangements should be disrupted. As seen in Figure 4a, DOD of 0 represents a perfect symmetric arrangement, while a DOD of 1 leads to a random shift within a maximum circle radius. Since the tunneling distances are set to 1nm, the maximum circle radius can be 0.5 nm in accordance to the hardcore-softshell model.
Figure 3. a) random distribution of GNPs b/c) agglomerated distribution by considering the 1st constraint and 2nd constraint for different $R$ and $C$ in an explanatory manner

Figure 4. Particle arrangement quantified by the degree of disorder (DOD): a) a perfect symmetric arrangement with a tunneling distance of 1 nm between hardcores (DOD=0), b) GNP arrangement for DOD of 0.5, c) GNP arrangement for DOD of 1
2.2 Conductivity analysis

In the presented 2D model the conductivity and piezoresistive effect is determined as a function of the tunneling resistivity between adjacent GNP in form of the quantum tunneling mechanism. For a low-voltage range the tunneling resistivity is given by Simmon’s equation [27] as:

\[ \rho_{\text{tunneling}} = \frac{\hbar^2}{e^2 \sqrt{2m\gamma}} \exp\left(\frac{4\pi d}{h\sqrt{2m\gamma}}\right) \]  

(5)

Here \( e \) is the elementary charge, \( m \) is the mass of an electron and \( h \) is the Planck constant. The tunneling distance \( d \) is the smallest possible distance between adjacent nanoparticles. \( \lambda \) is the potential barrier of the insulator through which the tunneling mechanism occurs. The network represents a circuit of nodes, where each hardcore represents a node. In accordance to Kirchhoff’s circuit law, the node analysis can be used by,

\[
\begin{pmatrix}
G_{i1} & -G_{i2} & \ldots & -G_{in} & \phi_i \\
-G_{i2} & G_{i2} & \ldots & -G_{in} & \phi_j \\
\vdots & \vdots & \ddots & \vdots & \vdots \\
-G_{in} & -G_{m2} & \ldots & G_{mn} & \phi_n
\end{pmatrix}
\begin{pmatrix}
\phi_1 \\
\phi_2 \\
\vdots \\
\phi_n
\end{pmatrix}
= \begin{pmatrix}
I_1 \\
I_2 \\
\vdots \\
I_n
\end{pmatrix}
\]

\[ G_{ij} = G_{ji} \forall i, j \]  

(6)

where \( G_{ij} \) is the admittance, \( \phi_i \) the potential between two nodes between the i-th and j-th GNP and \( I \) the current input to the network. We define a supplied voltage potential between the first and last node. Inside the electrode the particles are connected without any resistance between the nodes. The contact-resistance to the electrode is not considered in this investigation since it does not represent the network behavior and it can be eliminated by a four-point probe measurement system [33]. The area of the electrodes is considered over the entire width of RE.

Since the potential between the nodes are calculated, the current between the nodes is determined by the Ohmic law. The current paths are visualized and represented by the line width and colour. Paths with higher current strength are represented with thicker lines in yellow/red colour while paths without any current paths correspond to blue lines (see Figure 1). The formation of current paths as a function of the potential barrier has been already investigated by Yokaribas et al [9].

2.2 Sensitivity analysis

The gauge factor (GF) is a general measure for the sensitivity of the strain sensors and quantifies the relative change of the resistance \( R \) due to the applied strain \( \varepsilon \) [34] by

\[ GF = \frac{1}{\varepsilon} \frac{\Delta R}{R} \]  

(7)

The GNP do not deform during deformation of the substrate due to slippage effects between the GNP's [35]. The comparison of the Raman spectra for strained and unstrained states of GNP in Yokaribas et al. confirm this assumption for the aforementioned GNP network in Figure 2 [9]. Simplifying the GNP to circular rigid bodies, the motion of the particles can be estimated in accordance to the two-dimensional strain fields.
3. Results and Discussion

On the basis of the developed numerical model above, the PRE for three different kinds of distribution is investigated. The predicted results of each data point are determined by 30 simulations. It is taken into account that near the percolation threshold the resistance change becomes asymptotic and nonlinear [20], which is not favourable for validation of the presented simulation results, aiming at reproducible sensor performance beyond the percolation threshold.

3.1 Random network and representative element

Firstly, randomly deposited GNP are investigated for different number of GNP by varying the area fraction $AF$. The standard deviations of GF are calculated respectively, in order to find a measure (e.g., number of particles) for a representative element (RE). As it can be seen in Figure 5a, the results of the standard deviation are given as a function of the area fraction and number of particles, respectively. As a lower limit, a percolated network with linked GNP requires an area fraction of 0.22. By increasing the number of GNP and area fraction, the data points run into saturation. Beyond an area fraction of 0.3 and 4000 GNP a lower gradient is determined. A deeper analysis of these parameters by fixing one parameter, while the other is changed, confirms the saturated nature beyond the percolation threshold (see Figure 5b). For a simulation of 150 runs with randomly deposited GNP inside the RE, a mean GF of 16.48 with a standard deviation of 11.3% is predicted.

![Figure 5. a) standard deviation of the gauge factor for different number of particles and area fraction (hatched area represents the mean standard deviation for the RE), b) deeper analysis for the chosen RE](image-url)
3.2 Agglomerated GNP network

Secondly, the effect of “pseudo”-agglomeration is investigated by varying the parameters \( R \) and \( C \) in Table 1 (see Section 2.2.). As seen in Figure 6, it is interesting to note that agglomeration does not result in significant influence to the mean gauge factor by comparing with the random distribution. Furthermore, the random distribution shows a lower deviation at the same time, which is a crucial point in sensor performances. Enhancing the sensitivity can be realized by increasing the potential barrier or area fraction, as shown in the previous analysis of Yokaribas et al. [9]. The results reveal that the potential barrier (1.5 eV instead of 1eV) has a more prevalent effect on the sensitivity than the agglomerated distribution. Based on these results, it can be outlined that the design of GNP nanocomposites and films should aim a random distribution. Avoiding agglomeration is beneficial for the sensitivity and reproducibility at the same. These results are in good agreement with the results by Gong et al., who investigate spherical agglomeration inside a nanocomposite of carbon nanotubes, derived by a numerical 3D model [22]. It confirms clearly that the electrical conductivity of the nanocomposites is more sensitive to the internal density of agglomerates than the piezoresistivity does. GNP network does not percolate for some parameters shown in Table 1. By this way the network becomes non-conductive, which is also a weak point.

Table 1. Simulation parameters (note that parameters marked with * do not percolate for all 30 runs and therefore are not considered further)

<table>
<thead>
<tr>
<th>Constraint</th>
<th>( R ) for ( C=20 )</th>
<th>( C ) for ( R=3 )</th>
<th>( \lambda )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(^{st})</td>
<td>3*,4,5,7,10</td>
<td>0,2,5,10,20*,30*</td>
<td>1 eV, 1.5 eV</td>
</tr>
<tr>
<td>2(^{nd})</td>
<td>3,4,5,7,10</td>
<td>0,2,5,10,20,30</td>
<td>1 eV, 1.5 eV</td>
</tr>
</tbody>
</table>

![Figure 6. Mean gauge factor and standard deviation of gauge factor for two different potential barriers](image)

3.3 GNP network quantified by DOD

Finally, in order to understand the mechanism of conductivity and piezoresistivity a symmetric arrangement with DOD of 0 should be stepwise disordered to a DOD of 1.
Furthermore the relevance of the Poisson ratio to GF and its standard deviation are considered in accordance to the strain field. The results in Figure 7 predict the network behaviour and show the current paths for DOD of 0 and 1. It is interesting to note that the Poisson’s ratio decreases the gauge factor and increases the standard deviation at the same time. The Poisson’s ratio effect will reduce the transversal distance between the adjacent GNPs in transversal direction, which corresponds to a more transversal orientation of tunneling vector $t_{xy}$. Thus, a higher gauge factor within a network can be achieved by a better alignment of the tunneling vector in the measured strain direction. The symmetrical arrangement in the measured strain direction has a high relevance for the sensitivity and reproducibility simultaneously. With higher degree of disorder the distribution of current paths becomes more complex. Single current paths become important while other parts minimize their contribution to the network behaviour and the resistivity increases at the same time (see Figure 7).

![Graphs showing mean gauge factor, standard deviation, and normalized resistivity](image)

Figure 7. a) mean gauge factor/ standard deviation/ normalized resistivity of 30 simulations for different degrees of disorder b) schematically shown current paths inside the network with a degree of disorder 0 and 1, subjected to a two dimensional strain field

4. Conclusions

In summary, a computational study for deeper analysis of distribution of a GNP inside a network of nanocomposites was performed. The developed numerical model represents the mechanism of piezoresistivity in GNP networks of nanocomposites and films in an accurate way. By introducing tunneling vectors for describing the network behavior, an
important direction in the development of sensitive strain sensors with practical relevance for tailoring properties is given.

Besides the sensitivity and the effect of distribution, we investigate the reproducible sensor performances. The symmetrical arrangement in the measured strain direction has a high relevance for the sensitivity and reproducibility simultaneously, but poses problems in practical application. With higher degree of disorder the distribution of current paths becomes more complex. The comparisons of random and agglomerated states predict that agglomeration has no significant influence to the piezoresistivity, while other parameters such as the tunneling distances and potential barrier show a more sensitive characteristic to the change of resistivity. The novel insights may show relevance for future investigation by implementation of sensitive materials based on graphene nanoplatelets in smart structure application and Structural Health Monitoring.

References