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Numerical analysis of electric conductivity and percolation threshold of graphene-reinforced nanocomposites by finite element method

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Résumé — A nonlinear Finite Element formulation and a numerical methodology to model the nonlocal and nonlinear effects introduced by the tunneling effect conduction model within the polymer matrix between close graphene sheets is proposed, which could explain the percolation phenomenon and nonlinear electric behavior of graphene-reinforced nanocomposites with polymer matrix. The computed effective conductivity is evaluated over representative volumes containing arbitrary distributed graphene sheets. The effect of applied electric field, barrier height and graphene aspect ratio are analyzed.
Mots clés — graphene/polymer nanocomposites, tunnel effect, highly conducting surface model, electric properties.

1 Introduction

Graphene, a two dimensional sheet composed of sp^2 carbon atoms arranged in a honeycomb structure, has been recently used as filler in polymer-matrix composites for a wide range of applications, due to its giant electrical and mechanical properties [1, 2]. Even though polymeric materials are considered to be electrical insulators due to their extremely low electric conductivities, the introduction of graphene can lead to a percolation behavior at a very low volume fraction and can increase the conductivity of the resulting composites by several orders of magnitude [3, 4]. In recent studies, the percolation threshold for graphene can be as low as 0.07% in volume fraction due to its extremely low aspect ratio [5]. In addition, with the increase of applied voltages, the I-V curve of the polymeric composites exhibits regions with nonlinear behaviors. To explain these phenomena, many studies have been conducted to understand tunnel effect in composites [6, 7, 8].

Predicting the physical properties more precisely taking into account the tunnel effect can have great impact for the future design of the nanocomposite. In order to better understand the mechanism and design new nanocomposite materials, numerical simulation methods are required. For this purpose, we propose in the present work a finite element method (FEM) to predict the overall electric conductivity of graphene/polymer nanocomposites as well as the percolation threshold. A procedure based on numerical calculations on a Representative Volume Element (RVE) containing randomly distributed graphene sheets is proposed. A FEM formulation involving the nonlinear electric conduction effects is developed. To take into account the specific non-localities related to the tunnel effect, a distance function map is computed numerically within the RVE model. In addition, an imperfect surface model [9] is introduced to model the graphene sheets as surfaces within the RVE model and avoid meshing the thickness of graphene sheets, while incorporating the discontinuities in electric filed in the normal direction of graphene sheets. Finally, the influence of the applied electric field, barrier height and graphene aspect ratio is analyzed in details.

2 Modeling of the electric behavior of graphene-reinforced composites

We consider an RVE defined in a domain Ω whose external boundary is denoted by $\partial\Omega$. The RVE contains planar graphene sheets which are distributed randomly inside the polymer matrix, as depicted in Fig. 1. We assume that the RVE is decomposed into M subdomains Ω_m such that $\Omega = \bigcup_m \Omega_m$, $m = 1, 2, ..., M$. Each subdomain is surrounded by a boundary, whose portions contain surfaces Γ_n $n =$

$1,2,...,N$ associated with graphene, where N is the number of graphene sheets inside the RVE. The intersection of the graphene sheets with the external boundary $\partial\Omega$ are denoted by $\partial\Gamma_k$ $k = 1,2,...,K$ where K is the number of graphene sheets that intersect $\partial\Omega$ (see Fig. 1). The distribution of graphene sheets is assumed to be periodic.

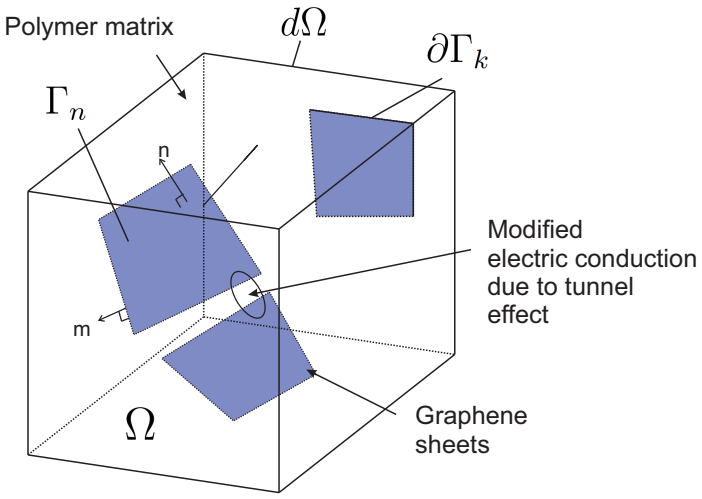


FIGURE 1 – RVE model of the graphene-reinforced composite.

2.1 Microscopic problem

At the scale of the RVE (microscopic scale), the governing equations are described as follows :

$$\nabla \cdot \mathbf{j} = 0 \text{ in } \Omega \tag{1}$$

$$-\nabla_s \cdot \mathbf{j}_s = -[\![\mathbf{j} \cdot \mathbf{n}]\!] \text{ on } \Gamma_n, \quad n = 1,2,...,N \tag{2}$$

where $\mathbf{j}$ and $\mathbf{j}_s$ denote the bulk and surface electric displacement fields, or current densities. The surface electric displacement field is defined along the tangential direction of the graphene sheets, which are assumed to be planar. Eqs. (1) and (2) refer to the Maxwell equation for the bulk and its analogy to surfaces, respectively. In the above,

$$\mathbf{E}(\mathbf{x}) = -\nabla\phi(\mathbf{x}) \tag{3}$$

is the electric field and ϕ is the electric potential. We introduce the surface divergence operator

$$\nabla_s \cdot \mathbf{a} = \mathbf{P} : \nabla\mathbf{a} \tag{4}$$

and surface quantities

$$\mathbf{a}_s = \mathbf{P}\mathbf{a} \tag{5}$$

where $\mathbf{a}$ is a differentiable real-valued vector, where

$$\mathbf{P}(\mathbf{x}) = \mathbf{1} - \mathbf{n}(\mathbf{x}) \otimes \mathbf{n}(\mathbf{x}) \tag{6}$$

characterizes the projection of the vector $\mathbf{a}$ along the tangent plane to Γ_n at $\mathbf{x}$ and $\mathbf{n}$ is the unit normal vector to Γ_n. The problem (1)-(2) is completed with constitutive relationships relating $\mathbf{j}$ and $\mathbf{E}$, and $\mathbf{j}_s$ to $\mathbf{E}_s$, which will be defined in the following, as well as the condition

$$\langle \mathbf{E}(\mathbf{x}) \rangle = \overline{\mathbf{E}}, \tag{7}$$

where $\langle . \rangle = \frac{1}{V} \int_\Omega (.) d\Omega$ is the spatial averaging over Ω, with V the volume of Ω. This condition is verified for the following boundary conditions over $\partial\Omega$:

$$\phi(\mathbf{x}) = -\overline{\mathbf{E}} \cdot \mathbf{x} + \tilde{\phi}(\mathbf{x}) \text{ on } \partial\Omega \tag{8}$$

with $\tilde{\phi}(\mathbf{x})$ is a periodic function over Ω. In the present paper, the second type of boundary conditions has been adopted.

2.2 Constitutive equations

The analytical expression obtained by Simmons[10] gives the tunnel current $\mathcal{G}$ as a function of electric field

$$\begin{aligned}\mathcal{G}(E,d) = &\frac{2.2e^3E^2}{8\pi h\Phi_0}\exp(-\frac{8\pi}{2.96heE}(2m)^{\frac{1}{2}}\Phi_0^{\frac{3}{2}})\ldots \\ &+[3\cdot\frac{(2m\Phi_0)^{\frac{1}{2}}}{2d}](e/h)^2Ed\exp[-(\frac{4\pi d}{h})(2m\Phi_0)^{\frac{1}{2}}]\end{aligned} \tag{9}$$

In the polymer matrix, the electric displacement $\mathbf{j}$ is related to the electric field through the nonlinear relationship :

$$\mathbf{j} = \begin{cases} \mathbf{k}_p^0\mathbf{E} & \text{if } d(\mathbf{x}) > d_{cut}, \\ \mathcal{G}(\mathbf{E},d)\frac{\mathbf{E}}{|\mathbf{E}|} & \text{if } d(\mathbf{x}) < d_{cut}, \end{cases} \tag{10}$$

where d_{cut} is a cut-off distance above which the tunnel effect can be neglected, and $\mathbf{k}_p^0$ is the electric conductivity tensor of the polymer matrix when neglecting tunnel effect.

Due to the very large aspect ratio of graphene, we propose to replace the graphene sheets with finite thickness by a surface whose equilibrium is described by (2) (see in Fig. 1), that the surface electric displacement is related to the surface electric flux through [9, 11] :

$$\mathbf{j}_s(\mathbf{x}) = -\mathbf{k}_s\nabla_s\phi(\mathbf{x}) \tag{11}$$

where

$$\mathbf{k}_s = h\mathbf{S}, \quad \mathbf{S} = \mathbf{k}_g - \frac{(\mathbf{k}_g\mathbf{n})\otimes(\mathbf{k}_g\mathbf{n})}{\mathbf{k}_g : (\mathbf{n}\otimes\mathbf{n})}. \tag{12}$$

In (12), $\mathbf{k}_g$ denotes the second-order electric conductivity tensor, which is here anisotropic, h is the thickness of graphene.

2.3 Effective behavior

At the macroscopic scale, the effective behavior can be written in an incremental form as

$$\overline{\mathbf{k}}(\overline{\mathbf{E}}) = \frac{\partial\overline{\mathbf{J}}}{\partial\overline{\mathbf{E}}}(\overline{\mathbf{E}}) \tag{13}$$

where $\overline{\mathbf{k}}$ is the tangent effective behavior, and

$$\overline{\mathbf{J}} = \frac{1}{V}\int_\Omega \mathbf{j}(\mathbf{x})d\Omega + \frac{1}{V}\sum_n\int_{\Gamma_n}\mathbf{j}_s d\Gamma. \tag{14}$$

In the present work, we evaluate $\overline{\mathbf{k}}(\overline{\mathbf{E}})$ numerically by perturbation.

3 Algorithm for solving the problem

3.1 Geometric modeling of graphene/polymer nanocomposites

The microstructure of the composites is composed of randomly distributed graphene sheets within the polymer matrix. The probability of distribution in each RVE is the same. Therefore, the geometric structure of the composites can be prescribed by the probability distribution in a RVE, which satisfies the

periodic boundary conditions. Without taking the lattice of graphene into account, the single graphene sheets can be looked as a square plane with the side length L. For generating a 3D homogeneous nanocomposite model, the Markov chains method is chosen based at atomistic level. And the graphene sheets are controlled to have no intersection with each other as illustrated in Fig.2.

We use GMSH [12] to make the mesh and insure that each triangular element of graphene surface conforms with the tetrahedral element of polymer matrix.

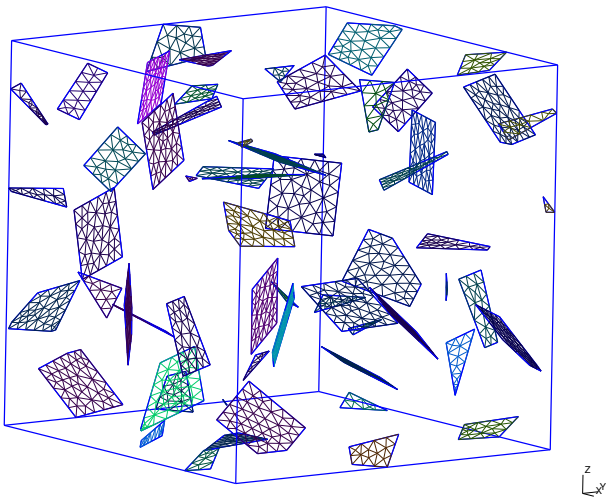


FIGURE 2 – RVE for the graphene/polymer nanocomposites involving 30 graphene sheets in a cube of $80\times80\times80\ nm^3$

3.2 Distance function

In what follows, we propose a simple definition for the distance function $d(\mathbf{x})$ in (9), which can be computed at all nodes of the mesh once before the calculations for a given distribution of graphene sheets within the RVE. Specifically, we consider a point $\mathbf{x}\in\Omega$ and denote by $\mathbf{x}^\Gamma$ a point lying on the surface Γ formed by the set of N graphene sheets. We define the distance function $d(\mathbf{x})$ as follows :

$$d(\mathbf{x}) = \min_{\substack{\mathbf{x}^\Gamma\in\Gamma^i\\ i=1,2,\ldots,N}} \left\|\mathbf{x}-\mathbf{x}^\Gamma\right\| + \min_{\substack{\mathbf{x}^\Gamma\in\Gamma^j\\ j=1,2,\ldots,N,\ \ j\neq i}} \left\|\mathbf{x}-\mathbf{x}^\Gamma\right\|. \tag{15}$$

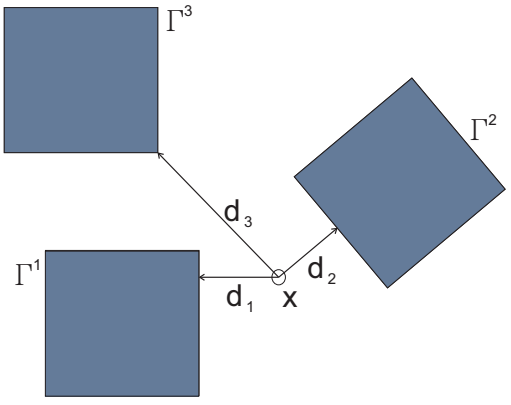


FIGURE 3 – Distances of a point $\mathbf{x}$ from surrounding graphene sheets to compute the distance $d(\mathbf{x})$.

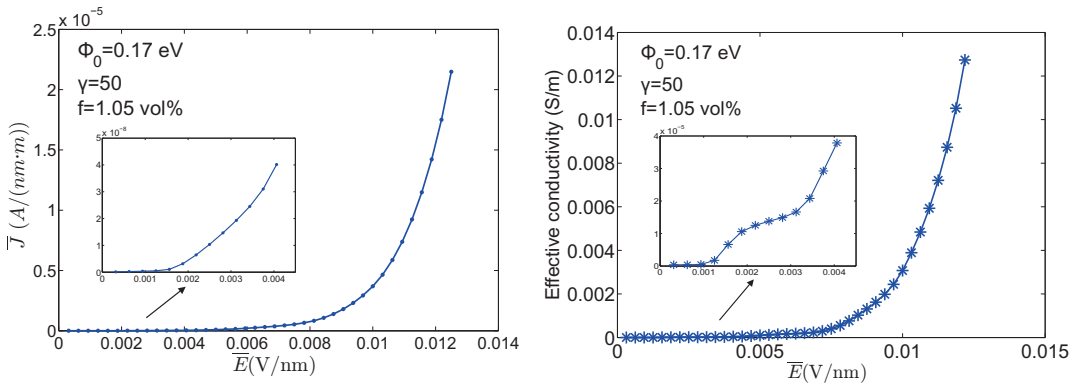
In other words, for a given point $\mathbf{x}$, we first compute the distance with all N graphene sheets, then the function $d(\mathbf{x})$ is defined as the sum of the two smallest distances between the point and two different neighboring graphene sheets. An illustration of this methodology is schematically depicted in Fig. 3 in the 2D context. For one point $\mathbf{x}$, the distances d_1, d_2 and d_3 represent the shortest distance with graphene sheets Γ^1, Γ^2 and Γ^3. The function $d(\mathbf{x})$ for this point is the sum of d_1 and d_2, which are the smallest values in the set d_i, $i=1,2,3$.

4 Numerical results

4.1 Electric field effect

In the following simulations, the conductivity of polymer is 10^{-10} S/m, and the in-plane and out-plane conductivities of graphene are taken to be 8.32×10^4 S/m and 83.2 S/m respectively.

Setting the barrier height Φ_0 and the aspect ratio γ to be 0.17 eV and 50 respectively, we can get the effective current flux as a function of microscopic electric field as shown in Fig.4 (a) with graphene volume fraction $f = 1.05$ vol%, which is in agreement with the tendency of experimental data [13]. And the corresponding effective conductivity-electric field function is shown in Fig.4 (b),where a sharp increase could be seen when the electric field is large enough.



(a) (b)

FIGURE 4 – (a) Effective current flux-effective electric field characteristics (b) Effective conductivity as a function of effective electric field

4.2 Barrier height effect

In this example, we analyze the influence of barrier height on the effective conductivity and the percolation threshold. The numerical results are provided in Fig. 5 for graphene/polymer nanocomposite with varying barrier height which are 0.17 eV, 0.3 eV and 1.0 eV respectively with an applied electric field of 0.0025 V/nm and the graphene aspect ratio of 50.

Taking into account the tunnel effect, the numerical values of $\overline{k}_{11}$, $\overline{k}_{22}$ and $\overline{k}_{33}$ are plotted for each volume fraction as shown in Fig.5 (a-c), where the average values are obtained for 30 realizations. For better comparison, we have superimposed the mean values of $\overline{k}_{11}$, $\overline{k}_{22}$ and $\overline{k}_{33}$ with $\Phi_0 = 0.3$ eV in Fig. 5 (d) and also plotted the average value $\frac{1}{3}\left[\overline{k}_{11} + \overline{k}_{22} + \overline{k}_{33}\right]$ when the tunnel effect is neglected. It can be shown that the tunnel effect is responsible of an increase in the apparent conductivity of several orders of magnitude, which is expected as the polymer matrix alone is almost isolating and that in our model, the graphene sheet are not in contact with each other. We estimate the percolation threshold around about 0.8 % which indicates that a very small volume fraction of graphene can leads to a giant increase in the effective conductivity of the composite when $\Phi_0 = 0.17$ eV. And it increases to 1.1 vol% and 2.4 vol% with the barrier height being $\Phi_0 = 0.3$ eV and $\Phi_0 = 1.0$ eV respectively. Therefore, it is obvious that higher barrier height can result in bigger percolation threshold when the graphene sheets are homogeneously distributed. The experimental results of percolation threshold have been reported ranging from 0.1 vol% to 1.6 vol% based on different polymer matrix and graphene type[14, 15, 16, 17]. These results also depend on the processing as well as the graphene dispersion.

4.3 Graphene aspect ratio effect

To analyze the effect of graphene aspect ratio on the percolation threshold, we calculate the conductivity tensor components as a function of graphene volume fraction for different graphene aspect ratio with $\Phi_0 = 0.17$ eV and $\overline{E} = 0.0025$ V/nm. The results are shown in Fig. 6 (a-c), which indicate the percolation threshold to be 0.4, 0.8 and 1.65 vol% respectively for graphene aspect ratio of 100, 50 and 20.

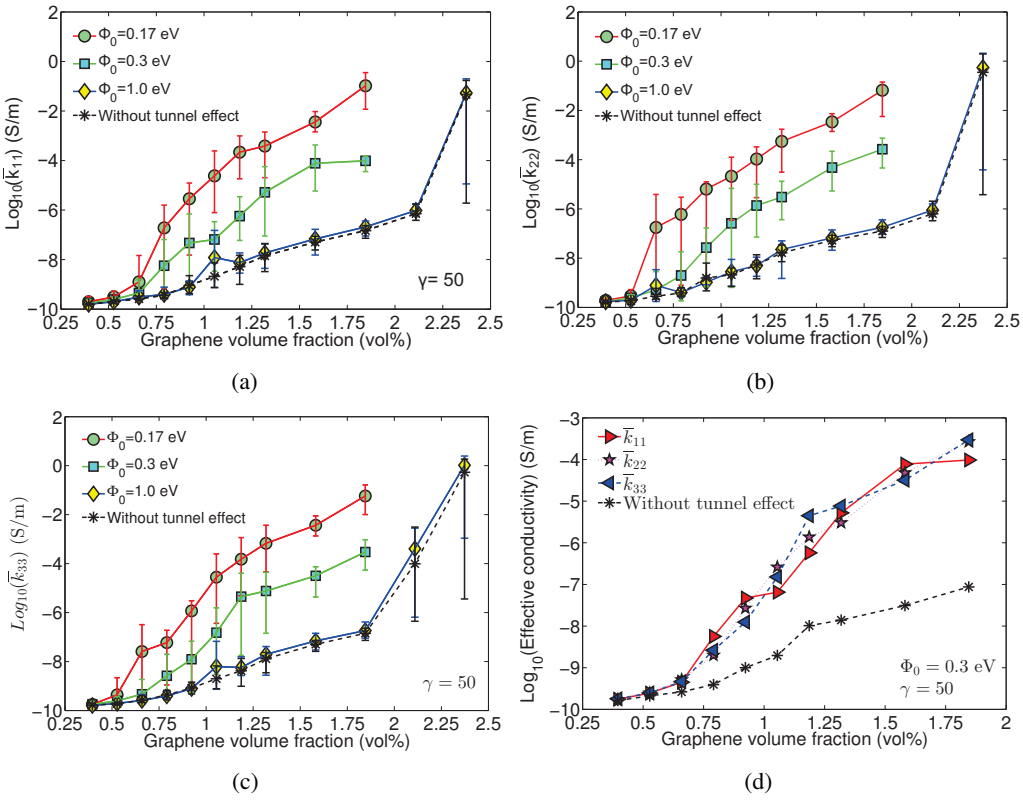


FIGURE 5 – (a) $\left(\overline{k}_T\right)_{11}$ (b) $\left(\overline{k}_T\right)_{22}$ (c) $\left(\overline{k}_T\right)_{33}$ (d)Comparison of effective electric conductivity as a function of the graphene volume fraction.

The three components are compared in Fig. 6(d) with $\gamma = 100$, which demonstrates that the mean values of $\overline{k}_{11}$, $\overline{k}_{22}$ and $\overline{k}_{33}$ are nearly equal except around the percolation threshold.

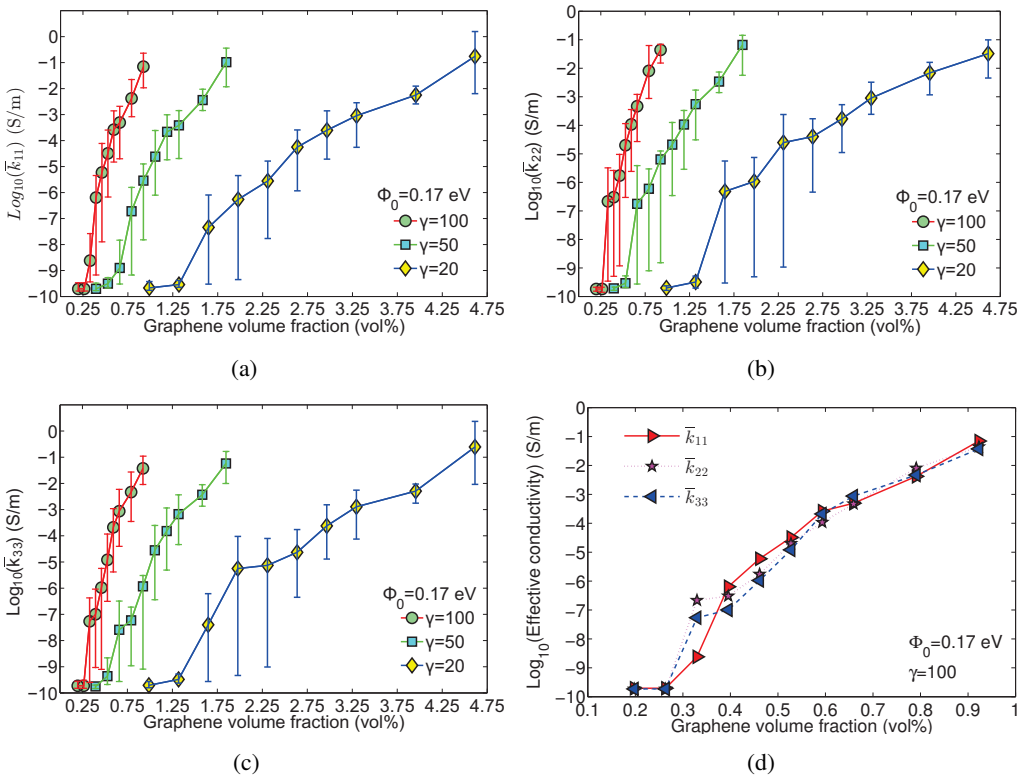


FIGURE 6 – (a) $\left(\overline{k}_T\right)_{11}$ (b) $\left(\overline{k}_T\right)_{22}$ (c) $\left(\overline{k}_T\right)_{33}$ (d)Comparison of effective electric conductivity as a function of the graphene volume fraction.

5 Conclusion

We have proposed a numerical procedure to compute the effective electric conductivity of graphene/polymer nanocomposites. The tunneling effect law has been introduced in a FEM model due to the small distance with the magnitude of angstrom between two graphene sheets. A methodology to get this distance in random structure has been defined with the definition of distance function. Moreover, to solve the mesh problem due to the low aspect ratio of graphene, a HC surface model is used, leading to an additional stiffness matrix.

Applying the procedure into the RVE of graphene/polymer nanocomposites generated by Markov-chains method, the overall electric conductivity of composites with random distributed graphene sheets can be determined at various graphene volume fraction. Furthermore, the effects of applied electric field, barrier height and graphene aspect ratio are explored. The effective current density-effective electric field characteristics are in good qualitative agreement with the experimental data. The results show that both lower barrier height and higher graphene aspect ratio can lead to very small percolation threshold.

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