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Incorporation of electron tunnelling phenomenon into 3D Monte Carlo simulation of electrical percolation in graphite nanoplatelet composites

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Received 20 July 2011, in final form 30 September 2011
Published 28 October 2011
Online at stacks.iop.org/JPhysD/44/455306

Abstract

The percolation threshold problem in insulating polymers filled with exfoliated conductive graphite nanoplatelets (GNPs) is re-examined in this 3D Monte Carlo simulation study. GNPs are modelled as solid discs wrapped by electrically conductive layers of certain thickness which represent half of the electron tunnelling distance. Two scenarios of ‘impenetrable’ and ‘penetrable’ GNPs are implemented in the simulations. The percolation thresholds for both scenarios are plotted versus the electron tunnelling distance for various GNP thicknesses. The assumption of successful dispersion and exfoliation, and the incorporation of the electron tunnelling phenomenon in the impenetrable simulations suggest that the simulated percolation thresholds are lower bounds for any experimental study. Finally, the simulation results are discussed and compared with other experimental studies.

(Some figures may appear in colour only in the online journal)

1. Introduction

Insulating polymers doped by nanoconductors such as graphite nanoplatelets (GNPs) are a class of engineering materials which are superior to the pristine polymer matrix in the sense of electrical conductivity [21, 34]. In addition to electrical conductivity, such nanoadditives usually contribute to improve other properties of the final nanocomposite such as mechanical, thermal or magnetic properties which promises the advent of new multifunctional tailor-made composites sought in many applications. Developing new electrically conductive or semi-conductive polymer composites can address most requirements of future products specifically in microelectronics [6, 27, 39]. Amongst many applications that one might list for such materials, electrostatic discharge (ESD) and electromagnetic interference (EMI) shielding are the notable ones which can be furnished for new generations of electronic products simply by employing these materials in their casing [20].

According to the experimental observations, the electrical conductivity of polymers enriched with conductive additives typically shows a classical S-curve behaviour with the volume fraction of fillers also known as the ‘filler loading/content/concentration’ [21]. Based on these observations the conductivity increases monotonically from
almost zero with the filler loading up to critical transition limit. In experimental observations, this limit is a narrow range of volume fractions which is called the percolation threshold, \( p_c \). At \( p_c \), which may vary slightly from one experiment to another, the conductive ingredients start to percolate within the sample thereby the conductivity undergoes an abrupt increase (of several orders of magnitude). At post percolation threshold levels, the electrical conductivity again follows a rather weaker dependence with the volume fraction of the conductive additive. This behaviour is attributed to the establishment of multiple continuous paths through the medium after the percolation threshold [21].

GNP, a nanoscale conductive filler produced by exfoliating natural flakes of graphite, like other nanoparticles has been the subject of interest for many recent works [19]. Structurally, natural graphite flakes can be thought of as offsetting several layers of graphene which in itself is comprised of carbon atoms arranged in a regular hexagonal lattice [25, 30]. GNPs are usually prepared from the intercalation of graphite flakes in highly concentrated acids at high temperatures [11, 14, 26, 40]. This process causes high expansion between flakes which results in the separation of the graphite sheets into nanoscale flakes with very high aspect ratio. In terms of physical properties, graphite has a unique combination of properties. Very high modulus in its graphene plane and excellent electrical as well as thermal conductivity due to its layered structure [24] combined with low cost make it an attractive additive for developing conductivity in insulating polymers. High aspect ratio of the GNPs promotes conducting electrons in polymer via the formation of uninterrupted conducting network(s) [24]. The conductivity of GNPs may reach levels of \( 4 \times 10^3 \) Siemens cm\(^{-1}\) (S cm\(^{-1}\)) [28] as compared with the typical conductivity values of \( 10^{-14} \) to \( 10^{-17} \) (S cm\(^{-1}\)) reported for polymers [9].

A crucial phenomenon in the study of conductive polymers is the tunnelling effect. The term ‘tunnelling’ refers to the jump of a charge carrier from one conductor to another neighbouring one and in general includes both jumps over a potential barrier and quantum mechanical tunnelling [32]. In systems where the particles do not touch ‘geometrically’ but do touch ‘electrically’ the measured finite macroscopic conductivity must be attributed to the existence of the interparticle tunnelling. Thus, in a composite material containing conductive fillers, the electric conductivity may well depend on the average distance between the particles. In a recent study, Balberg [2] addressed the issue in greater detail. Therefore, the percolation threshold in the conductive filler-based composite materials should also be a function of the topological aspects of the particles.

A variety of computational studies on electrical percolation problem is available in the literature [7–9, 12, 31]. One of the early applications of the Monte Carlo study on the percolation is due to Pike and Seager [31]. This study was limited to the problem of the percolation of randomly oriented sticks in 2D. In a step further, Balberg and Binenbaum [3, 4] studied anisotropic systems with a preferred fibre orientation. Their study proposed an increased percolation threshold which is highly dependent on the aspect ratio of the composing fillers. The percolation thresholds of polymer composites containing high aspect ratio fillers such as microscale disc-shaped graphite flakes and carbon fibres were also studied based on the excluded volume approach [4, 23]. In the follow-up studies, the Monte Carlo technique was employed by other researchers for percolation threshold analyses [12, 23].

The basic problem of object percolation in a medium has already been investigated by other researchers (see, e.g. [3–5, 15, 22, 23, 31]) but in this study the percolation threshold of a polymeric composite filled with conductive GNPs is re-examined using a new computational technique. The details of the proposed Monte Carlo-based method are provided in section 2. In a similar study carried out by Li and Kim [23] it is assumed that GNPs are perfect thin disc-shaped particles homogeneously distributed in the matrix. Then a specific interparticle distance (IPD) with a new definition was adopted to represent the electrical percolation. Afterwards the electrical percolation has been studied as a function of the geometry and volume fraction of conducting particles. Comparison with other results (e.g. Kuila et al [21]) indicates that their assumptions give unsatisfactory results. In a step forward in our study, the dispersion process can be switched between penetrable dispersion in which the particle penetration is allowed and impenetrable dispersion in which no physical penetration between particles is allowed. Analysis of the percolation threshold carried out by our proposed method is believed to yield more realistic results. By applying this method the effect of different aspect ratios of GNPs as well as the tunnelling distance on the percolation threshold is investigated in subsequent sections of this paper. The results derived by this analysis are then discussed and compared with other relevant studies in section 5.

2. Monte Carlo simulation

Implementation steps of the Monte Carlo methodology are delineated in the following lines. Numerical simulations are carried out inside a cubic unit cell of constant side length of 1000 units (units may be equally interpreted as nm). The partially exfoliated GNPs are then modelled as simple discs of tunable thickness dispersed uniformly inside the unit cell. This means that the statistical distribution of both the spatial position and orientation of discs is uniform. Although the option for creating a non-constant distribution of diameters had been worked out in the developed computer code, the diameter of GNPs is kept fixed at 100 nm in all simulations. The remaining simulation parameters consisting of the GNP thickness and the maximum tunnelling distance are allowed to vary as the influencing parameters. For microstructure generation, two scenarios are followed: the impenetrable scenario in which the GNPs are not allowed to penetrate each other, and the penetrable scenario in which the GNPs may penetrate and overlap each other. In the next step for the percolation check, the maximum allowable tunnelling distance, which is modelled as an auxiliary envelope wrapping the GNPs, is varied and then the percolation is checked according to the algorithm elaborated in section 4.
3. Generating GNPs

The geometry of each GNP is modelled as two parallel circular planes separated by the thickness of the GNP. Each circular plane in space may be identified by a normal, some point belonging to the plane, say the centre point, and a radius value. To achieve a uniformly random scatter of GNPs using the Monte Carlo method, the centre of each GNP is selected randomly inside the sample unit cell. Then the associated normal vector is specified by means of random homogeneous functions given below which produce uniformly random points on the surface of a sphere.

\[
\begin{align*}
\theta &= 2\pi v \\
\phi &= \text{Arc} \cos(2u - 1).
\end{align*}
\]

In the above equations \( \theta \in [0, 2\pi] \) and \( \phi \in [0, \pi] \) are spherical coordinates as shown in figure 1, and \( u, v \) are random variables belonging to \([0, 1]\). The normal vectors thus selected guarantee a uniform random distribution of GNP orientations [37]. For generating each GNP the procedure of random selection of its centre and normal direction is followed successively and then the next GNP is identically created.

2.2. Penetrable scenario

In the penetrable scenario, the GNPs are allowed to penetrate each other (see figure 2). Thus a new GNP is randomly lodged somewhere in the unit cell irrespective of the presence of the formerly generated GNPs. In other words, regions of space may be occupied by more than one GNP. This idea makes the algorithm of generating GNPs simple and fast. Moreover, using this algorithm one can simulate nearly every volume fraction of GNPs. As another extra advantage, the penetrable algorithm can help to check the electrical percolation directly when no tunnelling is taken into account. Nevertheless, this scenario suffers from some notable drawbacks. Firstly, the assumption of penetrable fillers leads to very low volume fractions when calculating the percolation threshold of the system. As another disadvantage, the penetrable scheme is not successful in modelling and simulating the entanglement and agglomeration of fillers.

For evaluating the real volume fraction of randomly distributed permeable objects, the well-known statistical method of Monte Carlo integration which relies on repeated random sampling is employed. To implement the method, a number of random or pseudo-random points are scattered inside the unit cell. Then the ratio of the number of points falling within the regions of space occupied by fillers to the total number of points is calculated as an estimate for the concentration of the filler phase. Then the number of random points inside the unit cell is increased (by up to \( \sim 10 \) orders of magnitude) as a criterion to check the convergence of the calculated GNP concentration. For calculating the real volume fraction in all simulations, this algorithm is employed.

2.3. Impenetrable scenario

In the Monte Carlo simulation of heterogeneous materials, the impenetrable scenario is the opposite scenario of penetrable fillers. The major distinguishing feature of this second scenario is that the overlapping or intersection of GNPs is not allowed. In other words, GNPs are required not to cut other GNPs and this condition is checked during the generation of every new GNP. If it cuts any neighbouring GNP, the selected centre and orientation is rejected and a new set of random centre and orientation is picked and this procedure is continued through the entire procedure of generating GNPs. To check the intersection of two GNPs, we propose the following efficient algorithm. For every circular plate of a newly generated GNP, the intersections between its infinite encompassing plane and circular plates of other GNPs are found. These intersections, if there are any, are two line segments of two chords belonging to the intersected circles. It can be shown that the following conditions govern the intersection state of two circular plates of interest

\[
\begin{align*}
\text{if } D > r + R & \Rightarrow \text{No contact.} \\
\text{if } D \leq r + R & \Rightarrow \text{Contact exists.}
\end{align*}
\]

where \( r \) and \( R \) are half of the chord lengths and \( D \) is the distance between the centres of the chords. In the appendix, the mathematical details of the derivation of these inequalities are provided.

The impenetrable scenario, however, possesses several drawbacks recapitulated in the following lines. As can be intuitively concluded, the algorithm is far too complex to develop and time consuming to run with respect to the
penetrable algorithm. On the other hand, for $t \gg h$, where $t$ is the GNP thickness and $h$ is the maximum allowable tunnelling distance, the algorithm is likely to get locked. Additionally, when the tunnelling is either nil or not to be taken into account, the percolation threshold may not be evaluated directly using this algorithm. As a solution to avoid this problem one may extrapolate the percolation threshold results to zero from simulations with non-zero $h$ which is discussed in section 5. Moreover, as we have forcefully precluded the penetration of fillers and remarkably lowered the probability of contact between the GNPs, the impenetrable algorithm results in upper bounds for the percolation threshold when compared with the penetrable algorithm results.

Compared with the hindering drawbacks, the advantages of the algorithm are significant and appealing. In contrast with the penetrable algorithm, in the impenetrable scenario volume fraction calculations are easy and straightforward (neglecting the fillers cut by the unit cell boundaries). In addition, the impenetrable scenario is more suitable for finite element simulations in that there is no intersection between fillers and mesh discretization is carried out easily. As another advantage, the predictions made by the impenetrable algorithm are expected to be closer to the true percolation thresholds obtained in experiments.

3. Collapse criterion

The tunnelling effect is a quantum mechanics phenomenon which contributes to the electrical conductivity of composites made of an insulating matrix and conductive particles. Based on this phenomenon two non-touching nanoflakes of GNP inside an insulating matrix will conduct electricity without direct physical contact if the distance between them is small enough for electrons to tunnel through. The maximum tunnelling distance varies based on the properties of the medium [10, 33, 35]. For most polymers, organics and oxides this distance is rather independent of the resistivity of the medium. In this study, this maximum distance, $h$, is allowed to vary to find its effect on percolation threshold, $p_c$. Once the GNPs are scattered within the unit cell, an imaginary envelope representing half of the tunnelling span is assumed around them (see figures 3 and 4). In other words, the two opposite circular faces of each GNP are offset outward creating a larger disc which is only used for percolation threshold calculation purposes. As discussed in the following section, the two GNPs are regarded as touching if their imaginary envelopes intersect. It is evident that the incorporation of the tunnelling phenomenon always lowers the percolation threshold (see, e.g. [29]).

4. Percolation check

Mathematically, percolation relates to the formation of connected clusters in a non-conducting medium. Percolation algorithms are applied to check the continuity of an ensemble of conducting objects in touch encapsulated inside a medium [1]. A variety of methods have been proposed in the literature for percolation check [17]. The criterion for evaluating the percolation is to look for at least a cluster of fillers which makes a closed pathway between the entire lateral surfaces of the unit cell.

In this study, the percolation analysis is done continually and simultaneously with the generation of each GNP. In fact, once a GNP is created, a cluster number equal to the GNP number is attributed to it. Then all the possible interconnections with the existing objects will be checked and the cluster numbers will be updated. Updating is performed according to the following rule: if, upon addition of a new object to the system, several objects become electrically

- **Figure 3.** A cut section of a simulated disc-shaped GNP. The effective electron tunnelling range is shown as a jacket around the core platelet.
- **Figure 4.** Two arbitrary cross sections of a typical 3D microstructure. GNPs and electron tunnelling jackets are marked in red and blue, respectively.
connected, the least cluster number in the ensemble is assigned to all the connected objects. Two particles are considered electrically touching if their electron tunnelling envelopes satisfy the second relation of inequality (2). The adopted algorithm is specifically accurate for high aspect ratio of GNPs. For low aspect ratio particles, however, other considerations like those employed for nanotubes are required.

5. Results and discussion

In all simulations, the side length of the cubic unit cell was taken as 1000. The diameter of GNPs was kept fixed at 100 and then $t$ and $h$ were allowed to vary to find their effect on $p_c$. Figure 5 exhibits the dependence of the percolation threshold on $h$ for various thicknesses using the impenetrable scenario. The diagrams suggest that for large values of $h$, the percolation threshold plateaus to some asymptotic values. As discussed earlier, the impenetrable algorithm fails to give any satisfactory result for small values of $h$. Therefore, for small values of $h$, the diagrams are extrapolated to zero.

As an interesting sideline result, we plotted the diagram of trial numbers required for adding a new GNP to the system versus the GNP number in a typical simulation based on the impenetrable scenario. As displayed in figure 7, although the trial numbers increase non-monotonically with the GNP number, the trend of the bar chart diagram looks fairly reasonable in that by the growth of the population of the system, it becomes more difficult to randomly find a suitable unoccupied region inside the unit cell to insert a new GNP. For large volume fractions of fillers which are equivalent to large numbers of inhomogeneities, the algorithm gets locked at around a specific volume fraction and the trial number required for inserting another object to the system goes to infinity. As a primary conjecture, one may think of this volume fraction as an upper bound for the maximum obtainable volume fraction when a really random dispersion is achieved and the system is free of agglomerations.

The diagrams of the percolation threshold versus $h$ obtained by the two scenarios are superposed in figure 8. In this figure the GNP thickness is predetermined at 10. It is immediately evident that the impenetrable algorithm yields an upper bound for small values of $h$ which agrees with our intuition. The percolation threshold predicted by the impenetrable algorithm, however, falls below the other one for larger values of $h$ although the difference is not as pronounced as the first part. To explain this difference, one may think of
Figure 7. Trial numbers required for adding a new GNP to the system versus the GNP number in the impenetrable scenario for three distinct simulations.

Figure 8. The percolation threshold versus $h$ for the two scenarios of penetrable (blue) and impenetrable (red)? GNPs.

Table 1. Comparison between simulated percolation thresholds assuming impenetrable GNPs and experimental results.

<table>
<thead>
<tr>
<th>Study case</th>
<th>Aspect ratio</th>
<th>Sample properties</th>
<th>$d$ (nm)</th>
<th>$t$ (nm)</th>
<th>Predicted percolation threshold</th>
<th>Exp. percolation threshold</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weng et al [38]</td>
<td>600</td>
<td>High density polyethylene 6 10 600 10 wt% (4.46 vol%)</td>
<td>6000</td>
<td>10</td>
<td>0.668%</td>
<td>4.6%</td>
</tr>
<tr>
<td>Fukushima and Drzal [13]</td>
<td>1579</td>
<td>Epoxy 15 9.5 1579 (1.13 vol%)</td>
<td>15 000</td>
<td>9.5</td>
<td>0.294%</td>
<td>1.13%</td>
</tr>
<tr>
<td>Chen et al [8]</td>
<td>5000</td>
<td>Polypropylene 50 10 5000 (0.67 vol%)</td>
<td>50 000</td>
<td>10</td>
<td>0.110%</td>
<td>0.67%</td>
</tr>
</tbody>
</table>

the tunnelling envelope as larger discs embracing GNPs. In penetrable algorithm, these larger discs can essentially occupy every position inside the unit cell without any restriction and irrespective of the earlier existing objects whereas in the impenetrable algorithm there is virtually a restriction on their positioning. In fact, these new entities can penetrate each other provided that their inner cores do not intersect. Intuitively, for large values of $h$ which corresponds to large tunnelling envelopes, the percolation threshold, which is equivalent to the least number of fillers making a closed pathway between the two opposite faces of the unit cell, takes place sooner and with fewer GNPs in the impenetrable algorithm.

A comparison between the simulation and experimental results is provided in table 1. In all three simulations, the diameter, $d$, and thickness, $t$, of GNPs were selected as cited in the experimental studies [23]. The tunnelling distance, $h$, was taken to be 10 which coincides with the approximate value reported in [23]. Based on the previous arguments and also to be on the safe side, the impenetrable algorithm was employed for the simulations. Comparison between the experimental percolation threshold values and their respective simulation predictions reveals that simulation results provide a lower bound value for the percolation threshold. The difference between the experimental and simulation results is dramatic. This wide gap can be well justified by looking through the assumptions behind the simulations. The non-uniform geometry of the simulated GNPs in the experiments and the constant value of the tunnelling distance along with the perfect dispersion and uniform distribution of the GNPs are among the major reasons which can explain this wide gap.
This is while agglomeration, non-uniform distribution and unsuccessful dispersion of GNPs in experiments are very likely to take place and difficult to capture in theoretical simulations. Thus, to reach the percolation threshold, the amount of GNPs added in experiments must be more than the simulation values to compensate for the effects of agglomeration and unsuccessful dispersion. However, some other researchers report percolation threshold values which are close enough to our simulation results. The percolation threshold values reported in [16, 18, 36] vary from 0.1% to 0.6%. Unfortunately, the authors have not provided adequate information on the geometrical and physical properties of the composing particles to allow for running appropriate simulations and making a comparison, but the proximity of the results are encouraging.

6. Conclusions

The effect of electron tunnelling distance on the electrical percolation threshold of GNP-based nanocomposites was the centre of attention in this simulation study. GNPs were modelled as thin discs randomly scattered inside a simulation cube. Two scenarios of ‘penetrable’ and ‘impenetrable’ objects were implemented for GNP scattering. Comparison with the experimental results indicates that the impenetrable scenario, which is closer to reality, yields a lower bound estimate for the percolation threshold. Additionally, the difference between the experimental and simulation results may well be attributed to the non-uniform geometry of the dispersed GNPs and their agglomeration in the experiments and/or the assumed invariance of influencing parameters in the simulations, such as GNPs’ geometry and electron tunnelling distance.

Acknowledgment

The authors would like to acknowledge the financial support from the Fond National de la Recherche (FNR) du Grand Duché de Luxembourg (AFR Research Assistantship for Majid Baniassadi).

Appendix A: Examining the intersection state of two spatial circular plates

For two arbitrary circular plates in three-dimensional space, first we find the line of intersection between the two infinite planes passing through the two circles (figure 9). For two distinct unparallel planes, say A and B, there exists a unique line of intersection. This line of intersection being found, the lines passing through the centre of each circle, O and O’, and normal to this line are found from vector calculus. The intersection of these two lines with the line of intersection produces two points, say M and M’ if either \( |OM| > \rho \) or \( |OM'| > \rho' \) where \( | | \) indicates the length of the line segment and \( \rho, \rho' \) are the associated radii of the two circles, then there is no intersection between the two circles; otherwise \( M \) and \( M' \) would be the medians of the chords created from the intersection of the line of intersection and the two circles. Having the coordinates of the centres and the medians as well as the radii of the two circles, the half-chord lengths, \( r \) and \( R \).

Figure 9. The intersection state of two spatial circular plates.

\[
D \leq r + R
\]

where \( D \) stands for the distance between the two medians, i.e. \( D = |MM'| \), then the circles intersect.

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