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The Optimization at Studying of Electrical Conductivity in the Dielectric Nanocomposites with Disordered Nanotubes

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Abstract—We study the electrical conductivity of a three-dimensional (3D) nanocomposite with incorporated random carbon nanotubes (CNT). A large length of the remote nanotubes generates a lot of intersections that induce a rather small percolating threshold of the global conductivity in this medium. We simulate such a system by random cylinders placed in a percolating parallelepiped with the use of Monte Carlo method. The conductivity of such a structure is associated with the critical phenomena, where the main transition parameter is defined by the value of the percolation threshold. We calculate the minimal percolating threshold and determine the functional form of the conductivity by the global optimization technique. Such an approach allows studying the details of the electrical conductivity in nanocomposites even at significant level of the percolating fluctuations.

1. INTRODUCTION

The incorporation of disordered carbon nanotubes (CNT) in a dielectric nanocomposite leads to formation of spatial percolating channels. Groups of such nanotubes are jointed in clusters, located in a chaotic fashion in a nanocomposite. The integration of separated clusters happen when the concentration of nanotubes approaches a certain critical value. As a result in the system spreading (infinite) cluster is formed, which leads to appearance of the electric contacts between external electrodes in such a compound [1–16]. Experimental studies [1] have shown that the conductivity in nanotube polymeric and ceramic matrix materials follows a percolation-like behavior. Specifically, at a relatively low concentration of nanotubes the conductivity follows the scaling law of percolation theory [17]. The percolation in a dielectric nanocomposite with carbon nanotube is of high interest due to the potential to create electrically conductive systems with an extremely low mass of carries.

It is important to note that in the system with long cylinders the nearest neighbors approximation is not applicable. A large length of the nanotubes (e.g., in [10] it is reported that ultralong CNTs over 18.5 cm long were grown on Si substrates) leads to the fact that the global conductivity occurs in nanocomposites due to contacts of remote objects. The upper boundary of the contacts numbers can be estimated in the following simple way. Two straight (no parallel) lines (nanotubes with high aspect ratio) have only one point of intersection. Three straight lines can have three contacts. It is easy to see that n (not parallel) straight lines have in general $n(n-1)/2$ intersections which at $n \gg 1$ produce $n^2/2$ contacts. In the case of $n = 100$, there can be 5000 contacts. Such a large number of contacts increases conductivity and reduces the influence of details of internal contacts for nanotubes. Besides, as shown in our paper, the independent randomness in height and radius of the cylinders becomes an important factor in vicinity of the percolating threshold. In what follows, we refer to the system with configuration similar to experiment [1] where the samples were connected to incorporated nanotubes by external metallic electrodes. The electric conductivity in such a compound

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sharply increases and exceeds the conductivity of the host dielectric matrix in many orders when the concentration of nanotubes (fractional volume) approaches the critical threshold value [1].

We study such a compound nanocomposite with the use of a 3D numerical grid with incorporated long cylinders (see Fig. 1) that simulate the random nanotubes with normal distribution on the height and radius. The latter inevitably arises at the CNTs growing, but it is weakly studied in vicinity of the electric conductivity threshold. We investigate the value of the percolating threshold as a statistically significant quantity. Normally in the experimental setups, parallelepiped samples are used. Therefore, we use the Monte Carlo method to calculate the cylinders percolation in a numerical grid (a parallelepiped $N \times N \times M$) and apply the technique of unconstrained nonlinear optimization [18, 19] to study the critical properties of the conductivity for normally distributed cylinders close to the percolating threshold. The conditions of intersections for such cylinders are studied in [2, 4, 7, 8]. We use here a simple condition when both i, j cylinders (with radii r_i and r_j) are in touch that can be written as $r_i^2 + r_j^2 - d^2 = -2r_i r_j \cos(\theta) \leq -2r_i r_j$, where d is the minimal distance between axes of cylinders, and $\pi \geq \theta \geq \pi/2$ is the angle. Such a condition allows drastically reducing time of Monte Carlo simulations. For the case of intersection of parallel cylinders ($\theta = \pi$) from the above one can easily obtain the well-known condition $r_i + r_j \leq d$.

2. BASIC EQUATIONS

Figure 1 shows the vicinity of some 3D cluster with random cylindrical nanotubes where some of cylinders have various intersections.

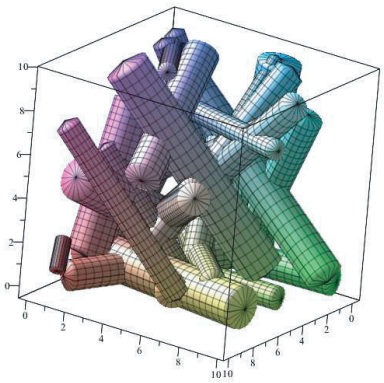

Figure 1. (Color on line.) The 3D cluster of disordered cylindrical nanotubes having normal distribution on height h and radius r. It is considered that the parameters of nanotubes are distributed normally, see Eq. (1).

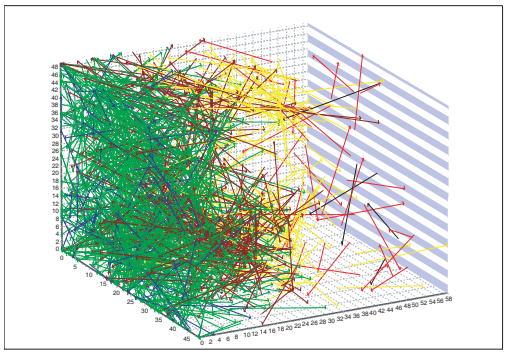

Figure 2. (Color on line.) Details of the spatial structure of the normal distribution of percolating cylinders with $\mu_h = 20, \sigma_h = 2, \mu_r = 0.1, \sigma_r = 0.025$ that belong to the infinite cluster slightly above the percolation threshold $p = 0.1 > p_c = 0.05$. The grid is $50 \times 50 \times 60$ is used. Only the cylinders connected to the infinite cluster are shown.

Figure 2 shows the details of the spatial structure of the percolating cylinders with $\mu_h = 20, \sigma_h = 2, \mu_r = 0.1, \sigma_r = 0.025$ (see Eq. (1) that belong to the infinite cluster slightly above the percolation threshold. The grid is $50 \times 50 \times 60$. Only the cylinders connected to the infinite cluster are shown. Cylinders that are not a part of the infinite cluster are omitted. The height and radius of the cylinders have a normal distribution, shown in Figs. 3 and 4. We observe that the disordered infinite cluster in Fig. 2 has a tree-like structure in a macro-scale. (But rerunning the simulations may generate a different cluster's shape.) For better viewing, the cylinders in the figure are painted in different colors, depending on the distance from the input contact. In the vicinity of input (left side) all cylinders have blue color, but in the vicinity of output (right side) the cylinders are shown in black. We observe from Fig. 2 that

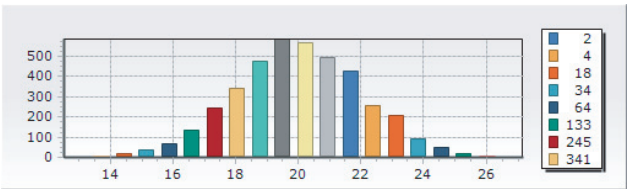

Figure 3. (Color on line.) The histogram of normal distribution of the high h of cylinders generated for $\mu_h = 20, \sigma_h = 2$ (with $h_{\max} = 27.7, h_{\min} = 13$). One observes an inhomogeneous shape of the distribution.

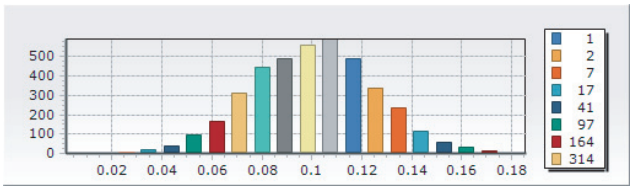

Figure 4. (Color on line.) The histogram of normal distribution of the radius r for cylinders generated for $\mu_r = 0.01$ and $\sigma_r = 0.025$ (with $r_{\max} = 0.18, r_{\min} = 0.01$).

even remote nanotubes can contact and produce a cluster. The average length of cylinders in general may be of order of the system sizes. Thus the nearest neighbors' approximation in such nanocomposites is not applicable, and one has to apply the complete Monte Carlo approach.

In the literature, the case of random cylinders is studied with fixed ratio aspect value $h/2r$. However, it is very difficult to grow such nanotubes technologically. Therefore, in what follows we consider a more general case when the independent parameters of nanotubers h and r are distributed normally, see Eq. (1):

$$\left(1/\sqrt{2\pi}\sigma_i\right) \exp(-\left(a-\mu_i\right)^2/2\sigma_i^2),\ i = h, r. \tag{1}$$

Such distributions are shown in Fig. 3 for the case $\mu_h = 20, \sigma_h = 2$ (with $h_{\max} = 27.7, h_{\min} = 13$) and in Fig. 4 for $\mu_r = 0.01$ and $\sigma_r = 0.025$ (with $r_{\max} = 0.18, r_{\min} = 0.01$). One observes, from Fig. 3 and Fig. 4, a quite inhomogeneous structure of such a distribution that cannot be replaced by the uniform one. All the cylinders have a random (uniform) orientation with respect to the polar and azimuthal angles in the unit sphere. Also we consider that in the boundary of system all external parts of nanotubes are cut off to fit the sample volume.

3. NUMERICS

It is well known that the percolation phase transition is described by the order parameter $P(p)$ where p is the fractional volume occupied by a spreading (infinite) cluster [17].

The electrical conductivity $S(p)$ assisted by the percolation also has a critical behavior defined by functional form $S(p) = b(p - p_c)^\beta$ (with constants b, p_c, β) that describes the critical threshold for percolation. The conductivity S is very small when the concentration of nanotubes p is less than the threshold $p < p_c$. However, the conductivity $S(p)$ sharply increases at the overcritical concentration at $p \geq p_c$, see [1]. Nevertheless, till now the technique of how to obtain the analytical expression for such a critical formalism in terms of not smooth functions (at vicinity $p = p_c$) to fit the shape of critical conductivity and allow obtaining the statistically significant values b, p_c, β at considerable level of fluctuation close to the percolation threshold is not sufficiently investigated.

Below by the use of Monte Carlo method we investigate behavior of the percolation order parameter $P(p)$ and the electric conductivity $S(p)$ close to the percolation threshold. Also we apply the constrained nonlinear optimization method [19] that does not use the gradient of functions (it is important in vicinity of the threshold p_c) and allows obtaining appropriate analytical expressions for the conductivity from results of simulation. We also use the algorithm [21] which, however, we have considerably extend and redesign for our purposes.

The idea is to fit the numerical experiment data to minimize an objective function, which is defined as the difference between the numerical data and the fit function $b(p-p_c)^\beta$ at variations of the parameters b, p_c, β. The results of such an approach are shown in Figs. 5 and 6. Fig. 5 shows the order parameter of percolation P as a function of the cylinder concentration (fractional volume) p at various parameters of the initial normal distribution $\mu_h = 25, \sigma_h = 0.3(a); 0.4(b); 0.2(c); 0.5(d)$ at $\mu_r = 0.1, \sigma_r = 0.025$, see Eq. (1). In this figure, the red dashed line (with asterisks) depict the data of 3D numerical simulation, and the blue line (with circles) shows the fitting line obtained by unconstrained nonlinear

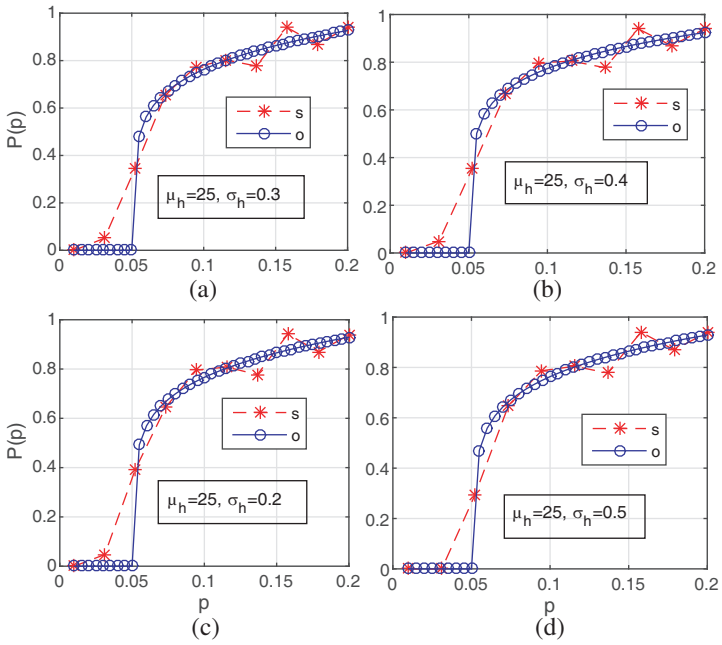

Figure 5. (Color on line.) The order parameter of percolation P as a function of the cluster cylinders fractional volume p at various parameters of the normal distribution $\mu_h = 25, \sigma_h = 0.3(a); 0.4(b); 0.2(c); 0.5(d)$, and $\mu_r = 0.1, \sigma_r = 0.025$, see Eq. (1). Red dashed lines (with asterisks) depict the data of numerical simulations, blue line (with circles) show the fitting obtained by the unconstrained nonlinear optimizations. The result of fit $P(p) = b(p-p_c)^\beta$ is: (a) $b = 1.25, p_c = 0.05, \beta = 0.16$; (b) $b = 1.29, p_c = 0.05, \beta = 0.17$; (c) $b = 1.29, p_c = 0.05, \beta = 0.17$; (d) $b = 1.30, p_c = 0.05, \beta = 0.17$. We observe that the blue lines correctly approach the critical dependence of the percolating at various parameters of random cylinders distribution.

optimization technique. We observe from Fig. 5 that the optimized blue line correctly approaches the critical dependence of the percolating at various parameters of random cylinders distribution. It is more important that it allows calculating the statistically significant values of the percolation threshold p_c and the critical exponent β.

To study the conductivity S of such a system, we calculate the length of total spreading cluster L_{cl}. Since the normalized electrical conductivity of the carbon nanotubes is 10^6–10^7 [S/m] [see review [3] and references therein], it is reasonable to assume that $S/S_0 \simeq L_{cl}$ between contacts. Fig. 6 shows the conductivity of the system S/S_0 as a function of the cylinder fractional volume p at the same parameters of the normal distribution of cylinders as in Fig. 5. In Fig. 6, red dashed lines (with asterisks) depict the data of numerical simulation, and blue lines (with circles) show the fitting line obtained by unconstrained nonlinear optimization technique. We observe that the conductivity S exponentially increases with respect of fractional volume p that is in the reasonable agree with the experiments [1].

4. THE STRUCTURE OF THE PROGRAM AND PARALLEL CALCULATIONS

For our simulation we use the approaches [19], [20], and [21] which are elaborated and redesigned for our purposes. The code of program is developed in C# language, and it has the following structure of classes: $|UserInterface\rangle \rightarrow |WorkWithCylinderParallel\rangle \rightarrow |WorkWithCylinder\rangle \rightarrow |Cylinder\rangle$. The class $|Cylinder\rangle$ contains all necessary parameters for the shape and position of a cylinder in the total system. The class $|WorkWithCylinder\rangle$ contains the fields and all methods to study the clusters of percolating cylinders in all the nanocomposite at fixed value of the percolation probability p. In class $|WorkWithCylinderParallel\rangle$ we have incorporated the facilities for generating of the parallel threads (see TPL in MS VS-2015) including the $|WorkWithCylinder\rangle$ objects to calculate the lengths and total

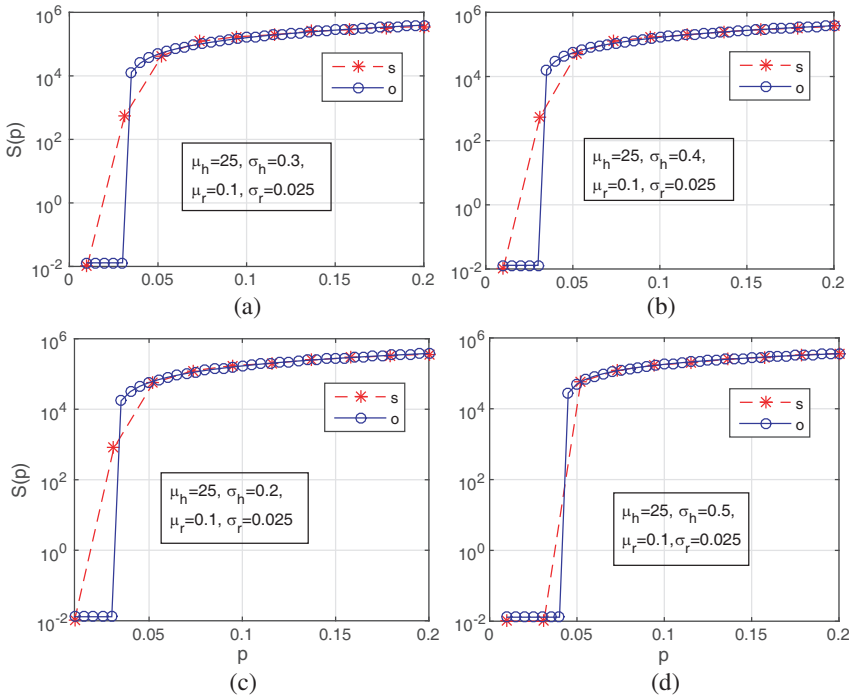

Figure 6. (Color on line.) The conductivity of the system $S(p)/S_0$ as a function of the cluster cylinders' fractional volume p at various parameters of the normal distribution as in Fig. 5. The result of fit $S(p) = b(p - p_c)^\beta$ is: (a) $b = 14.7, p_c = 0.03, \beta = 0.07$; (b) $b = 14.6, p_c = 0.03, \beta = 0.07$; (c) $b = 14.1, p_c = 0.0.05, \beta = 0.05$, and (d) $b = 14.2, p_c = 0.04, \beta = 0.06$. Red dashed lines (with asterisks) depict the data of numerical simulation, blue lines (with circles) show the fitting obtained by unconstrained nonlinear optimization technique.

volume of the percolating cluster, and the order parameter P for all the values of population probability p (fractional volume) in parallel. Such a structure of the parallel calculations allows drastically decreasing the time of our extended Monte Carlo simulation. For a computer PC with processor i7/7700 and 16 GB RAM the time of parallel calculation every plot in Figs. 5 and 6 (in panels (a)–(d)) was about 40–60 minutes.

5. CONCLUSION

We have investigated the electrical conductivity of 3D nanocomposite with incorporated random carbon nanotubes where the global conductivity occurs due to many intersections of long cylinders. The system was simulated by normally distributed cylinders, and the structure of infinite cluster in a vicinity of the percolation transition is studied with details. We applied the Monte Carlo method and the technique of the global optimization to determine the functional forms for the order parameter and electric conductivity close to the percolating transition. The latter allowed us calculating the minimal percolating threshold and the structure of infinite cluster for conductivity at significant level of the percolating fluctuations.

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