Modeling and calculation of the distribution of the minimum distance between carbon nanotubes with different degrees of orientation in a polymer matrix

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A technique for computer simulation of a random 3D distribution of carbon nanotubes (CNTs) with different orientations in a polymer matrix and calculation of the distance between nearest neighboring CNTs is described. It is shown that at low volume concentrations of CNTs, with an increase in CNT ordering, the character of the distribution of the minimum distance between CNTs changes significantly (from exponential to logarithmically normal), and the average minimum distance between CNTs noticeably increases. The proposed method and calculation results can be used to simulate the electrical conductivity, thermal conductivity, and other physical properties of polymer nanocomposites.

Keywords: carbon nanotubes, orientation, computer modelling, random location, distance.

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To describe the physical properties of nanocomposites with carbon nanotubes, it is important to have an idea of the nature of the CNT distribution in the polymer matrix. For example, in models of hopping (or tunneling) conductivity of nanocomposites with inclusions of conducting particles [1], the probability of tunnel transitions (jumps) is characterized by two parameters only: the height of the energy barrier between particles η and the distance between them d (or rather the type of distribution of the minimum distance between neighboring CNTs) [2,3]:

$$T_N \simeq \exp(-\eta^{1/2} d). \tag{1}$$

To estimate the macroscopic measured conductivity value, integration over the ensemble of CNTs is obviously necessary.

Changing the orientation (alignment in a certain direction) of CNTs in a polymer matrix, as it is known, significantly changes the properties of nanocomposites [4,5]. When the orientation of CNTs in the polymer matrix changes, the distance between the nearest neighboring CNTs will obviously change. However, in known papers, the analysis of changes in the distribution pattern of the minimum distance between neighboring CNTs depending on their orientation (order) in the polymer matrix was not carried out.

The computer modeling method, we use in this paper, is based on the well-known method of specifying (generating) a random distribution of CNTs in the representative polymer cuboid $L_x \times L_y \times L_z$ [2,3]. Each CNT in such a model can be described by a straight line segment. The starting points (x_i, y_i, z_i) of the CNTs are generated as follows:

$$\xi_i = L_\xi \times rand \quad (\xi = x, y, z). \tag{2}$$

Here $rand$ — uniformly distributed random numbers in the interval [0,1].

The length of l_i i-th CNT is according to the Weibull distribution [6], the distribution function of which has the form:

$$F(x) = 1 - e^{-(x/\lambda)^k} \text{ by } x \geq 0. \tag{3}$$

where k — distribution curve shape parameter, λ — scale parameter.

So, l_i can be generated using the expression:

$$l_i = F^{-1}(rand). \tag{4}$$

Corresponding azimuthal angles φ_i and cosines of polar angles θ_i (Figure 1, *a*) are also uniformly distributed in ranges $[0, 2\pi]$ and $[\cos\theta_{\max}, 1]$ respectively, namely:

$$\varphi_i = 2\pi \times rand, \ \cos\theta_i = (1 - \cos\theta_{\max}) \times rand + \cos\theta_{\max}. \tag{5}$$

Here, $\theta_{\max}$ — the maximum alignment angle of the CNTs used to evaluate the degree of alignment. If $\theta_{\max} = \pi/2$, CNT distribution is isotropic. At $\theta_{\max} = 0$ CNTs are perfectly ordered. It is more convenient to introduce the concept of the degree of alignment of CNTs as follows:

$$\theta_{\max} = \left(1 - \frac{A}{100}\right)\frac{\pi}{2}, \tag{6}$$

where A — leveling degree in percentage. At $A = 0\%$ the CNT distribution is isotropic, at $A = 100\%$ the CNTs are ideally ordered.

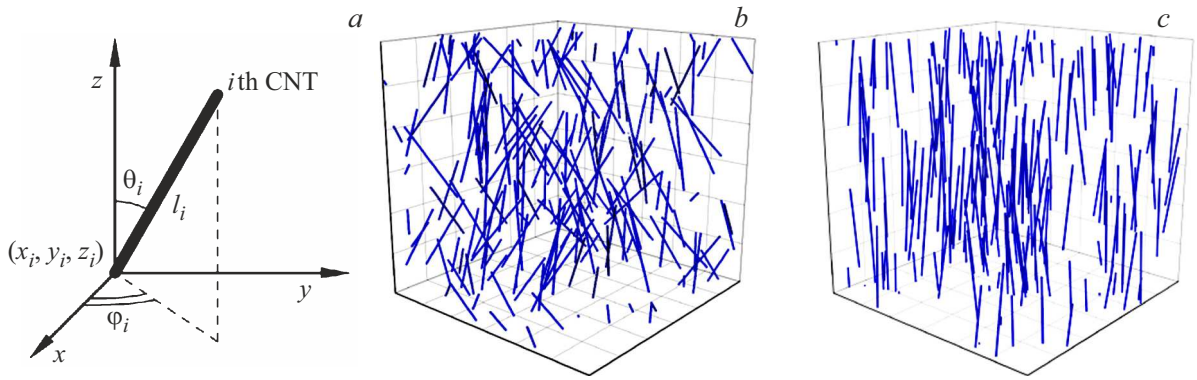

Figure 1. Model used to describe the arrangement of CNTs (a) and examples of CNT generation in a representative volume with varying degrees of alignment ($A = 50\%$ (b), $A = 90\%$ (c)).

If the coordinates of the end point of i-th CNT

$$(x_i + l_i \cos\theta_i,\ \ y_i + l_i \sin\theta_i \cos\varphi_i,\ \ z_i + l_i \sin\theta_i \sin\varphi_i)$$

extend beyond the boundaries of the representative cuboid, periodic boundary conditions are applied to simulate a larger system.

In the proposed model, CNTs are added to a representative volume one after another. At each step, the distance between the new CNT and the previously added CNTs is calculated. This problem is, in essence, determination of the minimum distance between two segments in three-dimensional space and was discussed many times before [7]. If the distance turns out to be less than CNT diameter, it is considered that the tubes intersect is present, the current CNT is discarded, and the generation of new CNT is repeated from the beginning. Thus, CNT systems are considered up to the percolation threshold and without taking into account the effects of agglomeration. Curvilinear CNTs and CNTs with kinks were not considered in this paper.

Examples of CNTs generated using this model with different degrees of alignment are shown in Figure 1, b and c.

To calculate the distribution of the minimum distance between the nearest neighboring CNTs the following parameters were used: the size of representative cuboid $6 \times 6 \times 6$ mkm, the average length of nanotubes $\langle d \rangle \geq 1$ or $2\,\mu$m ($\lambda = 2.2\,\mu$m, $k = 10$), nanotube diameter 30 nm, volume concentration of CNT — 1%.

Figure 2 shows histograms of the minimum distances between tubes (in other words, the distances between nearest neighbors) for the cases of isotropic and ordered distribution of CNTs. The calculation shows that for isotropic distribution of CNTs the average value $MinD$ is approximately equal to the standard deviation, which indicates the exponential nature of the distribution. For ordered (oriented) distribution of CNTs, the distribution $MinD$ changes its nature. Estimates showed that the value $\ln MinD$ with a confidence probability of 0.95 is distributed according to a normal law, i. e. the hypothesis of a lognormal distribution is fulfilled.

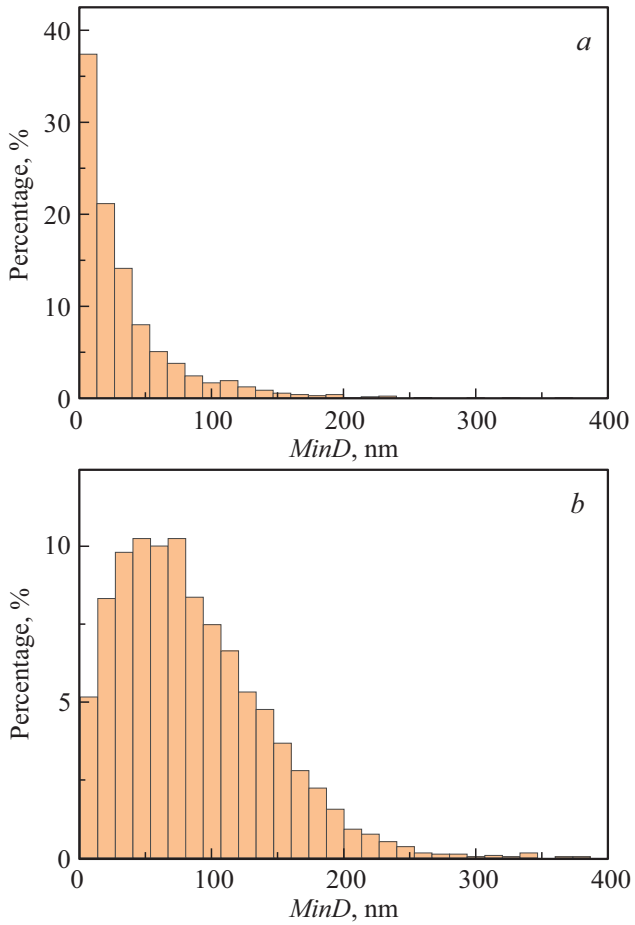

Figure 2. Histograms of the distribution of the minimum distance between neighboring nanotubes depending on the degree of CNTs alignment in the matrix (a — isotropic distribution, b — alignment 99%).

Figure 3 shows the change in the average minimum distance between CNTs depending on the degree of CNTs alignment in the matrix. It can be seen that an increase in the degree of ordering of CNTs leads to increase in

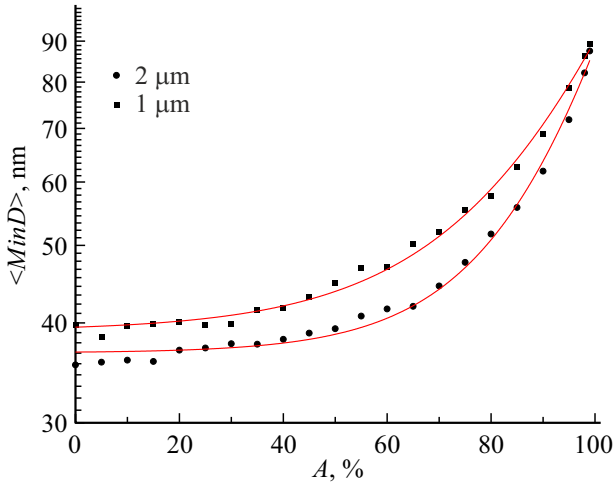

Figure 3. Change in the average distance between the nearest neighboring nanotubes depending on the degree of CNTs alignment in the matrix for tubes with different average lengths {lines — approximation by exponential function of the form $y = y_0 + A\exp\left((x - x_0)/t\right)$.

the average minimum distance between neighboring CNTs, which in turn shall lead to increase in the resistance of the nanocomposite (or a decrease in conductivity). Note that when calculating the conductivity, the determining factor will be the distribution of the angle between the direction of the electric field and the vectors between the two closest points of neighboring CNTs. With isotropic distribution of CNTs, the distribution of this angle will also obviously be isotropic, but in a system of highly ordered CNTs, anisotropy in the distribution of the angle and, as a consequence, conductivity will appear. Apparently, one of the main conditions for the conductivity increasing of nanocomposite is not so much the alignment of CNTs but the alignment of CNTs into conductive chains „head to tail". For example, CNTs alignment in magnetic field does not lead to significant alignment of CNTs into conductive chains, and the experimentally observed change in conductivity in such nanocomposites is quite weak [4,8]. At the same time, during orientation in an electric field, a rather significant change in conductivity [9] is often observed.

Thus, it is shown that with increase in the degree of CNT orientation, the nature of the distribution of the minimum distance between CNTs changes significantly (from exponential to logarithmically normal), and the average minimum distance between CNTs increases noticeably. The proposed methodology and calculation results can be used to model electrical conductivity, thermal conductivity and other physical properties of polymer nanocomposites.

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Conflict of interest

The authors declare that they have no conflict of interest.

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