Impact of defects on electrical connectivity of monolayer of ideally aligned rods

Yu Yu Tarasevich$^1$, D O Dubinin$^1$, V V Laptev$^{1,2}$, N I Lebovka$^{3,4}$

$^1$Astrakhan State University, Astrakhan, Russia
$^2$Astrakhan State Technical University, Astrakhan, Russia
$^3$Institute of Biocolloidal Chemistry named after F.D. Ovcharenko, NAS of Ukraine, Kiev, Ukraine
$^4$Taras Shevchenko Kiev National University, Department of Physics, Kiev, Ukraine
E-mail: tarasevich@asu.edu.ru

Abstract. The processes of formation of electrically conductive films filled by aligned elongated nanoparticles, i.e. nanotubes, nanowires or fibers attract great attention in nanotechnological applications. The alignment can be controlled by external electric fields, evaporation-driven self-assembly and assisted by different other techniques. This work studies the impact of defects on electrical connectivity of ideally aligned monolayer of rods ($k$-mers). By means of Monte Carlo simulation the problem of percolation for conductive rods on a discrete insulating substrate (square lattice) is analyzed. The aspect ratio of the particles changes within the interval 1–64, the insulating defects were distributed both on the lattice and on the particles. We found that even a very small amount of the insulating defects on the particles can destroy the electrical connectivity. The critical concentration of the defects decreases as the aspect ratio of the particles increases.

1. Introduction

Over the past decade, single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs), heteronanotubes and similar objects attract the great attention due to their exceptional properties [1]. Hybrid and functionalized tubular structures have been constructed via several modification paths. These modifications include the presence of molecules, generation of defects, and partial or full replacement of the carbon atoms, always maintaining a nanotube structure [2]. The promising applications have motivated efforts to produce thin films filled with the ordered nanotubes. These films inherit anisotropy of the one-dimensional carbon nanotube structure. Various methods for aligning nanotubes have been explored [3]. Evaporation-driven self-assembly (EDSA) is one of these methods [4]. EDSA is based on the well-studied ‘coffee-ring effect’ [5]. When a particle-laden droplet desiccates on a horizontal hydrophilic substrate, the particles suspended in the droplet tend to aggregate at the edges of the droplet, forming a ring-like structure. EDSA provides an opportunity to fabricate large-area, electronically monodisperse, aligned single-walled carbon nanotube thin films [6].

During EDSA, droplets of nanorods dispersed in solvents are deposited on substrate surfaces and the solvent is allowed to evaporate. Strong contact line pinning in combination with evaporation induces an outward flow inside the droplet. This flow can produce dense nanorod deposition inside coffee stain fringes, where large scale lateral ordering of the nanorods can be
observed. The long axis of the rods is oriented parallel to the contact line [7]. Self-assembly of single-walled carbon nanotubes into a sheet by drop drying has been reported [8].

A solution-based method produces highly oriented carbon nanotube (CNT) arrays. Inside these arrays, long-range nematic-like ordering of carbon nanotube stripes was observed [9]. Structures of aligned single-wall carbon nanotubes can be produced using a template-based fluidic assembly process [10]. Recently, a novel solvent evaporation method to align SWNTs in patterns having nanoscale width and micrometerscale length has been reported [11]. Novel means of building hybrid assemblies of crystalline $C_{60}$ and carbon nanotubes (CNTs) has been presented, wherein aligned CNT films direct the crystallization and orientation of $C_{60}$ rods from solution [12].

Another method to produce aligned single-wall carbon nanotube structures is based on application of the electric field. This method was used to form SWCNTs polymer composites [13]. Controlled placement of carbon nanotubes may be performed using alternating-current electric field [14].

Many efforts have been done to simulate the properties of layers of aligned rod-like objects. Thin film formation from a suspension of rod-like nanoparticles via solvent evaporation was studied by simulation [15]. When particles were strongly charged, they spontaneously aligned in suspension forming well-aligned thin film after complete drying.

Effect of nanotube alignment on percolation conductivity in carbon nanotube or polymer composites was investigated both experimentally and theoretically by Monte Carlo simulations [16]. The investigations showed that percolation conductivity of a stick network depends on alignment as well as concentration. Both dependencies exhibit critical (power-law) behavior. The highest conductivity occurs for slightly aligned, rather than isotropic, sticks.

Monte Carlo simulations has been used to study the effects of nanotube alignment and measurement direction on the resistivity in single-walled carbon nanotube multiple layers [17]. The minimum resistivity occurs for a partially aligned rather than a perfectly aligned nanotube film. The film resistivity becomes highly dependent on the measurement direction when nanotubes are strongly aligned.

A lattice gas model with Monte Carlo simulation has been used to study the morphological self-assembled patterns [18]. Moreover, percolation in two-dimensional nanoparticle films from colloidal self-assembly has been investigated numerically in this work.

Numerous both theoretical investigations and computer simulations have been devoted to the common physical behaviour of the systems of rod-like particles. Exact calculations and enumerations of systems of hard rigid rods distributed at closed packed density have been performed [19]. Monte Carlo simulations have been carried out for a system of straight rigid rods on a square lattice with only hard-core interactions [20], for the isotropic-nematic phase transition in a system of long straight rigid rods on two-dimensional square and triangular lattices [21, 22], for the isotropic-nematic phase transition in a system of self-assembled rigid rods on a lattice [23, 24], and for the self-assembled rigid rods on triangular lattices [25]. Particularly, it was demonstrated that a system of straight rigid rods on a square lattice with only hard-core interactions undergoes a phase transition from the low-density disordered phase to a nematic phase and then again undergoes a re-entrant phase transition from the nematic phase to a disordered phase [20]. Particularly, percolation of aligned rigid rods on two-dimensional square lattices has been investigated [26, 27].

Recently, impact of defects on the percolation of partially oriented rigid rods ($k$-mers) deposited of a square lattice has been reported [28, 29, 30]. Nevertheless, influence of the combined defects on percolation of perfectly aligned rods needs additional attention. This report presents the results of the Monte Carlo simulation plied to the problem of percolation for conductive rods on a discrete insulating substrate (square lattice). The insulating defects were distributed both on the lattice and on the particles. The impacts of the aspect ratio of the
particles and concentration different types of insulating defects on the electrical connectivity are discussed.

2. Details of simulation
A problem on a discrete two-dimensional substrate (square lattice $L \times L$ sides) is analyzed. We applied periodic (toroidal) boundary conditions to eliminate the effect of the border. The substrate was assumed as insulating. The substrate was initially randomly filled with the insulating point defects at given concentration $d_l$. The defects prevent the deposition of the particles. The deposited objects were linear $k$-mers (particles occupying $k$ adjacent sites of the square lattice). In fact, the value of $k$ is the aspect ratio of the particles. The objects were oriented strongly along one direction, e.g., along vertical axis $y$. We used random sequential adsorption to deposit the particles [31]. Interparticle hard-core repulsion was assumed, i.e. overlapping of the particles was strictly prohibited, as a result a monolayer was formed. The particles were treated as conducting. For each given value of $d_l$, we filled the lattice with the particles to the jamming state. At the jamming state, there is no possibility to adsorb even one additional particle, because any empty space of the appropriate size and shape is absent. The jamming concentration is denoted as $p$. Then, we randomly replaced some sites of the particles by the insulating defects; the defect concentration, $d_k$, being defined as the fraction of insulating sites on the particles, i.e. the number of such defects is $d_k p L^2$, and checked whether a path over the conducting particles spanning entirely the substrate. If the such path can be found, the electrical connectivity is present and the monolayer conducts the electricity. This situation is defined as the percolation [32]. We checked the percolation in two perpendicular directions, $x$ and $y$, and used two criteria: there is percolation in both directions (criterion AND), there is percolation at least along one direction (OR). In contrast to [33], we chose to treat spiral clusters as wrapping (percolating). We repeated the process 1000 times for different configurations of defects and particles and found the probability, $R(d_k)$, that percolation would occur at given concentrations of defects on the deposited particles. The abscissa of the inflection point of the curve was treated as the estimation of the critical concentration of defects for the given lattice size. We performed a scaling analysis to obtain the critical concentration at the thermodynamic limit

$$d_k(L) - d_k(\infty) \sim L^{-1/\nu_c},$$

where $\nu_c = 4/3$ is the critical exponent [32]. For $k \leq 32$, we used the lattice sizes $L = 100k$, $200k$, and $400k$. For $k = 64$, we used only two lattice sizes $L = 100k$ and $200k$ but the scaling analyzes were performed using the two criteria (AND, OR).

The highly efficient algorithm, proposed by Frank and Lobb [34] was utilized for finding conductivity of a square lattice, filled with the $k$-mers. The Frank and Lobb algorithm utilises the repeated application of a sequence of series, parallel and star-triangle ($Y-\triangle$) transformations to the bonds of the lattice. The final result of this sequence of transformations is reduction of any finite portion of the lattice to a single bond that has the same conductance as the entire lattice. We used four equivalent resistors (conductors) with $\sigma_f = 10^6$ and $\sigma_i = 1$ for occupied and empty sites [35], respectively, instead of each cell. The details of the calculations can be found in [36].

3. Results and Discussion
Below the critical concentrations of the defects, the monolayer is conducting (Fig. 1a) since the conducting parts of the particles form a spanning cluster. Above the critical concentrations of the defects, the monolayer is insulating since despite the existence of large conducting regions, these regions are not connected with each other (Fig. 1b).

Fig. 2a presents a phase diagram on the plane $(d_l; d_k)$. The regions below the curves correspond to the conducting (percolation) states. Even a small concentration of defects inhibits
Figure 1. The fragment $(80 \times 80)$ of adsorbed monolayer $800 \times 800$ of elongated particles. Particle aspect ratio is 8. (a) The monolayer is conducting. $d_l = 0.05$, $d_k = 0.05$. (b) The monolayer is insulating. $d_l = 0.075$, $d_k = 0.075$. The conducting subsystem is shown in blue. Insulating substrate is shown in white. The insulating point defects on the substrate are shown in black. The insulating regions of the particles are shown in light blue. The isolated clusters of the conducting particles are shown in red; these clusters do not contribute in the conductivity of the monolayer.

the deposition of long objects. The curves separating percolating and non-percolating states are convex for short objects ($k \leq 8$) and concave for the larger objects. As the aspect ratio, $k$, increases, the area of the percolating region on the phase plane $(d_l; d_k)$ decreases faster than the product of $0.5d_l d_k$. We can expect that in the case of long objects, the area will be extremely narrow and located along the axes. The result suggests that for objects with a large aspect ratio, even a very small concentration of defects can inhibit the percolation when both kinds of defects are present. Fig. 2b suggests that the monolayers constructed from the aligned rod-like particles cannot conduct even any kind of defects is absent when the aspect ratio of such particles is large enough. Our rough estimation gives the critical aspect ratio $k \gtrsim 100$.

Figure Fig. 3 presents examples of electrical conductivity $\sigma$ in the vertical ($y$) and horizontal ($x$) directions as a function of defects concentration, $d_k$, at fixed values of $d_k$ for $L = 800$ and $k = 8$. Behaviour of electrical conductivity $\sigma(d_k)$ corresponds with direct estimations of the percolation threshold from the phase diagram at the Fig. 2a. There is a sharp transition of electrical conductivity near the percolation threshold. Moreover, the behaviours of $\sigma_x(d_k)$ and $\sigma_y(d_k)$ are slightly different. Data evidence (see, inset to Fig. 3) that at fixed value of $d_l$ the percolation concentration $d_l$ for $x$ direction was higher that for $y$ direction. It reflects the presence of anisotropy of electrical conductivity for strictly ordered systems.

4. Conclusion
Using the model of random sequential adsorption, we studied the electrical conductivity of the monolayers of perfectly aligned elongated particles with aspect ratio up to 64. We considered deposition of the particles onto a substrate with preliminary placed insulating point defects. Some regions of the particles may be insulating. It should be kept in mind that no real interaction between the particles is taken into account in the model; the anisotropic monolayer is formed ‘by hand’. We found that even a very small amount of the insulating regions on the particles can destroy the conductivity of the monolayer. The critical concentration of the defects decreases as
Figure 2. (a) Phase diagram presented as the concentration of the defects on the particles, \(d_k\), versus the concentration of the defects on the substrate, \(d_l\). The areas below the curves correspond to the conducting (percolation) states. (b) Area of the conducting state on the phase diagram as a function of the inverse of the aspect ratio of the particles.

Figure 3. Examples of electrical conductivity \(\sigma\) in the vertical (\(y\)) and horizontal (\(x\)) directions as a function of defects concentration, \(d_k\), at fixed values of \(d_k\) for \(L = 800\) and \(k = 8\). The \(k\)-mers are perfectly oriented dimers along the vertical direction. Inset shows the percolation concentration of the defects on the particles, \(d_k\), versus the concentration of the defects on the substrate, \(d_l\).

the aspect ratio of the particles increases. The behaviour of the monolayers of aligned particles is very similar to the behaviour of the isotropic monolayers [29, 30]. The obvious shortcoming of our model is that the model shows only the fact of presence or absence of the conductivity, rather than the numerical value of the resistivity of the layer.
The future efforts should be focused on the calculations of the resistivity values for different defect concentrations and aspect ratios. Moreover, computer simulations of monolayers formed by particles with the larger aspect ratio ($k > 64$) is of interest because the real nanotubes have the large aspect ratio, e.g. the MWCNTs have the aspect ratio $\geq 100$ [37].

Acknowledgements
The reported research is supported by the Ministry of Education and Science of the Russian Federation, Project No. 643, the Russian Foundation for Basic Research, Grant No. 15-02-90402 Ukra, and the National Academy of Sciences of Ukraine, Project No. 43-02-15(U).

References
[1] Charlier J C, Blase X and Roche S 2007 Rev. Mod. Phys. 79(2) 677–732
[2] Ayala P, Arenal R, Loiseau A, Rubio A and Pichler T 2010 Rev. Mod. Phys. 82(2) 1843–1885
[3] Goh P, Ismail A and Ng B 2013 Compos. Part A: Appl. S. 56 103–126
[4] Lin Z (ed) 2010 Evaporative Self-assembly of Ordered Complex Structures (World Scientific Publishing Company) ISBN 9814304689
[5] Deegan R D, Bakajin O, Dupont T F, Huber G, Nagel S R and Witten T A 1997 Nature 389 827–829
[6] Shastry T A, Seo J W T, Lopez J J, Arnold H N, Kelter J Z, Sangwan V K, Lauhon L J, Marks T J and Jung Y J 2013 Small 9 45–51
[7] Nobile C, Carbone L, Fiore A, Cingolani R, Manna L and Krahne R 2009 J. Phys. Condens. Matt. 21 264013
[8] Du F, Fischer J E and Winey K I 2005 Phys. Rev. B 72(12) 121404
[9] Behnam A, Guo J and Ural A 2007 J. Appl. Phys. 102 044313
[10] Hsu C L, Chu S M, Wood K and Yang Y R 2007 phys. status solidi a 204 1856–1862
[11] Huang B 1988 J. Physique Lett. 46 659–666
[12] Haas A and Dhar D 2007 Europhys. Lett. 78 20003
[13] Park C, Wilkinson J, Banda S, Ounaies Z, Wise K E, Sauty G, Lillehei P T and Harrison J S 2006 J. Polym. Sci. Part B 44 1751–1762
[14] Chen Z, Hu W, Guo J and Saito K 2004 J. Vac. Sci. Technol. B 22 776–780
[15] Ohta S, Inasawa S, Koike O, Fujita M and Yamaguchi Y 2009 Appl. Phys. Express 2 065002
[16] Du F, Fischer J E and Winey K I 2005 Phys. Rev. B 72(12) 121404
[17] Behnam A, Guo J and Ural A 2007 J. Appl. Phys. 102 044313
[18] Hsu C L, Chu S M, Wood K and Yang Y R 2007 phys. status solidi a 204 1856–1862
[19] Baumgärtner A 1985 J. Physique Lett. 46 659–666
[20] Ghosh A and Dhar D 2007 Europhys. Lett. 78 20003
[21] Matoz-Fernandez D A, Linares D H and Ramirez-Pastor A J 2008 Europhys. Lett. 82 50007
[22] Almarza N G, Tavares J M and Telo da Gama M M 2011 J. Phys. Conf. Ser. 633 012064
[23] Evans J W 1993 Rev. Mod. Phys. 65(4) 1281–1329
[24] Stauffer D and Aharony A 1992 Introduction to Percolation Theory (London: Taylor & Francis)
[25] Newman M E J and Ziff R M 2001 Phys. Rev. E 64(1) 016706
[26] Frank D J and Lobb C J 1988 Phys. Rev. B 37(1) 302–307
[27] Yuge Y and Onizuka K 1978 J. Phys. C Solid State 11 L763–L766
[28] Cherkasova V A, Tarasevich Y Y, Lebovka N I and Vygornitskii N V 2010 Eur. Phys. J. B 74 205–209
[29] Guo J, Liu Y, Prada-Silvy R, Tan Y, Azad S, Krause B, Pötschke P and Grady B P 2014 J. Polym. Sci. Pol. Phys. 52 73–83