Influence of defects on the effective electrical conductivity of a monolayer produced by random sequential adsorption of linear \( k \)-mers onto a square lattice

YU. YU. TARASEVICH\(^1\), V. V. LAPTEV\(^{2,1}\), V. A. GOLTSEVA\(^1\) and N. I. LEBOVKA\(^{3,4}\)

\(^1\) Astrakhan State University, 20A Tatishchev Street, Astrakhan, 414056, Russia
\(^2\) Astrakhan State Technical University, 16 Tatishchev Street, Astrakhan, 414025, Russia
\(^3\) F. D. Ovcharenko Institute of Biocolloidal Chemistry, NAS of Ukraine, 42 Boulevard Vernadskogo, 03142 Kiev, Ukraine
\(^4\) Taras Shevchenko Kiev National University, Department of Physics, 64/13 Volodymyrska Street, 01601 Kyiv, Ukraine

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Abstract – The effect of defects on the behaviour of electrical conductivity, \( \sigma \), in a monolayer produced by the random sequential adsorption of linear \( k \)-mers (particles occupying \( k \) adjacent sites) onto a square lattice is studied by means of a Monte Carlo simulation. The \( k \)-mers are deposited on the substrate until a jamming state is reached, i.e. a state where no one additional particle can be placed because the presented voids are too small or of inappropriate shapes. The presence of defects in the lattice (impurities) and of defects in the \( k \)-mers with concentrations of \( d_l \) and \( d_k \), respectively, is assumed. The defects in the lattice are distributed randomly before deposition and these lattice sites are forbidden for the deposition of \( k \)-mers. The defects of the \( k \)-mers are distributed randomly on the deposited \( k \)-mers. The sites filled with \( k \)-mers have high electrical conductivity, \( \sigma_k \), whereas the empty sites, and the sites filled by either types of defect have a low electrical conductivity, \( \sigma_l \), i.e., a high-contrast, \( \sigma_k/\sigma_l \gg 1 \), is assumed. We examined isotropic (both the possible \( x \) and \( y \) orientations of a particle are equiprobable) and anisotropic (all particles are aligned along one given direction, \( y \) ) deposition. To calculate the effective electrical conductivity, the monolayer was presented as a random resistor network (RRN) and the Frank–Lobb algorithm was used. The effects of the concentrations of defects \( d_l \) and \( d_k \) on the electrical conductivity for the values of \( k = 2^n \), where \( n = 1, 2, \ldots, 5 \), were studied. Increase of both the \( d_l \) and \( d_k \) parameters values resulted in decreases in the value of \( \sigma \) and the suppression of percolation. Moreover, for anisotropic deposition the electrical conductivity along the \( y \) direction was noticeably larger than in the perpendicular direction, \( x \). Phase diagrams in the \(( d_l, d_k )\)-plane for different values of \( k \) were obtained.

Introduction: electrical conductivity of inhomogeneous media. – The physical properties of inhomogeneous media have attracted significant attention in the scientific community since the 19th century.\(^{[1]}\) Mainly, those efforts have been concentrated on binary inhomogeneous materials. One of the main problems in the theory of disordered systems is the calculation of the electrical conductivity for a random mixture of insulating and conducting materials.\(^{[2]}\) In particular, the singular behaviour of the electrical conductivity near a percolation threshold is of interest.\(^{[3]}\) Investigations of the physical properties of inhomogeneous media are significant for numerous applications such as the production and use of nanocomposites.\(^{[4]}\) Theoretical prediction of the effective properties for multiphase material systems is very important for the analyses of material performance and for the design of new materials.\(^{[5]}\)

An inhomogeneous medium can be considered as either
continuous or discrete. Accordingly, two complementary approaches are used to describe the electrical properties of such disordered media, i.e. the continuous approach and the discrete approach. The continuous approach originates from Maxwell’s works. In a Maxwell approximation, the impurities are supposed to be at a low concentration and to have a regular compact form, e.g. sphere or ellipsoid (“...spheres ... placed in a medium ... at such distances from each other that their effects in disturbing the course of the current may be taken as independent of each other” [1, p. 440–441], thus the mixture is diluted. The Maxwell approximation implies a linear dependence of the electrical conductivity on the concentration of inclusions. An extended approximation obtained in terms of the Maxwell approximation allows the electrical properties of composites to be described for a wide concentration range and even demonstrates the presence of the percolation threshold [2].

One widely used approach is the effective medium approximation (EMA) [2]. The classical EMA provides a good description of the physical properties for any concentration except for a narrow range around the percolation threshold [3]. At present, a more advanced version of the EMA, known as the generalized effective medium approximation (GEMA) [4], offers fairly good description of the physical properties even near the percolation threshold. An alternative description, i.e. the percolation approach, has been applied to a system consisting of randomly distributed metallic and dielectric regions [3]. Notice, in the percolation approach, an inhomogeneous material can be treated both as a continuous and as a discrete medium. The general percolation problem of cutting randomly centred insulating holes of arbitrary shape in a two-dimensional conducting sheet and its electrical conductivity has been investigated [5]. The review [2] is devoted to the AC electrical response of binary inhomogeneous materials, modelled as bond percolation networks. Percolation and the EMA, as they apply to the electrical conductivity of composites, are reviewed in [3].

A special group of inhomogeneous media are flat (2D) systems. Simulation of the electrical properties of 2D inhomogeneous systems (thin films) is motivated by their numerous applications. The resistance of a two-dimensional system of conducting sticks depends on systems anisotropy [6]. It was shown that the conductivity of a two-phase thin film, with both equal concentrations of the phases and their random distribution, is equal to the geometric mean of the conductivity of the phases [6]. The effective conductivity of random two-phase flat systems has been studied using an approach that differ from the effective medium approximation [7].

The physical properties of monolayers produced by RSA have been widely studied and discussed with special attention being paid to the effects of defects [8–11] and particle size distribution [12,13]. Recently, the percolation behaviour of the effective conductivity for a lattice model with interacting particles was reported [14]. Percolation and jamming phenomena have been investigated for the random sequential adsorption (RSA) of dimers on a square lattice, where the influence of dimer alignment on the electrical conductivity was examined [15]. A systematic study of the electrical conductivity of a monolayer produced by the RSA of linear k-mers (with values of k up to 128) onto a square lattice was, additionally, performed by means of computer simulation [16].

In real-world systems, the surfaces may be chemically heterogeneous and contain defects [17]. Some of the occupying k adjacent sites are considered as insulating and some of the lattice sites are occupied by defects (impurities). In this model, even a small concentration of defects can inhibit percolation for relatively long k-mers. Recently, some results concerning percolation and the electrical conductivity of monolayers produced by the RSA of aligned linear k-mers with defects onto a square lattice with impurities have been presented [18].

A generalized variant of the RSA model where both the k-mers and the lattice have defects has been proposed [19]. Some of the occupying k adjacent sites are considered as insulating and some of the lattice sites are occupied by defects (impurities). In this model, even a small concentration of defects can inhibit percolation for relatively long k-mers. Recently, some results concerning percolation and the electrical conductivity of monolayers produced by the RSA of aligned linear k-mers with defects onto a square lattice with impurities have been presented [20].

In this paper, we quantitatively examine the electrical conductivity of monolayers, paying special attention to the influence of defects on the electrical properties. We consider the monolayers as random resistor networks (RRN).

Methods. – In our computer simulation, we utilized RSA [21] to produce a monolayer. We employed a discrete two-dimensional substrate, namely a square lattice with periodic boundary conditions (a torus). The linear k-mers, i.e. particles occupying k adjacent lattice sites, were randomly deposited on the substrate. The values of k were 2^n, where n = 1, 2, ..., 5. Some fraction of the lattice sites (d_i) may be forbidden for the deposition of objects. We treated these sites as defects or impurities. These impurities had no effect on the electrical conductivity of the substrate but did affect the deposition of particles. The linear k-mers were randomly deposited on the substrate until a jamming state occurred, i.e. a state when no one additional particle can be placed because the presented voids are too small or of inappropriate shape. We examined the isotropic as well anisotropic deposition of the particles. During isotropic deposition, both the possible orientations, x and y, of a particle are equiprobable. During anisotropic deposition, all particles are aligned along one given direction, y. Overlapping with previously deposited particles was strictly forbidden, as a result, a monolayer was formed. Adhesion between the particles and the substrate was assumed to be very strong, so once deposited, a particle could not slip over the substrate or leave it (diffusion and detachment of the particles were impossible).
As a first step, point defects (impurities) were randomly embedded in the lattice sites up to a given concentration $d_l$. After that, $k$-mers with identical electrical properties of all their sites were deposited onto the substrate using the RSA algorithm until the jamming state was reached. Finally, defects were added to these deposited particles, i.e., some randomly chosen $k$-mer sites were marked as insulating. We studied how the effective electrical conductivity varied with the concentration of defects, $d_k$.

Figure 1 presents a fragment of a square lattice with four deposited 4-mers (horizontal and vertical). Impurities on the lattice are shown by black circles, and defects on $k$-mers are indicated by crosses. Different electrical conductivities of the bonds between the empty sites, $\sigma_l = 1$ (thin lines), filled sites, $\sigma_k = 10^6$ (thick lines), and empty and filled sites, $\sigma_{kl} = 2\sigma_k\sigma_l/(\sigma_k + \sigma_l) \approx 2\sigma_l$ (dashed lines) were assumed.

![Fig. 1: Fragment of a square lattice with four deposited 4-mers (horizontal and vertical). Impurities on the lattice are shown by black circles, and defects on k-mers are indicated by crosses. Different electrical conductivities of the bonds between the empty sites, $\sigma_l = 1$ (thin lines), filled sites, $\sigma_k = 10^6$ (thick lines), and empty and filled sites, $\sigma_{kl} = 2\sigma_k\sigma_l/(\sigma_k + \sigma_l) \approx 2\sigma_l$ (dashed lines) were assumed.](image)

To find the effective electrical conductivity, the torus was unrolled into a plane and two conducting buses were applied to its opposite sides. The electrical conductivity of the resulting RRN was calculated between these buses using the Frank-Lobb algorithm [37]. This RRN is an image of the original monolayer, it has a regular structure but randomly distributed conductivities. A preliminary scaling analysis of the electrical conductivity behaviour at different values of $k$ and $L$ has recently been performed for the defect-free problem [20]. The difference between the approximated value of electrical conductivity in the limit of the infinite system and $L = 100k$ was of the order of several percent. This is the reason why in our computations, for any value of $k$, the lattice size $L$ was $L = 100k$. For each given value of $k$, the computer experiments were repeated 10 times, then, the logarithm of the effective electrical conductivity was averaged.

For each value of $k$, we studied three situations. When any lattice site is allowed for deposition ($d_l = 0$), the curve $\sigma(d_k)$ is a typical sigmoid.

At the given value of $d_l$, the observed transition of electrical conductivity $\sigma(d_k)$ from the high-conducting to non-conducting state was fairly smooth and corresponded to the behaviour of the order parameter in a second-order phase transition in the presence of an external field. In the problem under consideration, the reciprocal electrical contrast $h = \sigma_l/\sigma_k$ plays the role of the “external field”, $h \ll 1$. The external field smears the phase transition [38]. An infinitely large electrical contrast, when $h = 0$, corresponds to the absence of an external field.

For isotropic deposition, the critical “geometrical” concentrations $d_k^{xy}$ that correspond to the points of mean geometric conductivity

$$\sigma_g = \sqrt{\sigma_k\sigma_l}$$

are fairly close to the percolation thresholds. This corresponds exactly to the prediction for 2D systems in the case of systems with equal concentrations of the phases [11].

When the concentration of impurities on the lattice is so large that it almost blocks the formation of a spanning cluster ($d_l = 0.02$), the effective electrical conductivity drops from $\sim 10^3$ to $\sim 1$ without a visible inflection point. The behaviour of the effective electrical conductivity confirms that, in the case of the deposition of long particles, even a very small concentration of defects on the substrate can prevent the formation of a conducting chain of particles.

With anisotropic deposition of the particles onto the lattice, the behaviour of the effective electrical conductivity is much more surprising. In this case, all the deposited particles are aligned along the $y$ axis. As expected, the
longitudinal effective electrical conductivity (i.e., the conductivity, measured along the y axis, $\sigma_y$) and the transversal one (i.e., the conductivity, measured along the x axis, $\sigma_x$) may differ. This effect has recently been reported for the case when all kinds of defects are absent [20]. It was more pronounced for long particles (for large values of $k$).

In Figure 3, the above-mentioned case corresponds to the point $d_k = 0$ for the curves for $d_l = 0$. Figure 3 clearly demonstrates that the electrical anisotropy of the monolayer increases as the value of $k$ increases.

We found that defects in the lattice increase the electrical anisotropy. At any given value of $k$, the difference between the electrical conductivities along the x and y directions increases as the concentration of defects $d_l$ grows. Insulating defects on the k-mers destroy connectivity when their concentration exceeds a critical value. Figure 4 presents examples of phase diagrams in the $(d_l, d_k)$-plane for $k = 4, 8, 16, 32$. The results for $k = 2$ are omitted because the anisotropy of the electrical conductivity near the percolation threshold is negligible. Here, the solid lines correspond to the critical “geometrical” concentrations $d^x_k$ and $d^y_k$ for the x and y directions, respectively, and the dashed lines were obtained using the Hoshen–Kopelman connectivity analysis at the thermodynamic limit [39]. For each value of $k$, there is a conducting state when the concentration of defects is located below the curve. When the concentrations is located above the curve, the monolayer is insulating. Quite surprising is the region around the critical curve. This region corresponds to a monolayer with a high electrical conductivity along the y direction and a low electrical conductivity along the x direction.

For characterization of the electrical anisotropy of monolayers, we used the same quantity as in [20]

$$\delta = \frac{\log (\sigma_x / \sigma_y)}{\log (\sigma_k / \sigma_l)}.$$  \hspace{1cm} (2)

This quantity equals 0 when a monolayer is electrically isotropic, and tends to 1 for a strongly anisotropic monolayer. For a defectless lattice ($d_l = 0$), the anisotropy is large and constant for small values of $d_k$; it has a peak near the percolation threshold and tends to zero when the concentration of defects on the k-mers, $d_k$ increases (Figure 5). The larger the value of $d_l$ the larger the initial anisotropy and the anisotropy near the percolation threshold, while the width of the initial plane part of the

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Fig. 2: Electrical conductivity, $\sigma$, vs defect concentration on the k-mers, $d_k$, for different values of defect concentration, $d_l$, on the lattice. The arrow shows an example of the critical “geometrical” concentration $d^y_k$ for $d_l = 0$. The isotropic deposition, $k = 32$, $L = 100k$, results are averaged over 10 independent runs. The statistical error is of the order of the marker size.

Fig. 3: Electrical conductivity, $\sigma$, vs defect concentration on the k-mers, $d_k$, for different values of defect concentration on the lattice, $d_l$. The anisotropic deposition, a) $k = 16$, b) $k = 32$, $L = 100k$, results are averaged over 10 independent runs. The statistical error is of the order of the marker size. The arrows show the examples of the critical “geometrical” concentration $d^x_k$ and $d^y_k$ in the x and y directions.
which samples exhibiting high electrical anisotropy could
diagonal direction. This observation suggests a means by
and, at the same time, a bad conductor along the perpen-
dinal field” [38]. There are certain concentrations of defects
earlier anisotropy reflects the smearing
Near the percolation threshold, the electrical anisotropy
greatly to destroy percolation, the monolayers with larger
concentration of defects on the lattice,
anisotropic deposition, calculation showed that when the
activity of the monolayers under consideration. In the case of
an imperfect substrate, i.e. a square lattice with embed-
ded impurities. Calculation of the electrical conductivities
of the percolation transition in the presence of an “exter-
thermodynamic limit. [39]. The anisotropic de-
position, \( k = 4, 8, 16, 32, \ L = 100k \), results are averaged over
10 independent runs. The statistical error is of the order of the
marker size.

curve decreases. The effect is less pronounced for shorter
particles (compare parts a) and b) in Figure 5.

Conclusion. – In our research, the electrical conductivities of monolayers of rod-like conducting particles adsorbed on an insulating substrate were calculated using the Frank–Lobb algorithm [37]. We considered both the anisotropic and isotropic deposition of particles onto an imperfect substrate, i.e. a square lattice with embedded impurities. Calculation of the electrical conductivities gave an explicit confirmation of the predictions obtained on the basis of percolation theory [38] viz. any kinds of defect have drastic negative effects on the electrical conductivity of the monolayers under consideration. In the case of anisotropic deposition, calculation showed that when the concentration of defects on the lattice, \( d_l \), is sufficiently large to destroy percolation, the monolayers with larger electrical anisotropy correspond to the larger values of \( d_l \). Near the percolation threshold, the electrical anisotropy is greater. The evident anisotropy reflects the smearing of the percolation transition in the presence of an “external field” [38]. There are certain concentrations of defects where the sample is a good conductor along one direction and, at the same time, a bad conductor along the perpendicular direction. This observation suggests a means by which samples exhibiting high electrical anisotropy could be designed.

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