Effect of aging on electrical conductivity of two-dimensional composite with rod-like fillers

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Abstract. Two-dimensional composite with rod-like fillers has been simulated using a lattice approach. The fillers were assumed to be conductors, whilst the substrate (host matrix) was assumed to be an insulator. Rod-like fillers were considered as linear $k$-mers of two mutually perpendicular orientations ($k_x$- and $k_y$-mers) on a square lattice with periodic boundary conditions applied along both directions of the lattice. A random sequential adsorption was used to produce an initial homogeneous and isotropic distribution of fillers. By means of the Monte Carlo (MC) technique, translational diffusion of the fillers was simulated as a random walk, while rotational diffusion was ignored. At each given MC step, the system under consideration was transformed into a random resistor network (RRN); the Frank–Lobb algorithm was applied to calculate the electrical conductivity of such RRNs. Diffusional relaxation of the system leads to a kind of aging. For example, when concentration of fillers exceeds the percolation threshold, the aging leads to decreasing of the electrical conductivity and, in some cases, the inhibition of percolation was observed.

1. Introduction
Among the alternatives for next-generation flexible, solution-processed transparent conductors, metal nanowire films attract a lot of attention as most promising (see, e.g., the reviews \cite{1, 2} and the references therein). To accelerate design of such the systems and their adoption for different applications, the predictive tools are required. This is the reason why computational and analytical studies of electrical properties of two-dimensional (2D) random networks composed of rod-like particles are of increasing interest \cite{3}.

An important part of various technological processes, including production of conducting nanocomposites such as transparent flexible conductors is adsorption of large molecules or nanoparticles, e.g., nanotubes at the liquid-solid interface. This process can be simulated as random sequential adsorption (RSA) \cite{4}. Numerous publications are devoted to 2D nanocomposites with rod-like conducting fillers (see, e.g., \cite{1, 2, 5}).

The time changes in the electrical conductivity during the kinetic gelation \cite{6} and aggregation of colloidal particles in aqueous solutions \cite{7, 8} have been theoretically and experimentally studied. The data were interpreted in the framework of the percolation theory, fractal nature of
the clusters, and cluster growth processes. The time changes in the electrical conductivity with composite aging have been observed in several experimental works. These changes were observed after transient shear during annealing of the polymer composites filled with carbon nanotubes (CNT) [9, 10]. The conductivity demonstrated noticeable increase with the time after the shear. The shearing can cause breaking and reformation of capacitors and resistors formed at the CNT–CNT contacts, and the conductivity recovery was explained by the reorganization of the conducting CNT network. The recovery of the conductivity was modelled using the electrical percolation approach combined with the cluster aggregation model [9, 11]. The time-dependent transition from insulating to conductive state was explained using the dynamic percolation concept [12]. The explanation was based on general effective medium model (GEM) coupled to a kinetic equation for CNT agglomeration. Thermal-induced dynamic percolation was observed in electrical conductivity behaviour in high-density polyethylene melt filled by carbon black [13, 14]. The dynamic percolation was modelled accounting for a first order aggregation model coupled with the classical percolation theory. Changes in electrical conductivity reflected the dynamic processes of destruction and re-formation of conductive filler networks in a low viscous CNT/epoxy suspension [15]. Dynamic percolation in highly oriented conductive networks formed with different carbon fillers (CNT and carbon black) was investigated during disorientation upon annealing [16]. The time-dependent changes of the electrical conductivity of carbon black filled polymethylmethacrylate were studied theoretically and experimentally [17]. The changes were attributed to the aggregation of freely dispersed aggregates into conductive pathways. The time dependence of the percolation in response to organic vapour was observed in water-borne polyurethane filled with carbon black [18].

Effects of fillers length, anisotropy and presence of defects on electrical conductivity of 2D systems were recently simulated [19, 20]. Although RSA with diffusion has been studied [21, 22, 23, 24, 25], effect of diffusion on electrical properties of 2D composites with rod-like fillers was not examined. In the present conference paper, we try to partially eliminate this gap. The rest of the paper is constructed as follows. In section 2, the technical details of the simulations are described. Section 3 presents our principal findings. Section 4 summarizes the main results.

2. Methods

The simulation was performed using a lattice approach. A low conducting substrate (host matrix) was approached as a square lattice of size $L \times L$ where $L = 256$. High conducting rod-like fillers were represented as linear $k$-mers (i.e., particles occupying $k$ adjacent lattice sites). The length of the $k$-mers (aspect ratio) was varied from 2 to 12.

An initial homogeneous and isotropic distribution of linear $k$-mers in a 2D film was produced using random sequential adsorption [4]. The $k$-mers were deposited randomly and sequentially onto the lattice, and their overlapping with previously placed $k$-mers was forbidden. The $k$-mers oriented along the $x$ and $y$ directions ($k_x$-mers and $k_y$-mers, respectively) were equiprobable in their deposition. To reduce finite-size effect, we used toroidal boundary conditions upon deposition, i.e., periodic boundary conditions (PBCs) along both the $x$ and $y$ axes. The concentration (packing density) of the particles varied in the range $p \in [0.1, p_j]$ where $p_j$ is the jamming concentration. However, the concentrations corresponding to a concentration slightly greater than the percolation threshold, $p_c$, were of our primary interest. Example of a system at initial state is presented in figure 1.

When the concentration of deposited particles reached the given value, the deposited particles were allowed to diffuse. The diffusion of $k$-mers was simulated using the kinetic MC procedure. In our simulation, only translational diffusion was taken into consideration. This is essentially the case for fairly dense systems in the jamming state [26], where rotational diffusion is impeded, especially for large values of $k$. Naturally, for dilute systems, rotational diffusion can occur,
Figure 1. Example of the initial pattern. $k = 10$, $p = 0.5$.

Figure 2. Representation of 3 deposited 3-mers as a RRN. Conductivities of the bonds between conducting sites are $\sigma_k$, between the insulating sites are $\sigma_m$, and between one insulating site and one conducting site are $\sigma_{mk}$.

however, this was ignored in our study. Although percolation threshold corresponds to a packing density less than jamming coverage, the packing density is high enough to essentially suppress rotations.

In our simulation, an arbitrary $k$-mer was randomly chosen and a translational shift by one lattice unit along either the longitudinal or the transverse axis of the $k$-mer was attempted. Equal probabilities to choose any of all the four possible directions to shift the $k$-mer were assumed. One time step of the MC computation, which corresponds to an attempted displacement of the total number of $k$-mers in the system, $N = pL^2/k$, was taken as the MC time unit. We started time counting from the value of $t_{MC} = 0$, being the initial moment (before diffusion). This model corresponds to [21, 23].

For characterization of the rearrangement of the system under consideration, the electrical conductivity, $\sigma$, were monitored at each given MC step. We used the model described in [27] to transform the system under consideration into a RRN. The torus was unrolled in a plane and two conducting buses were applied to its opposite sides. The electrical conductivity was calculated between these buses. The Frank–Lobb algorithm [28] was applied to calculate the electrical conductivity of such RRNs.

We considered an empty lattice as a regular resistor network. Each site is associated with four resistor. The conductivities of all resistors in the network are equal, $2\sigma_m$. Hence, the conductivity of a whole bond between two sites is $\sigma_m$. Each site of a $k$-mer is associated with four identical resistor, too. The conductivity of such the resistor is $2\sigma_k$. When a $k$-mer deposits onto the lattice, there are only three possible combinations of the resistors (figure 2).

**Two insulating** The conductivity of the entire bond is $\sigma_m$.

**Two conducting.** The conductivity of the entire bond is $\sigma_k$.

**Conducting insulating.** The conductivity of the entire bond is $\sigma_{km} = 2\sigma_m\sigma_k/(\sigma_m + \sigma_k)$.
In our study, we supposed $\sigma_m = 1$ a.u. and $\sigma_k = 10^6$ a.u., hence, $\sigma_{km} \approx 2$ a.u. Conductivities both along $x$ axis and along $y$ axis were taken into consideration.

Moreover, structure of percolation clusters was studied. The percolation clusters were identified using Hoshen–Kopelman algorithm [29]. After that, we extracted a backbone [30], i.e., a subset of the percolation cluster that carries an electrical current when a potential difference is applied between two its sites [31, 32, 33]. We used so-called ‘burning algorithm’ to find the backbone of the percolation cluster [34].

3. Results
We found that, for concentrations of fillers below the percolation threshold and close to the jamming concentration, the electrical conductivity of 2D composites with rod-like fillers is almost independent on time. In contrast, diffusion has a drastic impact on electrical conductivity when concentration of fillers slightly exceeds the percolation threshold, $p_c$, (figure 4). The latter case ($p \gtrapprox p_c$) has attracted our special attention.

![Figure 3. Examples of electrical conductivity (log scale), $\sigma$, vs MC steps, $t_{MC}$, for different concentrations, $p$. $k = 10$, $L = 256$. $\triangle$: $p = 0.4$, $\bigcirc$: $p = 0.5$, $\Box$: $p = 0.6$. The results are averaged over 100 independent runs.](image)

First of all, enormous error bars when $p \gtrapprox p_c$ should be explained. These errors reflect permanent jumps of the electrical conductivity near the phase transition conductor-to-insulator. For the same MC step, some samples are conductors, whereas other samples are insulators. Thereby, a direct averaging of the electrical conductivity over all independent runs is meaningless. To obtain sensible behaviour, at each MC step, 100 independent runs were divided into two groups, viz., conducting samples and the insulating samples. The data inside each group should be averaged independently. In this case, the electrical conductivity vs MC steps is presented by two branches; the first one is corresponded to the conductor whereas the second one corresponds to insulator (figure 4).

Initially, the system is a conductor. At large times ($t_{MC} \gtrapprox 10^3$), the system approximately with equal probabilities may be an insulator or a conductor. During a transient mode ($10 \lesssim t_{MC} \lesssim 10^2$), the system is more probably to be a conductor than an insulator. This behaviour of the electrical conductivity can be explained by the structure of percolation cluster. At initial state, almost all occupied sites belong to backbone and make a contribution to conductivity. During a few dozens of MC steps, fairly dense initial backbone turn into a quasi-one-dimensional chain (figure 5).
Figure 4. (a) Example of the electrical conductivity, $\sigma$, vs MC steps, $t_{MC}$, for $k = 12$ and concentration of particles $p = 0.575$, box-and-whiskers plot in log-log scale. Upper branch corresponds to conducting states, whilst lower branch corresponds to insulating states. (b) Probability, $P$, that a conducting state occurs.

Figure 5. Example of temporal evolution of backbone of the percolation cluster. $k = 12$, $L = 256$, (a) $t_{MC} = 0$, (b) $t_{MC} = 10$, $d_f = 1.672$, (c) $t_{MC} = 100$.

At the same time, number of sites belonging to the backbone decreases (figure 6). This has the drastic effect on electrical conductivity, because diffusion can easily both destroy such the weak backbone and recover it again. At $t_{MC} \gtrsim 10^2$, a dynamical percolation occurs, i.e., percolation arises and fades. Whilst during several first MC steps, the monolayer is a conductor, after $t_{MC} \sim 10^2$, the monolayer may be both conductor and insulator with different probabilities (figure 4).

4. Conclusion
In our study, a lattice approach has been applied to simulate effect of diffusion on electrical conductivity of a 2D composite with rod-like fillers. For concentrations of fillers above the percolation threshold but below the jamming concentration, we observed a kind of aging, i.e., decreasing of the electrical conductivity due to diffusion of fillers. This behaviour can be explained by evolution of the structure of the percolation cluster and its backbone. Diffusional relaxation leads to sparser percolation cluster with quasy-1D backbone. The diffusion of fillers
can easily destroy this backbone and recover it again. As the result, electrical conductivity of the monolayer varies with time. Such the behaviour of electrical conductivity observed in our study can be treated as a kind of the dynamical percolation [35].

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**Figure 6.** Example of fraction of lattice sites belonging to the backbone, $p_{BB}$ vs MC steps, $t_{MC}$. The results are averaged over 100 independent runs. $k = 12$, $L = 256$, $p = 0.6.$
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