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Electrical properties of nanocomposites near percolation threshold – dynamics

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ABSTRACT

The paper deals with analysis of morphology and electrical properties of (nano)composite films. It describes a computer simulation tool for morphological and transport analysis of the films. Two models of composite structures are prepared — a hard disk and soft disk model. Their morphology is studied by the covariance, Quadrat Counts method, and Voronoi tessellation. Some specific characteristics of the methods are introduced. The electric properties are studied by the Monte Carlo simulations via tunnel charge transport. The results for d.c. conductivity as well as in case of changing voltage are done.

1. Introduction

Composites and nanocomposites, which are formed from two or more distinct materials, have desirable combinations of properties that are not found in the individual components. Their mechanical and electrical properties could be very uncommon. Moreover, there can be found remarkable correlations between morphological and the other properties of such structures. A close connection between morphological and electric properties of composite films was found in electric conductivity analysis [1,2].

A problem of morphology of various materials with complex structure such as various nanocomposite structures becomes ever increasingly significant in different areas. Specification of such structures requires topological and geometrical descriptors so we are able to characterise the connectivity and spatial configuration. In the last years, new advanced techniques have been developed in spatial statistics [3]. Generally, it may be stated that today there is strive for use of multipoint statistic correlation functions for morphology analysis.

The electric properties of composite or nanocomposite films come in on foreground of interest, especially near the percolation threshold. The parameter which influences the electric properties of composite structures is the metal volume fraction [1] contained in dielectric material. The metal particles are completely insulated from each other at low values of metal volume fraction, near the critical value of it they form a percolation structure, and the structure embodies the metallic behaviour with dielectric inclusions above this value. However, the percolation threshold can have a wide range, from a little as 15% metal all the way to 80%. One can suppose ohmic or tunnelling conductivity in the structures. In the case of ohmic conductivity so called infinite cluster – objects connected to both electrodes applied to opposite sides of the structure – is analysed by the help of modified burning method [4], which takes into account spherical objects with real centre coordinates. This method enables to discover the structure of the infinite cluster — its backbone, dead-ends and critical bonds. In the case of tunnelling conductivity the objects are separated by the dielectric matrix. The value of electric potential of these objects depends on their electric capacity and electric charge. Since the capacity of the objects is very small (comparable to elementary charge) the values of potential are discontinuous. The values of potential fluctuate even when the system is very close to the steady state. Analysis of these fluctuations can afford us an experimentally observable quantity – the noise of the electric current passing through the structure. This noise could be then measured, analysed and compared for structures with various volume fractions and arrangements of objects. The electric current passing through the composite/nanocomposite structures follows trajectories, which create so called fuzzy cluster — the analogy of the infinite cluster in the case of the ohmic conduction. The morphology of the fuzzy cluster determines the electric properties of composite structure, thus it is desirable to deal with it. The real structures close the percolation threshold embody both mechanisms of conductivity ohmic and tunnelling [1].

2. Models

We used two different models to generate structures. First one is a hard disk model in two-dimensions (2D) or a hard sphere model in three-dimensions (3D). It is based on a random generation of objects to a working area with respect to so-called diffusion zone D. The diffusion zone is the main parameter of this model and states the minimal distance between edges of two objects. Alongside it, we use a relative parameter $D_{rel} = D/D_{max}$, where D_{max} is the maximal possible diffusion zone for a given structure. This parameter varies between

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values 0 and 1, whereas structures with $D_{rel}=0$ are random and structures with $D_{rel}=1$ are maximally arranged.

The second one, a soft disk (in 2D) or soft sphere (in 3D) model, is based on a molecular dynamics method with forces obtained from the inter-particle Lennard-Jones potential $\varphi=4\varepsilon[(\sigma/r)^{12}-(\sigma/r)^{6}]$. The main parameter of this model is so-called effective temperature T_{eff} used in simulated annealing – temperature was measured in relative units corresponding to the constant 4ε in Lennard-Jones expression. This parameter controls the arrangement of objects – the higher value of the final temperature T_{eff} the more disordered structures.

The dimensions of the working areas in both models varied between 1000× 1000 and 10,000× 10,000 pixels in 2D with boundaries, similarly in 3D, pixel being the length unit in our simulations. Examples of generated structures in 2D are demonstrated in Fig. 1. Several sets of model structures for study of both morphological and transport properties were generated.

3. Morphological analysis

Both the models allow preparing structures with various degrees of arrangement. The disordered or partially arranged structures can be generated successfully by both the hard and soft disk/sphere models. More arranged structures up to complete monocrystallic or polycrystallic can be generated by the soft disk/sphere model only. To test an influence of degree of object arrangements in the structure on its electrical properties, we need to quantify the arrangement. There are methods based on mathematical morphology suitable for it. Most popular are the covariance method, Quadrat Counts method, and Voronoi tessellation. The Quadrat Counts method [5] gives directly its feature as a degree of arrangement of the structure: a value between 1.0 (random structure) and 0.0 (totally arranged structure). However, contrary to this advantage, results given by this method are rather noised. Thus, structures with 10^4–10^5 objects must be processed in order to get sufficiently accurate results.

However, the number of objects in common samples (2D sections of composite structures) is distinctively lower; therefore, we have tested a sensitivity of the methods mentioned above to statistical noise. The structure samples containing 1000 objects were generated always 5 times with the same parameters and then the sensitivity was compared (Fig. 2). We have tested all the three morphological methods: covariance, Voronoi tessellation (VT), and Quadrat Counts (QC). The last two are compared in the Fig. 2. The covariance similar to majority of others represented here by the Quadrat Counts method gives very noisy results. The best results among them gives the Voronoi tessellation method, thus it was used in the following morphological analysis. It was used most robust specific characteristic

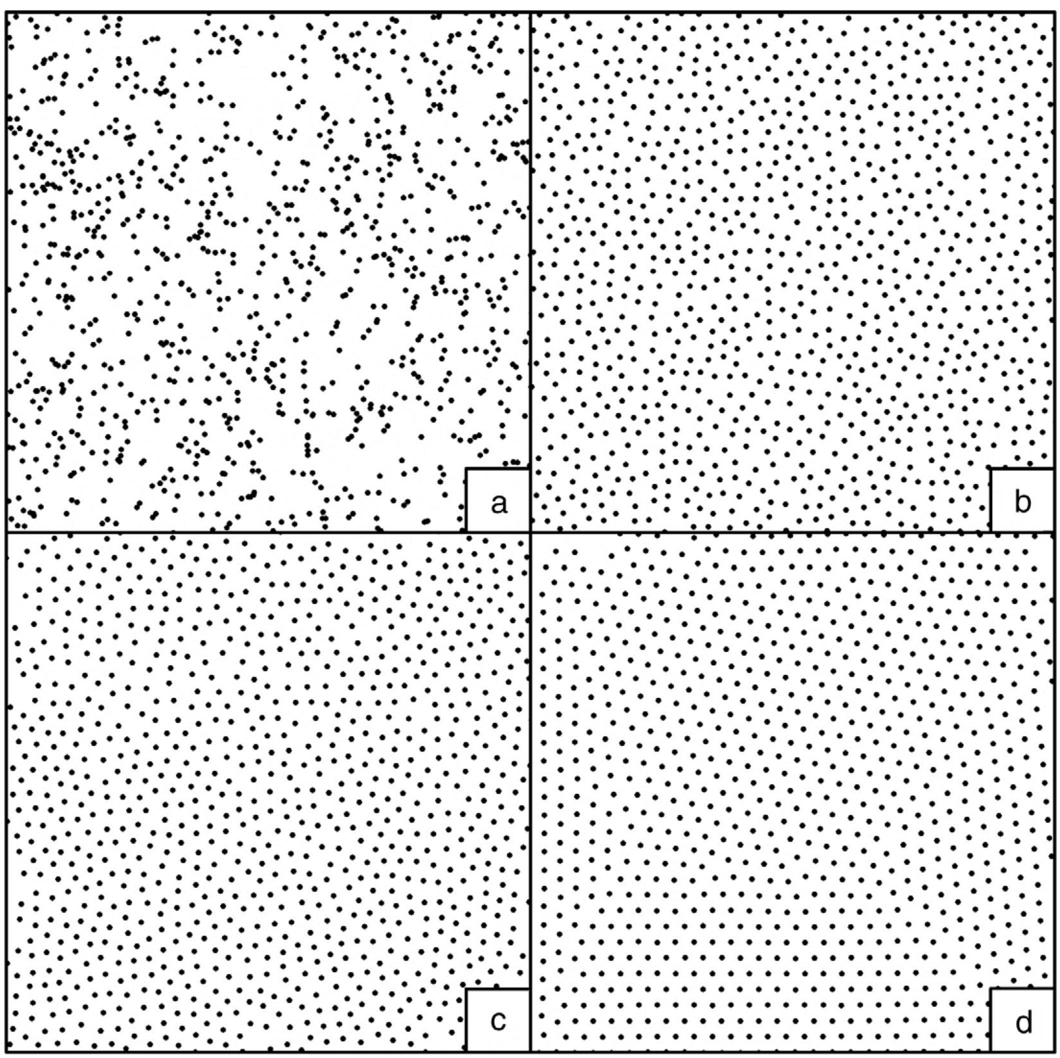

Fig. 1. Examples of generated structures in 2D: (a) completely disordered structure generated by hard-disk model with parameter $D_{rel}=0$ or soft disk model with parameter $T_{eff}=1\times 10^{10}$; (b) maximally arranged structure generated by hard disk model with $D_{rel}=1$; (c) partially arranged structure generated by soft disk model with $T_{eff}=1\times 10^{1}$, it is comparable to the previous structure; and (d) high ordered structure generated by soft disk model with $T_{eff}=1\times 10^{-10}$.