Modelling of a Time Dependent Electron Diffusion Problem for Nanocrystalline One-dimensional Carbon-Palladium Structures *via* Homogenization

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Abstract. Analytical and numerical phenomena of the electron resistance in the time dependent electron flow in Pd nanocrystals embedded in a carbonaceous matrix are studied. The asymptotic homogenization theory and Finite Element Method are applied to analyse and solve the problem.

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INTRODUCTION

In many physical science problems it is very important to know the effective properties of composites and/or inhomogeneous materials. When small areas of inhomogeneity are covering all of the material and their volume is very small in comparison with the volume of the material it is very difficult to solve analytical problem. In such situation it is proposed to change such inhomogeneous material with a homogeneous one representing the same properties in a macro scale.

We are studying a case of nanocomposite material built of nanograins of palladium placed in a carbonaceous matrix. In two dimensions a schematic representation of such nanocomposite is presented in Fig. 1 and real TEM image of a fragment of such material is presented in Fig. 2.

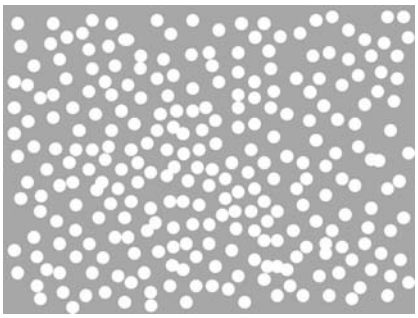

FIGURE 1. A schematic representation of nanocomposite material (grey colour - carbonaceous matrix, white colour - Pd nanograins)

In ideal case such composite material could be seen as periodic structure (see Fig. 3).

Such material is called a two-phase composite material. The problem of conductivity through this material can be explained in many ways. For example some authors [1, 2] suggest that the electrical conductance for the agglomerated metallic particles or the deposited nano-sized thin films depends on the filling factor of the connected and empty spaces. At low filling factor, the particles may be separated individually. The mechanism of conductivity on the thin film can be extensively addressed by a simple tunnelling between localized insulating states that imply a high resistivity

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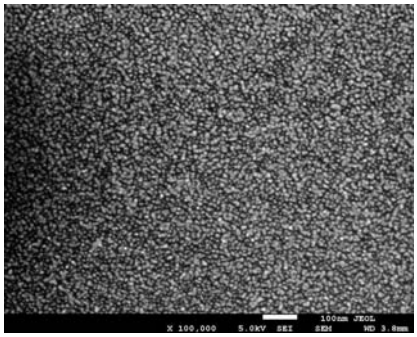

FIGURE 2. TEM image of a fragment of real Pd-carbonaceous nanocomposite material

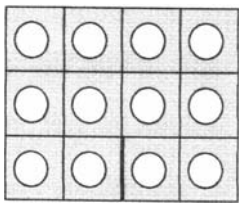

FIGURE 3. Periodic structure of a composite material

at low temperatures. When the filling factor is large enough for the particles to aggregate into clusters, and at least a conducting path is connected from one side of the sample to the other, the sample begins to exhibit current conduction. The resistivity $\rho(R, f.A)$ will be dependent on the particle size R, the filling factor f, and the aggregation factor A, which represents the extent to which the particles are connected with each other to those are discrete. This is a two dimensional case. For two-phase material we can estimate the problem with one-dimensional material and then investigated structure can be represented by a scheme presented in Fig. 4.

FIGURE 4. One dimensional representation of the structure

The key idea behind the physical derivation of the effective electrical conductivity (or resistivity) of a periodic two-phase composite is that we want ultimately to be able to treat the two-phase material as an "equivalent" homogeneous anisotropic one. For concreteness, we shall restrict our discussion to the 1-dimensional case; the n-dimensional case is handled similarly.

Useful technique which allows obtaining accurate results is that of asymptotic homogenization, cf. [3], [4]. A nanowire has a periodic microstructure composed of palladium nanocrystals embedded in a carbonaceous matrix. Our nanowire is a one-dimensional model and the electron flow is described by the one-dimensional diffusion equation. We assume that the nanowire consists of finite number of cells (containing Pd and C) of the length l periodically repeated on the interval $[0,L]$, and Pd nanocrystal has the length λl in each cell, $\lambda \in (0,1)$.

MODEL EQUATION

The charge concentration and the current flow in the nanowire is described by the one-dimensional equation, where u denotes the charge concentration and where $A\colon [0,L] \to \mathbb{R}$ is the electric conductivity of the nanowire,

$$\frac{\partial u}{\partial t}(x,t) = \frac{\partial}{\partial x}\Big(A(x)\frac{\partial u}{\partial x}(x,t)\Big) \qquad (x,t) \in [0,L] \times \mathbb{R}^{+}. \tag{1}$$

This equations can be solved by the separation of variables method. The system has a unique solution under the initial $u(0,x) = u_0$ and boundary $u(t,0) = u_1$, $u(L) = u_L$ conditions.

The microstructure of the nanowire imposes the following form of the space dependent term of the conductivity function

$$A(x) = \sigma_{Pd}(x)\chi_\lambda(x) + \sigma_C(x)(1-\chi_\lambda(x)), \tag{2}$$

where σ_{Pd} and σ_C denote the electric conductivities of palladium and carbonaceous matrix respectively and χ_λ is a characteristic function of the region occupied by the palladium nanocrystals. For simplicity we assume in our model that the conductivity functions σ_{Pd} and σ_C are constants. In the more general setting we can assume that the function σ_{Pd} considered on a single nanocrystal of Pd is defined by some second degree polynomial, whose coefficients should be calculated from the experimental data.

Homogenization - stationary and nonstationary case

At first, let us consider the stationary case and assume that the body is characterized by a periodic microstructure. It means that a large body with a characteristic dimension, say L, consists of a number of periodic cells whose characteristic dimension is l. Let $\frac{l}{L} << 1$; we introduce into our considerations a small parameter ε which is $\varepsilon = l/L$.

The homogenization method ([3, 5, 6, 7]), which we apply to solve the problem, means finding an asymptotic solution of the equation

$$\frac{d}{dx}(A^\varepsilon(x)\frac{du^\varepsilon}{dx}) = f(x). \tag{3}$$

In a periodic setting we write $A^\varepsilon(x) = A(\frac{x}{\varepsilon})$ and we will identify $\frac{x}{\varepsilon} = y$, where y is referred to as a *microscopic variable*, while x is a *macroscopic variable*. So we have $A(\frac{x}{\varepsilon}) = A(y)$, where the function A is periodic with respect to microscopic variable y. In other words, if we have a function $A(y)$ defined on $(0,1)$ we extend the function A to $\mathbb{R}$ by a periodic way, namely $A(y) = A(y+1)$, $\forall\, y \in \mathbb{R}$, for one-dimensional structures.

The method of homogenization consists in the elimination of the microscopic variable by the appropriate averaging or by passing to zero with a small parameter ε. To obtain a macroscopic description of the problem, we apply the following approximation, cf. [7]. We look for a solution of the problem (3) in the form

$$u^\varepsilon(x) = u^0(x) + \varepsilon u^1(x,y), \tag{4}$$

where for $x \in [0,L]$. The term $u^1(x,y)$, is a periodic functions with respect to microvariable $y \in Y = [0,1]$.

Applying the homogenization procedure based on two-scale asymptotic expansion (4) we obtain in 1D case the macroscopic equation, and macroscopic properties of the homogenized material:

$$A^{hom}\frac{d^2u^0}{dx^2} = f \ \text{ in } (0,L), \quad \text{where} \quad A^{hom} = \Big(\int_0^1 \frac{1}{A(y)}\,dy\Big)^{-1}. \tag{5}$$

The solution of the equation (3) exists and it has the following form

$$u^\varepsilon(x) \simeq u^0(x) + \varepsilon u^1(x,y) = u^0(x) + \varepsilon N(y)\frac{du_0(x)}{dx}, \tag{6}$$

where the unknown function $N(y)$, periodic in y is determined by the *local problem*

$$\frac{d}{dy}\left(A(y)\frac{dN(y)}{dy}\right) = -\frac{dA(y)}{dy} \qquad y \in Y. \tag{7}$$

Now let us pass to an one-dimensional time-dependent diffusion problem

$$\frac{\partial u^\varepsilon}{\partial t}(x,t) - \frac{\partial}{\partial x}\left(A(\frac{x}{\varepsilon})\frac{\partial u^\varepsilon}{\partial x}(x,t)\right) = f(x). \tag{8}$$

The equation should be supplemented by proper initial-boundary conditions.

Applying the same procedure as in the stationary problem above, and assuming $u^\varepsilon(x,t) = u^0(x,t) + \varepsilon u^1(x,y,t)$, instead of (4) and considering t as a parameter, we obtain the following homogenized or macroscopic relations

$$\frac{\partial u^0}{\partial t}(x,t) - A^{hom}\frac{\partial^2 u^0}{\partial x^2}(x,t) = f(x). \tag{9}$$

A^{hom} has the same form as previously. The last equation is a fundamental macroscopic relation for our considerations.

NUMERICAL SIMULATIONS

The numerical simulations are performed using the discontinuous Galerkin method. It is applied to solve numerically both problems: original one (1) and homogenized (9) with $f(x) = 0$ for $x \in [0, L]$, which differ only in the definition of the conductivity function. The discontinuous Galerkin method is based on a finite element formulation both in space and time variables.

Let the time interval $I = [0, T]$ be divided into disjoint subintervals I_n of the length Δt and the space interval $\mathscr{L} = [0, L]$ be divided into disjoint subintervals L_k of the length h.

Here we approximate the solution of the equation (1) or (9) by a function $v \in V_h^t$:

$$V_h^t = \{v : I \to V_h : \ \forall t \in I_n \ \ v|_{I_n}(t) = v_n \in V_h \text{ for each } I_n\}, \tag{10}$$

where $V_h = \{w \in C(\mathscr{L}) : w|_{L_k} \text{ is a linear function}\}$.

Let $U^n(x)$ denote the approximation of the function $u(t,x)$ on the time interval I_n. Now we can formulate the method as follows:

For $n = 1, \ldots, N$ find $U^n \in V_h$ such that

$$(U^n - U^{n-1}, v) + \Delta t\, a(U^n, v) = 0 \quad \forall v \in V_h, \tag{11}$$

where $(w, v) = \int_0^L w(x)v(x)\,dx$, $a(w, v) = \int_0^L K(x)\frac{dw}{dx}(x)\frac{dv}{dx}(x)\,dx$ for $w, v \in V_h$ and U^0 is the projection of the initial condition function on the space V_h.

CONCLUSIONS

We performed several numerical experiments to validate the method of homogenization. Calculations were carried out for 5 and 10 Pd-C cells and for corresponding effective material. The results of calculations for the homogenized material are consistent with the results for the cases of heterogeneous body and confirm the usefulness of this type of the averaging method in the considered problem.

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