DESCRIPTION OF EXISTING AND NEW TECHNIQUES FOR ELECTROMAGNETIC CHARACTERIZATION OF DIFFERENT NANOSTRUCTURED METAMATERIALS BASED ON THEIR CHEMICAL AND GEOMETRICAL STRUCTURES AND DOMAINS OF THEIR VALIDITY

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1 Known methods of electromagnetic characterization of metamaterials

The electromagnetic characterization of nanostructured materials can be considered a major part of the emerging field of nanotechnology. The practical importance and industrial interest in these materials demand optimization of several types of properties in these materials. These properties include polarization and magnetization responses, stability of the materials to mechanical, electrical, and constant magnetic fields applied during processing and operation. One of the fundamental goals in this field should be the understanding of the relationships of these properties on the composition, particle size and boundaries variations, defect structure and separation of the residual pores, but in most cases they are not well understood. In classical electrodynamics, the response of a material to electric and magnetic fields is characterized by two fundamental quantities called as effective material parameters: the permittivity ε and the permeability μ. In spite of the advances made, there is still no general agreement on interpretation of the experimental data of these values for nanostructured materials, especially for metamaterials whose volumetric electric and magnetic resonances lie within the frequency range of interest. These quantities depend sensitively on how to define them. Also they depend on how the material is organized at the microscopic level and even for the same material the *effective* material parameters (EMP) can be dependent on the size and shape of the sample. In the last case one speaks about mesoscopic materials.

Traditional effective medium approaches and insights generally are not applicable for metamaterials. Instead, collective electromagnetic behaviors in nanosystems are challenging in terms of both experimental observation and development of theoretical analyzes. In the previous reports we summarized most known approaches to the electromagnetic characterization of nanostructured metamaterials.

The procedures of the characterization of finite thickness metamaterial lattices (layers of metamaterials with a regular inner structure) whose analysis was done in our previous surveys are as follows:

1. EMP are obtained by a direct extraction of ε and μ from plane-wave reflection and transmission $(R-T)$ coefficients of a composite slab, assuming the slab to be effectively continuous and uniform medium. This is the so-called Nicholson-Ross-Weir (NRW) method which had been earlier applied only for the microwave characterization. The NRW method was first applied for nanostructured metamaterials by J.B. Pendry and S. O'Brien (UK, London Imperial College) and D.R. Smith (USA, Duke University).

2. EMP are obtained by an indirect extraction of ε and μ from plane-wave reflection and transmission $(R-T)$ coefficients of a composite slab, assuming the slab to be a 3-layer structure, where all 3 layers are effectively continuous and uniform media. The central layer is characterized by Lorentz's ε_L and μ_L of the bulk medium, and two other layers (so-called Drude transition layers) are characterized by other EMP. EMP of both central layer and Drude layers can be retrieved for a class of MTM called in some papers as Bloch lattices. This method had been introduced by the author of the present overview (Russia, Institute of Fine Mechanics and Optics – Finland, Helsinki University of Technology).

3. EMP for thin MTM layers (1-3 scatterers across the layer) are defined as describing the electric and magnetic response of the layer (considered as at effective artificial surface) unit area. In other words, the electric and magnetic dipole responses are calculated over

the whole layer thickness. The corresponding papers were coauthored by the author of the present review (Finland, Helsinki University of Technology).

4. EMP are obtained from exact simulations of the electromagnetic wave propagation in the lattice using a special procedure of the averaging of microscopic Maxwell equations. The method was introduced for theoretical characterization of metamaterial layers and implied the use of specially derived additional boundary conditions. The method has been suggested and developed by M. Silverinha (Portugal, Coimbra University).

5. First the effective permittivity of a metamaterial layer is introduced through the exact solution of the lattice cell problem. This solution is used to define the so-called homogenization operator which is applied to find the permeability. This purely mathematical and sophisticated method was suggested and developed by D. Felbacq with coauthors (France, University of Toulon).

6. EMP of the infinite metamaterial lattice with plasmonic constituents are calculated taking into account the typical for the plasmon resonance features of the polarization current distribution. The method was suggested by G. Shvets and A. Urzhumov (USA, University of Texas at Austin).

7. EMP are introduced through special line and surface averaging procedures (different procedures for field vectors **E**, **H** and **B**, **D**). As well as in three previous cases, to use this method for the experimental extraction of EMP seems hardly possible, and no corresponding attempts are known. The method belongs to J. B. Pendry.

8. EMP are introduced through refraction index and the wave impedance of a given eigenwave (no matter does the strong spatial dispersion exist in the material or not). The refraction index and the wave impedance are retrieved from theoretical study of the infinite lattice dispersion complemented by the simulations or measurements of the $R-T$ parameters of the finite-thickness lattice[1]. The method was suggested simultaneously and independently by C. Tserkezis (Greece, University of Athens) and by C. Smigaj and B. Gralyak (France, Fresnel Institute, Marseille). The differences between two corresponding works (both of them were briefly reviewed in our previous report) are minor.

9. EMP are introduced by approximate fitting of unknown parameters in Lorentz's dispersion laws for any permittivity and permeability to the results of measurements or simulations of $R-T$ parameters of the layer. Here the metamaterial layer is replaced by an approximately equivalent continuous media whose local EMP are to be found. The method was suggested by T. Driscoll with coauthors (USA, University of California at San Diego and Duke University).

10. EMP of a metamaterial are introduced using the quasi-static approach, i.e. Maxwell Garnett or Bruggeman formulas expressing the permittivity and permeability through individual electric and magnetic polarizabilities of constituent particles. However, individual polarizabilities of particles are recalculated through sheet electric and magnetic impedance of a metamaterial monolayer. These impedances are retrieved through $R-T$

[1] Or scattering coefficients of the layer in the high frequency range where the layer impinged by a plane wave re-radiates several ones.

parameters of the single monolayer. The method belongs to A. Scher and E. Kuester (USA, University of Colorado at Boulder).

The variety of these methods and the absence of any agreement in the scientific community which method is better suitable for given metamaterials made the writing of our reviews be very hard and the responsibility for our recommendations very heavy. We have shown evident shortcomings of all listed methods and outlined their applicability. In more details Method No 2 has been considered as deserving promotion within the framework of the ECONAM project (at least this is the opinion of the author). In the present report one will concentrate on the common restrictions of all these methods resulted from chemical and geometrical peculiarities of nanostructured metamaterials.

2 Restrictions in the electromagnetic characterization of nanostructured metamaterials

2.1 Geometrical restrictions

Metal nanoparticles are the most popular constitutive elements of nanostructured metamaterials operating in the optical frequency range. It is so because the ratio size/wavelength at the plasmon resonance can be very small which creates good presuppositions for the homogenization of a material and, consequently, its description in terms of EMP. However, the minimal ratio size/wavelength is still restricted. This results from an important quantum effect: the weak localization of conduction electrons at the surface of the metal nanoparticles [1, 2]. Due to this restriction macroscopic parameters such as complex permittivity and complex conductivity (usually uniquely related with one another) cannot be introduced in the usual way for particles whose minimal size is less than 5-6 nm [2, 3]. In principle, one still can describe the electromagnetic response of metal particles with sizes with the interval 1-6 nm through complex permittivity or complex conductivity, however these parameters are mesoscopic and can be found only after a special quantum modelling [4]. In any case these parameters do not obey the Drude dispersion law whereas larger metal nanoparticles do [3, 4]. Furthermore, the strong confinement of conductivity electrons at the surface of so small nanoparticles leads to the significant increase of their losses and damages the plasmon resonance. Therefore, so small particles are not so promising for obtaining metamaterials as particles larger than 5-6 nm.

Metal particles with sizes less than 1 nm cannot be described through own permittivity or conductivity and their properties are different from those of samples of bulk metals [5]. Such small ensembles of atoms possess certain regularity but are not yet crystal lattices. These are only embryos of the metallic state. Depending on the host medium such sub-nanoparticles can be attributed to conductors or insulators [6]. Optical properties, especially non-linear ones, such as fluorescence, luminescence, higher harmonics generation, etc. are also mesoscopic and dependent on the background [7]. It is difficult to characterize them theoretically. Of course, in principle one can find dipole polarizabilities of metal sub-nanosized particles, and these polarizabilities are also resonant in the optical range (though their resonance cannot be called as plasmon one). However, the threshold of their non-linearity is strongly lower than that of bigger (crystalline) nanoparticles.

Respectively, it is difficult to retrieve linear EMP of arrays of sub-nanosized metal particles. To ensure the linear regime one needs low fields, however the strong absorption of these field will lead to the very low level of the transmitted field which will hardly allow one to measure the transmission phase. Composites of metal particles with sizes less than 1 nm [5, 6, 7] are exotic metamaterials, for which no methods of electromagnetic characterization are available in the accessible literature. Composites (including lattices) of metal particles whose size is between 1 and 6 nm can be characterized in terms of EMP, however due to strong absorption in such structures it is still difficult to measure the transmission phase in them [8]. Therefore researches working with such composite concentrate on the spectroscopic studies [9]. From spectroscopic data under certain assumption one can find the complex permittivity as it is done in classical optics [11, 12]. The main assumption in this quasi-static characterization procedure is the absence of magnetic properties and of spatial dispersion which opens the door to the use of Kramers-Kronig relations. Another assumption is the absence of Drude transition layers which as it was explained in our previous reports implies the negligible phase shift per unit cell of the composite medium. In [10] one presented a structure in which the touching gold nanoparticles of diameter 2 nm form nanochains of length few tens nm in liquid crystal matrices are not studied even theoretically. Properties of such a nanochain are not yet studied even theoretically. Since the dissipation level in such nanochains has not been estimated, it is not clear (for the instance) can the NRW method or any other phase method be applied with practical accuracy for the electromagnetic characterization of such metamaterials or not.

Notice, that the weak localization of plasmonic electrons makes difficult the description of clusters of metal nanoparticles. It becomes impossible in terms of classical electrodynamics if the distance between metal nanoparticles in a cluster is between 0.01 nm and 1 nm [6]. Then the tunnel effect is strong and the quantum model should be developed for the whole cluster. The description of the cluster in terms of the permittivity is probably possible but is a challenging task. This permittivity will be, of course, strongly mesoscopic [13]. The distance between nanoparticles less than one tenth of Angström is equivalent to their direct contact [5]. Such a nanopair or a nanocluster (e.g. a nanochain mentioned above) can be considered as a complex shape nanoparticle, and its internal complex permittivity can be introduced in a quasi-classical way [14, 15].

Semiconductor nanoparticles can be described through internal complex permittivity (that of the corresponding bulk medium) only in the amorphous state. In the crystal state a semiconductor nanoparticle is an Ekimov-Onushchenko quantum dot [16] and the description in terms of the internal permittivity becomes difficult. First, permittivity as such cannot describe the size-sensitive quantization (the basic physical effect responsible for the coherent light generation and fluorescence in quantum dots). Therefore an attempt to describe an Ekimov-Onushchenko quantum dot excited by the light at its eigenfrequencies or excited by the intensive light in terms of the permittivity would be completely inadequate [17]. This assertion refers also to the permittivity with the inverse sign of the imaginary part as it is adopted for the active medium in the laser theory, since the radiation of a quantum dot has totally different nature. Second, the non-linearity of a quantum dot in the whole optical range is very strong and can hardly be neglected even if the light intensity is not sufficient for pumping and the frequencies are far from the nanocrystal eigenfrequencies [18]. Arrays of semiconductor nanocrystals cannot be then characterized in terms of bulk EMP.

2.2 Chemical restrictions

The methods of nanofabrication split to physical and chemical ones [19]. There are also combined physical-chemical nanotechnologies, for example nano-imprint lithography including plasma-enhanced chemical vapor deposition [20]. Chemical technologies are mainly associated with self-assembly of nanostructures.

The typical consequence of the self-assembly of nanoparticle arrays is the adhesion of molecules (e.g. organic ones as in [10]) on the particles surface. This process is important for the robustness of nanochains obtained in [10]. However, the mesosopic shield formed by these molecules changes drastically the electromagnetic properties of nanoparticles. For example, it leads to a shift of the plasmon resonance frequency and to a reduction of the resonance magnitude [23]. This effect is significant for organic molecules.

For semiconducting nanocrystals the covering with organic or hydrophobic molecules is very important since preserves the quality of the crystal. Otherwise the regularity of the crystal lattice is very soon destroyed by chemically active molecules coming from the host medium [21]. The alternative method to preserve the Ekimov-Onushchenko quantum dots is the immerse them into a chemically inert medium, for example grow them inside a polymer microsphere [22].

3 Conclusions

The full theoretical electromagnetic characterization of nanostructured metamaterials in terms of EMP implies, obviously, that the permittivity of their constituents have the unambiguous meaning of local complex material parameter. In other words, the nanoparticle should be a sample of a bulk medium which should be characterized by bulk permittivity. This permittivity can be found from quantum modelling, however once it is found the characterization of a nanoparticle is a subject of classical electrodynamics. However, this is not always so. The most important restriction is related with the size of metal nanoparticles and the distance between them. Both of them should not be less than one nanometer, otherwise it is practically impossible to theoretically calculate the permittivity and permeability of a metamaterial with needed accuracy. For metamaterials based on nanoparticles with size between 1 and 6 nm we can in principle calculate these parameters, however, it is a very difficult task including both quantum modelling of the nanoparticle polarizability and homogenization procedure referring to the classical electrodynamics.

As to the extraction of material parameters for metamaterial with sub-nanosized inclusions, it is in principle possible. However due to the low threshold of nonlinearity and high losses in such nanostructures, practical possibility to extract their complex material parameters is for the instance doubtful. For metamaterials with inclusions of size 1-6 nm it is possible but is a challenging task, and no reliable results of such an extraction are known in the available literature.

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