Nanostructured Metamaterials

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Nanostructured Metamaterials

Exchange between experts in electromagnetics and material science

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Foreword

It is my pleasure to present the publication *Nanostructured Metamaterials – Exchange between experts in electromagnetics and material science.*

Metamaterials are one of the new discoveries of the last decade. They present exceptional properties, dominated by their geometrical structure and this publication will allow the reader to learn more about these ‘artificial’ materials and about their interesting (and yet unexploited) potential applications. The design and manufacturing of such materials has been made possible thanks to progress made in both materials science and electrical engineering. With the help of bottom-up manufacturing techniques, a large number of micrometer scale designs can now being scaled down to nanometer scale and therefore completely new solutions can be investigated. The tools needed to create metamaterials include modelling, geometry and property design, bottom-up manufacturing and structural and electron microscopy characterization at the atomic- and nano-scale. By controlling the reactivity of atoms and molecules to create inclusions and by controlling the positioning of these nano-inclusions, nanostructured metamaterials can be realised with interesting fields of applications where waves are involved, such as ICT applications and noise reduction.

The 7th Framework Programme for Research (FP7), the European instrument for funding scientific research and technological development up to 2013, is targeting synergy between traditional scientific disciplines and this resulted in fostering four bottom-up manufacturing projects and a coordinated action on characterisation of metamaterials. Their total budget is EUR 20M with a FP7 contribution of EUR 15M. A workshop has been dedicated to metamaterials in December 2009 and its main outcome is presented in this publication.

So often materials are the bottleneck or, positively, the enabler for technological progress resulting in novel and sustainable products made available to all citizens. Within the larger family of industrial technologies, material science and engineering show paramount potential to allow such progress with benefits for industry and the society as a whole.

Metamaterials had a current market size of EUR 133 million in 2007 and are expected to grow to EUR 2.1 billion in 2013 (1), a compound annual growth rate (CAGR) of 26.5 %. I hope that the interdisciplinary and creative collaboration between material scientists and engineers together with ICT researchers will support this growth by allowing secure understanding and rapid progress in the innovative field of metamaterials, as this would allow exploiting their industrial (and later on, commercial) potential to the benefit of European industrial growth and the creation of jobs.

Renzo Tomellini
European Commission
Head of Unit ‘Value-added Materials’

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Introduction

Recently there has been great interest in developing materials, which could control the flow of electromagnetic waves (e.g. light) in unprecedented ways. Clever engineering has provided us means to create artificial materials with responses that are difficult to find in naturally appearing and earlier-known, classical materials. The design relies on inclusions and the new properties emerge due to specific interactions with electromagnetic fields. These designs can be scaled down and realised with nanotechnology. Such metamaterials can really be viewed as ‘effectively continuous materials’!

Metamaterials are composed of their elements in the same sense as matter consists of atoms (see Fig. 1). The structural elements themselves are made of conventional materials, i.e., finally, of normal atoms. Accordingly, metamaterial represents the next level of structural organization of matter, hence the prefix ‘meta’.

The structural elements or inclusions are small building blocks or unit cells (‘artificial molecules’) in large 1D, 2D or 3D arrays. The possibilities of combining various inclusion shapes, such as spheres, ellipses, helices, bent wires, and even various small electronic components are infinite and so are the possibilities for the artificial material behaviour. Many examples have been presented in the electronic engineering and physical literature.

There are many definitions of metamaterials, which highlight various aspects of this concept. In this booklet we assume metamaterials are an arrangement of artificial structural elements, designed to achieve advantageous and/or unusual (electromagnetic) properties.

Both effective continuous behaviour shown for wavelengths larger than the periodicity of the inclusions (low frequencies) and band gap behaviour for short wavelengths (high frequencies) are discussed.

Figure 1. Metamaterials with the many options for inclusions.
Metamaterials are often associated with negative refraction and this property has gained substantial attention because of its potential for cloaking invisibility devices and microscopy with super-resolution. In this booklet we do not restrict ourselves to negative refraction indices, but we include metamaterials with superior properties as compared to what can be found in nature. The expansion of previously allowed regions of material parameter values could e.g. result in better conductors or more ideal insulators.

The application possibilities of metamaterials are found in industrial sectors like Information and Communication Technologies, Space and Security & Defense, but also applications in Health, Energy and Environmental areas are foreseen. Examples of devices that have been realised during the past years are

- Sensors
- Superlensing
- Cloaking
- Light emitting diodes/
cavities for low-threshold lasers

and these were based on controlling the wave propagation and used dynamic, re-configurable and tunable materials. This technology will be driven further towards the market place by metamaterials that give added value over and above current approaches.

**Characterisation**

Metamaterial properties are not only determined by their material parameters, shape, and concentration of the constituent inclusions and due to this increased complexity characterisation has become a science in itself.

Effective parameters can be extracted from numerically simulated or experimentally measured reflection and transmission coefficients. Traditionally, these effective parameters are the phenomenological material parameters permittivity and permeability. In the case for natural materials these parameters give a good description of the behaviour, but metamaterials can not always be characterised this way. Many metamaterials need more parameters for their characterisation and in general, the validity of material parameters is to be questioned.

The traditional phenomenological material parameters permittivity and permeability are not fundamental physical constants, but they are engineering constants expressing an assumed proportionality. One of the future challenges for characterisation research is to establish the validity limits of material parameters and to develop means to properly describe media that are ‘beyond limits’.

**Manufacturing**

Up to today, metamaterials have mostly been manufactured by top down technologies like electron beam lithography. These techniques have the disadvantage of being quite expensive and slow and obtaining large areas and regular (3D) arrangements is difficult.

The potential of nanotechnology and material science to realise designs at a very small scale offers a very promising alternative. Material Science and Technologies currently under investigation to fabricate metamaterials are self-assembly and hybrid chemistry approaches.

**EC FP7 Call and the selected projects**

The NMP Programme of the EC launched the call NMP-2008-2.2-2 Nanostructured meta-materials to develop and demonstrate the potential of bottom-up technologies in Material Science and Technology for the preparation of nanostructured metamaterials.

The call allowed a wide interpretation of the concept ‘metamaterials’, where these materials with nanostructured inclusions would either mimick properties existing in nature with higher efficiency or exhibit radically new properties. The first type could e.g. show enhancement of magnetic responses in composites made out of non-magnetic components or and/or artificial chirality or better conductors, more ideal insulators, or larger values for other material parameters. The second type of metamaterials would exhibit radically new properties like negative or extreme electric permittivity and/or permeability.

As a result of the call 4 projects were selected to develop materials S&T technologies for metamaterials:
Introduction

- MAGNONICS developing protein-based materials for EM and spinwave metamaterials, both band gap and effectively continuous metamaterials will be studied;
- NIM-NIL developing graphene-based materials for negative refraction applications;
- METACHEM developing self-assembly and hybrid chemistry technologies for artificial optical magnetic and dielectric properties, optical left-handed materials, near-zero permittivity/permeability, negative index materials and low-loss plasmonic structures;
- NANOGOLD developing gold-chemistry for band-gap and a strong negative permeability metamaterials with reduced losses.

Applications of Metamaterials

Biosensors
Metamaterials can be used to provide more sensitive guiding modes (based on plasmon-mediated interaction between the inclusions which shows resonant excitation conditions). Surface plasmons occur at a metal/dielectric interface and are extremely sensitive to the refractive index of the dielectric medium within the penetration depth of the evanescent field. The metamaterial inclusions can be functionalised with receptors on their surface. If the matrix consists of nanoporous material it allows analytes to reach the receptor and the refractive index will be changed upon binding. The reflection spectrum depends on this refractive index.

Superlens
A superlens (or perfect lens) is a lens, which uses metamaterials to go beyond the diffraction limit. The diffraction limit is an inherent limitation in conventional optical devices or lenses. A lens consisting of a negative index metamaterial could compensate for wave decay and could reconstruct images in the near field. In addition, both propagating and evanescent waves contribute to the resolution of the image and resolution underneath the diffraction limit will be possible.

Cloaking
A cloaking device is an advanced stealth technology that causes an object to be partially or wholly invisible to parts of the electromagnetic (EM) spectrum (at least one wavelength of EM emissions). Scientists are using metamaterials to bend light around an object.

Tags to store and process information
A remote detection via high-frequency electromagnetic fields will be possible due to the collective response of magnonic crystals at elevated frequencies.

Exchange Workshop for new FP7 projects on metamaterials
In each of these projects there are materials scientists and electromagnetic engineers at work, as the field of nanostructured metamaterials requires a merge of the electronic engineering and material science. It is clear that at this stage both communities should work together, and the first step is mutual education of specialists in these fields. To this end a workshop was held in Brussels on December 9-11, 2009. The workshop was organized by a FP7 Coordination Support Action (CSA) project called ECONAM providing support on characterisation to the NMP field. Also the Virtual Institute for Artificial Electromagnetic Materials and Metamaterials called ‘Metamorphose VI AISBL’ contributed to the workshop.

The workshop combined tutorial lectures, overviews of the state of the art, and interactive discussions on design, synthesis, manufacture, experimental characterization, and understanding of electromagnetic properties of metamaterials. All this information we would like to share with you in this booklet. We hope this information will find widespread dissemination and use.

Dr Anne F. de Baas
Programme Officer
DG Research NMP Programme
Value-Added Materials
\[
\text{Re}[\chi(\omega)] = -\frac{2}{\pi} \text{PV} \int_{0}^{\infty} \frac{\text{Im}[\chi(\omega')] \omega'}{\omega'^2 - \omega^2} d\omega'
\]

\[
(\omega)] = -\frac{2}{\pi} \text{PV} \int_{0}^{\infty} \frac{\text{Im}[\chi(\omega')] \omega'}{\omega'^2 - \omega^2} d\omega'
\]

\[
= \varepsilon_0 \sum_{j=1,2} \int_{-\infty}^{t} R_{ij}(r, t-t') E_j
\]

\[
P(r, t) = \varepsilon_0 \int_{-\infty}^{t} \]
Chapter 1

Theory

\[ \int \delta (\mathbf{r}, t') dt' \]

\[ R(\mathbf{r}, t - t')E(\mathbf{r}, t') dt' \]
Chapter 1: Basic theory of nanostructured metamaterials

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Introduction

In this brochure we would like to present interesting aspects of metamaterials for material scientists. We will try to explain everything, but of course we have to assume a certain background in basic physics. To help the reader we have assembled descriptions of basic concepts in annex in Chapter 1.9.

1.1 Governing equations describing electromagnetic behaviour of materials

Artificial electromagnetic materials, often called metamaterials, show their properties when exposed to an electromagnetic field to which they provide peculiar responses. Electrical, microwave, and optical engineers rely on electromagnetic field theory to analyse and to predict this behaviour. To familiarize the reader with this branch of physics, we provide below a short introduction into electromagnetic wave theory and refer to relevant textbooks.

Maxwell’s equations in the time domain

All (classical) electromagnetic phenomena can be described by Maxwell’s equations. They were first formulated by James Clerk Maxwell in the 1860’s. At their heart they relate electric and magnetic field quantities [Maxwell], [Jackson], [Born]. Although various formulations exist, expressed in terms of partial differential equations they read as:

\[ \nabla \times \mathbf{E}(\mathbf{r}, t) = -\frac{\partial \mathbf{B}(\mathbf{r}, t)}{\partial t} \]  \hspace{1cm} (1)

\[ \nabla \times \mathbf{H}(\mathbf{r}, t) = \frac{\partial \mathbf{D}(\mathbf{r}, t)}{\partial t} + \mathbf{J}(\mathbf{r}, t). \]  \hspace{1cm} (2)

\[ \nabla \cdot \mathbf{D}(\mathbf{r}, t) = \rho(\mathbf{r}, t). \]  \hspace{1cm} (3)

\[ \nabla \cdot \mathbf{B}(\mathbf{r}, t) = 0. \]  \hspace{1cm} (4)

All quantities are functions of space \((\mathbf{r})\) and time \((t)\), and the spatial and temporal differentiations are denoted as \(\nabla\) and \(\frac{\partial}{\partial t}\). The quantities in these equations and their units in the SI system are the following: \(\mathbf{E}\) the electric field vector \([\text{V/m}]\), \(\mathbf{H}\) the magnetic field vector \([\text{A/m}]\), \(\mathbf{D}\) the electric flux density (displacement) vector \([\text{As/m}^2]\), \(\mathbf{B}\) the magnetic flux density (displacement) vector \([\text{Vs/m}^2\text{ or tesla (T)}]\), \(\mathbf{J}\) the current density

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vector \([A/m^2]\), and \(\rho\) the scalar charge density \([As/m^2]\). Since all quantities are physical and observable, they are real valued.

In a general case, these equations are underdetermined. Knowledge is required about how the electromagnetic field quantities \(E\) and \(H\) in a material result in electric and magnetic flux densities, \(D\) and \(B\). Therefore, to fully describe the interaction of electromagnetic fields, including light, with matter, Maxwell’s equations have to be supplemented by so-called constitutive relations. They relate the flux densities to the fields and both \(D\) and \(B\) may depend both on the electric and the magnetic field \(E\) and \(H\), respectively:

\[
D = D(E, H) \quad \text{and} \quad B = B(E, H).
\]  

Here the functional dependency is dictated by the nature of the material in which the fields exist and it may be rather complicated, especially in case of certain metamaterial types. In vacuum, the constitutive relations become trivial due to the absence of any matter and read as

\[
D(r,t) = \varepsilon_0 E(r,t) \quad \text{and} \quad B(r,t) = \mu_0 H(r,t) \tag{6}
\]

with the free-space permittivity \(\varepsilon_0\) and permeability \(\mu_0\) which have the values

\[
\varepsilon_0 = \frac{1}{\varepsilon^2 \mu_0} \approx 8.854 \times 10^{-12} \text{ As/Vm}, \tag{7}
\]

\[
\mu_0 = 4\pi \times 10^{-7} \text{ H/m}. \tag{8}
\]

The parameter \(c\) appearing above is the speed of light in vacuum \((c=299792458 \text{ m/s})\). Any contribution to the fluxes that arises from the polarisation of the matter is then usually included as electric polarisation \(P(r,t)\) and magnetization \(M(r,t)\). The constitutive relations therefore read as

\[
D(r,t) = \varepsilon_0 E(r,t) + P(r,t) \tag{9}
\]

\[
B(r,t) = \mu_0 (H(r,t) + M(r,t)),
\]

where \(P(r,t)\) and \(M(r,t)\) depend again explicitly on the electric and the magnetic field.

**Maxwell’s equations in the frequency domain**

Treating electromagnetic field solutions for given frequencies, can best be done with complex vector fields. Let us consider the case when all fields oscillate harmonically in time with an angular frequency denoted here as \(\omega\). Then by assuming the time-dependence to be \(\text{exp}(j\omega t)\), the time differentiation becomes an algebraic multiplication by \(j\omega\) and, since all fields share this time-dependence, it can be stripped and the equations simplify to:

\[
\nabla \times E(r) = -j\omega B(r), \tag{10}
\]

\[
\nabla \times H(r) = j\omega D(r) + J(r), \tag{11}
\]

\[
\nabla \cdot D(r) = \rho(r), \tag{12}
\]

\[
\nabla \cdot B(r) = 0. \tag{13}
\]
Note that the price to be paid is that these fields (which are now independent of time but depend instead on the frequency) are complex-valued. The real-valued time-dependent fields which are physical observable quantities can be calculated from

\[ E(r, t) = \text{Re}\{E(r)e^{i\omega t}\} . \]  

(14)

The notation of \( j \) as the imaginary unit is the convention common in electrical engineering; in physical science also \( i \) is often used. Note, however, that nearly always when this latter tradition is followed, the time-dependence for complex vectors is assumed to be \( \exp(-i\omega t) \). Hence, the sign of the imaginary parts change when moving from one notation to the other which causes often difficulties in interpreting the dissipative character (sign of the imaginary part of material parameters) of metamaterials. In this text we use the convention (14).

**Temporal dispersion**

The dielectric response in materials is due to charge separation mechanisms which may have various origins and which take different amount of time to develop and any response from matter may strongly depend on the frequency of the electromagnetic field. E.g. electronic polarisation is more sensitive to higher frequencies than ionic polarisation, and in metamaterials that are made of macroscopic artificial molecules, the response may be very strong in the microwave range. This phenomenon is called temporal dispersion. In consequence, the polarisation at an instant \( t \) is written as a convolution over all past events. Please note that future events will not affect the polarisation, a property usually connected to causality. By assuming for the moment a linear (the flux densities depend only linearly on the fields) and a local response of the medium (the flux at point \( r \) is only induced by the field at the same spatial position), and stationary (material properties do not change in time), the constitutive relation can be expressed as a convolution with a response function \( R(r, t - t') \) being a tensor. This relation for its components \( R_{ij} \) is given by

\[ P_i(r, t) = \varepsilon_0 \sum_{j=1,2,3} \int_{-\infty}^{t} R_{ij}(r, r - t')E_j(r, t')dt'. \]  

(15)

For an isotropic medium the equation even reduces to:

\[ P(r, t) = \varepsilon_0 \int_{-\infty}^{t} R(r, r - t')E(r, t')dt'. \]  

(16)

It has to be stressed that any response of the medium is fully expressed by this response function. Lifting any assumptions as formulated above, complicates the functional dependency but will not lead to substantial modifications of the functional relations. If e.g. the assumption on the locality would not hold anymore, the convolution needs to be taken over the entire spatial domain. When the assumption on the linear response is not valid, higher-order response functions need to be considered, which are multiplied by squares or cubes of the electric or magnetic field. Although written here only for the electric polarisation, dual expressions exist for the magnetization response of natural magnetics.

The description of the induced polarisation in the time domain is seemingly complicated and from a practical point of view not very handy. As the equation is a convolution in the time domain, the equation is however reduced to some simple algebraic multiplication in the frequency domain. Therefore, by Fourier transforming all quantities of the above equation into the frequency domain we obtain:

\[ P(r, \omega) = \varepsilon_0 \chi_e(r, \omega)E(r, \omega) \]

and

\[ M(r, \omega) = \chi_m(r, \omega)H(r, \omega) \]  

(17)
where the electric and magnetic susceptibilities $\chi_{e,m}(r,\omega)$ (pronounced chi) are defined as

$$\chi_{e,m}(r,\omega) = \int_{-\infty}^{\infty} R_{e,m}(r,\tau)e^{i\omega\tau}d\tau$$  \hspace{1cm} (18)

The fact that the susceptibility is a function of frequency $\chi(\omega)$ expresses that the medium has ‘memory’; in other words, the polarisation density is not only proportional to the instantaneous field amplitude but also depends on its past values.

The temporal dispersion also brings about losses expressed by the imaginary parts. Both the real and imaginary parts of $\chi(\omega)$ are functions of the frequency. It is important to note that there is a rigorous connection between the frequency behaviour of the real and imaginary parts given by the basic physical principle of causality. This principle expresses that the polarisation response of a medium to an electric excitation cannot precede its cause. This principle was above explicitly expressed by taking the convolution in the time domain only over past events. From the principle of causality the Kramers–Kronig relations follow. These have to be fulfilled for the real and imaginary parts of the susceptibility function [Landau]

$$\text{Re}[\chi(\omega)] = \frac{2}{\pi} \text{PV} \int_{0}^{\infty} \frac{\text{Im}[\chi(\omega')]\omega'}{\omega^2 - \omega'^2} d\omega'$$  \hspace{1cm} (19)

$$\text{Im}[\chi(\omega)] = \frac{2\omega}{\pi} \text{PV} \int_{0}^{\infty} \frac{\text{Re}[\chi(\omega')]d\omega'}.\text{PV}$$  \hspace{1cm} (20)

Here PV stands for the principal value part, which means that in the integration, the singular point $\omega' = \omega$ is symmetrically excluded. These relations, connected to the Hilbert transform, are useful in the analysis of the dispersive properties of materials.

(Spatial dispersion will be discussed in Chapter 1.4)

**Constitutive relations**

The functional dependency of the constitutive relations in the frequency domain may have arbitrary higher order terms whereas each of them has a particular meaning. By allowing also electro-magnetic coupling and by allowing also for a static contribution to the polarisation of the materials, we will obtain constitutive relations such as

$$P(E,H) = P_s + \xi E_{0,\chi_e}(\omega)E + \xi'(\omega)H + \beta_H(\omega)HH + \gamma_e(\omega)HE + \ldots$$

$$M(E,H) = M_s + \xi_{0,\chi_m}(\omega)H + \xi'(\omega)E + \beta_m(\omega)EH + \gamma_m(\omega)EE + \ldots$$  \hspace{1cm} (21)

Here, $P_s$ and $M_s$ are electric polarisation and magnetisation which exist in the absence of external (high-frequency) fields. Such response can be observed in, e.g., in ferroic and multi-ferroic materials. $\chi_e$ and $\chi_m$ are electric and magnetic susceptibilities as introduced above. Tensors $\xi$ and $\xi'$ (pronounced ksi or ksaj and zeta, resp.) express the induction of electric polarisation by a magnetic field or magnetisation by an electric field, which is called the linear magneto-electric effect. Higher order terms are tensor products. Today a lot of research is done to understand magneto-electric effect found in several oxide materials as well as in reciprocal bi-anisotropic materials and metamaterials. Although higher order terms appear in principle in these equations, for most relevant materials it is fully sufficient to consider only a few terms of the expansion above. Then, only some frequency dependent constants appear in the constitutive relations as proportionality coefficients which are usually taken as material constants.
The constitutive relations are essential to find solutions to Maxwell’s equations. They provide a link between the micro- or nanostructure of a fabricated metamaterial, that may be composed of arbitrary complex shaped unit cells, and an electromagnetic material with particular properties in which an ensemble of well documented physical phenomena can be observed. Obtaining the largest possible degree of freedom over these material parameters may be formulated as one of the primary goals in the field of metamaterials research.

**Description of the behaviour of the metamaterial**

Analysis of the electromagnetic behaviour of metamaterials usually starts from the constitutive relations model for a particular design of a metamaterial. Note that this step is far from trivial and in many cases metamaterials cannot be modelled by conventional material parameters [Menzel]. Next, we can solve Maxwell’s equations equipped with the appropriate constitutive relations for an infinite space filled with this metamaterial in the absence of sources and determine all the eigenwaves that can exist in the medium. By enforcing appropriate boundary conditions (in simple cases of weak or negligible spatial dispersion, continuity of the tangential electric and magnetic field components), the amplitudes of these eigenmodes are found for a finite-size sample of a given shape, and the field inside the metamaterial sample is expressed as superposition of eigenmodes. It has to be stressed that this superposition can be expressed in the temporal domain if finite temporal pulses are used to illuminate the metamaterial, or in the frequency domain, if the finite spatial beams are used to illuminate it. Simultaneously, the amplitudes of the eigenmodes used to decompose the reflected field are obtained, and so a solution to the entire problem is found.

**1.2 Spin wave theory underpinning magnonic metamaterials**

Magnonic metamaterials consist of magnetic structures possessing desired properties with respect to the spin wave propagation and confined spin wave resonances leading to specific values of permeability in the desired frequency range. Here we will give an introduction to the study of propagating and confined spin waves in 2D and 3D magnetic structures.

Most of current research in metamaterials mainly concerns the design of ‘magnetic’ resonances using non-magnetic materials. In the literature, one can also find a number of attempts to exploit uniform magnetic resonances in naturally magnetic materials, e.g. ferromagnets [Belov2002] and antiferromagnets [Tarkhanyan].

Magnetic particles can interact in two ways: via magneto-dipole field (no ‘magnetic connection’ between particles required) and via exchange field (much stronger; ‘magnetic connection’ between particles required). Waves with larger wavenumbers for which the exchange interaction starts to play a role are called exchange spin waves. The quantum approach deals with magnons, and hence this field is also called Magnonics. This exchange interaction modifies the resonance, and thereby the effective properties. One can also think about metamaterials consisting of artificial molecules rather than artificial atoms (could be said to be ‘meta-meta-materials’). On the ground, these are arrays of particles with more than one particle in the unit cell, with particles within each unit cell interacting among themselves.

The physics of magnetisation dynamics (‘spin waves’) in magnetic nano- and micro-structures is very complex, and therefore, there should be rich opportunities to design such artificial magnetic structures so as to enhance/tailor their resonance to nearly uniform magnetic fields as required for the metamaterials
design. The very fact that spin waves confined in magnetic nanostructures have been successfully studied by techniques employing excitation by uniform ac magnetic fields [Kruglyak2010] shows that this approach is feasible.

Magnetic metamaterials respond to electromagnetic waves with spin waves. Spin waves can be excited by and therefore interact with the magnetic field of electromagnetic waves. Spin waves play a role in the reflection and transmission of an electromagnetic wave and hence in the permeability because whenever the frequency of an electromagnetic wave coincides with the resonant frequency of a spin wave confined in a nano-particle AND the spin wave is ‘responsive’ to uniform (or nearly uniform – note that the electromagnetic wavelength is much greater than that of the spin wave) magnetic field of the electromagnetic wave, there is a resonance in the permeability – a so called ‘spin-wave resonance’. In addition, magnonic metamaterials can be designed to react to spin waves as the incident waves.

1.3 Bandgap and effectively continuous metamaterials

Waves (excitations) show different dynamics depending on whether they have wavelengths comparable to or much greater than the characteristic size of the building blocks (unit cells or inclusions) forming artificial or natural materials. The former case is associated with studies of artificial ‘band gap structures’, e.g., photonic, plasmonic, phononic, and magnonic crystals, and some authors include these materials in the definition of metamaterials, while others do not. The latter case (waves with wavelengths much greater than the characteristic size of the building blocks) are the focus of metamaterials science as they show effectively continuous properties and can without any debate be called ‘materials’.

Bandgap materials

Materials with artificial periodic modulation of the refractive index with periodicity comparable to the wavelength of electromagnetic waves in the visible range are known as photonic band gap structures. In analogy, periodical structures designed for the microwave frequency range are called electromagnetic bandgap structures. Magnetic materials with periodically modulated properties show that a tailored spin-wave band structure consisting of bands of allowed magnonic states and band gaps. This class of artificial bandgap materials is called magnonic crystals.

Note that spin waves can be also considered as a branch of electromagnetic waves in magnetic media, as they are a solution of coupled Maxwell and Landau-Lifshitz equations. The solution has two branches. The higher frequency one is ‘light like’, while the low frequency is ‘spin wave like’. When the ‘distance’ between the branches is large enough, one can talk about uncoupled light and spin waves, and each can be derived in the approximation of absence of the other. However, spin waves have usually much smaller wavelengths than the ‘usual’ electromagnetic waves at the same frequency.

Electronic bandgap materials are semiconductor crystals exhibiting a periodic potential which affects the electron motion by defining allowed and forbidden electronic energy bands. The concept can be further extended to sound waves (phonons) in periodical structures, as well as waves of other physical nature. Sound waves in piezoelectrics are generated by electromagnetic fields, which makes a connection to the science of artificial electromagnetic materials.
In order to operate, bandgap materials need material contrast in each unit cell: a combination of two different dielectrics or dielectric and metal, for example. Using such artificial structures, it is possible to enable propagation of light in particular directions or to localize it in chosen channels or zones upon introducing defects, or even completely prohibit propagation of light at the frequencies within a bandgap.

These bandgap materials are said to be strongly spatially dispersive (see Chapter 1.4.2) as non-local effects play a decisive role. This field of bandgap materials is a part of photonics and magnonics and while the photonics part is well researched [Joannopoulos], [Sakoda], the magnonics part is an innovative field under rapid development. This part of metamaterial science is however not elaborated in this brochure. But of course the same structures will behave as effectively continuous materials for larger wavelengths and the novel manufacturing technologies discussed in this booklet have equal potential for this class of materials.

**Effectively continuous media**

If the inclusions are small compared to the wavelength (typically from $\lambda/10$ to $\lambda/1000$), the theory of weak spatial dispersion applies. Here, the local effects dominate, and non-local effects can be in many cases described introducing chirality (bi-anisotropy) coefficients and the effective permeability parameter. In this case the medium is considered as an effective continuum and modelling of complex media is then done by homogenisation (averaging) of the microscopic Maxwell equations to derive material properties. This case will be further elaborated below.

### 1.4 Effectively continuous materials

#### 1.4.1 Classes of effectively continuous materials

**Isotropic media**

The simplest material response in terms of the constitutive relations (5) is the one where there is only a scalar relating the field and displacement vectors:

$$
\mathbf{D} = \varepsilon \mathbf{E}, \quad \mathbf{B} = \mu \mathbf{H},
$$

(22)

where $\varepsilon$ is the permittivity and $\mu$ is the permeability of the medium. This means that the medium is isotropic (the response does not depend on the direction of the field vector).

Let us look for a plane wave solution of Maxwell’s equations in a homogeneous (the material parameters $\varepsilon$ and $\mu$ are constant in space scalars, and there are no sources ($\mathbf{J} = 0$, $\rho = 0$). From (10)-(13) we can write

$$
\nabla^2 \mathbf{E}(\mathbf{r}) + \omega^2 \mu \varepsilon \mathbf{E}(\mathbf{r}) = 0.
$$

(23)

For a plane wave, we can choose a Cartesian coordinate system so that the fields depend only on one coordinate, say $z$. This leaves us with

$$
\frac{d}{dz} \mathbf{E}(z) + \omega^2 \mu \varepsilon \mathbf{E}(z) = 0
$$

(24)

and with the definition $k = \omega \sqrt{\mu \varepsilon}$ one can write the two solutions

$$
\mathbf{E}(\mathbf{r}) = E_1 e^{-jkz} \quad \text{and} \quad \mathbf{E}(\mathbf{r}) = E_2 e^{+jkz}
$$

(25)
Using (14), one can see that the first solution is a wave propagating in the positive $z$-direction, and the second one propagates in the negative $z$-direction.

Note that in (25), $E_1$ and $E_2$ are constant vectors that determine the amplitude and polarisation of the electric field. For example, a real vector $E_1$ means a linearly polarised field, and if $E_2$ is a complex vector, whose real and imaginary parts are equal in length and perpendicular to each other, the polarisation is circular. The electric field has to be free of divergence, as required by (12) from here we see that vectors $E_1$ and $E_2$ are orthogonal to the axis $z$. For this reason these wave solutions are called **transverse** electromagnetic waves.

If the medium is lossless, the material parameters $\varepsilon$ and $\mu$ are real numbers. However, $k$ may be either real or purely imaginary, in case if the two material parameters have different signs. If $k$ is real, the waves in (25) only suffer phase change, and the wavelength $\lambda_{ph}$ in the $z$-direction after which the phase attains the same value is given by the condition $k\lambda_{ph} = 2\pi$, or in terms of the material parameters,

$$\lambda_{ph} = \frac{2\pi}{\omega\sqrt{\mu\varepsilon}} = \frac{2\pi c}{\omega n}.$$  \hfill (26)

Here the refractive index $n$ is defined by the latter equality. Hence, the phase wavelength becomes shorter for higher frequencies, and also for materials with higher permittivity and permeability. The notions of the phase and group velocities are discussed in Annex II.

On the other hand, dielectric (magnetic) losses mean that the permittivity (permeability) is complex. Then also $k$ becomes complex, and its imaginary part causes the amplitude of the propagating wave to decay exponentially, which can be calculated from (25). If no dissipation occurs, the medium is lossless.

In Chapter 1.7 examples of metamaterial geometries of isotropic artificial dielectrics and magnetics will be given.

**Materials described only by permittivity**

First we will consider materials that can be described by the permittivity $\varepsilon$ only. If we say that a material can be described by permittivity only, we mean that the material has a permeability equal to that of vacuum and thus that the relation between $B$ and $H$ is $B = \mu_0 H$. Most common examples of such natural materials are dielectrics, conductors and piezoelectric materials.

> **Dielectrics**

In dielectrics the incident electromagnetic field moves the charges and in doing so, it induces a polarisation of the medium (See also the Annex). The induced polarisation is a complex function depending on the electric field but can be expanded into a Taylor series. Assuming the electric field to be small, only a few expansion terms need to be retained.

In the realm of linear electromagnetic and optics, the Taylor series can be truncated for dielectric materials and in the first approximation we get

$$D = \varepsilon_0 E + P.$$ \hfill (27)

The polarisation $P$ expresses the extent to which the incident EM field is capable of separating the positive and negative charges in the material. For each type of material $P$ has a specific relation to $E$. 
A bound electron in a dielectric would bounce forwards and backwards with the oscillating incident field as its driving force and this would be expressed as a harmonic oscillation ($f = \omega/2\pi$ and $\lambda = c/f$). The polarisation being the product of unit-volume displaced charge and distance would then also oscillate harmonically. For each frequency the response will be different and this is expressed as

$$P(\omega) = \varepsilon_0 \chi(\omega) E(\omega).$$  \hspace{1cm} (28)

Note that we now work in the frequency domain, which is often done for wave phenomena. Combining (27) and (28) we find

$$\varepsilon(\omega) = \varepsilon_0 \left(1 + \chi(\omega)\right)$$  \hspace{1cm} (29)

and we have derived an expression for the permittivity in a simple dielectric material. The parameter $\chi$ (pronounced kai) is called the electric susceptibility. If the dielectric is not isotropic then $\chi$ is a tensor and we have to write that

$$P = \varepsilon_0 \bar{\chi} E$$  \hspace{1cm} (30)

and this will be the case for many metamaterials.

Possible geometry designs for artificial dielectric materials will be discussed in Chapter 1.7.

\textbf{Conductors}

Also the free electrons in a metal will oscillate harmonically under the influence of an incident electromagnetic wave and this can be described by an oscillating current density $J$, which is the product of the charge density per unit volume and the velocity of charge movement. When the effect of the electromagnetic wave on the metamaterials is linear, the relation between $J$ and $E$ is given by a material constant called conductivity $\sigma$:

$$J(\omega) = \sigma(\omega) E(\omega).$$  \hspace{1cm} (31)

To derive an expression for the permittivity, we remember that $P$ in (27) is proportional to the charge displacement $x$ and $J$ is proportional to the charge speed $v$ (that is $P = Ne x$ and $J = Ne v$, with $N$ being the particle density and $e$ being the electric charge). In the complex notation for time-harmonic fields $v = j\omega x$, and we can express $P$ as a function of $J$ and insert that in (31). We get for a conductor that

$$\varepsilon(\omega) = \varepsilon_0 + \sigma(\omega)/j\omega.$$  \hspace{1cm} (32)

In the real world a certain material might have polarisation due to both free and bound charges, and we describe that as

$$\hat{\varepsilon}(\omega) = \varepsilon(\omega) + \sigma(\omega)/j\omega.$$  \hspace{1cm} (33)

Here $\varepsilon(\omega)$ measures the polarisation response due to bound charges and it is also a complex number. The permittivity in a conductor has a large imaginary part (the second term, proportional to the conductivity sigma) and this means that the losses are large. But this also means that the penetration depth of the electromagnetic waves into a material sample is small. The fields attenuate rapidly within the conductor and the fields are confined to a thin surface layer; this allows the definition of surface current and surface impedance, which are notions often used by electronic engineers. The quantity $\hat{\varepsilon}(\omega)$ is often called the generalized permittivity.
Piezoelectric materials

Piezoelectricity is a phenomenon in materials where electric fields can be created by mechanical compression in some directions. This can be explained by a relative displacement of positive and negative charges resulting in an induced dipole. On thermodynamic grounds, one can expect that for such materials also the opposite effect exists, which is indeed the case: the application of a potential difference in the material creates a mechanical distortion. This effect is often labeled as the direct piezoelectric effect. The mechanical relation relating the stress and strain is cross-coupled to the electrical effect and this appears in the (electrical) constitutive equations. The constitutive relations for piezoelectric materials are more complicated than for ordinary anisotropic materials because the mechanical stresses and strains themselves are second-order tensors, and hence their relations with electric field and flux density have to be presented by cross-coupling third-order tensors.

Magnetic materials

For magnetic materials the permeability is the dominating parameter expressing the relation between $B$ and $H$

$$B = \mu_0 (H + M) = \mu H ,$$

(34)

where $M$ is the magnetic moment density (magnetization) and $\mu$ is the permeability. (Almost in all magnetic materials the medium is also electrically polarisable, and the name magneto-dielectric is used.) Possible designs for artificial magnetic materials will be discussed in Chapter 1.7.

Magneto-dielectric materials

Materials described by permittivity and permeability are called magneto-dielectric and these will be discussed in detail in the Chapter 4 Characterisation.

Magneto-dielectric materials with negative permittivity and permeability

The sign of the real parts of permittivity and permeability is not restricted by any physical law, and can be negative. The real part of the permittivity is negative, for example, in metals, and this takes place because there are free electrons that move in the applied electric field and create a polarisation which is out of phase with the applied field. The resonant frequency of free-electron oscillations is called the plasma frequency and depends on the electron density and effective electron mass. For metals, this frequency lies in the ultraviolet range, which means that at the microwave frequencies (range of GHz) and below, the real part of the permittivity takes very large negative values. However, the conductivity of metals is so high, that at these frequencies the imaginary part of the permittivity dominates.

In natural materials negative permeability occurs in materials with resonant phenomena (see section 1.6). The real part of permeability may take negative values near a resonance of sufficient strength, as for example in ferrites near the ferromagnetic resonance frequency. For artificial materials manipulation of magnetic charges is not an option, but a negative permeability response can be realised using electrically small resonant metal inclusions of special shapes, e.g. split rings. In the visible part of the spectrum this is the only possibility of realising negative permeability (as well as any relative permeability values different from 1). This will be discussed in more detail in section 1.6.
Anisotropic and bi-anisotropic materials

Isotropic media do not possess any special direction in their structure (a high degree of spatial symmetry), meaning that the electromagnetic response (and any other response, for that matter) does not depend on how the material is rotated with respect to the field. For isotropic media, the material parameter tensors are multiples of the unit tensor, and scalar multiplications suffice.

Metamaterial are often anisotropic, as the geometric symmetry is broken. The impact on the constitutive parameters is, that a tensor description is necessary.

For materials that can no longer be considered isotropic, relations (22) cannot be used. The next step is to consider permittivity and permeability as tensors. Such materials are called *anisotropic materials*.

Often a linear relation exists between all the four vectors of the electromagnetic fields and such materials are called *bi-anisotropic materials*. The constitutive relations for bi-anisotropic materials read

\[
\begin{align*}
D &= \bar{\varepsilon} \cdot E + \bar{\delta} \cdot H \\
B &= \bar{\zeta} \cdot E + \bar{\mu} \cdot H.
\end{align*}
\]  

(35)

In these relations, the four material parameter tensors necessary to characterise the material are: the permittivity \(\bar{\varepsilon}\), the permeability \(\bar{\mu}\), and the magneto-electric coupling is expressed by two magneto-electric tensors \(\bar{\delta}\) and \(\bar{\zeta}\). Note that the most general bi-anisotropic material requires 36 complex parameters for a full constitutive electromagnetic description.

We would like to linger for a second on magneto-electric coupling. It can be observed in materials in which magnetic field creates electric polarisation in the medium, and vice versa, an electric excitation brings forth magnetic response (bi-anisotropic materials, introduced above). Materials which lack a preferred direction, but which do show magneto-electro coupling are called *bi-isotropic* and the amount of free parameters in (35) decreases to four.

This motivates us to draw Table 1 that shows a four-field division of materials into subclasses when the criteria are isotropy-anisotropy and whether the medium displays magneto-electric coupling.

<table>
<thead>
<tr>
<th></th>
<th>Direction independent</th>
<th>Direction dependent</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>No magneto-electric coupling</strong></td>
<td>2 ((\varepsilon, \mu)) ((\text{isotropic}))</td>
<td>18 ((\bar{\varepsilon}, \bar{\mu})) ((\text{biaxial anisotropic}))</td>
</tr>
<tr>
<td>magneto-electric</td>
<td>4 ((\varepsilon, \mu, \bar{\delta}, \bar{\zeta})) ((\text{bi-isotropic}))</td>
<td>36 ((\bar{\varepsilon}, \bar{\mu}, \bar{\delta}, \bar{\zeta})) ((\text{bi-anisotropic}))</td>
</tr>
</tbody>
</table>

Table 1. Classes of linear electromagnetic materials and the number of free material parameters in their full characterisation [Capolino].
The bi-anisotropic theory holds for most metamaterials, but even so a large number of parameters might be needed to describe the material.

**Spin-wave/Magnonic metamaterials**

Periodic magnetic structures exhibit band gaps if ‘probed’ with a wave of the order or smaller than the period, but they show effectively continuous properties if ‘probed’ with a large-scale wave (microwaves or long-wavelength spin waves). Both phenomena are theoretically described by the same theory where ‘effectively continuous’ behaviour is the long-wavelength limit of the band gap theory.

The effective parameters are those that are required to describe the collective spin waves as if the array were a continuous material. They determine dispersion of spin waves in continuous samples, e.g., the effective exchange constant, effective anisotropy, effective magnetisation, and effective gyro-magnetic ratio [Kruglyak2005]. Historically, the research of spin waves in magnetic nanostructures has always been connected with measuring spin wave spectra or associated high-frequency magnetic susceptibilities. Nonetheless, for example media containing nano-dots can have interesting ‘effective material properties’. Indeed, effective electromagnetic properties of a medium containing ferromagnetic inclusions was theoretically investigated e.g. in [Belov2002]. However, the response of the magnetic inclusions was entirely due to uniform ferromagnetic resonance, and hence bound to lie in the low GHz range. The useful frequency range will be significantly expanded if non-uniform resonances (so called spin-wave resonances) were exploited. To take full advantage of the latter, strategies improving coupling of essentially uniform electromagnetic fields to non-uniform spin waves will have to be adopted from the field of spin dynamics and this is at the moment a topic of advanced research.

1.4.2 Important Concepts

**Backward-wave materials**

Materials that have both negative permittivity and permeability have been the subject of much research lately, as the negative refractive index associated with such media is a phenomenon that does not occur in nature, according to the present knowledge. These materials were first theoretically introduced in a systematic way by Veselago [Veselago]. These materials are sometimes called left-handed (LH), which in this context refers to a material in which the two field vectors of a plane wave and the wave vector form a left-handed triplet (see Fig. 1). The electromagnetic wave will convey energy in the direction opposite to phase velocity. The notion of ‘left-handedness’ in the connection of Veselago media is unfortunate since there is no handedness in the geometrical structure of such media.

Backward-wave media are media in which the energy velocity direction is opposite to the phase velocity direction (or –at least- the scalar product between the corresponding vectors is negative). In particular, this takes place in isotropic materials with negative
permittivity and permeability (double negative media). Negative refraction takes place on interfaces between ‘usual’ materials and backward-wave media.

Surface waves (waves propagating along a surface but exponentially decaying in the directions orthogonal to the surface) can exist on interfaces between media having material parameters of the opposite sign. In optics of metals, these surface waves are called ‘surface plasmons’. Surface plasmons correspond to a collective excitation between electrons in a metal and photons just outside the metal. From a macroscopic point of view, the phenomenon can be expressed in classical electrodynamics with the help of a negative real part of the relative permittivity. This is for instance the case for silver and gold at optical frequencies.

**Perfect lens**

Material with negative permittivity and negative permeability can be utilized to realize ‘lenses’ that beat the well-known diffraction limit of resolution, resolving details smaller than the wavelength [Veselago]. It can be shown that at an interface between free space and an isotropic losses material with the relative material parameters equal to –1 (both permittivity and permeability), surface waves with any wavenumber along the interface (surface plasmons) are eigenwaves. Thus, every evanescent plane-wave component of the incident field resonantly excites oscillations on the interface. Furthermore, it can be shown that a parallel-plate slab made of such material acts as a perfect lens. The incident propagating plane waves are focused due to negative refraction at two interfaces, while the evanescent incident waves are restored in the focus thanks to resonant excitation of surface plasmons. However, finite period of the metamaterial structure, anisotropy and losses in such structures remain important challenges.

More recently, wire media structures with high-resolution imaging capabilities have been devised [Belov2008, Ikonen]. In this case, the TE components (with electric field transverse to the wires) are not affected by the material, while TM waves are transported (channeled) through the half-wavelength structure, i.e. they are the same at the output as compared to the input, except for a phase shift. This is due to the strong spatial dispersion of the material [Belov2003]. In those materials, propagating TM waves are just transferred through the material, while evanescent waves are transformed into propagating ones in the material and become again evanescent at the output. As a result, the TM component of fields at the input is simply reproduced at the output. Reflection is avoided at the input by exploiting a Fabry-Perot resonance, obtained when the structure has a length equal to a multiple of half the wavelength. It is interesting to notice that the resolution of the collimating structure is limited only by the spacing between wires. Such structures are extremely difficult to realize at optical frequencies, mainly because of the high losses in metals at those frequencies.

**Reciprocal materials**

Another important concept in the electromagnetic material response is reciprocity. All media can be separated into two big classes: reciprocal and nonreciprocal media.

The notion of reciprocity is closely related with the symmetry with respect to time reversal: reciprocal media are symmetric under this transformation, while nonreciprocal materials are not. In radio communications technology, reciprocity means an invariance of a system performance when the positions of the transmitter and receiver are interchanged [Kong], [Van Bladel]. Most natural materials are reciprocal, exceptions being naturally magnetic materials, such as ferrites and antiferromagnetics, and materials biased by external magnetic fields.

If the medium is **reciprocal**, the conditions for the bi-anisotropic material parameters are [Kong]:

\[
\varepsilon = \varepsilon^T, \quad \mu = \mu^T, \quad \gamma = \gamma^T, \quad (36)
\]
where $T$ denotes transpose of the tensor. For reciprocal media, therefore, permittivity and permeability are symmetric tensors, and the magneto-electric cross-coefficients $\xi$ and $\xi'$ are each other’s negative transposes. Hence a full characterisation of reciprocal bi-anisotropic materials requires 21 (complex) parameters.

Nonreciprocal effects are measured by antisymmetric parts of $\bar{\varepsilon}$ and $\bar{\mu}$, and by the tensor of nonreciprocal magneto-electric coupling, denoted $\bar{\kappa}$ in the following equations [Sihvola]:

$$D = \bar{\varepsilon} \cdot E + \left( \bar{\varepsilon}' - j\kappa \right) \cdot H,$$

$$B = \left( \bar{\chi} + j\kappa \right) \cdot E + \bar{\mu} \cdot H.$$  \hspace{1cm} (37) \hspace{1cm} (38)

The two magneto-electric tensors (which measure reciprocal and nonreciprocal coupling) are connected to the previous ones through the following relations:

$$\bar{\chi} = \frac{\xi + \xi'}{2}, \quad \bar{\kappa} = \frac{\xi - \xi'}{2j}.$$  \hspace{1cm} (39)

Of these two tensors, the $\bar{\kappa}$ is usually termed the chirality tensor, and it is responsible for the reciprocal magneto-electric phenomena (in fact, not only for chirality effects), and $\bar{\kappa}$ is the nonreciprocal cross-polarisation (Tellegen) tensor. Time-harmonic dependence of the fields brings forth complex-valued quantities. With the definitions of (37)-(38), the tensors $\bar{\kappa}$ and $\bar{\kappa}$ are real for lossless materials (zero imaginary part).

The tensor $\bar{\kappa}$ can be nonzero only if there is some external parameter which changes sign (non-symmetry) under time inversion, so that nonreciprocal effects are possible. Most often this is either some external bias field or internal magnetisation in the medium which exists due to exchange interactions between electron spins.

All bi-anisotropic materials can be categorised with 7 reciprocal and 7 non-reciprocal parameters into 14 classes based on the reciprocal or nonreciprocal nature of their constituents [Serdyukov].

### Spatially inhomogeneous materials and materials with spatial dispersion

Spatial dispersion is the name of an effect based on non-locality of electromagnetic response in materials. It expresses that material polarisation at a certain point in space is influenced by what happens at neighbouring points.

Spatial dispersion is one of the key notions in the theory of artificial electromagnetic materials and we will show that the first order spatial dispersion results in chirality, while the second order dispersion results in artificial magnetism. Following [Serdyukov], we will next briefly describe approaches to effective material parameter modelling of weak spatial dispersion and explain how spatial dispersion determines chirality and artificial magnetism in metamaterials.

To describe a metamaterial with its nanoinclusions, we need the microscopic Maxwell equations. Finally, we are however only interested in the macroscopic (material) properties of the metamaterials. The macroscopic Maxwell equations (1-4) follow from volume averaging of the microscopic Maxwell equations. We will see that this averaging can only be done easily if the material is weakly spatially dispersive.
It is important to distinguish weak spatial dispersion from strong spatial dispersion. Weak spatial dispersion is when the polarisation current at a certain point of the medium is influenced only by what happens at neighboring points inside the same unit cell of the medium (in practice inside one particle). Strong spatial dispersion is when phenomena at a certain point of the medium are also influenced by what happens outside the unit cell, that is by (many) neighboring unit cells.

Averaging ‘smoothes’ the current and charge distributions and the actual microscopic fields, determined by movements of individual electrons, are replaced by averaged charge and current densities, which are uniform over one unit cell of the structure. Direct averaging of microscopic equations in source-free regions results in

\[ \nabla \times \mathbf{E} = -j \omega \mathbf{B}, \quad \nabla \times \mathbf{B} = j \omega \varepsilon \mathbf{E} + \mathbf{J}^{\text{ind}} \quad (40) \]
\[ \varepsilon \nabla \cdot \mathbf{E} = \rho^{\text{ind}}, \quad \nabla \cdot \mathbf{B} = 0 \quad (41) \]

If we now formally define induction vectors as

\[ \mathbf{D} = \varepsilon \mathbf{E} + \mathbf{J}^{\text{ind}}/j \omega \quad \text{and} \quad \mathbf{H} = \mathbf{B}/\mu \quad (42) \]

the field equations will take the familiar form of macroscopic equations in source-free materials

\[ \nabla \times \mathbf{E} = -j \omega \mathbf{B}, \quad \nabla \times \mathbf{H} = j \omega \mathbf{D} \quad (43) \]
\[ \nabla \cdot \mathbf{D} = 0, \quad \nabla \cdot \mathbf{B} = 0. \quad (44) \]

Here we took into account that the averaged induced charges and currents satisfy the continuity equation (conservation of charge). If external sources are present, we should add the respective currents and charges into the right-hand sides, which results in (1)-(4).

The averaged induction vector \( \mathbf{D} \) depends on the induced averaged current density, and in general linear media, induced current density depends linearly on all past values of electric fields everywhere in space. Dependence on the past (dependence of the induced current on electric fields \textit{in the past}) is expressed as frequency dependence of all parameters, but here we suppress this for brevity and the induced averaged current is written as

\[ \mathbf{J}^{\text{ind}}(\mathbf{r}) = \int_{V} \mathbf{K}(\mathbf{r}, \mathbf{r}') \mathbf{E}(\mathbf{r}') dV \quad (45) \]

where the spatial nonlocality of the response is expressed as a dependence of induced current at point \( \mathbf{r} \) on electric fields elsewhere, at points \( \mathbf{r}' \).

If the spatial dispersion is \textit{weak}, the kernel \( \mathbf{K}(\mathbf{r}, \mathbf{r}') \) quickly decays when the distance between points \( \mathbf{r} \) and \( \mathbf{r}' \) increases. This regime is of interest for metamaterials which behave as ‘effectively continuous media’ and can be described by material parameters like permittivity and permeability, and we concentrate on this case here.
If spatial dispersion is weak, current at a certain point depends only on electric fields in a near vicinity of this point, and the ‘global’ integral dependence (45) can be replaced by dependence only on the field and its low-order derivatives at the observation point (Taylor expansion):

$$J^{\text{ind}} = j\omega(\alpha_0 E + \alpha \nabla \times E + \beta \nabla \cdot E + \gamma \nabla \times \nabla \times E). \quad (46)$$

For simplicity of writing, we only consider isotropic media here (for general anisotropic materials there will be all combinations of derivatives along all directions and tensorial expansion coefficients, see [Serdyukov]). It is important to note that here all the vectors and their derivatives are taken at the same point in space.

Substituting in the definition of $D$ above, we get the constitutive relations in the following form:

$$D = \varepsilon E + \alpha \nabla \times E + \beta \nabla \cdot E + \gamma \nabla \times \nabla \times E, \quad H = \frac{B}{\mu_0} \quad (47)$$

Here $\varepsilon = \varepsilon_0 + \alpha$. These equations can be successfully used to study plane waves in spatially infinite media (for plane waves spatial derivatives are replaced by multiplication by the wave vector, which results in the dispersion equation, which can be then solved). However, the problem is that for anything else these relations are not very useful. As soon as there is an interface between the material sample and something else (free space, for example), the presence of spatial derivatives in the constitutive relations requires additional boundary conditions which need to be derived specifically for every type of material. Thus, it is of primary importance to re-formulate the material equations so that there would be no explicit spatial derivatives. Instead, spatial dispersion effects would be ‘packed’ into some extra material parameters.

**First-order spatial dispersion and chirality**

Let us first assume that spatial dispersion is so weak that only the first-order derivatives in (47) would be sufficient to describe the medium nonlocality, and the second-order terms can be neglected:

$$D = \varepsilon E + \alpha \nabla \times E, \quad H = \frac{B}{\mu_0} \quad (48)$$

We can re-define the auxiliary vectors $D$ and $H$ so that the explicit dependence on the spatial derivatives disappears. This is possible because these vectors are not uniquely defined: Maxwell’s equations are invariant with respect to transformation

$$\begin{align*}
    D' &= D + \nabla \times Q \\
    H' &= H + j\omega Q
\end{align*} \quad (49)$$

Indeed,

$$\begin{align*}
    \nabla \times H &= j\omega D \\
    \nabla \times H' - j\omega \nabla \times Q &= j\omega D' - j\omega \nabla \times Q \\
    \nabla \times H' &= j\omega D'.
\end{align*} \quad (50)$$
If we now choose the arbitrary (differentiable) vector \( \mathbf{Q} = -\frac{\alpha}{2} \mathbf{E} \), and using (43), (48) and (49) the material relations transform into

\[
\mathbf{D}' = \varepsilon \mathbf{E} + \frac{\alpha}{2} \nabla \times \mathbf{E} = \varepsilon \mathbf{E} - j\omega \frac{\alpha}{2} \mathbf{B},
\]

\[
\mathbf{H}' = \frac{\mathbf{B}}{\mu_0} - j\omega \frac{\alpha}{2} \mathbf{E} \tag{51}
\]

As a result, we arrive to the constitutive relations of isotropic chiral materials:

\[
\mathbf{D}' = \varepsilon \mathbf{E} - j\xi \mathbf{B}, \quad \mathbf{H}' = \frac{\mathbf{B}}{\mu_0} - j\xi \mathbf{E}, \tag{52}
\]

where the chirality parameter \( \xi = \omega \frac{\alpha}{2} \). Obviously, the effect of chirality is a manifestation of first-order spatial dispersion and the chirality parameter is simply proportional to the first-order expansion coefficient in (47). Finally, solving (52) for \( \mathbf{B} \) and \( \mathbf{D} \) in terms of \( \mathbf{E} \) and \( \mathbf{H} \), we arrive at a simplified form of the bi-isotropic material relations (37-38), where the chirality tensor is reduced to a parameter \( \kappa \), which is proportional to \( \xi \), and the nonreciprocal magneto-electric coupling coefficient \( \chi = 0 \), because we consider reciprocal media here.

In the chapter below we will show that geometrical designs for materials with exceptional \( \varepsilon \) and \( \mu \), but also with novel \( \kappa \) and \( \chi \) can be created. Having sufficient freedom in realizing material parameter values, we can achieve desired wave properties in various ways. For instance, instead of realizing negative \( \mu \) (which is very difficult in the optical region), one can use chiral and bi-anisotropic media with positive \( \mu \) to realize negative refraction [Tretyakov2003]. So the process goes both ways: realizing media with interesting \( \kappa \) and \( \chi \) and using media with \( \kappa \) to realize interesting phenomena (simulating effects of difficult \( \varepsilon \) and \( \mu \)).

### Second order dispersion and artificial magnetism

Let us now consider the next approximation, where spatial dispersion is stronger and second-order spatial derivatives of electric field in (47) are significant. Dropping the prime sign in (52) and including the second-order terms, we write the constitutive relations for the re-defined vectors \( \mathbf{D} \) and \( \mathbf{H} \) as

\[
\mathbf{D} = \varepsilon \mathbf{E} - j\xi \mathbf{B} + \beta \nabla \cdot \mathbf{E} + \gamma \nabla \times (\nabla \times \mathbf{E}), \tag{53}
\]

\[
\mathbf{H} = \frac{\mathbf{B}}{\mu_0} - j\xi \mathbf{E}.
\]

Again, the presence of spatial derivatives makes these relations very much useless in solving electromagnetic problems. Can we again re-define the induction vectors so that also the second-order derivatives ‘disappear’? The answer is ‘yes’ and ‘no’ (unfortunately). Indeed, transforming the auxiliary vectors with \( \mathbf{Q} = -\gamma \nabla \times \mathbf{E} = j\omega \gamma \mathbf{B} \), we can eliminate the second-order curl terms in the constitutive equations, introducing instead effective permeability \( \mu \):

\[
\mathbf{D} = \varepsilon \mathbf{E} - j\xi \mathbf{B} + \beta \nabla \cdot \mathbf{E}, \quad \text{and}
\]

\[
\mu = \frac{\mu_0}{1 - \omega^2 \mu_0 \gamma}, \quad \text{with} \quad \beta = \frac{\gamma \mu_0}{\mu_0 - \omega^2 \gamma}, \tag{54}
\]

\[
\mathbf{H} = \frac{\mathbf{B}}{\mu} - j\xi \mathbf{E}.
\]
Thus, the artificial magnetism is a second-order spatial dispersion effect, and the permeability value is determined by the second-order expansion coefficient $\gamma$ in (47). It is of prime importance to recognize that the other second-order term (proportional to $\beta$) cannot be eliminated in this way, so, in general, spatial derivatives still remain in the material relations. Since both artificial magnetism (described by $\mu$) and other second-order terms are of the same order, it is not possible to drop the remaining spatial derivatives in (54) except when the inclusion shape is such that the response to the curl part of electric field strongly dominates. This issue is discussed in more detail in the section about artificial magnetics.

Magnetism is a good example, as the response to a magnetic field can be translated into the response to a nonuniform component of electric field. This is because the Maxwell’s equations show that $B = \frac{1}{\mu_0} \nabla \times E$ and this equivalence is used in the design of metamaterials [artificial magnetism is weak spatial dispersion of 2nd order, while natural magnetism has a different origin (spin)]. In metamaterials inclusions are often made rather large in order to exploit spatial dispersion, for example, to realise artificial magnetism. This nonlocality might be different for different frequencies and wave vectors and this effect is expressed by the name ‘dispersion’.

**Order of magnitude of effects**

The magneto-electric tensor (3×3 matrix) $\kappa$ measures the effects of the first-order spatial dispersion: The amplitudes of all its components are proportional to $l/\lambda$, where $l$ is the inclusion size and $\lambda$ is the wavelength. However, for particles of complex shapes, the magneto-electric coefficients can have resonances at specific frequencies, so that it is possible to engineer materials with very strong bi-anisotropy.

The strongest effect is the electric polarisation of particles (molecules) in uniform electric field. That effect exists even in the static limit (when the frequency tends to zero and the wavelength goes to infinity). The effects of bi-anisotropy (chirality) are the first-order spatial dispersion effects, and it is much weaker. For example, for particles shown in Fig.11 Chapter 1.7, the scaling factor equals $\tau = kS/l$, where $S$ is the loop area and $l$ is the arm length. The effect of artificial magnetism [difference between $\mu$ from $\mu_0$ in (4)] is the second-order spatial dispersion effect (amplitude proportional to $(kl)^2$), and it is much weaker than bi-anisotropy. We can conceptually write the relation:

Artificial magnetism terms ~
$\tau$ multiplied by bi-anisotropy terms ~ $\tau$ multiplied by dielectric response terms.

(55)

Because the sizes of natural molecules are much smaller than the wavelength even in the visible, this factor $\tau$ is very small and all bi-anisotropy effects are weak, while artificial magnetism is negligible. One of the main reasons behind the development of metamaterials is that this hierarchy can be ‘broken’: By proper design of particle shape and size it is possible to highlight and suppress specific weak spatial dispersion effects. Recently it has been shown that the scaling factor $\tau$ can equal unity for particles of particular shape and size, so called ‘optimal spirals’ [Saenz]. In such metamaterials it is possible to realise extreme effective parameters of chiral media, when the permittivity and permeability are both close to zero, while the chirality (bi-anisotropy) is strong. These media exhibit negative refraction index, negative refraction, and they can lead to realisation of optical superlenses [Tretyakov2003].
Nonreciprocal magneto-electric coupling

Note that in addition to weak spatial dispersion, there exists a very different physical mechanism leading to bi-anisotropic coupling: nonreciprocity. Bi-anisotropy is also possible in materials containing both naturally magnetic inclusions biased by some external magnetic fields coupled to some metal or dielectric inclusions. The magneto-electric coupling coefficient $\chi$ is a time-odd parameter proportional to the bias magnetic field (or other external parameter that changes sign under time inversion). See more in the section about classification of bi-anisotropic materials.

Wave phenomena in the quasi-static limit

In some special cases the wavelength of waves propagating in the medium can be extremely small compared to the free-space wavelength at the same frequency. In such situations the wave phenomena can be described by Maxwell’s equations in the static limit (time derivatives are negligible with respect to spatial derivatives). Typical examples of such waves are magnetostatic waves in thin magnetized ferrite layers and spin waves in ferrites and ferromagnetics.

Materials meeting the locality requirement

If the effective properties of the material can be adequately described by the bi-anisotropic constitutive relations (35), where all the material parameters depend only on the frequency and possibly on the coordinates (but not on the wave vector), we say that the material satisfies the locality requirements. This means that the material relations relate volume-averaged field vectors defined at the same point of space, that is, they are ‘local’.

Of course, the material response is local when spatial dispersion effects are negligible, but the definition of locality is wider than this limiting case of dielectrics and natural magnetics. It is important to remember that the ‘local’ bi-anisotropic constitutive relations model not only local dielectric response, but also physically nonlocal effects of chirality and artificial magnetism. In terms of the spatial dispersion theory, the locality requirement for the constitutive parameters means that the spatial dispersion is weak, so that only the terms up to the second order in (47) are significant, and also that the coefficient $\beta$ in (54) is negligible.

Electromagnetic response of bi-anisotropic inclusions of ‘local media’ usually can be modelled using the quasi-static approximation (see more in Annex on basic concepts), because the overall particle size is electrically small.

The relation between locality, spatial dispersion and optical density

There is no simple relation between locality in material response, spatial dispersion and optical density. For example, a material can be very dense optically in the sense that the distance between inclusions is very small compared to the wavelength in free space, but the particle shape is such that at some resonant frequency the coefficient $\beta$ in (54) is more significant than artificial magnetism. Anyway, below we give some general comments on this relationship.

Optical density can be defined in two ways

1) $(ka) << 1$, where $k$ is the wavenumber in the host medium (for natural media $k$ corresponds to free space wavenumber).

2) $(qa) << 1$, where $q$ is the wavenumber in the effective medium.
If the material is optically dense according to definition 2), then no strong spatial dispersion occurs at frequencies where \((qa)<1\), and local (bi-anisotropic) material relations can be used, provided that the inclusion shape allows that. If at least one of the conditions 1) and 2) is not satisfied, the material is strongly spatially dispersive (‘photonic crystal’ regime), and a local description is not possible.

The quasi-static model of unit cells is usually possible for bi-anisotropic media; although we need to model response not only to spatially uniform fields but also to non-uniform excitations (the phase shift of the exciting field over one particle size is essential for chirality and artificial magnetism).

### 1.5 Mathematical and numerical modelling

**Mixing rules**

Homogenisation theories attempt to assign effective material parameters (in metamaterials studies, especially effective permittivity and permeability) to materials of mixed and heterogeneous microstructure. This is possible to a certain extent, if the characteristic length of the inhomogeneities in the mixture is sufficiently smaller than the wavelength of the operating electromagnetic field. This is the case at least for the case when the mixture is composed of non-resonant inclusions and positive-permittivity materials. However, it has been shown [Wallen] that also for negative-permittivity mixtures, basic mixing rules which are based on quasistatic principles, give fairly accurate predictions, when measured against full-wave simulations. This happens even astonishingly close to regions where plasmonic resonances appear, although of course the failure in accounting for all the detailed resonance structure cannot be avoided. In the following, the simplest classical mixing rules are described. The mixtures considered are composed of two isotropic phases (background medium and inclusions), and the inclusions are assumed to be in the form of spheres.

The first-order response of an isotropic dielectric sphere that is small in comparison with the wavelength is given by its polarisability \(\alpha\). It is the ratio between the induced dipole moment and the amplitude of the external electric field and reads as

\[
\alpha = V(\varepsilon_i - \varepsilon_e) \frac{3\varepsilon_e}{\varepsilon_i + 2\varepsilon_e}, \tag{56}
\]

where the permittivities of the inclusion and its environment are denoted by \(\varepsilon_i\) and \(\varepsilon_e\), respectively. The volume of the sphere is \(V\). Note that the polarisability is a scalar. This is because the inclusion material is isotropic and its shape is spherically symmetric.

> **Maxwell Garnett formula**

Consider a mixture where small (in comparison with the wavelength) spherical dielectric inclusions (with permittivity \(\varepsilon_i\)) are embedded in an environment of permittivity \(\varepsilon_e\). The number density of the inclusions is \(n\). Then the effective permittivity of the mixture, according to the so-called Clausius-Mossotti formula [ClausiusMossotti], reads

\[
\frac{\varepsilon_{\text{eff}} - \varepsilon_e}{\varepsilon_{\text{eff}} + 2\varepsilon_e} = \frac{n\alpha}{3\varepsilon_e}, \tag{57}
\]

The dilute-mixture approximation can be written by taking the limit of small \(n\):

\[
\varepsilon_{\text{eff}} \approx \varepsilon_e + n\alpha \tag{58}
\]
In practical applications quantities like polarisabilities and scatterer densities are not always those most convenient to use. Rather, one prefers to play with the permittivities of the components of the mixture. When this is the case, it is advantageous to combine the Clausius-Mossotti formula with the polarisability expression (56). Then we can write

\[
\frac{\varepsilon_{\text{eff}} - \varepsilon_e}{\varepsilon_{\text{eff}} + 2\varepsilon_e} = f \frac{\varepsilon_i - \varepsilon_e}{\varepsilon_i + 2\varepsilon_e},
\]

(59)

where \( f = nV \) is a dimensionless quantity signifying the volume fraction of the inclusions in the mixture. Note that because only the volume fraction and the permittivities appear in the mixing rule, the spheres are not required to have the same size if only all of them are small compared to the wavelength.

Perhaps the most common mixing rule is the Maxwell Garnett formula (1) which is the rule (59) written explicitly for the effective permittivity:

\[
\varepsilon_{\text{eff}} = \varepsilon_e + 3f \varepsilon_e \frac{\varepsilon_i - \varepsilon_e}{\varepsilon_i + 2\varepsilon_e - f(\varepsilon_i - \varepsilon_e)}.
\]

(60)

This formula is in wide use in very diverse fields of application. The beauty of the Maxwell Garnett formula is its simple appearance combined with its broad applicability. It satisfies the limiting processes for vanishing inclusion phase \( f \to 0 \) giving \( \varepsilon_{\text{eff}} \to \varepsilon_e \) and for vanishing background \( f \to 1 \) we have \( \varepsilon_{\text{eff}} \to \varepsilon_i \).

The perturbation expansion of the Maxwell Garnett rule gives the mixing equation for dilute mixtures \( (f<<1) \):

\[
\varepsilon_{\text{eff}} \approx \varepsilon_e + 3f \varepsilon_e \frac{\varepsilon_i - \varepsilon_e}{\varepsilon_i + 2\varepsilon_e} + 3f^2 \varepsilon_e \left( \frac{\varepsilon_i - \varepsilon_e}{\varepsilon_i + 2\varepsilon_e} \right)^2.
\]

(61)

Lord Rayleigh [Rayleigh] has given an improved version of the Maxwell Garnett formula:

\[
\varepsilon_{\text{eff}} = \varepsilon_e + \frac{3f \varepsilon_e}{\varepsilon_i + 2\varepsilon_e - f + \frac{1.305 \varepsilon_e}{\varepsilon_i + 2\varepsilon_e}}.
\]

(62)

The difference between the predictions by the Maxwell Garnett (60) and Rayleigh (62) mixing rules; for example, the series expansions in terms of the volume fraction around \( f = 0 \) have the same coefficients up to the fourth power of \( f \). But for higher volume fractions of the inclusion phase, the deviation becomes large. In fact the Rayleigh mixing rule predicts a value for \( \varepsilon_{\text{eff}} \) approaching infinity for increasing \( f \) if the permittivity contrast is large enough \( (\varepsilon_i/\varepsilon_e > 4.735) \).

**Bruggeman mixing rule**

Another philosophy of homogenisation lies behind the so-called Bruggeman mixing rule. There one does not distinguish between host and guest in the mixture. The basic form of this formula for spherical scatterers is

\[
(1 - f) \frac{\varepsilon_e - \varepsilon_{\text{eff}}}{\varepsilon_e + 2\varepsilon_{\text{eff}}} + f \frac{\varepsilon_i - \varepsilon_{\text{eff}}}{\varepsilon_i + 2\varepsilon_{\text{eff}}} = 0.
\]

(63)

(1) Note that this was first derived by J.C. Maxwell-Garnett in 1904 [Maxwell-Garnett], it is not named after the ‘famous’ J.C. Maxwell.
This Bruggeman formula has the special property that it treats the inclusions and the environment symmetrically. The interpretation of (63) is that the formula balances both mixing components with respect to the unknown effective medium, using the volume fraction of each component as weight ($f$ for the inclusions and $1-f$ for the environment). This symmetry property of (63) makes the radical distinction between the Maxwell Garnett rule and the Bruggeman rule. The Maxwell Garnett approach is inherently non-symmetric. The difference can be observed in the series expansion for dilute mixtures ($f \ll 1$):

$$
\varepsilon_{\text{eff}} \approx \varepsilon_e + 3f\varepsilon_e\frac{\varepsilon_i - \varepsilon_e}{\varepsilon_i + 2\varepsilon_e} + 9f^2\varepsilon_e\frac{\varepsilon_i\varepsilon_e}{\varepsilon_i + 2\varepsilon_e}\left(\frac{\varepsilon_i - \varepsilon_e}{\varepsilon_i + 2\varepsilon_e}\right)^2.
$$

(64)

Here the term of the second order in $f$ differs from the expansion of the Maxwell Garnett rule (61). Figs 2 and 3 illustrate the comparison of the predictions of the effective permittivity of the two mixing rules. As can be observed, for low volume fractions, the rules give very similar results. Likewise, for low-contrast mixtures (the permittivities of the inclusions and the environment are not large), the predictions agree very well. However, when the contrast increases, and especially as it comes to the imaginary part, the predictions differ strongly. The Maxwell Garnett prediction stays lower than the Bruggeman result which displays the phenomenon of percolation.

**Figure 2.** The relative permittivity of a mixture for permittivity ratio $\varepsilon_i/\varepsilon_e = 3$ as a function of the inclusion volume fraction $f$. Maxwell-Garnett prediction (solid blue) and Bruggeman prediction (dashed red).

**Figure 3.** The imaginary part of the relative permittivity of a mixture for permittivity ratio $\varepsilon_i/\varepsilon_e = 5 - j100$ as a function of the inclusion volume fraction $f$. Maxwell Garnett prediction (solid blue) and Bruggeman prediction (dashed red). Note the large difference above the percolation threshold $f \approx 1/3$ where, according to the Bruggeman prediction, the effective permittivity suddenly starts to increase.

### Spin-wave metamaterials modeling

Dynamic micromagnetic theories are used to describe spin wave resonances in metamaterial samples. First, the equilibrium magnetisation configuration of a ferromagnet under given external conditions is calculated. At present, quasi-static micromagnetic simulations are a reliable tool for the evaluation of equilibrium configuration of ferromagnetic samples with mesoscopic sizes (thin films and multilayers with lateral sizes up to 5 μm, 3D samples with typical sizes of several hundreds nm). The dynamic behaviour involves simulation of the time evolution of the magnetisation when external conditions (mostly the external field) rapidly change.
The most common equation of motion for the ferromagnet magnetisation is the Landau-Lifshitz-Gilbert equation [Landau]:

$$\frac{\partial \mathbf{M}}{\partial t} = - \frac{\gamma_0}{1 + \alpha^2} [\mathbf{M} \times \mathbf{H}^{\text{eff}}] - \frac{\gamma_0}{M_s} \frac{\alpha}{1 + \alpha^2} \mathbf{M} \times [\mathbf{M} \times \mathbf{H}^{\text{eff}}].$$  \hspace{1cm} (65)

The first term in (65) describes the magnetisation precession around the effective field $\mathbf{H}^{\text{eff}}$, while the second term models dissipation losses.

An important problem is the inclusion of thermal fluctuations in the model. Such fluctuations are especially important when studying magnetisation dynamics in small magnetic systems (with the typical sizes ~ 100 nm), where the thermal energy $kT$ has the same order of magnitude as the energy barriers separating various metastable magnetisation states. These methodical difficulties have been resolved during the last decade, so that dynamical micromagnetic simulations both with and without thermal fluctuations demonstrate remarkable agreement with experimental findings at least for the linear magnetisation dynamics (small magnetisation deviations from the equilibrium state) – see, e.g., [Bayer]. Remarkable progress is also achieved in studying non-linear magnetisation excitations like those caused by the injection of a spin-polarised current [Ralph], [Berkov2008]. We note that at present there exist several commercial and non-commercial packages, which allow users with moderate background in magnetism to carry out standard micromagnetic simulations [Berkov-MM], [Donahue], [Scheinfein].

Once the dynamic behaviour of the spins is known everywhere in the metamaterial, the effective continuous metamaterials properties can be derived.

**Circuit theory as a model for metamaterials**

The behaviour of metamaterials can be sometimes modeled by equivalent electrical circuits. We will discuss how this is done e.g. for the magnetic permeability of artificial magnetic structures.

The response of an artificial magnetic inclusion is due to resonant oscillating currents, and a common way to describe this is to model the inclusion by an equivalent effective resistor-inductor-capacitor (RLC) circuit, and to apply the equations of circuit theory. Using this theory for a lattice of 'magnetic' elements one can obtain an expression for the current in the structure, and through it for the magnetic moment and the frequency dependence of the effective magnetic permeability $\mu(\omega)$. In such an RLC circuit the functional forms of the resistance $R$, the capacitance $C$, and the inductance $L$ will depend on the inclusion geometry of the metamaterials.

Let us consider a system of slab pairs, of which one is shown in Fig. 4a (of length $l$ and separation $t_b$), excited by a magnetic field which has the harmonic time dependence $\mathbf{H} = H_0 e^{i \omega t}$ and is applied perpendicular to the pair plane (see Fig. 4a). At the magnetic resonance of the structure resonant antiparallel currents are excited in the two slabs of the pair, as is shown in Fig. 4b, creating an effective loop current. Moreover, this current results in accumulation of opposite charges at the two upper (and at the two lower) sides of the pair, creating capacitive regimes there. The structure thus can be approximated by an effective circuit (as is shown in Fig. 4b), of inductance $L$, the inductance of the loop current, and capacitance $C = C_1/2$, the capacitance of the two capacitive regimes.
Under these conditions, and according to the Kirchhoff loop rule (stating that the sum of the potential differences around a closed circuit is equal to the total electromotive force), the sum of the self-inductance voltage drop $U_L$ over the inductance $L$, the voltage drop $U_C$ across the capacitance $C$, and the voltage drop $U_R$ across the resistance $R$, equal the voltage $U_{\text{ind}}$ induced by the external magnetic flux, i.e.

$$U_L + U_C + U_R = U_{\text{ind}}$$

or

$$LI + \frac{1}{C}\int I \, dt + IR = U_{\text{ind}} = -\dot{\phi},$$

(66)

where $\phi$ is the external magnetic flux $\phi = \mu_0 I t_b H$, and $I$ is the current. Taking the time derivative of (66) and dividing by $L$ we obtain

$$\dot{I} + R \frac{1}{L} + \frac{I}{LC} = \frac{U_{\text{ind}}}{L} = \omega^2 \frac{\mu_0 I t_b}{L} H_0 e^{j\omega t}.$$  

(67)

The obvious solution is $I = I_0 e^{j\omega t}$ with

$$I_0 = -\frac{\omega^2}{\omega^2 - 1/LC - j\omega R/L} \frac{\mu_0 I t_b}{L} H_0.$$

Having calculated the current, one can easily obtain the pair magnetic dipole moment, via the formula area $\times$ current $= I t_b$, and the magnetisation results from $M = (N_{\text{LC}}/V) I t_b$, where $N_{\text{LC}}$ is the number of 'LC' circuits and $V$ is their corresponding volume. Note that

$$N_{\text{LC}}/V = 1/(a_x a_y a_z) = 1/V_{\text{uc}}$$

where $a_x, a_y, a_z$ are the lattice constants, with $a_x \geq w, a_y > l, a_z \geq t + 2t_w$ and $V_{\text{uc}}$ is the volume of the unit cell. Finally, using

$$M = \mu_0 \chi_m(\omega) H, \quad \mu(\omega)/\mu_0 = 1 + \chi_m(\omega),$$
with $\chi_m$ the magnetic susceptibility, one obtains that

$$
\mu(\omega) = \mu_0 \left[ 1 - \frac{(1/V_{uc}) \left( \mu_0 (lt_b)^2 / L \right) \omega^2}{\omega^2 - \omega_{LC}^2 - j\omega\gamma} \right],
$$

where $\omega_{LC} = 1/\sqrt{(LC)}$ and $\gamma = R/L$.

For a solenoid of area $lt_b$ and length $w$, the magnetic field inductance $L$ is given by $L = \mu_0 lt_b / w$, and the $\mu$ expression turns to

$$
\mu(\omega) / \mu_0 = 1 - \frac{F \omega^2}{\omega^2 - \omega_{LC}^2 - j\omega\gamma}, \quad \text{with } F = \frac{lt_bw}{V_{uc}} = \frac{\text{interpair volume}}{\text{unit cell volume}}
$$

Apart from the $\omega^2$ in the numerator, this formula represents a Lorenz oscillator resonance for a magnetic atom. Here we have lumped the various parameters into the dimensionless quantity $F$, which is less than one. As is done in most cases, all the losses and the scattering mechanisms can be lumped into a damping factor $\gamma$, added in the denominator of (68).

### Numerical electromagnetic modelling and post-processing

With Maxwell’s equations and the appropriate description of our metamaterials we can analyze what happens if metamaterial samples are excited by a source of electromagnetic radiation. For simple materials the appropriate material description can be expressed in terms of material parameters, but this is not always the case, especially for complex nanostructures. Often, the solution in the form of $E(r,t)$ and $H(r,t)$ can only be found numerically. Materials scientists have thus to be prepared to use electromagnetic wave propagation theory concepts, such as reflection and transmission coefficients, group and phase velocity, impedance and admittance. The most relevant electromagnetic wave theory concepts are briefly explained in section 1.9 Annex to Theory Chapter.

The analysis of metamaterials remains a challenging task in view of the complexity of the inclusions and very strong mutual coupling among them. Often the electrical size of the sample to be computed is very large and requires large computer resources. Numerical models rely on analytical approximations and each class has its own limits, so that for all metamaterial configurations the results have a limited applicability range. The most well-known numerical methods are based on FDTD (Finite-Difference Time-Domain) [Chen], FE (Finite Elements) [Zhao], IE (Integral-Equation) [Craeye], and FIT (Finite Integration Technique) approaches [Weiland]; the latter is sometimes regarded as a variation on FDTD, with several fundamental differences, however. Each of these methods gave rise to different commercial software packages and each method is still subject to new developments in several laboratories.

In this brochure we do not aim to explain numerical modelling to material scientists, but feel that material scientist working with numerical mathematicians need an answer to the following questions:

- What input does the simulation model need from the material scientist?
- What are the quantities produced by the model?
- What characteristic parameters can post-processing derive from calculated quantities?
The answer to the first question is certainly that the input to the model is the exact material configuration; i.e. the geometry of the structure, along with the bulk or sometimes size-dependent effective parameters of all constituents. In practice, most structures can be considered as piecewise continuous. In those cases, the structures are described by the shapes and locations of all components, along with their effective parameters. The shapes to be considered can be canonical shapes (spheres, cylinders, parallelepipeds, ...) or they can also be described by a mesh, i.e. a list of points and interconnecting segments. A few standard formats are available for their description. In most cases, the structures are made of a repetition of identical inclusions. In the case where the arrangement of such inclusions is irregular, the position of every inclusion needs to be provided with high accuracy (of the order of $\lambda/50$). In that case, it should be kept in mind that samples larger than a few wavelengths in every direction rapidly become a challenge in terms of computer resources (computation times and memory). When the structures are periodic, the lattice arrangement (rectangular, hexagonal...) should be provided, along with the overall dimensions of the global structure. One should also mention whether the structures are infinite in one or several directions. Finally, the structure of the excitation should also be provided, e.g. plane-wave excitation or excitation from localised sources, like elementary electrical dipoles.

The quantities produced by the model in general correspond to $E$ and $H$ fields scattered by the structures mentioned above under the given excitation. In the following, we provide a non-exhaustive list of possible outputs.

- $E$ and $H$ field distributions in every unit cell with periodic excitation.
- Specific decompositions of fields, in terms of spherical, cylindrical and plane waves. Here, the fields are provided in terms of modal coefficients. Dipolar or multipolar decompositions are also possible. A limited subset of those representations corresponds to the transmission and reflection coefficients through a slab of metamaterial.
- Eigenmode representations for fields in periodic structures. These involve for instance dispersion curves (or ‘hyper-surfaces’). Some more details are given just below regarding the way in which those dispersion curves can be represented.
- $E$ and $H$ field distributions due to a single point source exciting an infinitely periodic medium. This representation may also be called ‘Point Spread Function’ in imaging terms, or ‘Synthetic Green’s function’ in differential mathematics terms. This is probably the most complete way of representing metamaterials. It also provides direct insight into the imaging functionality of metamaterials.
- Distributions of scattered fields around a finite periodic or non-periodic array of inclusions.
- Reflection and transmission coefficients (also called S-parameters).

Finally, we need to answer the question of which post-processing can be applied to obtain effective material parameters and these should be either estimated from calculated response of individual inclusions (using mixing rules, for example), or extracted from, for example, reflection and transmission coefficients in the same way as we do in experimental characterisation. This operation is called post-processing. The critical remarks discussed in Chapter 4.1.3 on the interpretation of measurements apply of course also to the interpretation of numerical simulations. In Chapter 4.1.3 we show that the conditions under which Characteristic Material Parameters (CMPs) can be extracted from the plane-wave reflection coefficient $R$ and transmission coefficient $T$ of the composite layer are very narrow. This can in fact only be done if the composite layer is a so-called Bloch lattice. In the case of Bloch lattices these CMPs can be obtained with commercial software, while other more powerful and less limited codes are under development. As discussed in Chapter 4.1.3., it is not yet known how to extract CMP parameters for non-Bloch lattices, and even if this is at all possible. In non-Bloch cases the post-processing cannot go any further than the calculated $R$ and $T$ for all angles of incidence with the near field at the interfaces. The response to point sources (Point Spread Function) appears to be the most complete representation.
Decomposition of fields into Bloch waves

Eigenwaves are waves that, once excited, can propagate through an infinite material without any further external excitation, and they can have any amplitude. To excite a given eigenwave, an incoming plane wave must have the same wavenumber along the interface between metamaterial and surrounding space, as the eigenwave. This is only theoretical, since the structures need to be both infinite and perfectly lossless for this situation to occur. In practice, i.e. for structures with non-zero losses, the excitation of eigenmodes will only occur if the incident wave has a non-zero energy component with the same wavelength. This can be expressed as the requirement that the incident field has a non-zero projection on the eigenmode. In homogeneous isotropic media the eigenwaves can be plane waves, spherical and cylindrical waves. For materials with periodically positioned inhomogeneities the eigenwaves are of a different type and these waves are called Bloch waves or Bloch modes. The eigenmode properties reflect the periodicity of the structures and they are periodic functions of the spatial coordinates, with constant phase shifts between fields in consecutive unit cells.

The eigenmodes can be described via the dependence of the phase shifts per unit cell along the coordinate directions on the frequency. For 3D-periodic structures, this function can be visualized as a hyper-surface in the four-dimensional space made of the three wavenumbers and the frequency. More precisely, for a given eigenmode, let us denote by $\psi_x$, $\psi_y$, and $\psi_z$ the phase shifts between consecutive cells along $x$, $y$ and $z$ axes, respectively, and by $a$, $b$ and $c$ the corresponding periods. Then, the eigenmode has the wavenumbers given by $k_x = \psi_x/a$, $k_y = \psi_y/b$ and $k_z = \psi_z/c$. The eigensurface corresponds to the function $\omega = \omega(k_x, k_y, k_z)$, called the dispersion relation. The phase velocity of an eigenmode is per definition in the same direction as the wave vector and its value equals to $\omega/k$. Hence, it can be written as:

$$v_p = \frac{k \omega}{\|k\|^2},$$

where $k$ is the 3D, 2D or 1D wavevector. Along the eigenmode hyper-surface, the group velocity is parallel to the gradient of frequency versus wavenumbers: $v_g = \nabla_\omega \omega$.

In the case of a doubly infinite slab of a metamaterial the eigensurface corresponds to 2D surfaces in a 3D domain: $\omega(k_x, k_y)$. Materials behave as bandgap structures when for some frequencies there is no propagating solution, which is expressed by the fact that there is no corresponding real solutions for that particular phase shift. The reader is strongly encouraged to read [Enoch et al.] for more details about the information that can be obtained from dispersion curves.

Effective parameters and homogenisation

It should be stressed, that, in view of the fine details of local fields related to the presence of inclusions in each unit cell, the eigenfields inside a metamaterial are not plane waves. This should be born in mind when the microscopic fields are to be homogenised in order to arrive at macroscopic, effective parameters. Hence, the representation of the metamaterial by a homogenized medium in which plane waves propagate requires a carefull averaging of fields over the volume of the unit cell, as will be discussed in detail in Chapter 4 Characterisation.
1.6 Resonances in permittivity and permeability

In Chapter 1.1 we have introduced the notion of temporal dispersion. In the following, three basic dispersion models will be introduced and the notion of resonance will be explained.

**Lorentz model for dielectrics**

As introduced in Chapter 1.1, in dielectric materials the charges are displaced by an incident electric field. The amplitude is given by the restoring forces on the electrons and depends strongly on the time-variation of the field and this dipole (formed by the displaced electrons and the remaining ion) will oscillate. For frequencies around a certain frequency $\Omega$, the induced dipole moment might be very large and strongly depend on the frequency. This exceptional interaction (called ‘resonance’) of incident electromagnetic field with the structure will lead to strong scattering and absorption.

The behaviour of the oscillating dipole can be described on the base of a simple driven harmonic oscillator and the solution gives the relation between the polarisation $P$ and electric field $E$ (constitutive relation) expressed by the susceptibility $\chi$. The solution to the differential equation describing forced resonance are governed by a complex Lorentzian function and the relation usually reads:

$$P(\omega) = \frac{\varepsilon_0 f}{(\Omega^2 - \omega^2) + j\gamma \omega} E(\omega) = \varepsilon_0 \chi(\omega) E(\omega), \quad (69)$$

in which $f$ is a phenomenological strength of the resonance and $\gamma$ is the damping factor. The amplitude of this function depending on the detuning of the frequency from resonance and the damping is shown in Fig. 5 below.

As in all resonance processes in nature and technology, the driven harmonic oscillator is able to follow the excitation at frequencies smaller than the resonance frequency and in these case it is said to be in-phase (here we speak about the case of negligible losses: $\gamma \approx 0$ in (69)). At frequencies larger than the resonance frequency the response in the material is $180^\circ$ out of phase relative to the excitation. The lower the damping, the sharper the resonance and in that case the spectral domain in which this relative phase difference between the illuminating wave field and the dipolar excitation occurs will be narrow. When the damping is small, the resonance peak is also higher and the transfer of energy from the illuminating wave field to the dipole will be strongest directly at the resonance. This change in $180^\circ$ of the phase around the resonance frequency also suggests that for frequencies slightly smaller than the resonance frequency, the susceptibility is large and positive, whereas it is negative at frequencies larger than the resonance. To obtain the relative permittivity as the defining quantity we use the relation $\varepsilon = 1 + \varepsilon_0 \chi(29)$. The real and imaginary parts of the permittivity for a Lorentzian resonance as described above are shown in Fig. 5.

![Lorentzian resonance](image-url)
Drude model for metals

A special case of the Lorentz model is the Drude model. The Drude model is often used to describe the optical properties of noble metals, from which most optical metamaterials are made. The Drude model also models the properties of wire media for waves with no field dependence along the wires [Shvets], [Belov2003]. The Drude behaviour comes from (69) by letting the electrons be free and setting the resonance frequency to zero, \( \omega_0 = 0 \):

\[
\varepsilon(\omega) = \varepsilon_\infty - \varepsilon_0 \frac{\omega_p^2}{\omega^2 - j\omega\nu},
\]

(70)

Fig. 6 displays the frequency behaviour of the permittivity in the Drude model. As can be seen, at low frequencies the imaginary part dominates the response. Indeed, the typical conductivity behaviour for metals at low frequencies

\[
\varepsilon(\omega) \rightarrow \frac{j\sigma}{\omega}
\]

(71)

is included in the model (70) in the limit \( \omega \rightarrow 0 \), and the conductivity is \( \sigma = \omega_p^2 \varepsilon_0 / \nu \).

Debye model for dielectric fluids with permanent electric dipole moments

The model labelled after Peter Debye describes well the dielectric response of fluids with permanent electric dipole moments. For example, the dielectric behaviour of water follows the Debye model for frequencies up to millimeter wave frequencies. The Debye model is very much used in aquametric applications [Kraszewski], [Kupfer]. These dipole moments feel a torque in the electric field which means that the polarisation requires time to reach its equilibrium state. The permittivity in the frequency domain reads

\[
\varepsilon(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + j\omega\tau},
\]

(72)

where \( \varepsilon_s \) and \( \varepsilon_\infty \) are the low-frequency and optical permittivities of the material. The material is lossy, and the dissipativity of the material is seen from the fact that the imaginary part of \( \varepsilon(\omega) \) is negative for all frequencies. The magnitude of the imaginary part has its maximum at the relaxation frequency \( \nu = 1/(2\pi\tau) \). Fig. 7 shows the dispersion of the permittivity according to the Debye model.
Resonance of magnetic material

For magnetic materials the constitutive equation giving the relation between $\mathbf{M}$ and $\mathbf{H}$ is the equation of motion. For a spin in an external magnetic field this is the Landau-Lifshitz equation (65). We can use this equation to find the susceptibility tensor as follows.

We decompose the solution in harmonic functions with frequency $\omega$ and find that the solution relating $\mathbf{M}$ to $\mathbf{H}$ has a singular point at the frequency $\omega_0$. This phenomenon is called ferromagnetic resonance, as it expresses that the material specifically absorbs incident electromagnetic waves at this frequency. This resonance is seen in the susceptibility $\chi$ and the permeability $\mu$ as a singularity at frequency $\omega_0$. It also shows that the permeability is negative for frequencies just above the resonance frequency. In the presence of losses this singular point is smeared out and we get the resonant behaviour similar to the case for the permittivity as shown in Fig. 5 [Landau].

Mie scattering and resonant modes

Scattering by spherical particles of any size is generally described by the term Mie scattering also called Lorenz-Mie or Lorenz-Mie-Debye scattering. It is an analytical solution of Maxwell’s equations for the scattering of electromagnetic radiation. In contrast to Rayleigh scattering, the Mie solution to the scattering problem is valid for all possible ratios of diameter to wavelength. Rayleigh scattering is limited to the case of spheres much smaller than the wavelength such that the problem can be solved with sufficient precision within the quasi-static approximation.

When electromagnetic waves fall on a dielectric sphere, Maxwell’s equations will show that at certain frequencies of the incident wave field the light will be strongly scattered and/or absorbed. Such frequencies are resonance frequencies and the modes associated to the excitation are called Mie resonances.

Generally, to solve Maxwell’s equations, an electric potential and a magnetic potential are introduced. These potentials are expanded in a series and a very particular meaning exists for each coefficient in the expansion. The lowest order mode for the electric or the magnetic potential corresponds to an electric or magnetic dipole. Higher order modes correspond to respective higher order modes such as electric or magnetic quadrupoles or octupoles. The corresponding behaviours are called electrical and magnetic Mie resonances.

If a medium made of densely packed spheres is homogenisable, it can be described by effectively materials parameters. Strong dispersion in the permittivity occurs, if the material is illuminated at a frequency that corresponds to the lowest order electric resonant mode and strong dispersion in the permeability, if the
lowest order magnetic resonant mode is excited. One of the important goals in metamaterial research is therefore to excite these lowest order Mie resonances.

Metamaterials made of such spheres are at the focus of interest. In order to induce sufficient dispersion in the effective properties, it has to be assured that the resonances are excited with sufficient strength. This is assured by using a material for the sphere with very large positive permittivity. This will lead to sharp Mie resonances with large oscillator amplitudes.

1.7 Examples of metamaterial geometries

In order to inspire material scientists to use their bottom-up manufacturing technologies to realize unknown designs (geometry and properties), we would like to present a few of those designs as examples.

Artificial dielectrics and relevant inclusion geometries

In this section we will introduce the design of artificial dielectrics, which can be made of dielectric but also of metallic inclusions. Artificial dielectrics obviously require electrically polarisable inclusions (e.g., small metallic or dielectric spheres). In order to realise the effective-medium regime, inclusions should be electrically small (much smaller than the incident wavelength). Simple-shaped particles like spheres or ellipsoids are usually non-resonant, except if the material parameters of the inclusion take large or negative values of the permittivity (as in metals in the visible). For optical applications, the most relevant phenomenon is the plasmonic resonance of free electrons in small metal nanoparticles. The use of this phenomenon allows one to realise a strong resonant response (Lorentz resonance) in composites made of electrically small inclusions. The other possibility is to use particles of more complicated shapes. The idea here is to create a strong concentration of reactive electric and magnetic fields in some parts of the inclusion volume (or in the space surrounding the particle). This results in a down shift of the resonance frequency while the overall particle size remains small. Artificial dielectrics have many applications in microwave engineering and antennas [Kock], [Cohn]. For optical applications, artificial dielectrics with ‘usual’ properties are not needed, because natural materials are widely available. Research on optical artificial dielectrics with exotic values of parameters is taking off. For example, materials with permittivity smaller than unity or close to zero are needed for realisation of cloaks and optical nanocircuits. The relevant geometries are usually spheres, strips [Kock], [Cohn], and complementary structures with voids in an isotropic dielectric host [Ward], [Valentine]. The theory of artificial dielectrics with small dipolar inclusions is well developed, e.g. [Collin].

Figure 8. Resonances of gold spheres.

Figure 9. Typical geometries of artificial dielectrics [Collin].
Wire media

Artificial materials formed by electrically dense arrays of thin conducting wires were originally proposed as artificial dielectrics with the effective permittivity smaller than unity [Rotman] as shown in Fig. 10. Only recently it was realised that wire media possess strong spatial dispersion even in the quasi-static limit [Shvets], [Belov2003] (see Annex for the explanation of the notion of the quasi-static limit). This is because metal wire lattices support propagating transverse electromagnetic (TEM) or quasi-TEM waves along the wires. These fields of these waves depend on the longitudinal coordinate (along the wires) as the plane-wave fields defined in (25). Basically, they are transmission-line modes similar to those in two-wire transmission line or a coaxial cable. Because they behave as propagating plane waves, they propagate with very little decay at electrically long distances, thus creating strong nonlocality in the effective material response (strong spatial dispersion).

The effective permittivity component along the wires reads, for electrically dense grids of thin parallel wires [Shvets], [Belov2003]

$$\varepsilon(k, k_z) = \varepsilon_0 \left(1 - \frac{k_p^2}{k^2 - k_z^2}\right)$$  \hspace{1cm} (73)

Here $k$ is the wavenumber in the host medium, $k_p = \omega_p \sqrt{\varepsilon_0 \mu_0}$ is the effective plasma wavenumber, and $k_z$ is the propagation constant along the wires. The permittivity becomes very large for specific values of the longitudinal wave and this is called strong frequency dispersion.

![Figure 10. Typical geometries of wire media [Rotman].](image)

This strong frequency dispersion was utilised in the design of low-loss superlenses, including magnifying superlens [Belov2008].
Artificial bi-anisotropic media and related inclusion geometries

> **Reciprocal metamaterials**
Typical inclusion shapes for the design of artificial bi-anisotropic materials are shown in Fig. 11. Due to specific shapes of these particles, applied electric field induces both electric and magnetic dipole moments. Likewise, a magnetic field produces both magnetic and electric polarizations.

![Figure 11. Chiral inclusion (left) and omega inclusion (right).](image)

It can be shown that arbitrary reciprocal bi-anisotropic effect can be realised using composite material containing inclusions of only these two basic shapes [Serdyukov].

> **Nonreciprocal bi-anisotropic metamaterials**
Bi-anisotropy is also possible in materials containing naturally magnetic inclusions biased by some external magnetic fields coupled to some metal or dielectric inclusions. The magneto-electric coupling coefficient $\chi$ is a time-odd parameter proportional to the bias magnetic field (or other external parameter that changes sign under time inversion). An example of possible inclusion geometry is shown in Fig. 12. The realisation of metamaterials with very unusual properties (for example, emulating properties of moving media in composite materials at rest) can allow the realisation of arbitrary linear field transformations using metamaterials [Tretyakov2009].

![Figure 12. An inclusion shape for the realisation of artificial moving media [Tretyakov1998].](image)
Artificial magnetics and relevant inclusion geometries

Shapes of inclusions for artificial magnetic materials should be chosen carefully, so that 1) the stronger bi-anisotropy effects would be forbidden due to the geometrical symmetry and 2) among all the second-order effects the artificial magnetism would dominate. For microwave applications, this is relatively easy as the dimensions are in the order of a millimeter, but the theory is equally valid for nanostructured metamaterials. The key to the design is to choose the shape so that induced currents form loops with a rather uniform distribution of the induced current, which then produces a strong magnetic moment [Schelkunoff]. Several typical geometries are shown in Fig. 13.

![Fig. 13. Some geometries of metal particles used to realise artificial magnetic materials.](image)

Work is being done on development of similar approaches to realisation of optical artificial magnetic materials using clusters of plasmonic nanoparticles, e.g. [Alu], [Simovski], see Fig. 14 and the METACHEM and NANOGOLD projects (see Chapter 2). These geometries have the potential to show magnetic response under conditions of weak spatial dispersion, which would hopefully result in creating metamaterials with permeability different from unity at optical frequencies.

![Fig. 14. Some geometries promising for the realisation of optical artificial magnetics. Picture (a) from [Alu], pictures (b-d) from [Simovski].](image)

Known experimental realisations of infrared and optical metamaterials (with dimensions in the nanometre range) which demonstrate backward waves (negative phase velocity) and negative refraction are usually based on simpler geometries, such as dual bars or fishnet layers (2), see Fig. 15. In these structures, the induced magnetic moment strongly depends on the distribution of the exciting electric field in space, even if the particles and the structure periods are electrically small and the incident magnetic field can be assumed to be uniform -this is explained in detail in the section about spatial dispersion – in those notations,

(2) Backward waves and negative refraction exist also in periodic structures, where there is no effective magnetic response at all.
the other second-order coefficient $\beta$ is of the same order as the coefficient $\gamma$, which is responsible for artificial magnetism. Furthermore, fishnet layers possess strong spatial dispersion similar to wire media, because quasi-TEM waves can travel between the layers. These structures cannot be described only by effective permeability and permittivity tensors. At this stage there are no adequate effective medium models of optical dual-bar or fishnet composites, although there is considerable progress in their microwave modelling [Marques].

Figure 15. Some geometries used to realize backward waves and negative refraction [after Shuang].
1.8 References


[Rayleigh] Lord Rayleigh. On the influence of obstacles arranged in rectangular order upon the properties of a medium, Philosophical Magazine, 31, 481-502, 1892.


1.9 Annex to Theory Chapter

1.9.1 Important concepts used to describe the behaviour of metamaterials
Based on Wikipedia, the free encyclopedia, http://en.wikipedia.org, February 2010

Electromagnetic spectrum

The electromagnetic spectrum is the range of all possible frequencies of electromagnetic radiation. The electromagnetic spectrum extends from below frequencies used for modern radio to gamma radiation at the short-wavelength end, covering wavelengths from thousands of kilometers down to a fraction of the size of an atom. The visible spectrum is the portion of the electromagnetic spectrum that is visible to (can be detected by) the human eye. Electromagnetic radiation in this range of wavelengths is called visible light or simply light. A typical human eye will respond to wavelengths from about 390 to 750 nm.

Vector calculus, the basics

dot product: multiplication of two vector fields, yielding a scalar field: $\mathbf{v} \cdot \mathbf{w}$.
cross product: multiplication of two vector fields, yielding a vector field: $\mathbf{v} \times \mathbf{w}$.

<table>
<thead>
<tr>
<th>Operation</th>
<th>Notation</th>
<th>Description</th>
<th>Domain/Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gradient</td>
<td>$\text{grad} (f) = \nabla f$</td>
<td>Measures the rate and direction of change in a scalar field.</td>
<td>Maps scalar fields to vector fields.</td>
</tr>
<tr>
<td>Curl</td>
<td>$\text{curl} (F) = \nabla \times F$</td>
<td>Measures the tendency to rotate about a point in a vector field.</td>
<td>Maps vector fields to (pseudo)vector fields.</td>
</tr>
<tr>
<td>Divergence</td>
<td>$\text{div}(\mathbf{F}) = \nabla \cdot \mathbf{F}$</td>
<td>Measures the magnitude of a source or sink at a given point in a vector field.</td>
<td>Maps vector fields to scalar fields.</td>
</tr>
</tbody>
</table>
**Permittivity**

Permittivity is a measure of how an electric field affects, and is affected by, a dielectric medium, and is determined by the ability of a material to electrically polarise in response to the field, and thereby reduce the total electric field inside the material. It is directly related to electric susceptibility, which is a measure of how easily a dielectric polarises in response to an electric field.

In SI units, permittivity $\varepsilon$ is measured in farads per metre (F/m); electric susceptibility $\chi$ is dimensionless. They are related to each other through

$$\varepsilon = \varepsilon_r \varepsilon_0 = (1 + \chi)\varepsilon_0,$$

where $\varepsilon_r$ is the relative permittivity of the material, and $\varepsilon_0 = 8.85\ldots \times 10^{-12} \text{ F/m}$ is the vacuum permittivity.

In electromagnetism, the electric displacement field $\mathbf{D}$ represents how an electric field $\mathbf{E}$ influences the organisation of electrical charges in a given medium, including charge migration and electric dipole reorientation. Its relation to permittivity in the very simple case of linear, homogeneous, isotropic materials with ‘instantaneous’ response to changes in electric field is

$$\mathbf{D} = \varepsilon \mathbf{E},$$

where the permittivity $\varepsilon$ is a scalar. If the medium is anisotropic, the permittivity is a second rank tensor.

In general, permittivity is not a constant, as it can vary with the position in the medium, the frequency of the field applied, humidity, temperature, and other parameters. In a nonlinear medium, the permittivity can depend on the strength of the electric field. Permittivity as a function of frequency can take real or complex values.

The displacement field $\mathbf{D}$ is measured in units of coulombs per square meter (C/m²), while the electric field $\mathbf{E}$ is measured in volts per metre (V/m).

If the effective permittivity takes negative values, the eigenmodes are evanescent and the amplitude of plane waves decays exponentially upon traversing the structure. For a source with a frequency far away from any resonance or larger than the plasma frequency in metals, the permittivity of the medium is positive. The corresponding eigenmodes will be propagating waves, decaying only due to absorption, measured by the imaginary part of the complex permittivity.

**Vacuum permittivity**

The vacuum permittivity $\varepsilon_0$ (also called permittivity of free space or the electric constant) is the ratio $\mathbf{D}/\mathbf{E}$ in free space. It also appears in the Coulomb force constant $1/4\pi\varepsilon_0$.

Its value is

$$\varepsilon_0 \equiv \frac{1}{c^2 \mu_0} = \frac{1}{35950207149.4727056\pi m} F \approx 8.8541878176\ldots \times 10^{-12} \frac{F}{m}$$
where

\( c \) is the speed of light in free space,
\( \mu_0 \) is the free space permeability.

The constants \( c_0 \) and \( \mu_0 \) are defined in SI units to have exact numerical values, shifting responsibility of experiment to the determination of the metre and the ampere. (The approximation in the second value of \( \varepsilon_0 \) above stems from \( \pi \) being an irrational number.)

**Relative permittivity**

The permittivity of a homogeneous material is usually given relative to that of free space, as a relative permittivity \( \varepsilon_r \) (also called the dielectric constant, although this sometimes only refers to the static, zero-frequency relative permittivity). In an anisotropic material, the relative permittivity may be a tensor, causing birefringence. The actual permittivity is then calculated by multiplying the relative permittivity by \( \varepsilon_0 \):

\[
\varepsilon_r = (1 + \chi),
\]

where \( \chi \) (frequently written \( \chi_e \)) is the electric susceptibility of the material.

**Susceptibility**

The susceptibility is defined as the constant of proportionality (which may be a tensor) relating an electric field \( E \) to the induced dielectric polarisation density \( P \) such that

\[
P = \varepsilon_0 \chi E,
\]

where \( \varepsilon_0 \) is the electric permittivity of free space.

The susceptibility of a medium is related to its relative permittivity \( \varepsilon_r \) by

\[
\chi = \varepsilon_r - 1.
\]

So in the case of a vacuum

\[
\chi = 0
\]

The susceptibility is also related to the polarisability of individual particles in the medium by the Clausius-Mossotti relation.

**Electric displacement**

The electric displacement \( D \) is related to the polarisation density \( P \) by

\[
D = \varepsilon_0 E + P = \varepsilon_0 (1 + \chi)E = \varepsilon_r \varepsilon_0 E.
\]
Permeability

In electromagnetism, permeability is the degree of magnetisation that a material obtains in response to an applied magnetic field. Magnetic permeability is typically represented by the Greek letter \( \mu \). In SI units, permeability is measured in the henry per metre \( (\text{H m}^{-1}) \), or newton per ampere squared \( (\text{N A}^{-2}) \). The constant value \( \mu_0 \) is known as the permeability of free space, and has the exact (defined) value \( \mu_0 = 4\pi \times 10^{-7} \text{N} \cdot \text{A}^{-2} \).

In electromagnetism, the auxiliary magnetic field \( \mathbf{H} \) represents how a magnetic flux \( \mathbf{B} \) influences the organisation of magnetic dipoles in a given medium, including dipole migration and magnetic dipole reorientation. Its relation to permeability is

\[
\mathbf{B} = \mu \mathbf{H}
\]

where the permeability \( \mu \) is a scalar if the medium is isotropic or a second rank tensor for an anisotropic medium. The magnetic field \( \mathbf{H} \) has dimensions current per unit length and is measured in units of amperes per metre \( (\text{A m}^{-1}) \).

\( \mathbf{B} \) has dimensions inductance times current per unit area \( (\text{H} \cdot \text{A/m}^2) \) and is measured in webers (volt.seconds) per square-metre \( (\text{V} \cdot \text{s/m}^2) \), or teslas \( (\text{T}) \).

In general, permeability is not a constant, as it can vary with the position in the medium, the frequency of the field applied, humidity, temperature, and other parameters. In a nonlinear medium, the permeability can depend on the strength of the magnetic field. Permeability as a function of frequency can take real or complex values. In ferromagnetic materials, the relationship between \( \mathbf{B} \) and \( \mathbf{H} \) exhibits both non-linearity and hysteresis: \( \mathbf{B} \) is not a single-valued function of \( \mathbf{H} \), but depends also on the history of the material.

Vacuum permeability

The vacuum permeability \( \mu_0 \) has the value

\[
\mu_0 = 4\pi \times 10^{-7} \text{N} \cdot \text{A}^{-2} \approx 1.2566370614\ldots \times 10^{-6} \text{H} \cdot \text{m}^{-1} \text{ or N} \cdot \text{A}^{-2}
\]

in the SI system of units (or \( \text{T} \cdot \text{m/A} \)).

Relative permeability

Relative permeability, sometimes denoted by the symbol \( \mu_r \), is the ratio of the permeability of a specific medium to the permeability of free space

\[
\mu_r = \frac{\mu}{\mu_0}
\]

Magnetic susceptibility

In terms of relative permeability, the magnetic susceptibility is:

\[
\chi_m = \mu_r - 1.
\]
\( \chi_m \), a dimensionless quantity, is sometimes called volumetric or bulk susceptibility, to distinguish it from \( \chi_p \) (magnetic mass or specific susceptibility) and \( \chi_M \) (molar or molar mass susceptibility).

### Speed of light in medium and wave impedance

More convenient forms of the Maxwell's equations are written with the help of two parameters, the speed of light in the medium \( v_p \) and \( \eta \) (pronounced eta), the characteristic impedance of the material:

\[
\frac{1}{v_p} = \frac{1}{\sqrt{\varepsilon \mu}} \quad \text{and} \quad \eta = \sqrt{\frac{\mu}{\varepsilon}}.
\]

With these substitutions Maxwell’s equations can be written as ‘simple’ wave equations and techniques to solve secondary order differential equations can be applied.

### Field energy

A quantity of interest is the energy flux or Poynting vector \( \mathbf{P} \) defined as

\[
\mathbf{S}(\mathbf{r},t) = \mathbf{E}(\mathbf{r},t) \times \mathbf{H}(\mathbf{r},t).
\]

If an incident plane wave is radiated on to a metamaterial, then some of these waves are reflected back and some will be transmitted, usually now propagating under another angle. Some of the incident energy is carried by the reflected waves and some of it by the transmitted waves. The energy flux is always in the direction away from the source.

As to the stored field energy in materials, simple general expressions in terms of the permittivity and permeability exist only for the case of negligible losses. In the general case, knowledge of material microstructure is required for determination of the stored energy, and the corresponding expressions need to be derived for each particular geometry.

### Phase velocity

(see also section 1.9.2 Annex to Theory Chapter)

The phase velocity of a wave is the rate at which the phase of the wave propagates in space. This is the velocity at which the phase of any one frequency component of the wave will propagate. One could pick one particular phase of the wave (for example the crest) and it would appear to travel at the phase velocity. The phase velocity is given in terms of the wave’s frequency \( \omega \) and wavenumber \( k \) is given by

\[
V_p = \frac{\omega}{k}.
\]

The phase velocity of electromagnetic radiation may under certain circumstances exceed the speed of light in vacuum, but this does not indicate any superluminal information or energy transfer.

Note that the phase velocity is not necessarily the same as the group velocity of the wave (see below), which is the rate that changes in amplitude (known as the envelope of the wave packet) will propagate.
Group velocity
(see also section 1.9.2 Annex to Theory Chapter)

The group velocity is the rate at which the envelope of the waveform is propagating; that is, the rate of variation of the amplitude of the waveform. Provided the waveform is not distorted significantly during propagation, it is the group velocity that represents the rate at which information (and energy) may be transmitted by the wave, for example the velocity at which a pulse of light travels down an optical fibre. However, if the wave is travelling through an absorptive and strongly dispersive medium, this does not always hold. For example, it is possible to design experiments where the group velocity of laser light pulses sent through specially prepared materials significantly exceeds the speed of light in vacuum. However, superluminal communication is not possible, since the signal velocity remains less than the speed of light. It is also possible to reduce the group velocity to zero, stopping the pulse, or have negative group velocity, making the pulse appear to propagate backwards.

In isotropic media, the group velocity is defined by the equation:

\[ v_g = \frac{\partial \omega}{\partial k} \]

where:
- \( v_g \) is the group velocity
- \( \omega \) is the wave’s angular frequency
- \( k \) is the wave number

The function \( \omega(k) \), which gives \( \omega \) as a function of \( k \), is known as the dispersion relation. If \( \omega \) is directly proportional to \( k \), then the group velocity is exactly equal to the phase velocity. Otherwise, the envelope of the wave will become distorted as it propagates. This ‘group velocity dispersion’ is an important effect in the propagation of signals through optical fibres and in the design of short pulse lasers.

Refractive index \( n \)

The refractive index, \( n \), of a medium is defined as the ratio of the speed of light \( c \) to the phase velocity \( v_p \) in the medium itself:

\[ n = \frac{c}{v_p} \]

The refractive index is most commonly used in the context of light with vacuum as a reference medium, although historically other reference media (e.g. air at a standardised pressure and temperature) have been common. It is usually given the symbol \( n \). In the case of light propagating in a linear, isotropic, local media the refractive index equals

\[ n = \sqrt{\varepsilon_r \mu_r} \]

where \( \varepsilon_r \) is the material’s relative permittivity, and \( \mu_r \) is its relative permeability. For most materials, \( \mu_r \) is very close to 1 at optical frequencies, therefore \( n \) is approximately \( \sqrt{\varepsilon_r} \). Contrary to a widespread misconception, \( n \) may be smaller than 1.
In a lossless, non-magnetic medium, the phase velocity $v_p$ and the wavelength $\lambda$ are all reduced or enhanced by a scale factor $n$ compared to the free-space values:

$$v_p = \frac{c}{n}, \quad \lambda = \frac{\lambda_0}{n},$$
while the propagation constant is proportional to $n$:

$$k = k_0 n.$$

**Wave impedance**

The wave impedance is a quantity which is useful to describe the behaviour of multiple interfaces. For plane waves traveling along axis $z$, it is defined as $Z_x = E_x/H_y$ and $Z_y = E_y/H_x$. The impedance is a complex parameter. The real part is associated with the power carried by the wave. If a plane wave propagates in a lossless medium, its wave impedance is purely real. For evanescent waves the wave impedance in purely imaginary.

**Reflection, transmission and scattering parameter**

In case the medium contains discontinuities, the electromagnetic wave will be partly reflected and partly transmitted.

The reflection coefficient $R$ is the (complex) ratio of the amplitude of the reflected wave to the amplitude of the incident wave. It is the complex ratio of the electric field strength of the reflected wave ($E^-$) to that of the incident wave ($E^+$). This is represented with a $R$ and can be written as:

$$R = \frac{E^-}{E^+}$$

The reflection coefficient is closely related to the transmission coefficient, which describes either the amplitude or the intensity of a transmitted wave relative to an incident wave. With the notation for the amplitude of the transmitted electric field $E^t$, the transmission coefficient is defined as

$$T = \frac{E^t}{E^+}$$

The scattering matrix $S$ relates the incoming wave to the transmitted and reflected waves. The matrix elements of $S$ are the reflection and transmission coefficients $R$ and $T$ respectively. Any text book on electromagnetic wave theory gives the exact mathematical relation.

**Plasmon**

Plasmons are collective oscillations of the free electron gas density, for example, at optical frequencies. Plasmons can couple with a photon to create another quasiparticle called a plasmon polariton. Most of their properties can be derived directly from Maxwell’s equations.
Plasmons can be described in the classical model as oscillations of free electron density against the fixed positive ions in a metal. To visualise a plasma oscillation, imagine a cube of metal is placed in an external electric field to the right. Electrons will move to the left side (uncovering positive ions on the right side) until they cancel the field inside the metal. Now we switch the electric field off, and the electrons move to the right, repelled by each other and attracted to the positive ions left bare on the right side. They oscillate back and forth at the plasma frequency until the energy is lost in some kind of resistance or damping. Plasmon is a quantisation of this kind of oscillations.

Plasmons play a large role in the optical properties of metals. Light of frequency above a certain frequency called the plasma frequency is transmitted, because the electrons cannot respond fast enough. Light of frequency below the plasma frequency is reflected, because the electrons in the metal screen the electric field of the light. In most metals, the plasma frequency is in the ultraviolet, making them shiny (reflective) in the visible range and, therefore, useful in the design of optical metamaterials. Some metals, such as copper and gold, have electronic interband transitions in the visible range, whereby specific light energies (colors) are absorbed; yielding their distinct colour. In semiconductors, the valence electron plasma frequency is usually in the deep ultraviolet, which is why they too are reflective, while usually much more lossy as compared with metals.

**Surface plasmon**

Surface plasmons are those plasmons that are confined to surfaces and that interact strongly with light resulting in a polariton. They occur at the interface of a vacuum or material with a positive dielectric constant, and a negative dielectric constant (usually a metal or doped semiconductor). Surface plasmons have been used to control the colours of materials. This is possible since controlling the material’s surface shape controls the types of surface plasmons that can couple to it and propagate across it. This in turn controls the interaction of light with the surface. These effects are illustrated by the historic stained glasses which adorn medieval cathedrals. In this case, the color is given by metal nanoparticles of certain size which interact with the optical field to give the glass its vibrant colour. In modern science, these effects have been engineered for both visible light and microwave radiation. At microwaves, surface plasmons are usually called surface waves. They are well known in microwave engineering, including surface waves on patterned metal or dielectric interfaces (sometimes called ‘spoof surface plasmons’ in more recent literature). To produce optical range surface plasmon effects involves producing surfaces which have features <400 nm. This is much more difficult than in the microwave range and has only recently become possible to do in any reliable way.

### 1.9.2 Phase velocity, group velocity, energy velocity

S. Tretyakov and C. Simovski

Here we discuss the relation between phase and group velocities, and the physical meaning of and limitations on the notion of group velocity. This is important because group velocity in strongly dispersive and lossy media looses its meaning of being the velocity with which field pulses are transported, and one should be careful in interpreting observed phenomena.

We start from a reminder of definitions (given in Annex 1). Consider a monochromatic plane wave of frequency $\omega$ and wavenumber $k$ (for simplicity of writing we assume that the fields depend only on one spatial coordinate, say, $z$):

$$E(z, t) = E_0 \cos(\omega t - kz).$$
To have an idea of the progressive aspect of the wave, assume that we want to follow a maximum value of the monochromatic wave field, e.g. we keep the value of the argument of the cosine constant. This leads to

\[ z = \frac{\omega}{k} t, \]

which brings us to the definition of the phase velocity:

\[ v_p = \frac{\omega}{k}. \]

In materials without dispersion,

\[ k = \omega \sqrt{\varepsilon \mu} = \omega \sqrt{\varepsilon_0 \mu_0} n = \frac{\omega}{c} n = k_0 n, \]

where the refractive index \( n \) does not change with the frequency. Here, \( c \) is the speed of light in vacuum and \( k_0 \) is the wavenumber in vacuum. Thus, we can also write

\[ v_p = \frac{\omega}{k} = \frac{c}{n}. \]

In nondispersive media all monochromatic waves (only one wave frequency) propagate with the same velocity. As we can decompose any propagating wave into monochromatic waves (the Fourier decomposition), this means that all waves propagate without changing their shape. However, materials without dispersion (where the refractive index does not depend on the frequency and the wavenumber is directly proportional to the frequency) are an idealisation. All materials are dispersive to some extent. Apparently, in dispersive media field propagating waves (often we speak about propagating ‘pulse’ and its shape) get distorted in shape when they propagate. However, if this distortion is small on the scale of many wavelengths, it is possible to speak about the velocity with which the pulse as a whole propagates. This velocity is called ‘group velocity’, because a propagating wave pulse can be considered as a group of plane waves. The group velocity is given by (see any basic book on wave theory or electromagnetics, also [Landau])

\[ v_g (\omega_0) = \frac{d\omega}{dk} = \left( \frac{dk}{d\omega} \right)^{-1}. \]

Here the derivative is taken at the central frequency of the wave packet \( \omega_0 \). Because by definition of the phase velocity \( \omega = v_p k \), we can establish the following relation between the group and phase velocities:

\[ v_g = \frac{d(v_p k)}{dk} = v_p + k \frac{d(v_p)}{dk}. \]

In a similar way we can also write

\[ v_g = c \left( \frac{d(n\omega)}{d\omega} \right)^{-1} = \frac{c}{n + \omega_0 \left( \frac{dn}{d\omega} \right)}. \quad (1) \]

If losses are small, the refractive index is always growing with the frequency \( (dn/d\omega > 0) \) (this follows from the causality principle, [Landau]). In this case we speak about normal dispersion. Obviously, in a ‘usual material’ with positive refractive index \( n \), the group velocity is always smaller than the phase velocity and smaller than the speed of light in vacuum.
An interesting question is what happens if we have a low-loss double negative material in which \( n < 0 \).

Because the derivative \( \frac{dn}{d\omega} > 0 \) in all low-loss media, including materials with negative refractive index, it seems that the group velocity can take any value, including values larger than the speed of light in vacuum. However, from the causality principle it follows that

\[
\frac{d(\varepsilon\omega)}{d\omega} > \varepsilon_0, \quad \frac{d(\mu\omega)}{d\omega} > \mu_0.
\]

Furthermore, from passivity of the medium it follows that the wave impedance is positive:

\[
\eta = \sqrt{\frac{\mu}{\varepsilon}} > 0
\]

(losses are assumed to be negligible). Using these limitations, it is easy to prove [Smith and Kroll] that

\[
\frac{d(n\omega)}{d\omega} > 1
\]

at all frequencies where losses can be neglected. This tells that the group velocity in transparent dispersive media is always positive and smaller than the speed of light in vacuum, whatever is the sign of the refraction index. Actually, also the following holds [Landau] (note that although in [Landau] this inequality is derived for the case when \( \mu = \mu_0 \), the refractive index as such also is a linear response function and satisfies the same restrictions as permittivity)

\[
\frac{d(n\omega)}{d\omega} > n,
\]

from which we see that the group velocity is smaller than the phase velocity in the absolute value.

Let us discuss next the case of anomalous dispersion, when \( \frac{dn}{d\omega} < 0 \) which happens when the losses are large. According to (1), in this case can the group velocity in principle take any value, including values larger than the speed of light (superluminal) or negative values. Anomalous dispersion takes place close to resonance of inclusions, where losses are not negligible and frequency dispersion is strong, which results in strong distortion of the packet shape already over distances comparable with the wavelength. We have to conclude that the group velocity in this situation does not have the physical meaning of the velocity of packet propagation or of the velocity with which the energy propagates. It is important to remember that the field energy always propagates in the direction away FROM the source. Thus, if the group velocity takes, for example, negative values, this means that the group velocity necessarily does not tell anything about the energy propagation velocity. Group velocity can be interpreted as the energy velocity only in low-loss and low-dispersion materials.

For instance, superluminal group velocity basically means that during propagation the incoming wave shape is distorted such that the amplitude at the propagating wave front increases while the amplitude in the tail decreases. This can be interpreted as faster propagation of the propagating wave pulse as a whole, if the propagating wave position is measured at the position of the field maximum.

REFERENCES

Chapter 2

Design
Chapter 2: Design of metamaterials in the projects

Magnonic meta-material designs

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MAGNONICS targets to exploit magnetic resonances in naturally magnetic materials, e.g. ferromagnets [1] and antiferromagnets [2]. The physics of magnetisation dynamics (‘spin waves’) in magnetic nano- and micro-structures is very complex [3], and therefore, there should be rich opportunities to design such artificial magnetic structures so as to enhance/shape their resonance to nearly uniform magnetic fields as required for the meta-materials design. Nano-manufacturing will be used to shape the resonance of naturally magnetic materials and thereby lead to creation of novel meta-materials.

Effective electromagnetic properties of a medium containing ferromagnetic inclusions were theoretically investigated e.g. in Ref. 1. There, the response of the magnetic inclusions was entirely due to uniform ferromagnetic resonance (magneto-dipole interaction), and hence bound to lie in the low GHz range. For magnetisation waves with larger frequencies (shorter wavelengths), the exchange interaction is starting to play a role, and these waves are usually referred to as exchange spin waves. Taking these non-uniform resonances into account, metamaterials with higher resonance frequencies and with a wealth of new properties can be designed. The exchange interaction could be used to design arrays of particles, where more than one particle form a unit cell, and where the particles within each unit cell interact. These would be meta-materials consisting of artificial molecules rather than atoms (and these designs could be called ‘meta-meta-materials’).

Two types of response of the magnetic metamaterials (see e.g. Fig. 1) will be investigated: responses of the metamaterials with spin wave resonances to incident EM waves, and secondly responses of the metamaterials to spin waves themselves used as the incident waves [3].

Periodic structures will exhibit band gaps if ‘probed’ with a wave with a wavelength of the order or smaller than the period. Magnonic band gap materials only allow spin waves with frequency (wavelength) within allowed bands to pass.

‘Effectively continuous’ behaviour can be observed for wavelengths larger than the inclusions (periods), e.g. for microwaves or long wavelength spin waves and will also be studied.

As enticing new material science the project will create truly 3D magnetic nanostructures consisting of metallic nanospheres within protein shells ordered into 3D lattices with a regular spacing. We note that the protein arrays have periods of the order of 10 nm and spin wave sources of that length scale are currently unavailable. So, only effectively continuous behaviour of protein based arrays will be studied experimentally.

But also other designs will be studied like e.g. shown in Fig. 1 and 2.

We expect that the new spin wave theory relating electromagnetic excitation to spin wave dominated responses will result in fascinating new properties,

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not yet presented in the literature. The effective magnetic parameters describing the collective spin waves as if the inclusion arrays were a continuous material are a.o. the effective exchange constant, effective anisotropy, effective magnetisation and effective gyromagnetic ratio [4].

These entirely new electromagnetic meta-materials could be designed to tune the transmission, absorption and reflection of electromagnetic radiation in the GHz-THz frequency range.

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These entirely new electromagnetic meta-materials could be designed to tune the transmission, absorption and reflection of electromagnetic radiation in the GHz-THz frequency range.

Figure 1a. Sketch of a 1 dimensional (1D) proposed meta-material. Thin ferromagnetic films are separated by the host dielectric of a relatively large thickness. The electromagnetic wave propagates along z direction. The wavelength of the electromagnetic wave is much greater than the characteristic dimensions of the structure. (unpublished).

Figure 1b. The numerically calculated dispersion of spin waves in a zigzag shaped ferromagnetic magnetic structure is shown. The long wavelength spin waves ‘do not feel’ each individual period of the structure but their dispersion is modified by the total and hence reflects the effective behaviour of the magnonic structure. The magenta dots are experimental data points acquired using the Brillouin Light Scattering (BLS) technique. (unpublished).

REFERENCES
Design of nanostructured metamaterials in METACHEM

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The goal of the METACHEM collaborative project is to fabricate nanostructured metamaterial exhibiting extraordinary electromagnetic properties in the visible range. For the experimental work, METACHEM associates nanochemistry (for the synthesis of engineered plasmonic nanoparticles), self-assembly of colloidal objects (for the fabrication of three-dimensionally organized materials) and optical measurements (for the extraction of the effective electromagnetic parameters). Alternatively, theory plays a major role as it provides materials scientists with the design of the operational nanostructures that are expected to produce the targeted properties. This chapter reviews the main classes of nanostructures that will be produced within the METACHEM project.

1- Nanoclusters:

Nanoclusters of plasmonic particles surrounding a dielectric or plasmonic core have been proposed by C. Simovski (Fig. 2a and reference [1]) as isotropic nanoresonators at optical frequencies. Dense assemblies of such nanoclusters (with the metal core at the centre) are candidates for isotropic materials exhibiting negative refractive index in the optical frequency range. If the central particle has no metal core such composites exhibit the resonant permeability. Calculations were done using the Drude model for the permittivity of silver. Two alternative designs of the magnetic nanocluster where simple plasmonic scatterers (nanospheres) are replaced by plasmonic tripods prepared from intersecting or touching nanospheres are shown in Fig. 2b. This structure was proposed for the case if the Drude model for the permittivity of silver fails. With this design solution it is theoretically possible to attain the negative permeability (and negative refraction index if the central particle has the silver core) using the experimental data for the permittivity of silver from [2].

2- Metal-dielectric composites:

Assemblies of metallic nanorods (Fig. 3) and nanolayers embedded in a dielectric matrix have been considered. Such structures have two interesting properties: (i) they may lead to highly directive radiation – orthogonal to the rods – from a very localized source [3], (ii), they may transfer an image – along the rods – with a sub-wavelength resolution. Image magnification can be obtained if a spatial divergence of the rods or a curvature of the layers is imposed [4].

Another design proposed in METACHEM is a self-assembled version of the nanofishnet structure [5], [6] in which a metal-dielectric-metal sequence of nanolayers forms a nanopatterned film (Fig. 4). The top and bottom metal layers are expected to support an antisymmetric resonant mode, giving a resonant permeability response to an illuminating wave, similarly to the magnetic response recently reported in other fishnet structures. Differently from previous fishnet designs, the holes in the nanopatterned film are arranged periodically on a triangular lattice and the

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resulting periodic cell is hexagonal. The position and strength of the magnetic resonance is controlled by the extension of the metal regions around the holes. Additionally, the plasmonic response of the metal parts of the nanopatterned film to the incident electric field, analogously to the Drude-like response of continuous wires, should result in a negative permittivity over the wide frequency range below the effective plasma frequency. The lattice periodicity should be larger than the hole diameter to ensure that the effective plasma frequency of the structure is above the frequency of the magnetic resonance. By carefully choosing the length of the lattice vectors and the size of the holes so that the effective plasma frequency of the structure is above the magnetic resonant frequency, the small resonance band where the permeability becomes negative can be superimposed with the negative region of the permittivity, and, as a consequence, in the frequency band just above the magnetic resonance the metamaterial will exhibit a double-negative behaviour.

-3- Super-lattices:

Super lattices of engineered spherical particles have been proposed as model structures exhibiting dielectric and/or magnetic resonances. As dielectric and magnetic resonances do not show up at the same frequency in a spherical homogeneous nanoparticle, binary alloys of metallic and dielectric nanospheres are considered as model systems of NIM (Fig. 5). In particular, to accomplish negative permeability at optical frequencies we can exploit the large electric permittivity stemming from intrinsic material resonances of certain semiconductors [7]-[8]. When a crystal exhibiting negative permeability is at hand, in order to achieve a NRI behaviour we can combine the magnetic crystal with an electric crystal showing a negative permittivity so as to form a binary particle superlattice [6]. The required electric response is induced by a material with a Drude-type permittivity such as noble metals or doped semiconductors in the infrared.

As an alternative, one can coat the spheres of the magnetic crystal with a proper material in a way that the coated unit exhibits an electric resonance at the same spectral region of the magnetic one (Fig. 6) [8], [9]. The underlying physical mechanisms correspond to a negative effective permeability response due to a polaritonic or excitonic spherical core, while a negative effective permittivity effect results from an electric-dipole resonance of the sphere coating on its outer surface, whose dispersion follows a Drude model. Since this permittivity value is negative, the electric field is evanescent within the sphere so that such electric dipole resonance is a surface resonance in contrast to the volume effect of the magnetic resonance. Therefore, the coating can be designed to have a negative permittivity. Note that the magnetic resonance of the core is hardly affected, as long as the permittivity of the coating remains small in comparison to the large permittivity of the core.
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Figure 4. (a) Atomic force microscopy image and scheme of the metal-oxide nanopatterned film onto a metal layer; (b) etching of the metal sublayer to produce a fishnet structure; and (c) deposition of metal sub-layer to produce the double-fishnet structure.

Figure 5. bcc superlattice of a binary alloy of metallic (grey) and dielectric (green) nanoparticles.

Figure 6. closed packed cubic lattice of core-shell (dielectric-metal) nanoparticles.
NANOGOLD meta-material designs

C. Rockstuhl(1)

Self organized metamaterials that rely on metallic nanoparticles which are suitably integrated into a dielectric host are at the focus of the Nanogold project. If self organization by liquid crystal structures is used for material assembly, small metal particles are of special interest. A small particle is thought of disturbing less the self organization process but there are open questions about their effectiveness. Our materials concept is therefore presented with the frame of scientific and technological limitations that might appear. Our metamaterial design concept is based on combination of resonances and interferences of electromagnetic fields in nanostructured composite materials suggested in different publications [ROCK 2007, ROCK 2008, WU 2008].

Fig. 7 outlines the general strategy. The metamaterials we propose are composed of periodically arranged nanoinclusions on two different length scales. Whereas on the first length scale the effective permittivity of the medium is altered, the arrangement on the second length scale permits to modify the effective permeability of the medium. The different design stages are shown in Fig. 7. A noble metal, e.g., gold (Au) or silver (Ag), serves as the starting material. It provides a sufficiently large negative real part for the permittivity in the spectral domain of interest [Fig. 7(b)]. Forming small nanoparticles (NP) out of such a medium [Fig. 7(a)] allows to permit for the excitation of a localized surface plasmons at appropriate design wavelengths. The metamaterial we propose at first is made out of these small NPs periodically arranged in a host dielectric [Fig. 7(c)]. The dispersion of the effective permittivity of such a medium is modified according to a Lorentzian lineshape in close vicinity to the collective LSP wavelength [Fig. 7(d)]. As denser the particles are packed as stronger the induced dispersion is. Such MMs were already investigated in the past [RIIKO 2005, LIDO 2007]. The real part of the effective permittivity exhibits large negative values for wavelengths less than the localized surface plasmon wavelength but huge positive values for larger wavelengths.

It is important to visualize and understand the action exercised by the metamaterials on light that propagates through this medium. Simulations based on the finite-difference time-domain method allow extracting the effective permittivity of the medium and it can be shown that for certain combinations of the inclusion size and the wavelength, the permittivity is negative, while for other combinations it is positive. These simulations also show that in the spectral domain where the effective permittivity takes negative values, the field experiences effectively a medium that has metallic properties, leading to a rapid attenuation of the penetrating EM field. If the wavelength of the source is slightly larger than the resonance wavelength, the effective permittivity of the medium is positive and the penetrating EM field is a propagating wave (and no exponentially decaying amplitude will be seen).

We also want to obtain an effective medium with a strong negative permeability. A sphere formed by a metamaterial made of densely packed metallic nanoparticles supports strong Mie resonances at wavelengths where the effective permittivity is positive. The resonance is stronger the larger the permeittivity of the metamaterial is, which is usually understood as beneficial. The fundamental magnetic mode will dominate the response and it occurs at the largest ratio for wavelength over particle size.

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We envision a medium made of densely packed spheres which we call the meta-meta-material [Fig. 7(e)]. It will show strong dispersion in the effective permeability in the spectral domain of the lowest order Mie-resonance. The optical properties of such structures are either analyzed with Mie theory, taking the effective properties of the metamaterial but no periodic arrangement of the spheres into account, or they can be also computed rigorously, taking the distribution of the spherical metallic nanoparticles and the entire geometry \textit{ab initio} into account. In the spectral domain of the lowest Mie resonance for the magnetic mode, a strong negative permeability is encountered, again with a Lorentzian line shape for the dispersion [Fig. 7(f)].

To summarize: our metamaterial concept is based on combining different unit cells to obtain negative index materials. We will consider complex optical properties of the host and inclusion medium and describe plasmonics in fully anisotropic materials, considering size dependent material properties. We will also try to overcome the loss problem present for small nanoparticles. We approach these design challenges by using several simulation techniques and combinations thereof. The large variety of structures and dimensions needs to be considered carefully. We approach the scattering properties of the metamaterials by Mie and generalized Mie theory, evaluation of the dispersion relation (based on plane wave expansion techniques), calculations of the reflection and transmission properties of finite slabs (done by employing the Korringa Kohn Rostoker or the Fourier modal methods), and we back up the simulation by general purpose techniques such as finite-difference time-domain and finite-element methods. Applications will be designed by incorporating effective material properties directly in a demonstrator.

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NIM_NIL targets the development of negative index materials (NIMs) operating in the optical regime with the lowest possible losses. The research will start by employing well-known negative index material designs ([1-3]), such as fishnet, and using gold for the metallic components and the structures will be fabricated by nanoimprint lithography. But the target is to replace the metallic components by graphene. The use of graphene is expected to improve the metamaterials properties based on its high electron conductivity. Optimization of the metamaterials structures will involve further modeling and development of manufacturing processes.

A common way to describe an artificial magnetic metamaterial is to approach it with an equivalent magnetic field driven resistor-inductor-capacitor (RLC) circuit. In the RLC circuit model $R$ represents the resistance of the circuit, $L$ the magnetic field inductance and $C$ the capacitance. The functional forms of $L$, $R$, and $C$ depend on the structure geometry. Moreover $R$ is proportional to the resistivity, $\rho$, which describes the motion of the electrons inside the metal. For free electrons in the metal the resistivity takes the form (known as Drude formula)

$$\rho = \frac{\gamma}{\varepsilon_0 \omega_p^2} - i \frac{\omega}{\varepsilon_0 \omega_p^2},$$

with

$$\omega_p = \sqrt{\frac{e^2 n_e}{m_{\text{eff}} \varepsilon_0}}$$

$\omega_p$ is the metal plasma frequency (in the UV range) and $\gamma$ the metal collision frequency (in the near IR) ($n_e$ is the number density of electrons and $m_{\text{eff}}$ their effective mass). In the microwaves regime ($\omega \ll \gamma$) it is sufficient to consider only the real part of the resistivity. In the IR and optical regime, though, the imaginary part of $\rho$ also becomes important and should be taken into account. This will result in a complex resistance, $R = \rho F = R_r + i \omega L_r$ ($F$ is a function of the geometry) containing, besides the usual real term ($R_r$ representing the ohmic losses), an imaginary term proportional to frequency ($i \omega L_r$), which is an inductive term; there $L_r$ represents the inductance of the current carrying electrons, expressing their delay in following high frequency fields. Using this complex resistance in the effective circuit equations, one can observe that the inductance $L_r$ is added to the magnetic field inductance of the circuit.

Scaling the artificial magnetic structures from mm down to the sub-micron and nm scale in order to achieve negative permeability response in the optical regime, one can see that the electron inductance scales inversely proportional to the linear structure scale, in contrast to the magnetic field inductance and capacitance which scale proportionally to this linear scale (this can be observed for any appropriate formula for the capacitance and inductance); thus, $L_r$ dominates the response of the structures on small scales (while on large scales its role is insignificant).

Taking into account the electron inductance, one can conclude and explain the main features of the magnetic response of nano-scale metamaterials. The behaviour can be summarized as follows:

(a) The magnetic resonance frequency of nano-scale structures [4] shows a saturation behaviour (Fig. 8) rather than scaling linear to the inverse lattice constant, as occurs in the mm-scale structures. The saturation value of this frequency, $\omega_{\text{max}}$, depends both on the design and on the properties of the constituent materials. In particular, $\omega_{\text{max}}$ is proportional to the plasma frequency of

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the metal used for the fabrication of the metamaterial; also structures of small capacitance and low magnetic field inductance lead to higher $\omega_m^{\text{max}}$.

(b) The magnetic permeability resonance becomes weaker the smaller the metamaterials dimensions are, and when we reach the nanoscale domain the permeability ultimately ceases to reach negative values. The strength of the resonance depends both on the geometrical design and the materials properties. In particular, a strong resonance and wide negative permeability band are obtained using metals with high plasma frequency and low collision frequency. Fortunately also the ohmic losses, are lowest for a high metal plasma frequency and a low collision frequency.

The results described in (a) and (b), above, show that to achieve high quality optical NIMs, one should pursue not only geometry optimization, but also use conducting materials with both high plasma frequency, $\omega_p = \sqrt{e^2 n / m_{\text{eff}} \epsilon_0}$ (where $n$ is the concentration of the charge carriers and $m_{\text{eff}}$ their effective mass), and low collision frequency, $\gamma$. Graphene seems to promise both these two figures: Recent experimental and theoretical works for graphene have revealed conductivity values ($\sigma = \epsilon_0 \omega_p^2 / \gamma$) as high as 18 000 (experimental) and 200 000 (theoretical) cm$^2$/Vs [5] which is an indication for very low collision frequency ($\gamma$) values. On the other hand, the ballistic transport of the graphene carriers, which implies linear frequency-momentum relation, indicates ‘zero’ effective mass ($m_{\text{eff}} = \hbar (\partial^2 k / \partial \omega^2)$) of the carriers and thus high values of the plasma frequency. Both these features make graphene a promising material for replacing the metallic components in nanometer scale metamaterials, leading to improved ‘quality’ optical negative index response (i.e. high ratio of real to imaginary part of the refractive index).

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Manufacturing
Chapter 3: Manufacturing Technologies of the projects

MAGNONICS
Protein-guided assembly of (magnetic) nanostructures

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The MAGNONICS project will develop several novel technologies for fabrication of magnonic meta-materials. The protein based colloidal crystallisation will be explored for fabrication of truly 3D magnetic nanostructures. This approach will be assisted by exploration of the use of atomic layer deposition (ALD) for depositing magnetic materials within voids of the 3D arrays. The need to produce large area (mm to cm) samples (large areas are required by long wavelength electromagnetic waves) with nanoscale features, low dispersion in properties and long range ordering will be addressed by using the etched nano-sphere lithography in combination with electro-chemical deposition of magnetic materials. These novel and therefore bearing increased risk approaches will be backed up by such more conventional techniques as e-beam lithography, focused ion beam etching, magnetron sputtering etc.

Ordered arrays of nanoparticles have interesting properties [1,2] including metamaterials properties. Several methods are available to fabricate ordered 2-dimensional nanoparticle arrays, such as direct self-assembly, but truly 3-dimensional (3-D) ordered arrays of nanoparticles are considerably more difficult to make. They are usually prepared by slowly destabilizing a colloidal dispersion of nanoparticles, for example by adding a precipitating agent and permitting evaporation, to form facetted ‘colloidal crystals’ [3]. However, to form colloidal crystals requires a highly monodisperse distribution of nanoparticles, and the process is extremely slow: it takes 5-7 weeks to grow colloidal crystals of size up to 100 μm from ~ 10 nm diameter nanoparticles, using a three-layer supersaturation technique [4].

Proteins enable a different approach to fabricating 3-D nanoparticle arrays. As a first stage, nanoparticles with the desired function are synthesized inside individual protein molecules, using the protein shell as a nano-reactor [5]. Next, the protein is crystallized to give the desired array, as shown schematically in Fig. 1. With this approach, the periodicity and symmetry of the array is controlled solely by the protein. This method is quite general, as it can easily be applied to different proteins and to nanoparticles with a wide range of material properties. Protein crystallization has been used previously to prepare 2-dimensional arrays but till recently not 3-dimensional ones [6].

The feasibility of this approach was first demonstrated by preparing periodic arrays of ferrimagnetic nanoparticles, with all 3 array dimensions of the order of 100 μm, using the protein ferritin as a template [7]. Native ferritin consists of 24 protein sub-units that form a nearly spherical hollow shell of thickness ~ 2 nm, penetrated by channels, which encloses a hollow cavity of radius ~ 4 nm [8]. In native ferritin, this cavity stores excess intracellular Fe as a mineral,
the empty protein shell (apoferrittin) may be used as a nano-scale reactor to synthesize nanoparticles ranging from oxides and sulphides [5] to metals such as Cu [9], and MAGNONICS will concentrate on magnetic oxides and metals.

To demonstrate protein-guided assembly of magnetic nanostructures, nanoparticles of magnetite-maghemite \((\text{Fe}_3\text{O}_4 - \gamma - \text{Fe}_2\text{O}_3)\) were synthesized in apoferritin by oxidizing Fe (II) [10]. Ferritin containing nanoparticles of magnetite-maghemite is known as magnetoferritin [11] because magnetite-maghemite is ferrimagnetic and has a much greater magnetization than the antiferromagnetic ferrihydrite of native ferritin. Magnetoferritin was then purified and crystallized using \(\text{CdSO}_4\) as a precipitation agent [7]. Magnetic fractionation ensured that all the ferritin molecules incorporated in the crystals contained magnetic nanoparticles.

Fig. 2 shows that this method works: the crystals’ regular shape and clear facets indicate that synthesis of the ferrimagnetic nanoparticle within the protein cavity has not destroyed its ability to crystallize. Magnetoferritin crystals are being developed into metamaterials for magnonic applications.

The method demonstrated here for making large, regular 3-D arrays of nanoparticles should also be applicable to many other materials. For example, it would be of interest to study the optical properties of protein crystals containing metal or semiconductor nanoparticles and such studies will be conducted in the project to establish the effective continuous EM and magnonic properties.
The objective of the METACHEM project is to apply self-assembly methods of colloidal sciences to the fabrication of 3-dimensional nanostructured metamaterials operating in the range of visible light or near infrared. Besides the necessary theoretical work devoted to the fine definition of the structural parameters, the manufacturing work in METACHEM gathers nanochemists and soft condensed matter physicists. The toolbox of nanochemists enables the synthesis of a large variety of nanoobjects with adjustable morphology, size or surface function. These objects can be used as nanoresonators. They can be assembled in 3-dimensional super-lattices via self-assembly methods that are commonly found in soft condensed matter systems, namely clustering by specific interaction or slow evaporation, copolymer templates or Langmuir films.

-1- Introduction:

Developments in designs over the past couple of years have brought the field of metamaterials into a stage where, besides lithography-based approaches, new ‘bottom-up’ fabrication techniques based on nanochemistry and material science can now be effectively explored.

Recent advances in the chemical synthesis of engineered nano-particles and objects make it possible to consider them as the building resonating blocks that may create the desired local electromagnetic response. The nanoparticle-assembled structures can show original emergent properties that cannot be readily envisioned from the original properties of the building block. The physical properties of an assembly of nanoparticles, resulting from the strong interactions between their constituents, differ from those of isolated particles as well as from those of the bulk counterparts, and are function of the shape and type of assembly. Collective optical, electronic, and magnetic properties are observed when nanoparticles are organized in 2-/3-D periodic arrangements.

In order to manufacture a functional, three-dimensional bulk metamaterial out of these individual nano-objects, we thus face the difficult task of distributing them in space in well-organized sequences. For effective collective behaviour we need an average density of one to ten active units (nano-resonators) per wavelength. For operation with visible light this corresponds to about $10^9$ to $10^{12}$ nano-particles in a volumetric metamaterial sample of millimeter size. The individual, direct manipulation of such a huge number of nano-objects seems unrealistic for large-scale applications.

On the other hand, self-assembly appears as a common and highly efficient process well known in soft condensed matter physics. It results from the spontaneous organization of individual objects under the effect of complex pair interactions and can lead to well organized two-dimensional or three-dimensional structures of various symmetries. This is why it is currently one of the most promising routes to 3D metamaterials.

The objective of METACHEM is therefore to combine nanochemistry (to design and synthesize nanoparticles as individual resonators) and self-assembly techniques (to organize the nanoobjects at nanometer scale) in order to fabricate artificial materials possessing ‘meta’ electromagnetic properties.

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-2- Nanochemistry of nanoobjects:

The recent advance in material science provides extremely effective tools for nano-object fabrication. The increasing attention is fostered by the original exciting properties of materials in nanophase state, which are highly dependent on their geometry and can be dramatically different from those of the corresponding bulk phase materials. Such geometry dependent properties are essential for designing novel functional materials with tailored characteristics, revealing a high impact on fundamental aspects as well as on potential technological applications. Fine tuning of the nanomaterial chemical and physical properties opens possibilities for their application in several fields.

Among the numerous synthetic methods that have been developed, the chemical solution approaches have been demonstrated to be a valuable route for obtaining nanocrystals and nanoparticles with high control on size, shape and monodispersity, which are crucial parameters for defining the final properties of such nanosized matter (Fig. 3). Such materials present many advantages over those obtained by other means owing to the flexibility, not only in synthesis conditions but also, mainly, in post-synthesis processing.

Colloidal strategies, in particular, provide highly processable nanoobjects, thanks to the organic molecules layer present at the surface, which represents an adjustable interface with the external environment, thus allowing a careful control on their solubility and on their specific chemical reactivity toward the surroundings.

In the METACHEM project, several nanostructures will be developed corresponding to a different set of detailed scientific and technical objectives. Those can be summarized as follows:

(a) Spherical gold nanoparticles, with sizes bellow 10 nm, for incorporation in templates. The synthetic methods to produce these nanoparticles will be based on modification of the Brust method [2], where the Au salt is reduced with a strong reducing agent (sodium borohydride).
Silica-coated gold nanoparticles, with 15 nm Au core and different silica shell thickness, for their assembly by means of the Langmuir Blodgett technique and for their directed assembly in order to built 3D-isotropic metamaterials. Such individual structures will be obtained following the Turkevich [3] method for the production of the Au cores, and the Stöber [4] method for the latter silica coating. The Turkevich method comprises the reduction of the Au salt in the presence of sodium citrate acting as a reducing and stabilizer agent. The Stöber method will be used for controlling the silica shell thickness by means of the condensation reaction of tetraethyl orthosilicate (TEOS) on previously functionalized Au core nanoparticles with (3-Aminopropyl)trimethoxysilane (APS). This approach will allow a precise tuning of the silica shell thickness which remains a critical issue for controlling the distance between plasmonic metal cores.

Nanostructures composed of a metallic gold core and a fluorescent shell (of dyes or quantum dots) for loss compensation. The gold cores will be synthesised as explained above, following the Turkevich approach. The fluorescent shell will be deposited onto the metallic cores by means of two different strategies. The incorporation of dyes will be carried out through the condensation reaction of a mixture composed of a silica precursor and the desired dye onto functionalized gold nanoparticles. In the case of quantum dots, they will be directly attached to the silica-coated gold nanoparticles (with a different silica thickness) by means of the electrostatic forces or by covalent bonds.

Gold nanorods, and core-shell gold nanorods-silica nanostructures for their self-assembly to make plasmonic lightguides. Metallic gold nanorods will be synthesised by means of modifications of the El-Sayed approach [5]. His strategy is based on the slow growth of metallic Au seeds (3-4 nm) in the presence of CTAB by means of a slow reduction of Au(+3) with ascorbic acid. The same approaches described above for the spherical gold nanoparticles (with the modifications required) will be applied to the gold nanorods for their coating with silica or even polymers. Their perpendicular alignment with respect to the substrate will be obtained through their self-assembly using mimic surfactants [6].

Similar nanostructures to those described above by using silver instead of Au will be also investigated.

Three different routes are developed in parallel in the METACHEM project:

(i) Nano-clusters:
Individual electric and/or magnetic resonators can be obtained by associating a small number of plasmonic particles (typically of the order of ten) in a well controlled geometry [7, 8]. Fig. 4 shows the geometry of such nano-clusters proposed by C. Simovski and S. Tretyakov [8]. The fabrication of the nanoclusters is indeed more difficult than the synthesis of individual core-shell particles, but the self-assembly of the clusters is simpler as a regular periodic three-dimensional ordering is not required.

(ii) Template-assisted approaches:
Template-assisted approaches use nanostructured host-matrices (such as liquid crystals or block copolymers) in which the nanoparticles are embedded and spatially organized, the resulting material thus being a composite consisting of particles and the host. Block copolymers, in particular, present spontaneous molecular organization with long-range order with periodicities of order of a tenth of the wavelength of visible light (10-100 nm). Four equilibrium symmetries are known (Fig. 5): body-centered cubic array of spheres, bicontinuous cubic structures, hexagonally packed cylinders and lamellae. Ordering solid nanoparticles in such templates has been addressed, with steady progress, for more than a decade. This technique can be done with metallic nanoparticles. Provided the proper interactions are permitted between the particle surface and the polymer chains, the metallic particles can be confined within the nanodomains formed by one of the blocks of the copolymer, thus producing ordered metal-organic nanocomposites of chosen symmetry.
Moreover, block copolymers also form self-assembled objects, called micelles, in dilute dispersions in an appropriate solvent. Patterned surfaces can be obtained when such micelles, deposited on a substrate, are used to template material deposition or etching.

(iii) Direct techniques:
Direct techniques appear as the most desirable methods since they spontaneously organize the nanoobjects into dense, well-ordered packing. They include solvent evaporation, gravity-driven sedimentation, or convective deposition. Semi directed technique such as layer-by-layer Langmuir-Blodgett deposition combine self-assembly and directed growth.

Different schemes can be used to convey the instruction for assembly and organization into nanoparticles and nanostructures (Fig. 6). In the case of spontaneous assembly (self assembly) the organization is guided by the intrinsic information coded into the building blocks, namely size, shape and surface chemistry.

The complexity of the structure formed depends on a variety of factors, ranging from the type of single structural element, the length scale along which the assembly is achieved, and the kind of mechanism that is ultimately exploited to create the final architectures of matter. The basic nanosized building blocks of such complex structures play a crucial role, and the extent to which they can be engineered and their properties suitably tailored is central.

The colloidal chemistry approaches enables to fabricate nanostructures, taking advantage from the a priori design of the novel building blocks, programmed for assembly and synthesized with specific structure and requirements in mind. Recent advances in the fabrication of the building blocks for assembly process have been achieved by a deep understanding of the NC and NP shape control, introduction of asymmetry and multi-functionality, and careful control of the synthetic mechanism (monodispersity and surface chemistry control). Such investigations, combined with the vast understanding of fundamental mechanism of the assembly processes, have led to an enormous development in this field.
The extent to which the building blocks can be engineered has progressed tremendously in the last few years, and there are many works that have reported on new classes of 'supermolecules' and particles designed and fabricated with desired features, including encoded instructions for assembly, that help in designing a new generation of materials. In particular, precision fabrication of self-assembly components, introduction of orientational order and asymmetry, as well as programmability and addressability are issues that have been extensively explored.

Assembly of high-quality NCs of different types into complex ordered materials will provide unique chances for original functional structures and open the venue to a novel domain of bottom-up chemistry with enough potential to compete with the top-down approaches of nanolithography.

Figure 6. Transmission and scanning electron microscopy images of different structures resulting from the assembly of PbS nanocrystals (A-D), assembly of Au nanorods (E,F) and Au nanoparticles (G,D) onto carbon nanotubes, and the in situ growth and assembly of gold nanoparticles into a hollow silica sphere.

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To realize materials with unusual electromagnetic properties we use the idea of coupling resonances. We do need a resonant entity (nanoparticle) that will be incorporated in a building block (liquid crystal molecule or meta-atom) and further assembled in a structure (liquid crystalline phase or induced structure). The metamaterial behaviour (response) is due to resonance effects from the single building block (inclusion) and the 3D structure of the liquid-crystalline phase (geometry).

In our approach the particle size can even be relatively small and is therefore suited to be incorporated directly into a macromolecule. Larger nanoparticles allow for sharper resonances and will be studied too. To explore the whole range of possible structures three strategies are used:

- realize entire materials by chemical synthesis;
- design meta-atoms containing resonant entities and find ways for their assembly;
- use phase separation techniques based on polymer technology and liquid crystals to manufacture the desired material structure.

To obtain three dimensional meta-material structures based on the compound multiresonant material approach, three different scientific and technological backgrounds are needed:

1) Chemical synthesis of composite materials containing resonant entities. The organization of the incorporated resonant moieties is based on liquid crystalline phases (by Georg MEHL University of Hull and Toralf SCHARF EPFL). Nano-chemistry of composite metallic nano-entities based on chemical synthesis and physical chemistry (by Thomas BUERGI University of Heidelberg).

2) Technology of composite nanomaterials based on phase separation and induced spatial ordering (by Toralf SCHARF EPFL).

In what follows detailed information on these subjects to be used in NANOGOLD project are given.

-1- Chemical synthesis of composite materials containing resonant entities: Fabrication of liquid crystal gold nanoparticles

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Nanostructured Metamaterials

mainly determined by the condition to maintain auto-
organization, hence to find a liquid crystalline phase.

The idea is to include nanoparticles in a liquid crystal host, in order to create organic-inorganic composite materials with tailored metamaterials properties. The metamaterial behaviour (response) is due to resonance effects from the single molecular building block (inclusion) and the 3D structure of the liquid-crystalline phase (geometry).

The host could consist of mesogenic rod-like, disk-like and tapershaped (dendrimer) molecules, which form liquid-crystalline phases even when particles are included. For most of the approaches, like simple mixing of nanoparticles with a liquid crystal host, particles will disturb the order of the host. However, if the particles are incorporated into the molecules they might be hidden and the presence of the particle may induce a higher degree of order than exhibited by the native mesogen. The distance between the nanoparticles should be designed to be between 0.3 nm to over 10 nm.

In the NANOGOLD project we will attach macromolecular and low-molar liquid crystal (LC) ligands to the particles by chemical methods. The shapes of the macromolecule incorporating a nanoparticle are strongly dependent on the ligand structure, the number of dendrons and on the volume filled around the particle. Principles of close packing and radial distribution of density, introduced for spherical [UNGAR 2003] and rod-like [ZENG 2005] supramolecular dendrimers will be applied to guide the design of one-dimensional and three-dimensional ordered arrays of nanoparticles. The challenge is to design macro-

molecules and mesogens incorporating metal nano-
particles that show distinct mesophases with two- and three-dimensional order at high loads of particles.

The project will try to make highly monodisperse metal nanoparticles derivatized with alkane thiols, acids or amines as only then do they form bulk lattices with long-range order [WHETTEN 1996, SUN 2000]. The lattices targeted are those natural to packing of spheres, i.e. bodycentred cubic, hexagonal close packed or face-centered cubic. Bodycentred cubic lattices can also be made with bulkier mon-
odendron thiols via derivatization of gold nanoparticles [DONNIO 2007].

Until now, only very little is known about which parameters are the most influential for self-organization and the ensuing spatial assembly of gold nanoparticles wrapped with LCs. The expertise within the consortium gathered in recent years through research on LC multipodes with inorganic cores [CSEH 2006, CSEH 2007] and nematogen-coated gold nanoparticles [ZENG 2009], provides a solid background for designing realistic strategies with a good chance of success. An example is shown on the following figure.

In NANOGOLD we will study the influence of different material parameters on the materials properties.

We do need:

- high density of resonant entities within the material;
- different liquid crystalline phases with varying geometrical parameters.

To obtain a variety of phases and set the density for entities within the material, variation of different characteristic has to be studied. Of importance are:

- size and shape of nanoparticle;
- size of the organic ligands;
- length and stiffness of the spacer part of the ligand;
 Nanotechnology of composite metallic nanoentities based on chemical synthesis and physical chemistry

Thomas Bürgi (3)

Monolayer-protected metal nanoparticles (NPs) have attracted significant research interest in recent years due to their importance in both fundamental science and technological applications. The physical properties (optical, electrical) of these organic-inorganic hybrid materials are largely determined by their metal core, whereas the shell around the latter determines their chemical properties like solubility or recognition. The physical properties of these organic-inorganic hybrid materials are highly tunable by changing not only the size and the shape of the metal core but also the spatial arrangement of these building blocks with respect to one another within a material.

The literature dealing with metal NPs synthesis is uncountable and a wide variety of techniques have been reported using precursors from liquid, solid and gas phases. Metal NPs can be prepared by the top-down (physical) approach. However, the bottom-up (chemical) approach is considerably cheaper and allows one to prepare very small particles as well as larger ones.

The chemical approach is based on the nucleation and growth of metallic atoms in liquid media or in gas phase. The literature describes five general methods for the chemical preparation of transition metal NPs: [Gautier 2009]

- anchoring strengths at the nanoparticle (anchor chemistry, mobility on the particle...);
- characteristics of the ligand (stiffness, phase transition temperatures, stability...);
- molar ratio between the ligand and the co-ligand ‘diluent’ chains;
- order and phase sequence of the resulting mesophase.

Understanding the influence of each of these characteristics will allow to select liquid crystalline phases, getting influence on the arrangements of nano-entities and design materials. For meta-material design based on such materials wire grid approaches are most promising [Yao 2008, Simovski 2005, Pendry 1999]. It was already demonstrated that liquid crystal mesogens containing gold nanoparticles establish a structure that shows chains of nanoparticles with varying distances between them [Zeng 2009]. Different mesophase will lead to different particle arrangements. Chains were already demonstrated but also planes might be found in smectic phases that have layered structure. All depends on the design of the mesogenic which contain the resonant entity. We will study specific molecular design, characterize the structure of the resulting phases and support the design by molecular simulations. A wire grid metamaterial where grids are composed out of spheres will be the first candidate to be designed and optically studied. Such material will have high anisotropy and should have a resonant stimulated response to electromagnetic waves.

The effective electromagnetic response parameters like susceptibility and permeability of the materials depend on structural parameters such as particle distance and chain distance. These parameters are results of the mesophase formation. In recent publication 60-nm wire diameter and 110-nm center-to-center distance were used to demonstrate negative refraction effects [Yao 2008]. Our materials have much smaller distances and wire diameters. Typical values here are 1-5 nm particle chain diameters and 5-20 nm chain to chain distance. Detailed electromagnetic field simulations will be undertaken to find an optimal configuration. In resonance based composite metamaterials the range of accessible effective electromagnetic materials is usually wider when the resonances are more pronounced. This would be the case for particles larger than 2 nm. A main challenge in our research is therefore to increase the size of nanoparticles in such materials while maintaining the self organizing properties.
1) chemical reduction of metal salts;
2) ligand reduction and displacement from organometallic complexes;
3) electrochemical reduction;
4) metal vapor synthesis; and
5) thermal, photochemical or sonochemical decomposition.

The chemical reduction method is very versatile. For the preparation of gold nanoparticles by chemical reduction the methods proposed by Brust et al. [Brust 1994] and Turkevich [Enustun 1963] are most popular. The former results in particles up to about 4 nm, whereas the latter can be used for the preparation of larger particles of several tens of nm in diameter. Using the Brust method (Fig. 8) it became recently also possible to prepare truly monodisperse gold particles or clusters such as such as Au$_{25}$, Au$_{38}$, Au$_{68}$, Au$_{102}$, Au$_{145}$ and Au$_{225}$.[Walter 2008, Murray 2008]. The stability of these ‘magic’ particles can be explained by a superatom model.

The ligand shell of the particles is crucial for their stabilization against agglomeration. The ligand shell can however also be used to introduce functionalities and it can furthermore be modified to provide organization to the nanoparticles. The relatively strong gold – thiol binding makes thiol an adaptable ligand. Once thiolate covered gold nanoparticles are formed their surface and therefore their chemical properties can be engineered by several methods, such as through thiolate-for-thiolate exchange or chemical transformations such as esterification (Fig. 9).

An interesting opportunity of such organic – inorganic composite materials is their self-organization into supramolecular structures. The information needed to do so is already encoded in the monomeric units. Examples of such systems are liquid-crystalline gold particles, where some of the thiolates in the ligand shell are mesogenes or liquid-crystalline dendrimers [Frein 2008, Zeng 2009, Cseh 2006]. Even hierarchical structures may form by combining nanoparticles with amphiphiles [Shalkevich 2009] or block-copolymers [Glass 2003].

Figure 8. Sketch of the biphasic reaction according to Brust’s protocol. Au(II) is transferred from water to the organic phase, forms Au(I)/thiolates polymers when thiols are added and are reduced by sodium borohydride to yield (C$_{12}$–SH)-stabilized Au(0) nanoparticles according to a nucleation-growth-passivation mechanism.
Figure 9. Methods to introduce new functions to thiolate-protected gold nanoparticles.

EGMUDE: (1-Mercapto-11-undecyl) tri(ethylene glycol)

Figure 10. Left: Transmission electron micrograph (TEM) of gold nanoparticles (17 nm) covered by EGMUDE, an amphiphilic thiol. Right: Hierarchical structure formed from EGMUDE and gold nanoparticles covered by EGMUDE during the preparation in aqueous solution. Reproduced with permission of the PCCP Owner Societies.
-3- Technology of composite nanomaterials based on phase separation and induced spatial ordering

Toralf SCHARF (4)

It has been theoretically shown that the use of more complex structures combining nanometer and submicrometer scales allows to create metamaterials with negative refractive index near the visible [ROCK 2007]. Experimental validation of such a concept was done on surfaces with the help of self assembly techniques based on surface modification [Lee 2009, WU 2008]. Assembling three dimensional materials of such kind would need different approaches. Within NANOGOLD we will follow two pathways:

- self assembly techniques by physical chemistry principles for bulk and surface nanostructure fabrication; and
- conventional nano- and microtechnology for test and reference structures.

A recent review of conventional wafer based metamaterial fabrication is available [BOLTAS 2008] and shows clearly the limitation to small area applications of planar fabrication techniques. Microtechnology can be used for structures larger than 500 nm and electron beam writing of surface structures has to be used for smaller structures. Often this leads only to very small active areas. Imaging an entire substance with a dedicated phase sequence is possible. If liquid crystal phases are formed, mixing rules between different substances apply and more or less complex phase diagrams will describe the properties of mixtures. Then physical chemistry can be used. Micro-phase separation and emulsions are good tools to structure materials in three dimensions if the structure can be frozen. Phase separation experiments are of major interest and the concept follows the fabrication of polymer dispersed liquid crystals [DRAICZ 1995], where the phase of a mixture of liquid crystal and epoxy glue (homogeneous if the liquid crystal is in its isotropic phase) separates when transferred into the mesophase. Depending on process conditions nanometer sized structural features are formed. Phase separation can be by polymerization. Obtainable structured size and assembly parameters fit with the metamaterials design given in [ROCK 2008].

In this way, the preparation of cavities filled with densely packed nanoparticles can be envisaged what leads to realization of a metamaterial in the visible. A single particle of size above 10 nm filled with closely packed nanoparticles of size below 10 nm would act as a meta-atom with very interesting electromagnetic scattering properties. One challenge is to realize such structures base on chemistry and physical chemistry science presented before.

With the help of interference, structured UV laser radiation can be produced and used during polymerization [GORK 2005]. The technique for realizing such polymer-liquid crystalline periodic nano-structures by holographic means (HPDLCs) has actually become quite mature and reliable. One further step in this direction has been done in the past with the introduction of POLICRYPS [CAPUTO 2004a, CAPUTO 2004b]. The acronym indicates high quality structures consisting of polymer slices alternated to films of regularly aligned LC material (POLymer LIquid CRYstal Polymer Slices). A glass cell filled in with a mixture of monomer and Nematic Liquid Crystal (NLC) is brought up in temperature above the nematic-isotropic transition point of the LC and then exposed to a laser light interference pattern. At that temperature, the diffusivity of LC molecules is highly increased and it acts in synergy with the polymerization process (induced by the light curing) to determine an almost complete phase separation of polymer and LC [VELTRI 2004]. After curing, the cooling of the sample to room temperature induces a self-organization process of the LC molecules which results in well oriented liquid crystal layers.

The main challenge here is to obtain a material combination that allows to create dense nanoparticle assemblies of sizes between 10 and 50 nm in host materials and to arrange them. The conventional techniques to produce nanoparticles lead to densities that are very low compared to a densely packed system where volume fraction of more than 60 % have to be reached.

REFERENCES
NIM NIL
Fabrication of graphene inclusions

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Within NIM NIL the goal is to manufacture metamaterials based on graphene. Layers of graphene will be structured into metamaterials inclusions of nanometer size. Therefore fabrication and structuring techniques of graphene are investigated.

Fabrication of graphene layers

The usual reported method to achieve graphene is the micro-cleaving of highly oriented pyrolytic graphite, by using adhesive tape and/or manually rubbing graphite layers against SiO2 to obtain a monolayer or few layers graphene [2,3]. These techniques result in samples with micron dimensions. For scaling up the production, methods for large area graphene synthesis are developed which include

- ultrahigh vacuum annealing at T>1300°C for thermal decomposition of single-crystal SiC (0001) [4];
- CVD (chemical vapor deposition) on transition metals including Ni, Cu, Ru [5]; and
- the deposition of graphene oxide (GO) films from a liquid suspension followed by chemical reduction [6].

Since it has been demonstrated in literature that graphene properties and mobility strongly depend on the growth substrate and on the growth methodology, the NIM-NIL project aims at investigating and comparing different growth routes. The two methods to be compared are CVD and thermal decomposition based resp.

First, we use CVD to synthesize single- to few layer graphene films on evaporated polycrystalline Ni and Cu. The nucleation and growth of graphene occurs by exposure of the transition metal surface to CH4/H2 mixtures at temperatures typically around 1000°C. Since the solubility of carbon in Ni is temperature-dependent, carbon atoms precipitate as a graphene layer on the Ni surface upon cooling of the sample. Graphene films are then removed from the metallic Ni substrates and transferred to a Si/SiO2 substrate [7].

Secondly, epitaxial graphene films are also being produced on both the Si-face and C-face of single-crystal 6H- and 4H-SiC by thermal desorption of Si annealing SiC at T >1 300°C. After H2 plasma etching and oxide removal from the SiC surfaces, the surface is carbonized at high temperature to yield mono- and bi-layer graphene on the Si-face and few-layers (>5ML) of graphene on the C-face (Fig. 11). By this process, graphene is achieved directly on a semi-insulating substrate (instead of the CVD on metal that requires transferring).

Graphene obtained by CVD will be compared with that obtained by the thermal decomposition at T>1 300°C of both the Si-face and C-face SiC and by mechanical cleaving of graphite.

Fabrication of graphene metamaterials inclusions

To create metamaterials with inclusions made of graphene, the graphene has to be structured. The usual method to structure graphene is e-beam lithography [2], but this method cannot be used for mass production due to a low throughput.

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Different structuring approaches of graphene will be investigated:

- the transfer printing method and exfoliation;
- the pre-patterning of SiC and its transformation to graphene;
- structuring graphene layers created with chemical vapor deposition (CVD) methods.

In all three approaches use will be made of Nanoimprint Lithography (NIL) as structuring technique. NIL was developed in the early to mid 1990ies and soon proved to be capable of sub 10 nm resolution [11-14]. NIL is a fast and cost efficient technique which is listed in the international technology roadmap for semiconductors as a possible successor for optical lithography for the 32 nm node and beyond [15]. In the UV-NIL process (Fig. 12) a low viscosity resist is spin coated or droplet dispensed on a substrate and is deformed by a nano-patterned stamp. After UV-exposure and separation of stamp and substrate a negative copy of the stamp patterns on the substrate is achieved. To transfer the structures onto the substrate further steps like etching or metal deposition and lift-off are necessary.

**Transfer printing method and exfoliation**

To create structured graphene a transfer printing method has been developed by X. Liang as reported in [9]. A patterned stamp was used to exfoliate graphene layers from commercially available highly oriented pyrolytic graphite by pressing the stamp onto the graphite layer and transferred this layer to a quartz substrate. The feature sizes were about 10 μm.

Another method is to directly structure highly oriented pyrolytic graphite (HOPG) using NIL and to use the patterned HOPG for exfoliation similar as described in ref. [16]. Here HOPG was patterned using standard lithography techniques and brought into contact with a silicon substrate with 50 nm SiO₂ on top. By applying a voltage between HOPG and substrate the graphene layers which are in contact to the substrate are electrostatically exfoliated.

**Prepatterning of SiC and its transformation to graphene**

A different approach consists of structuring SiC using NIL and then transforming the SiC into graphene. It is known that SiC surface preparation (removal...
of SiO$_2$) is extremely crucial for obtaining homogeneous graphene. Therefore, we will optimise 4H- and 6H-SiC surface preparation using plasma dry methodologies taking advantage of the sub-monolayer sensitivity of in situ real time spectroscopic ellipsometry for optimising surface processes. Then thermal desorption of silicon from silicon carbide (6H-SiC) wafers at very high temperatures between 1250°C and 1450°C will be employed to form an inclusion consisting of a few layers of graphene [4].

**Structuring graphene layers**

If the deposition methods within NIM_NIL will be successful, patterned graphene can be achieved by imprinting directly on deposited graphene. The structures within the NIL resist will be transferred into the graphene by etching techniques.

NIM-NIL will explore all three methods for achieving metamaterial inclusions in the nanometer regime made of graphene. The best method will be optimized and used also for building up multiple layers into 3D NIMs. It has been shown that NIL is a suitable technique to stack subsequently several aligned layers on top of each other [17-19].

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Safety issues – Risks and hazards associated with the use and disseminations of nanoparticles

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For several years, nanomaterials became a centre of interest of academic research, but also from an industrial point of view. These nanostructured materials seem to be very promising for their unique physical and chemical properties due to their original nanostructure and their size (catalysts, composite materials, metamaterials...).

According to the current state of knowledge on nanomaterials exhibiting novel properties, it cannot be ruled out that exposure to such materials may have specific toxicological effects, different from those of larger particles in the micrometer range. General dust limit values do not necessarily apply in the case of ultra-fine dusts (i.e. dust fractions with a particle size of under 0.1 μm diffusion equivalent diameter).

Increased attention is drawn to Control Banding, as a practical approach to controlling hazardous agents in a changing world, as a complement to the traditional methods of air sampling and analysis and providing a formal process for incorporating professional judgment and monitoring.

Control banding (CB) is a system used to assess and manage workplace risks. It is a process in which a single control technology (such as general ventilation or containment) is applied to one range or band of exposures to a chemical that falls within a given hazard group. Control banding was originally developed by the pharmaceutical industry as a way to safely work with new chemicals that had little or no toxicity information.

Recently, Paik et al.[1] presented a pilot Control Banding tool called ‘Control Banding Nanotool’ which tried to take into account existing knowledge of nano-sized material toxicology and to use the Control Banding framework proposed in earlier publications.

Their method proposes to calculate a Risk Level as a result of, on the one hand, a severity score (hazard band) and on the other hand, a probability score (exposure band). For each of the four Risk Levels, a control strategy is proposed

> The severity score (0 to 100)

is determined by the toxicological properties of the bulk material (toxicity estimated by an Occupational Exposure Limit when available, carcinogenicity, reproductive toxicity, mutagenicity, dermal hazard), the same toxicological properties of the nano-sized material when available, and by some of the physical and chemical characteristics of the nano-sized material: surface chemistry, particle shape (fiber or tubular shape, irregular shape, anisotropic shape), particle diameter and solubility. A weighting factor is allocated to each of these parameters, 70% of the total score being related to the properties of the material in the nano-scale size. A lack of information for any of those parameters results in ascribing a score equal to 75% of the maximal score. According to the total score, nano-sized materials are allocated to one of four ‘severity bands’.

> The probability score (0 to 100)

relate to the likelihood for workers to be exposed to nano-sized materials. Calculation of this score involves several parameters: estimated amount of nano-sized material, dustiness/mistiness,
frequency and duration of operations, and number of workers potentially exposed. It must be noted that the amount of materials defined for the rating criteria are within the range that one can expect in a research laboratory (from milligrams to grams).

As a result of the calculation, one of the four ‘probability’ bands is allocated to the exposure scenario.

More recently, Zalk et al.[2] presented, how the CB Nanotool has been developed, implemented, and been proven to afford a qualitative risk assessment toward the control of nanomaterial exposures.

Even, if it should be recognized that CB toolkits must always be used with some degree of caution, CB strategies are known over decades to offer a simplified control of worker exposures when there is an absence of firm toxicological and exposure information. The nanomaterials R&D activities fit this classification perfectly. CB toolkit requires frequent use, validation, and evaluation of recommended control effectiveness. Moreover, an active dialog within the Industrial Hygiene community and users of such tools is strongly recommended.

REFERENCES
Characterisation
Chapter 4: Characterisation Theory and Measurements

Introduction

The possibilities of combining metamaterial inclusions are infinite and the possibilities for the realized effective material behaviour are vast.

Characterising the properties will be discussed by presenting the theoretical background and interpretation of measurements in section 4.1. A classification based on metamaterial behaviour is proposed with descriptive material parameters. The final aim would be that engineers, who have a wished for behaviour in mind, would be able to look up the different geometrical structures in the table and they would be able to choose the most suitable structure on e.g. fabrication related arguments (or be able to ‘place and order’ for development of the needed metamaterial).

Once the metamaterials are created, the geometric structure has to be verified. In section 4.2 (direct and indirect) structural characterisation is discussed.

Also the electromagnetic properties should be verified and this will be discussed in section 4.3. Measurement techniques need to be consistent with the procedure for the retrieval of characteristic parameters from the measurement data and it will be discussed that electromagnetic characterisation of different types of MTMs is one of the main challenges in modern applied electrodynamics.

4.1 EM characterisation Theory

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4.1.1 Classification of electromagnetic nanostructured materials

A classification based on the optical (more generally, electromagnetic) behaviour is needed with descriptive material parameters in order to facilitate the use of these materials. In this chapter we will take the first step towards this goal and try to establish the new nomenclature and classification.

In the literature and on the Internet there are many definitions of metamaterials, which usually stress their unusual electromagnetic (EM) properties. Perhaps in the most generic way, a metamaterial (MTM) can be defined as an arrangement of artificial structural elements, designed to achieve advantageous and unusual properties. Most of the literature deals with advantageous and unusual electromagnetic properties. But the term metamaterial is also used in the literature in connection with artificial materials designed to exhibit advantageous and unusual properties for waves of other nature, for example there is literature on phononics MTMs designed to control sound waves. Sometimes waves of other nature provoke electromagnetic waves (sound waves in piezoelectrics or spin waves in nanostructured magnetic materials), and there is no solid
boundary between electromagnetic and non-electromagnetic materials. Since the EC funded projects described in this booklet mostly work on electromagnetic MTMs, we focus on advantageous and unusual electromagnetic properties. An analogous classification can possibly be suggested for non-electromagnetic MTMs.

The concept of an effectively continuous material implies homogeneity, and we focus on materials in which the distance between elements is small enough (compared to the wavelength) to be considered homogenous. In this text we will include MTMs which are periodic structures, but we will only consider the case in which the lattice constants are considerably smaller than the wavelength in the medium. This distinguishes effectively continuous metamaterials from e.g. photonic (electromagnetic) crystals and from frequency-selective surfaces, whose useful and unusual (electromagnetic) properties originate mainly from the periodicity of their structure. Effectively continuous structures and their unusual properties are due to specific electromagnetic response of their ‘artificial molecules’ and not due to specific distances between them (geometric parameters of inclusions are more important than parameters of their arrangements). Furthermore, the electromagnetic properties of ‘molecules’ are determined not only by their chemical composition, but also by their geometrical shape. The chemical composition is usually chosen so that the response is strong (conductive material, plasmonic material, high permittivity material, ferromagnetic material, etc.) and losses are minimised. Specific engineered properties are designed primarily by choosing the inclusion shape and size. In this definition, MTMs are characterised by effective material parameters, e.g. (for bulk MTMs) permittivity, permeability, chirality parameter and other possible effective bulk parameters.

Sometimes photonic crystals or frequency selective surfaces are also called metamaterials. However, for these structures unified in the class of electromagnetic band-gap structures, the description of electromagnetic response is based on other concepts than effective material parameters (e.g. isofrequency plots or reflection phase diagrams). We do not include such electromagnetic band-gap structures in this chapter.

Inspecting different types of existing nanostructures (e.g. recent books [1-7]) and inspecting prospective nanostructures which are under discussion in the current literature we can find many types which satisfy the above definition of an MTM. To show the place of nanostructured MTMs among all nanostructured materials it is instructive to suggest a classification of nanostructures related to their linear electromagnetic properties. A possible classification is presented below in the form of a table and in an additional figure. This classification takes into account the internal geometry of the nanostructure, the most important linear electromagnetic properties of constituents/inclusions and those of the structure as a whole.

The first criterion of our classification is the dimensionality of the array of constituents which form the nanostructure (the vertical axis in Table 1) Bulk (3D) structures are structures with a large number of constitutive elements in any direction. Surface (2D) materials correspond to the case when the structure is a thin film with only 1-3 constitutive elements across its thickness.

The optical size of the unit cell/inclusion in the operational frequency range (usually, visible and near-IR for nanostructured MTMs) is the second criterion which determines the type of the nanostructure (the horizontal axis of the classification table) A large optical size implies \((qa) > 1\) where \(q\) is the wavenumber in the effective medium and \(a\) is the unit cell size, and these structures are called optically sparse. In this range the structure can not be presented as effectively continuous and can not be characterised by local material parameters (either bulk or surface ones). In the case of small optical size, characterised by \((qa) < 1\), the structure is called optically dense, can in principle be characterised by effectively continuous local parameters and can be referred to as an MTM. Of course, it depends on the wavelength of the excited waves whether a particular array of inclusions will behave as optically dense or optically sparse. Note that the notion of optical density is related to that of spatial dispersion. Optically sparse structures often show strong spatial dispersion, while spatial dispersion in optically dense media can be weak or negligible.
<table>
<thead>
<tr>
<th>Nanostructures</th>
<th>Optically dense ((q \cdot a &gt; 1))</th>
<th>Optically sparse ((q \cdot a &lt; 1))</th>
<th>Optically dense in one direction, while either optically sparse or with extended inclusions in other direction(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3D, bulk</td>
<td>Bulk MTM of small inclusions</td>
<td>Photonic crystals and quasi-crystals, Optically sparse random composites</td>
<td>Wire media, multilayer optical fishnet structures, alternating solid plasmonic and dielectric nanolayers</td>
</tr>
<tr>
<td></td>
<td>Bulk nanostructured materials without useful and unusual electromagnetic properties</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2D, surface</td>
<td>Metasurfaces/metafilms</td>
<td>Plasmonic diffraction grids, optical band-gap surfaces and optical frequency selective surfaces</td>
<td>Artificial impedance surfaces with long inclusions or slots</td>
</tr>
<tr>
<td></td>
<td>nanostructured optically dense surfaces without useful and unusual electromagnetic properties</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1D, linear</td>
<td>Metawaveguides</td>
<td>Not yet investigated, but possible</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Nanostructured materials, classified by their linear electromagnetic properties. Cells corresponding to metamaterials are highlighted in grey. Here \(q\) is the wavenumber in the effective medium and \(a\) is the unit cell size.

Note that MTMs of the surface type were called metasurfaces in [8, 9] and metafilms in [10-12]. Linear (directional) structures with nanosized inclusions are optical waveguides with nanoinclusions, plasmonic and polaritonic nanochains. They are called in this table metawaveguides.

In some cells of the table MTMs occur and we have shaded these in grey. The colour reflects the third criterion of the classification: the existence of useful and unusual electromagnetic properties of the nanostructured material (if the structure is consistent with the concept of material (i.e. can be homogenized). The richest content corresponds to the cell ‘Bulk MTMs of small inclusions’ which is probably also the most important cell of the table. This class is further detailed below.

Examples of optically dense surface nanostructures, which we do not classify as MTMs, are plasmonic island nanofilms and chemically roughened metal surfaces. The constituents are metal islands, random nanocorrugations, molecular clusters or even separate molecules. These materials are used mainly in sensing applications, utilising, for example, the so-called surface-enhanced Raman scattering (SERS). This application is based on the effect of the local field enhancement in the vicinity of such a surface and is caused by plasmon resonance. This enhancement effect is definitely useful. However, we do not classify chemically roughened metal surfaces as metasurfaces, because the local field enhancement is a local effect and not related to the properties of the structure. Their behaviour is fully determined by the properties of an individual nanocorrugation.

However, if the nanostructuring of the plasmonic surface is regular, the surface possesses an unusual property: strong enhancement of the averaged electric field at the surface. Such artificial surfaces we therefore include in our definition of metasurfaces. Also nanostructured surfaces of vertical (aligned) metal nanorods grown on a metal substrate [19] enhance, at the plasmon resonance, the field in the plane of the upper edges of the rods. In general, nanostructured self-resonant grids possessing certain regularity either in the arrangement of resonant elements or in their orientation are metasurfaces.

Such grids can comprise separate plasmonic scatterers on a dielectric substrate or plasmonic corrugations. They also can be realised as solid metal screens of nanometer thickness with slots or holes. For example, metal nanolayers with subwavelength slots support surface plasmon polariton waves whose dispersion is determined by these slots (see e.g. in Chapters 25 and 26 of [9]).
Another important example of a metasurface is a monolayer optical fishnet (see e.g. in Chapter 29 of [9]). This monolayer is formed by a pair of parallel silver or gold periodically slotted nanolayers with a nanogap in between. The slots in optical fishnet structures are obviously non-circular and are often optically rather large.

Abundant literature is devoted to nanostructured waveguides. Their useful and unusual property is the subwavelength channel for the guided wave observed in plasmonic nanochains (see e.g. in [20]) and nanostructured fibers with plasmonic insertions (see e.g. in [21]). This unusual and useful property results from the combination of the plasmon resonance and strong near-field coupling between constituents. These structures are thus classified as metawaveguides in our classification. They also can be used for frequency filtering of optical signals on the nanoscale level (e.g. in [22]).

Multilayer optical fishnets and multilayer metal-dielectric nanostructures (see e.g. [23-28]) are important types of MTMs. Multilayer optical fishnets demonstrate a negative phase shift of the wave across the structure (i.e. backward wave propagation) which is expressed by a negative phase velocity. Moreover, their group velocity can be also negative, i.e. the pulse peak can travel in the opposite direction to the energy transport direction. As to multilayer nanostructures of alternating solid metal and dielectric nanolayers, their unusual and useful property is the subwavelength optical imaging in the far zone of the optical object. This property has been experimentally demonstrated e.g. in [28].

Note that known fishnets do not offer subwavelength imaging in the backward-wave frequency range, and stacks of continuous layers do not support backward waves, so none of them can make a Pendry perfect lens. The thickness of the fishnet monolayer is much smaller than the wavelength. However, due to optically large period in the plane they possess strong spatial dispersion for waves propagating obliquely to the structure or along its surface. The strong spatial dispersion for these waves is also inherent to plasmonic nanostructures of alternating solid layers, where it is related to the infinite size of the layers in the plane. In both cases no unusual and useful properties of such structures are known which would be related to this spatial dispersion.

For another type of MTM – wire media – the effect of spatial dispersion is crucial for the unusual properties (see e.g. in Chapter 15 of [8]). Wire media in the optical range that are optically dense arrays of optically long metal nanowires or carbon nanotubes [23] can be grown on a substrate or prepared by embedding nanowires into porous glass or a porous plastic fibre matrix. If nanowires are grown on a substrate, the wires can be optically short and the structure qualifies as a metasurface (see above). Nanostructured wire media (arrays of aligned nanorods and nanotubes with long optical length) are spatially dispersive in the infrared range [24]. In the visible range optically dense lattices of parallel metal nanowires become a uniaxial dielectric medium without strong spatial dispersion [25] but with negative axial permittivity.

Plasmonic inclusions are resonant even if they have very small optical size. For example, silver or gold nanorods of 40 nm length of pyramidal shape in a liquid host medium resonate at a wavelength of 750 nm [26]. Nanocomposites with such inclusions refer to MTMs for both cases of regular and random arrangements. Random nanocomposites possess scattering losses whereas regular plasmonic composites do not. Therefore regular plasmonic composites are more promising. However, for very small silver and gold nanoparticles (considerably smaller than 10 nm in diameter) losses become so strong that the plasmonic resonance practically disappears.

Ferro- and ferri-magnetic nanocomposites can also be called MTMs, though they operate in the radio frequency range. Their granular or wired structure allows them to simultaneously possess non-trivial magnetic and dielectric properties. Ferroelectric nanocomposites are not yet studied much, but it is certain that also these can possess unusual and probably useful properties, and we included them into our chart together with magnetic nanostructured materials.
Magnetic nanostructured materials can be made optically very dense if we compare their spatial scale with the EM wavelength in free space. However, the length of the so-called spin waves which can be excited in them is usually very small compared to the size of magnetic nanoparticles. The exception is the so-called magnonic MTM, where the spin-wave wavelength may be comparable to, or larger than, the distance between nanoparticles (but still much smaller than the wavelength of electromagnetic waves at the same frequency). The design and the characterisation of these media is a subject of new research and a classification has not yet appeared (see separate chapter of this booklet). These structures are not included in our materials classification.

Now we will move on to discuss the class of ‘Bulk MTMs of small inclusions’.

In Fig. 1 a classification of bulk MTMs of small inclusions is given based on their material parameters. We distinguish 6 major branches:

1) Artificial dielectric media with unusual permittivity. Unusual values of $\varepsilon$ are values close to 0 or to (-1) or very high in the visible range where usual materials (except some liquid crystals existing only in the form of thin films) have rather low permittivity.

2) Artificial magnetic media, operating in the optical range. Not only media with negative $\mu$ deserve to be referred to as MTMs, media with $\mu=0$ or $\mu=2$ in the optical range are also MTMs.

3) Media with both negative permittivity and permeability. These media represent the most known type of MTM, however if $\varepsilon=0$ and $\mu=2$ in the visible range such materials should be also referred to as magneto-dielectric MTMs.

4) Nanostructured materials with constituents possessing natural electric (electrets, ferroelectrics) or natural magnetic (ferromagnetic, ferrimagnetic) polarisations.

5) Multipole media.

6) Bi-anisotropic media discussed in Chapter 1.4.1 of this chapter.

**Figure 1.** Classification of bulk nanostructured MTMs of small inclusions. The optical range in this scheme by definition covers IR, visible and near UV ranges. The abbreviation NSM in the figure means nanostructured materials.
4.1.2 Classical characterisation techniques: Limitations on retrieved effective parameters

*State-of-the-art of retrieval techniques*

Retrieval of electromagnetic characteristic parameters from measured data (also called *post-processing*) is necessary for experimental electromagnetic characterisation, since no electromagnetic characteristic parameters of a material can be measured directly. Most often, the retrieved parameters are the permittivity and permeability ($\varepsilon$ and $\mu$) which by definition pertain to magneto-dielectric media. The material equations are by definition:

$$\mathbf{D} = \varepsilon \mathbf{E}, \quad \mathbf{B} = \mu \mathbf{H}$$

In the classical scheme of linear electromagnetic characterisation a magneto-dielectric material is defined so that the material can be characterised by the effective material parameters $\varepsilon$ and $\mu$ and the usual Maxwell boundary conditions are satisfied at the interfaces [1-14]. Such effective material parameters (EMP) can be obtained, using the known extraction procedure, from experimental or computer-simulated data on complex plane-wave reflection ($R$) and transmission ($T$) coefficients of a sample of a natural or composite material in the form of a slab. This classical procedure is known as the Nicolson-Ross-Weir (NRW) method [1-4] and is based on the inversion of the Fresnel-Airy formulae for the plane-wave reflection and transmission in layers of continuous magneto-dielectric media. The NRW procedure was first applied to MTM layers in papers [5] and [6]. Its use for the characterisation of MTMs was later reported in hundreds of papers and books [7-9], and it is now the most common method of electromagnetic characterisation of composite media.
Samples of natural media can also be characterised by techniques other than the NRW method. For materials operating in the radio frequency range there are many resonator and waveguide methods, including a variety of electromagnetic *in situ* characterisation methods (see overviews [15-21]). Characterisation *in situ* is important for samples of media prepared for use in microwave components. In optics the NRW method is rarely applied, as it requires difficult precision measurements of the phase of optical signals. Instead, spectroscopic (e.g. [22]) or ellipsometric methods (mainly for optically thin films, see e.g. in [23]) are used. Spectroscopic ellipsometry allows to determine both film thickness and complex permittivity (e.g. [24, 25]). In most natural materials the measurement of the phase is not necessary because all natural materials have a trivial permeability $\mu=1$ in the optical range.

**Dependence of material parameters on the incident wave direction**

However, the user should be aware that in the NRW method it is implied that the incident wave is a plane wave normal to the composite layer. For anisotropic media the procedure thus gives only the tangential components of the tensors $\varepsilon$ and $\mu$. The retrieval method can be generalised for obliquely incident probe waves, but for most known metamaterial layers the extracted parameters appear to be dependent on the incident angle, which means that they cannot be used as conventional effective parameters.

**Transition from microscopic to macroscopic (effective parameters)**

Perhaps the most important observation is that this method is based on the theory for materials which can be considered as homogeneous at the frequency range of interest. This implies that the permittivity and permeability $\varepsilon$ and $\mu$ can be introduced in a unique way and measure the volume-averaged polarisations induced by macroscopic (also volume-averaged) electric and magnetic fields. For both natural and composite media this is so in the quasi-static limit $(qa)<<1$. Here $a$ is the characteristic distance between the inclusions and $q$ is the wavenumber of the electromagnetic wave in the material. In the quasi-static limit different methods for the transition from microscopic fields to the (effective) macroscopic ones give the same result, and this result coincides with that of the static theory. Beyond the quasi-static limit there is no unique method of eliminating the so-called short-wave oscillations of the microscopic field [10]. The EMPs are calculated in different ways by different authors, e.g., by using the equation of Clausius-Mossotti or other known static mixing rules [11]. This makes the post-processing of measured data (or data from numerical simulation of linear wave processes) an ambiguous procedure.

**Effective and characteristic material parameters**

Now let us introduce the concept of characteristic material parameters (CMPs). *Characterisation* in materials science refers to the use of external techniques to probe the internal material structure (geometric characterisation) and the properties of a material such as elemental content, chemical properties, electric conductivity, static permeability and hysteresis, mechanical, thermal properties, etc. Non-intrusive probing methods are preferable and often mandatory. The results of the characterisation of a bulk material do not depend on the sample shape and measuring setup, whereas for interface and surface phenomena the geometry is taken into account.

In the maximalist approach, the term CMPs can be granted only to those characteristic parameters which do not depend on the sample shape and size and on the electromagnetic field distribution in it, i.e. the CMPs should give a fully condensed description of linear electromagnetic properties of the material from which the sample is prepared.
However, in practice often a set of EMPs is used, which is capable of describing the interaction of the sample with at least a number of plane waves propagating in different directions. These EMPs deserve to be referred to as CMPs, even if they are not applicable for other excitations, e.g. for evanescent waves.

It is not a realistic task to find a fully condensed description of MTMs which would suit the whole infinite spatial spectrum of electromagnetic fields, especially not for nanostructured MTMs. Possibly, one can use one set of parameters applicable for propagating waves and another set of parameters for the evanescent waves. What is important is that effective material parameters (EMP) that are applicable for only one case of wave propagation cannot be called characteristic material parameters (CMP) of the material. It is, therefore, of prime importance to define and specify the applicability area and the physical meaning of every parameter that is used to characterise a material.

In order for retrieved permittivity $\varepsilon$ and permeability $\mu$ to have the physical meaning and ‘predictive power’ of characteristic material parameters (CMPs), they must obey the so-called locality condition. Locality is defined as the independence of material parameters on the wave vector $\mathbf{q}$ (more precisely, on the distribution of macroscopic fields in the sample), though the frequency dependence can be strong. For a given frequency the locality can be formulated as the independence of EMPs on the propagation direction. The locality practically means that $\varepsilon$ and $\mu$ are independent on the spatial distribution of wave fields excited in the material sample by external sources.

The locality requirement is respected for bulk EMPs only if the following (obvious) conditions are fulfilled:

1) **Passivity.** For the temporal dependence $\exp(-i\omega t)$ the locality requirement implies the limitation $\text{Im}(\varepsilon)>0$ and $\text{Im}(\mu)>0$ (both inequalities are obvious at all frequencies). For the temporal dependence $\exp(i\omega t)$ the locality requirement implies the limitation $\text{Im}(\varepsilon)<0$ and $\text{Im}(\mu)<0$.

2) **Causality.** For media with negligible losses the locality requirement implies the limitation $\frac{\partial \text{Re}(\varepsilon \omega)}{\partial \omega} > 1$ and $\frac{\partial \text{Re}(\mu \omega)}{\partial \omega} > 1$. This limitation means that, in the frequency regions where the imaginary parts of $\varepsilon$ and $\mu$ are negligibly small, real parts of these parameters must grow versus frequency.

These two conditions are necessary conditions for locality since they are derived (see, e.g., in [11, 12]) from the independence of bulk EMPs on the wave vector $\mathbf{q}$, where the EMPs $\varepsilon$ and $\mu$ are defined (in the index form) by the formulae

$$D_\alpha = \varepsilon_0 E_\alpha + P_\alpha = \varepsilon_0 \varepsilon_{\alpha\beta} E_\beta$$

$$B_\alpha = \mu_0 H_\alpha + M_\alpha = \mu_0 \mu_{\alpha\beta} H_\beta$$

Here $E$ and $H$ are the main macroscopic fields entering Maxwell’s equations, $D$ and $B$ are auxiliary vectors (note that sometimes $E$ and $B$ are considered as the main field vectors while $D$ and $H$ model the medium polarisation), $P$ and $M$ are, respectively, bulk polarisation and bulk magnetisation referred to the unit volume of the medium.

Passivity in the media without supply of electromagnetic energy is the electromagnetic formulation of the 2nd law of thermodynamics [13]. Both passivity and causality limitations for $\varepsilon$ and $\mu$ defined by formulae (1) can be expressed through the well-known Kramers-Kronig relations [10-14].
4.1.3 Effective material parameters: A discussion on the meaning and applicability limits of the retrieved parameters

A. Introduction

As already indicated in the preceding section, it is of prime importance to define and specify the applicability domain and the physical meaning of every material parameter that is used to characterise a material. We recall that only the parameters that describe the material properties in a condensed way consistently and unambiguously can be called 'characteristic'. Measured quantities are of 'effective' parameters, and often they are not the unique characteristics and their meaning and applicability limits will be discussed here.

The effective material parameters are introduced as a result of the homogenisation procedure, however, not every homogenisation model does guarantee that the electromagnetic parameters (EMP) fit the concept of characterisation (i.e. give a condensed description of the material response to electromagnetic waves). There are two main approaches to the homogenisation of lattices.

One approach is theoretical, and it starts from the averaging of microscopic fields and microscopic (local) polarisation/magnetisation. The result of the averaging (in the sense of the averaging of Maxwell equations) is a set of material equations and the set of relations for effective material parameters entering these equations. These relations express EMP through susceptibilities of individual particles and other parameters of the original heterogeneous structure. To assess whether these EMP are representative of the characteristic
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parameters, it is necessary to analyze the properties of waves of different polarisations propagating at different directions in the lattice. At first, the same set of EMP should describe eigenwaves propagating at different angles with respect to the lattice axes. However, this is not enough – applicability of these EMP to the interface problems should also be checked. If the same set of EMP is also suitable for describing the wave reflection and transmission at the interface at different angles of incidence, then we can finally conclude that this set of EMP is really the set of CMP.

All these issues have been addressed in the classical homogenisation model of natural crystals (P. Ewald, S. Oseen, M. Born, D. Sivukhin et al.). This model refers to the case when the optical size of the unit cell is very small \((qa)<0.01\) where \(q\) is wave number and \(a\) is the lattice constant. For composite media, especially for MTM which normally operate in the range \(0.01<(qa)<1\) [1, 2] a similar thorough theory is not developed yet. Moreover, many researchers working with MTM (especially, nanostructured MTM) prefer an approach suggested in [3, 4], which can be called *heuristic* homogenisation. In this approach the sample formed by an array of artificial particles in the dielectric matrix is heuristically replaced by a body of the same shape filled with isotropic uniform continuous magneto-dielectric medium with unknown \(\varepsilon\) and \(\mu\) to be determined. The latter two complex quantities are retrieved from measurement (or from exact numerical simulation) of two scattering parameters at a specific angle of the wave incidence and polarisation. Then it is assumed that the sample composed of the actual MTM will have all scattering characteristics identical to those of the effective continuous magneto-dielectric medium.

Is this approach justified? Any model, even crude, is justified if it works. However, authors of the present Chapter do not know any work, which would prove that \(\varepsilon\) and \(\mu\) retrieved in this way for any metamaterial are applicable to several angles of the wave incidence and for both TE and TM polarisations of the incident wave. On the contrary, from the available literature one can infer, that these quantities are apparently applicable only to the same case of the wave incidence in which they were retrieved. Therefore they do not fit the concept of CMP.

The heuristic homogenisation was however claimed successful in [3-9] and many other works (see review [1]). This claim was not totally wrong and deserves special comments. Works based upon the aforementioned parameter retrieval refer to a special class of MTM samples, composed of finite-thickness orthorhombic lattices of small resonant scatterers. These scatterers are not bianisotropic and at most frequencies (beyond the ranges of quadrupole and other multipole resonances) they can be adequately modeled by electric and magnetic dipoles. The finite thickness lattice forms a layer (infinite in a plane and finite in the normal direction) with integer number \(N\) of unit cells across it. Its scattering parameters are complex valued reflection \((R)\) and transmission \((T)\) coefficients. The retrieval of EMP from \(R\) and \(T\) coefficients of a layer of a continuous magneto-dielectric medium is the standard NRW method, which is reviewed in the separate Section C of this Chapter. In many papers (e.g. [3-9]) it was found that EMP \(\varepsilon\) and \(\mu\) retrieved for this class of MTM by the NRW method do not depend on \(N\), i.e. they remain unchanged for any layer thickness \(d=Na\). In the logics of many researchers this fact means that these parameters deserve to be called EMP. Their argument is as follows: these EMP are representative of the material inside the layer because they are independent of \(d\). Formally, this is the case. For a special class of MTM the parameters \(\varepsilon\) and \(\mu\), retrieved by the NRW method, do indeed comply with the definition of EMP. This class of lattices was called in [2] Bloch lattices (this name is related with the possibility to introduce the so-called Bloch impedance for these lattices). However, even for Bloch lattices these retrieved material parameters do not fit the concept of CMP, because the locality limitations are violated for these parameters. This is a clear indication, that the retrieved \(\varepsilon\) and \(\mu\) cannot be CMP of MTM. The non-local parameters obtained for the case of the normal wave incidence cannot be applied to other excitation cases. Even in the case of normal incidence they become inapplicable, if the same MTM layer is mounted on different substrate.
As it is evident now, the locality violation in the retrieved parameters was an indication that the heuristic homogenisation [3, 4] was flawed, and the prime attention should be paid to alternative homogenisation models. However, this problem was not duly understood at that time (2002). The absence of locality in the retrieved parameters was interpreted as a sign of strong spatial dispersion. Locality of the medium response can be easily checked through frequency dependence of $n_{\text{eff}}$ and $Z_{\text{eff}}$. Really, the two locality limitations (see more details in Section 1.2 of this Chapter) can be also formulated for $n_{\text{eff}}$ and $Z_{\text{eff}}$. Causality requires growth of the refractive index with frequency in the low-loss regions. This is called the Foster theorem. Additionally, passivity requires the sign of the imaginary part of $n_{\text{eff}}$ and of real part of $Z_{\text{eff}}$ to be consistent with lossy (i.e. not amplifying) medium. Inspecting works [3-9] and many other papers devoted to lattices of small separate (non-bianisotropic) scatterers, one can easily notice that within the frequency region $(q a) < 1$ locality is respected for $n_{\text{eff}}$ and $Z_{\text{eff}}$ and therefore strong spatial dispersion does not occur. Therefore new theoretical homogenisation models for such MTM are needed. Unfortunately, progress in theoretical homogenisation of MTM has been very modest. Only a few works are known, which link a theoretical model with the experimental electromagnetic characterisation of MTM.

As already noticed, in order to deliver the characteristic parameters of an artificial material, its theoretical model has to explicitly include the boundary conditions. As a result, it should establish relationships between CMP and scattering parameters, which can be really measured, e.g. $R$ and $T$ coefficients of a layer. When measured in the far-field zone, these two coefficients contain only macroscopic information about the material properties, because the contribution of evanescent waves (which contain the microscopic information) cannot be uniquely extracted from the far field of reflected and transmitted waves. As it will be explained below, for the special class of MTM (Bloch lattices) such incomplete information can be sufficient for their characterisation.

Even careful measurement of coefficients $R$ and $T$ for nanostructured layers is a difficult task. Two major practical difficulties should be overcome in these measurements. The first problem is concerned with small overall sample sizes, which require the use of very narrow wave beams. To measure phase at the center of a narrow light beam, special interferometers, unavailable commercially, are necessary. Alternatively, sophisticated measurement schemes are needed in order to utilize the existing Mach-Zender interferometers. The second problem is related to the presence of a substrate, when one measures the phase of $T$. Since this coefficient is, by definition, referenced to the interface between the nanostructured layer and its substrate, it is impossible to measure it directly. Instead, one measures coefficient $T'$, which is refers to the bottom surface of the substrate. Coefficient $T$ is then retrieved from already extracted coefficient $T'$. The transmission coefficient of the substrate itself should be exactly known. To determine the substrate transmission coefficient, it should be measured separately. It is possible, in principle, to measure the transmission coefficient of the substrate dielectric layer without the nanostructure, before its fabrication and then repeat the measurements of the whole assembly after the nanostructure fabrication. However, the substrate optical properties may change in the course of growing the nanostructure on its surface. This example demonstrates that even the standard NRW method poses major challenges in the measurements of the layered nanostructured MTM.

As to non-Bloch metamaterials, fine measurements of evanescent optical fields, which are needed for their characterisation are much more difficult: no consistent measurement techniques are known to us. Together with tremendous challenges of the theoretical homogenisation of this type of MTM, huge difficulties of the pertinent experimental measurements make their electromagnetic characterisation hardly possible in the near future. Therefore, at the present stage, it is reasonable to restrict the electromagnetic characterisation of bulk nanostructured MTM to the case of Bloch lattices, for which the knowledge of their complex $R$ and $T$ coefficients is sufficient. Below this problem is discussed in detail. Applicability of the same approach to thin films and to optically sparse structures is also addressed.
B. Prerequisites of homogenisation

Practical use of measured or calculated effective parameters implies a homogenisation model (theoretical or heuristic). It is sometimes wrongly thought, that the only possible homogenisation theories are Lorentz theory (purely electrostatic) and Ewald’s theory (quasi-static), which are known for natural media and for some artificial dielectrics. Homogenisation models have been verified experimentally for artificial media, e.g. for artificial dielectrics used in the microwave and mm-wave ranges. The possibility of homogenisation, i.e. the description of the medium composed of particles as a continuous medium, is determined by the following two conditions. The first condition requires that the medium be represented as an array or lattice with geometrically identical or nearly identical unit cells. Lattices containing one particle per unit cells are called orthorhombic. The nearly identical unit cells refer to random media (natural amorphous media, gases and random composites) where particles in the unit cells can deviate from their statistically average positions. However, in the majority of unit cells these deviations are small enough, so that the number of particles per unit cell is almost constant. This condition allows the homogenisation in terms of the spatially uniform material parameters. In this Chapter we do not discuss the homogenisation of media with non-uniform concentration of particles (scattering media), since this class of media does not represent any known nanostructured material.

The second condition of homogenisation is, that the microscopic spatial distributions of fields and polarisation currents are slowly varying between adjacent unit cells. If this condition is fulfilled, while the wave propagates through the medium, the microscopic oscillations of fields and polarisation currents (though very strong and sharp) can be smoothened. The small variation of microscopic field distribution from cell to cell is the key prerequisite for homogenisation. Homogenisation therefore becomes possible, if the wave phase shift qa between any two adjacent unit cells is much smaller than π. An array of inclusions with small qa (qa<1) is called optically dense, and arrays with qa>π/2 are called optically sparse. How small should this parameter qa be in order to allow homogenisation? The general theory does not answer this question. At present, it is broadly accepted, that homogenisation is possible only in the quasi-static limit, i.e. for (qa)<0.01.

Though the exact frequency bounds of homogenisation can hardly be determined experimentally for each particular MTM, they can be estimated theoretically. Probably, the most reliable criterion of the presence of strong spatial dispersion is the shape of the so-called iso-frequency (equi-frequency) surfaces, which are well known in crystallography [11]. In principle, for some lattices deviations of the surface shape from ellipsoid or hyperboloid (existing in the absence of spatial dispersion) can arise even at qa<1. However, the authors have never encountered such situations in the three-dimensional periodic arrays and think, that the frequency bound of the homogenisation for such arrays of isolated scatterers is, at least, qa=1 or even larger.

Thus, one can conclude, that the effective medium description in terms of bulk permittivity and permeability can be extended far beyond the quasi-static limit and can be expanded to the frequency region where the MTM operate, Namely, it can correspond to the frequency range determined by the condition qa<1, where the wave number q=ω neff/c can be retrieved by the standard NRW method. This is discussed in more detail in review [1] where results of the retrieval obtained in works [3-9] are discussed. In these works the basic physical requirements to the local material parameters are satisfied through the whole domain qa≤1. Therefore in the frequency range (qa<1) we call the lattices optically dense, though not quasi-static. In optically dense lattices, even if their inclusions are resonant, we do not observe strong spatial dispersion, and they can be adequately modeled by an equivalent continuous medium. In such cases the retrieved EMP (if they are retrieved correctly i.e. they are bulk material parameters) must obey the locality constraints formulated in Chapter 1.4.2.
C. Wave impedance and effective impedance of the homogenised lattice of particles

As is known from the Fresnel theory, the plane wave refraction at the interface of continuous media can be described in terms of the wave impedances and refractive indices. For a layer of continuous medium, these quantities can be uniquely related to the reflection and transmission coefficients. Since in the theory of continuous magneto-dielectric media bulk material parameters are uniquely related to the wave impedance $Z_w$ and refractive index $n$, the retrieval of bulk material parameters of a continuous magneto-dielectric medium is possible using these simple formulas:

$$n = \sqrt{\varepsilon \mu}, \quad Z_w = Z_0 \sqrt{\frac{\mu}{\varepsilon}} = \sqrt{\frac{\mu_0}{\varepsilon_0} \frac{\mu}{\varepsilon}}$$  \hspace{1cm} (1)

The wave impedance $Z_w$ in formulas (1) is defined as the ratio of electric and magnetic fields in a plane wave, which is uniform inside the continuous medium up to its interface. $Z_0$ in (1) is the free-space wave impedance. This uniformity means, that in the wave theory of continuous media there is no difference between the wave impedance of the medium and the surface impedance of a semi-infinite medium (for the normal incidence of the wave). The Fresnel theory is developed for continuous media, with no concepts of macroscopic and microscopic fields. To apply the Fresnel-Airy formulas together with formulas (1) to layers of particles (e.g. to natural media formed by atoms or molecules) the layer of particles should be replaced with the layer of equivalent continuous medium. It is possible to do this accurately using the theoretical homogenisation model. The classical homogenisation model applicable for natural transparent crystals in the optical frequency region was first introduced in 1915-1921 by P. Ewald. This theoretical model implies the replacement of true (microscopic) fields by macroscopic electric and magnetic fields, which represent the averaged microscopic fields. In this model $Z_w$ is formulas (2) is defined as the ratio of macroscopic electric and magnetic fields. In other words, the homogenisation theory starts from the consideration of microscopic fields and polarisation and results in Fresnel-Airy formulas and formulas (1) for macroscopic fields.

Since natural transparent crystals in the optical range are formed by electrical dipoles and their permeability is equal to 1, Ewald’s theory corresponds to the substitution $\mu=1$ in formulas (1). Later it was proven, that formulas (2) hold for magneto-dielectric natural media also in the radio frequency range (where $\mu$ can be different from unity). In this model it was proven, that the refractive index and wave impedance, calculated in terms of the bulk material parameters (i.e. by averaging microscopic fields), are really applicable to the Fresnel formulas for the reflection and refraction at the crystal interface. This result allows us to consider natural materials (though they consist of particles) as homogenous media, when we evaluate the scattering parameters. However, it is important to note that this theory was based on a set of low-frequency approximations and its accuracy was experimentally confirmed only for the frequency region $(q\alpha)<0.01$. This condition is met for most natural transparent crystals up to the upper end of the ultraviolet range.

Now let us consider how the situation changes in the frequency region $(q\alpha)>0.01$, where the approximations of the Ewald theory are no longer applicable. Our discussion is based on the observation, that the effective impedance of the lattice $Z_{\text{eff}}$, which is used in the Fresnel-like formula for reflection from the homogenized semi-infinite lattice of particles

$$R = \frac{Z_{\text{eff}} - Z_0}{Z_{\text{eff}} + Z_0},$$
is mathematically different from the wave impedance $Z_w$ of the same homogenized lattice. This feature was first mentioned explicitly in the classical work [10]. (In fact in this paper one considered the case of natural crystals when $\mu = 1$ and $\varepsilon = n_{\text{eff}}^2$. Respectively, the difference between $Z_{\text{eff}}$ and $1/n_{\text{eff}}$ was claimed, the term 'wave impedance' was not used in [10]). However, in that paper disparity of these two impedances was noticed together with the observations of polaritons excited at the surface in the same frequency region $(qa) > 0.01$. Therefore, in further literature, this impedance difference was understood, as if the effective impedance of a lattice is not equal to the wave impedance when the excitation of polaritons is significant. Perhaps, only in paper [2] it was shown, that the difference between the effective impedance of the lattice and its wave impedance has nothing to do with the effect of polaritons. The relative difference is of the order of $(qa)$ and its reason is as follows. The wave impedance, as defined through bulk effective parameters, corresponds to the volume averaging of the same fields in the bulk of the lattice beneath the interface. But electric and magnetic fields reflected by a bulk lattice correspond to the surface (transversal) averaging of the microscopic fields $E$ and $H$ over the unit cell front area $S$ shown in Fig. 2, right panel.

**Figure 2.** Left: an illustration to the Nicholson-Ross-Weir (NRW) retrieval procedure applied for a finite-thickness lattice of small particles. Right: illustration to the difference between the transversal (surface) and volume averaging of microscopic electric and magnetic fields. The first averaging method gives the reflected wave amplitude and corresponds to the Bloch impedance $Z_w$. The second averaging method does not give the correct result for the reflected wave amplitude (without transition layers) and corresponds to the bulk wave impedance $Z_{\text{eff}}$. Arrows show electric or magnetic resonant dipole moments of particles.

Therefore the effective impedance $Z_{\text{eff}}$ retrieved from the reflection coefficient of a semi-infinite lattice, corresponds to the surface averaging of microscopic fields in the plane of the lattice interface, i.e. is the surface impedance of the lattice. Assuming the incidence wave to be $x$-polarized one can write:

$$Z_{\text{eff}} = \frac{1}{S} \int_S E_x dS \neq \frac{1}{V} \int_V E_x dV = Z_w$$

Since $Z_{\text{eff}} \neq Z_w = Z_0 \sqrt{\mu \varepsilon}$, it would not be correct to calculate bulk $\varepsilon$ and $\mu$ substituting the surface impedance into formulas (1). Only in the quasi-static limit the error in the inequality small enough.

The physical reason for the difference between the bulk and the surface averaging is as follows. The field averaged over the volume $V$ contains information on the microscopic field distribution over the whole unit cell between its input surface $S$ and output surface $S'$. The surface averaging is the integration of the field over the constant-phase surface $S$. When the phase shift of the propagating wave over the unit cell is not negligible, the bulk averaging obviously gives a result, which is different from the surface averaging. In the quasi-static limit the wavelength is very large with respect to the unit cell size $a$, so that the phase of the EM fields over one unit cell practically does not change. Thus, the spatial distribution of fields inside one cell can be found from the static field equations. In that quasi-static limit (practically for $(qa) < 0.01$),
the numerical difference between the results of the surface and bulk averaging of microscopic fields disappears. This corresponds to the applicability of the Ewald’s theory.

We can see that the standard NRW retrieval procedure applied beyond the quasi-static limit contains a serious shortcoming. What is then the physical meaning and applicability limits of EMP retrieved with the help of the standard NRW retrieval procedure? We will show that these parameters are still meaningful, albeit only in a certain sense. A brief discussion is presented below, and for further details the readers are referred to the review and full analysis in [1] and [2].

D. Bloch lattices and Bloch material parameters

Consider an infinite orthorhombic lattice, where the wave propagates along a crystal axis. In Fig. 2, right panel, the propagation is depicted along the z-axis. As above, let us denote one surface of any arbitrary selected unit cell by $S$ and the opposite surface by $S'$. If the wave propagates along $z$ in the positive direction, $S$ is the front surface of this unit cell. If the wave propagates in the opposite direction, $S'$ is this front surface. If the transverse averaging of the microscopic electric and magnetic fields over the surface $S$ in the first situation and over the surface $S'$ in the second situation gives the same result, the effective impedance defined by the left identity of formula (2) (now for an unbounded lattice) is called the Bloch impedance. The introduction of Bloch impedance is possible for orthorhombic lattices with planar symmetry of inclusions. A special group of such lattices was called Bloch lattices in paper [2]. Some researchers dispute the correctness of the term ‘Bloch lattices’. However, since no alternative terminology has been suggested, we keep this term in the present booklet. By definition, the Bloch impedance of Bloch lattices [2] remains the same for finite-thickness lattices with different number $N$ of unit cells over the layer thickness, just as for an unbound lattice. This means, that for a Bloch lattice layer with a thickness equal to multiples of the lattice constant $a$, the refractive index and surface impedance $Z_{\text{eff}}$ of a layer are identical to those for the corresponding infinite lattice, i.e. $Z_{\text{eff}} = Z_{\text{eff}}$. Another important property of the Bloch lattice is, that the reflection coefficient $R$ is identical for both sides of the layer. In other words, the same values of $Z_{\text{eff}}$ and $n_{\text{eff}}$ are retrieved from the $R$ and $T$ coefficients at any layer thickness $d$ equal to multiples of $a$. Of course, also for Bloch lattices there remains a difference between bulk and surface averaging beyond the quasi-static limit.

Strictly speaking, Bloch lattices are a physical idealisation. A, certain (planar) symmetry of particles is required and the near-field interactions between adjacent lattice planes should be negligible. If the near-field interaction of adjacent crystal planes is strong, the higher-order Floquet harmonics significantly contribute to it. In this case, the microscopic field distributions at the front and rear surfaces of the unit cell centered at the layer interface are very different. Therefore lattices, where the near-field interaction between adjacent crystal planes is strong, are not Bloch lattices. As stated above, the class of Bloch lattices can be detected by simulations or measurements, if we compare the results for extracted effective wave impedances and refractive indices retrieved for different numbers of layers $N$.

The material parameters $\varepsilon$ and $\mu$ expressed in terms of the Bloch impedance were called the Bloch Effective Material Parameters (EMP) in [2]. Bloch EMP may depend on the angle of wave incidence and are thus not the characteristic parameters meeting our definition. Being obtained for the normal incidence, they cannot be universally used to predict the $R$ and $T$ coefficients at any other incidence angle.

Bloch EMP are defined by the formal relations, analogous to formulas (1):

$$
\varepsilon_B = \frac{n_{\text{eff}}}{Z_B Z_0}, \quad \mu_B = \frac{n_{\text{eff}}}{Z_0} Z_B,
$$

(3)
where $Z_B$ is given by the left part of formula (2). Since both $n_{\text{eff}}$ and $Z_B$ are retrieved by the NRW method, both Bloch EMP $\varepsilon$ and $\mu$ can be calculated either using the theoretically evaluated refractive index and Bloch impedance of the infinite lattice, or calculated from $R$ and $T$ coefficients of the layer. In other words, in the case of the Bloch lattice Bloch material parameters refer to both theoretical and heuristic homogenisation models.

The theoretical representation of the Bloch lattice as an effective homogeneous medium with the wave impedance $Z_B$ and refractive index $n_{\text{eff}}$ is in fact a transmission-line model. A Bloch lattice is formed by crystal planes (grids of electric and magnetic dipoles) whose electromagnetic interaction can be described by the far-field theory (coupling between planes is only via travelling waves). Such a set of parallel grids can be modeled by a periodically loaded transmission line [2], where the transversally averaged fields $E_{\text{fa}}$ and $H_{\text{fa}}$ act similarly to the voltage and current in the equivalent transmission line, respectively. The periodic lumped loads inserted in this line represent the crystal planes and the host line corresponds to the host medium (dielectric material matrix). Then the effective parameters (Bloch impedance $Z_B$ and refractive index $n_{\text{eff}}$) describe the equivalent homogeneous line whose segment of the length is equal to the unit cell and has the ABCD (transmission) matrix identical to that for the unit cell of the original loaded line.

The transmission matrix of the unit layer can of course be expressed through the refractive index and Bloch impedance without involving Bloch EMP. However, researchers prefer to calculate Bloch EMP for two reasons. First, many researchers treat Bloch EMP as bulk parameters. Secondly, researchers, who understand this difference, use Bloch EMP in order to partially characterise the material. Let us consider this last case in more detail. Nanostructured Bloch lattices are formed by nanoparticles or clusters of nanoparticles, whose response (in the frequency range where the lattice operates as a metamaterial) can be presented in the form of resonant electric and resonant magnetic dipoles. When the resonance band of electric dipole response of the lattice unit cell does not overlap with the resonance band of the magnetic dipoles, the following situation holds. The Bloch permittivity within the range of the electric dipole resonance experiences the Lorentz resonance, i.e. looks like a usual local permittivity (though it has the larger resonance magnitude than that of the bulk permittivity). The Bloch permeability within the same range experiences a specific non-Lorentz resonance, which is often called antiresonance [3-5]. Similarly, at the magnetic dipole resonance the Bloch permeability experiences the Lorentz resonance and the Bloch permittivity experiences an anti-resonance.

Before 2007 when researchers did not understand the difference between Bloch EMP and bulk EMP, the ‘antiresonance’ was perceived as violation of locality, i.e. as manifestation of strong spatial dispersion. The antiresonance of one retrieved EMP was considered as a physical effect and interpreted as resulting from the combination of the resonant response of particles and their periodicity in the lattice. In [1, 2] and other works of the same author it was shown that the antiresonance of the retrieved permittivity (or permeability) combined with the Lorentz-like resonance of the retrieved permeability (or permittivity) is an artifact. However, this artifact contains some useful information. In the case when one retrieved Bloch parameter is ‘antiresonant’ at the same frequencies where the other is normally resonant the frequency dependence for the Lorentz-like Bloch parameter gives the correct resonance frequency bands. Also one can see that the electric and magnetic resonances are separated in frequency.

If the two resonance bands (electric dipole and magnetic dipole resonances) overlap, both Bloch material parameters experience a non-Lorentz resonance. Though the shape of their frequency dependence is different from the ‘antiresonant’ one, both of them ‘violate’ the locality limitations. If the retrieved permittivity and permeability resonate in the same range and their resonance is non-Lorentzian, it simply means that the electric and magnetic dipoles of the lattice resonate in the same frequency band. Again, with Bloch EMP we obtain correct frequency bounds of this band. It can be asserted, that Bloch EMP can serve for
the partial characterisation of MTM, namely for obtaining the electric and magnetic resonance frequency bands. Also, these parameters can be used for the qualitative description of the MTM performance.

Now let us discuss the applicability of Bloch material parameters for quantitative calculations. Since they remain the same for any number $N$ of unit cells across the layer, one can retrieve Bloch EMP from $R$ and $T$ coefficients for the specific number $N$ (say, for a monolayer with $N=1$) and apply them to predicting $R$ and $T$ coefficients for any other $N$ (for the same normal incidence direction). This application of Bloch EMP implies that these layers are stacked on the same substrate. Of course, the prediction of the $R$ and $T$ coefficients for different $N$ is possible with retrieved Bloch impedance $Z_B$ and refractive index $n_{\text{eff}}$ instead of $\varepsilon_B$ and $\mu_B$. However, since Bloch EMP are also suitable for this purpose, they can be called effective material parameters.

E. Is it possible to retrieve bulk $\varepsilon$ and $\mu$ from measured (or exactly calculated) $R$ and $T$ coefficients?

In the case of Bloch lattices it is possible to derive bulk EMP, which satisfy the locality requirements and which are therefore, probably, characteristic parameters (and they are thus applicable to different cases of the wave incidence) [1, 2]. Bulk EMP, defined through the refractive index $n_{\text{eff}}$ and the wave impedance $Z_w$, are exactly equal to the corresponding parameters introduced by the usual definitions, i.e. formulas (1) of Section 1.4.3.C involving auxiliary field vectors $D$ and $B$. It becomes possible to retrieve bulk EMP from $R$ and $T$ coefficients due to the existence of the explicit relationship between the wave impedance $Z_w$ and the Bloch impedance. This means that a new theoretical homogenisation model of Bloch lattices can be found with the same EMP as the new heuristic homogenisation model. The new retrieved bulk material parameters are not the Bloch EMP. They have different frequency dispersion. It is of course impossible, that two different sets of EMP – Bloch EMP and bulk EMP – were introduced for the same heuristic homogenisation model. This means that the homogenisation model related to the bulk EMP is different from that adopted by the NRW method. The MTM layer is replaced not by uniform homogeneous magneto-dielectric layer as in the model related to Bloch EMP, but by a piece-wise homogeneous structure. The original method of their retrieval was presented in works [1, 2]. This method can be considered as a modification of the NRW method. The algorithm suggested by Simovski as the modification of the NRW method is illustrated in Fig. 3.

![Figure 3](image)

F. Can the NRW method be applied to thin metamaterial films?

The most dangerous pitfall in the characterisation of nanostructured MTM is, in our opinion, not recognising that artificial surface and bulk material behave differently. For example, it is not correct to apply the standard NRW algorithm, which is valid only for a bulk material, to nanostructured MTM layers with only
1-2 resonant inclusions over the layer thickness. We call such nanolayers *nanostructured metasurfaces*. Authors of e.g. [12-16] (and many other works) extract material parameters from $R$ and $T$ coefficients of a metasurface and the values found are interpreted as effective bulk parameters. This leads to inadequate descriptions of such structures.

An important example of nanostructured metasurfaces is the bilayer optical fishnet. This bilayer is formed by a pair of parallel periodically perforated nanofilms (silver or gold) with a subwavelength dielectric spacer between these two films. Apertures in the optical fishnet structures are often non-circular and optically large. EMP calculated or retrieved for this type of MTM (usually at the normal incidence) obviously violate the locality requirements (see e.g. [12-17]). Therefore these parameters do not comply with the concept of electromagnetic characterisation explained above. They are not applicable for oblique wave incidence, but only applicable to the normal incidence case. They cannot even be called material parameters, because $\varepsilon$ and $\mu$ retrieved for the fishnet bilayer differ substantially from those obtained for multilayer structures formed by stacking the same bilayer (see e.g. [17]). It can be misleading to associate such retrieved parameters with the conventional $\varepsilon$ and $\mu$ and to call them permittivity and permeability.

Notice, however, that these parameters can be used for illustrative purposes. At the frequencies where the retrieved $\text{Re} \varepsilon < 0$ and $\text{Re} \mu < 0$, the phase shift of the wave propagating through the fishnet structure in the normal direction (calculated and retrieved from measured data) corresponds to the backward wave (see e.g. in [12]). One can conclude from this negative phase shift, that the wave propagating across the bilayer fishnet is backward. It is known that in bulk doubly-negative media the wave is also backward. Therefore a bilayer fishnet, even though it is not a bulk material, can be interpreted in a limited sense as a doubly-negative material. This physical analogy is complemented by the study of plasmonic modes of the polarisation current induced in two self-resonant grids forming the fishnet structure. There is an electric mode, where the currents induced in two grids are in-phase and a magnetic mode, where they are out-of-phase. One can qualitatively associate the electric mode resonance with negative permittivity and the magnetic mode resonance with negative permeability. However, it is important to remember, that these $\varepsilon$ and $\mu$ cannot be used for the generic characterisation of the fishnet material or for predicting other than negative phase velocity properties of this structure.

**G. Can effective parameters be found for optically sparse structures?**

Another pitfall occurs in identifying the difference between optically sparse ($qa > \pi/2$) and optically dense ($qa < 1$) structures. It is well known (see e.g. [11, 18-20]), that photonic crystals cannot be fully described in terms of a few frequency dependent EMP. For their characterisation it is necessary to analyse the Brillouin dispersion diagram and the set of iso-frequency (equi-frequency) surfaces. In a number of works dedicated to photonic crystals (e.g. [21-23]) the effective $\varepsilon$ and $\mu$ parameters of these crystals were introduced without a proper discussion of their physical meaning. Nor was the applicability to boundary problems discussed and the parameters were presented in a form independent on the wave vector. Note, that it is possible, in principle, to characterise photonic crystals by permittivity and permeability. Spatially dispersive $\varepsilon$ and $\mu$ explicitly depending on the wave vector $q$ can be used for solving boundary problems for photonic crystals [24-26], though not at very high frequencies. However, this characterisation is only theoretical, because this approach requires knowledge of the explicit dependencies of the material parameters on the wave vector $q$. Moreover, one should specially derive boundary conditions for every lattice eigenmode excited at a given frequency. One should not restrict this to the fundamental Bloch harmonic but derive boundary conditions for all propagating Bloch harmonics and also for the polaritons (attenuated harmonics) which also influence the reflection and transmission of a photonic crystal layer. For these reasons this method is, probably, not appropriate for experimental characterisation. However, even if spatially dispersive $\varepsilon$ and $\mu$ of a photonic crystal can be obtained one way or the other, this can not be a reason to classify photonic crystals as effectively continuous MTM.
Conclusion

In this section we have considered the difference between the concepts ‘characteristic material parameters’ and ‘effective material parameters’. The concept CMP is more restrictive, than that of EMP and not all possible EMP represent CMP. We have discussed the applicability of homogenisation models, which allow one to describe composite structures through EMP and CMP and concluded that both these concepts make sense for MTM. EMP retrieved using the standard NRW method for bulk MTM are not CMP. However for a special, but very important, class of MTM these EMP (we called them Bloch’s material parameters) contain some information and can be used for partial characterisation of MTM. The physical meaning and applicability of these EMP have been discussed in detail. It is noticed that using the original algorithm of retrieval, it becomes possible also to obtain EMP which are probably consistent with the concept of CMP. The can be retrieved from the same R and T coefficients which are used in the NRW method to determine Bloch’s EMP.

There are many nanostructured ‘materials’ which cannot be characterised through bulk material parameters (even Bloch material parameters cannot be introduced for them). This applies for example to metasurfaces and structures with spatial dispersion effects. In these cases homogenisation models should be very different from bulk averaging and the NRW method becomes fully inadequate. The retrieved parameters, though often called ‘effective’, do not give in these cases any information which could be used for the characterisation. Fortunately for some bilayer metasurfaces (e.g. optical fishnets) the retrieved parameters can serve illustrative purposes.

REFERENCES

4.1.4 Metamaterials with weak spatial dispersions: Are two tensors enough?

In the Theory Chapter 2 we have introduced the constitutive equations relating field vectors $\mathbf{E}$ and $\mathbf{H}$ to $\mathbf{D}$ and $\mathbf{B}$ in composite or molecular bulk media. The general relation can be expressed as a Taylor expansion, in which spatial derivatives of macroscopic fields appear. This series is often truncated into a relation with two tensors

$$\mathbf{D} = \varepsilon \mathbf{E}, \quad \mathbf{B} = \mu \mathbf{H}$$

Media for which this truncation makes sense are called magneto-dielectrics. In this section we investigate the cases when this truncation is not possible.

It has been known since the early fifties that composites containing electrically small conductive inclusions of complex shapes can exhibit properties of artificial magnetics, usually described by magnetic polarisability of inclusions [2]. This relation is expressed as $\mathbf{m} = \beta \mathbf{H}$, where $\mathbf{m}$ is the induced magnetic dipole moment, $\mathbf{H}$ is the local magnetic field at the centre of the inclusion and the inclusion polarisability $\beta$ can be a tensor. The effective permeability of the composite is defined by the magnetic response $\mathbf{m}$ of the individual inclusions after appropriate averaging. This magnetic response is a manifestation of a spatial dispersion effect, because the response of a unit cell to a magnetic field can be described as the response to a non-uniform component of the electric field using the relation $\mathbf{B} = \text{rot} E/(\text{-j} \omega)$ which involves first-order spatial derivatives of $\mathbf{E}$. The key pre-requisite for the validity of this description with only one tensor $\beta$ is that the response to other spatial derivatives of $\mathbf{E}$ can be neglected (see [2, 3] and in Chapter 2-1 of [4]). Also, electric quadrupole responses as well as any other higher-order polarisation moments should be negligibly small compared to the magnetic dipole (strictly speaking the smallness in this case refers to the field produced by higher-order multipoles of the unit cell compared to the dipole fields [5]). However, these are only negligible for very specific inclusion shapes.

Let us for example consider arrays of dual plasmonic nanoparticles (two particles that remain together) e.g. two plasmonic spheres or dual bars (see Fig. 5). In the literature it is often assumed that the resonant magnetic response of such a unit cell is related to the phase shift of the wave over the distance $a$ between...
the two plasmonic elements. The problem with this claim is that the medium is assumed to be a regular magneto-dielectric \([7-21]\), while it is not, as we demonstrate below. A simple consideration below shows that modelling such media by only two material parameters (permittivity and permeability) leads to wrong conclusions and that the conclusion of negative permeability can be disputed.

Fig. 3 represents a plasmonic nanopair made of a metal with complex permittivity \(\varepsilon\) in a medium with permittivity \(\varepsilon_h\). Let this nanopair be a unit cell of a material (lattice). The magnetic moment of the unit cell of volume \(V\) is defined in electrodynamics as

\[
m = \frac{1}{2} \int_V \mathbf{r} \times \mathbf{J} \, dV \tag{4}
\]

Here \(\mathbf{r}\) is the radius-vector referred to the particle centre, and \(\mathbf{J} = j\omega(\varepsilon-\varepsilon_h)\mathbf{E}\) is the polarisation current density (in our case, inside plasmonic spheres). The nanospheres are assumed to be non-magnetic. The response of the pair of nanospheres to the time-varying magnetic field can be translated into the response of the nanopair to a spatially varying electric field and when the local electric field acting on one nanosphere \(A\) is different from the electric field acting on the other nanosphere \(B\), the nanopair can acquire a magnetic moment, as we will explain.

If the wave propagates in the \(x\)-\(y\) plane (see Fig. 5) and the wave has a magnetic field in the \(z\)-direction, then the magnetic moment \(m\) of the nanopair is always \(z\)-directed and equal to \(m = -j\omega p_{A,B}/2\), where \(p_{A,B}\) are the electric dipole moments of the two spheres and where the formula (4) is used.

If the wave propagates along the \(x\)-axis (\(q = q_x\) in Fig. 5), the excitation of the nanopair by the magnetic field is equivalent to the excitation by a non-uniform \(y\)-polarized electric field with anti-symmetric distribution along \(x\). Then \(E(B) = -E(A)\), \(p_B = -p_A\) and we have \(m = -j\omega p_A/2\). The local magnetic field \(H_H^z\) at the nanopair centre is related to the electric fields \(p_A/4E(A)\) through Maxwell’s equation:

\[
-j\omega H_H^z = \frac{\partial E_y}{\partial x} - \frac{\partial E_x}{\partial y} \approx 0 - \frac{E(B) - E(A)}{a} = \frac{2E(A)}{a}
\]

In this relation we took into account the small optical size of the nanopair \((ka) < 1\) and we replaced the derivative by a ratio of finite variations. The nanopair magnetic polarisability \(\beta\) can then be expressed through the electric polarisability of a single nanosphere \(\alpha\) as

\[
\beta = \frac{m}{H} = \sqrt{\frac{\mu_0}{\varepsilon_0}} (ka)^2 \left(\frac{p_A}{4E(A)}\right) = \sqrt{\frac{\mu_0}{\varepsilon_0}} (ka)^2 \alpha
\]
The magnetic polarisability in this special case of propagation turns out to be resonant at the same frequency as the plasmon resonance of an individual sphere given by factor $\alpha$. Actually, the magnetic resonance is slightly red-shifted with respect to that of the single sphere given by factor $\alpha$ (our simplistic model does not take into account the mutual coupling of spheres), but it is not important for our discussion.

However, if the wave propagates along the $y$-direction ($q = q_y$ in Fig. 5), the response of the nanopair to the same magnetic field $H$ is zero magnetic moment. In this case $E = Ex$ is zero on the $x$-axis i.e. at the centres of both nanospheres, and their electric dipole moments vanish. The magnetic field $H$ induces opposite electric polarisations of the upper and lower halves of both spheres, as shown in Fig. 5. This effect is practically negligible and has nothing to do with magnetic polarisation, i.e. in this case $\beta = 0$.

The optical size of a pair of spheres and the period of these pairs are assumed to be very small and there is thus no physical reason for strong spatial dispersion in the effective medium. The absence of strong spatial dispersion means that the permeability tensor $\mu$ being a material parameter cannot depend strongly on the direction of the vector $q$. But we have shown a dramatic dependence of the magnetic susceptibility $\beta$ on the propagation direction of the electromagnetic wave: $\beta$ is large for one direction and vanishes for another.

The answer to this apparent paradox is given in the theory of multipole media [5] which were also called media with weak spatial dispersion in works [2-4]. Multipole media show high-order multipole responses accompanying the magnetic dipole response. In the present case, for any direction of propagation, quadrupole susceptibility should have been taken into account. Media with resonant quadrupole moments cannot be described in terms of $\varepsilon$ and $\mu$ only. Correct constitutive equations for multipole media contain beside the macroscopic fields $E$ and $H$ also the spatial derivatives of $E$ [2-5] and hence more material parameters are needed. With this constitutive equation the unit cell magnetisation of such composites can be properly described, without involving non-physical spatially dispersive permeability $\mu(q)$. Constitutive equations of materials with significant quadrupole moments (media formed by resonant pairs, media formed by $S$-shaped metal particles [20], etc.) can be written in the index form:

\[
D_\alpha \equiv \varepsilon_0 E_\alpha + P_\alpha + \frac{1}{2} \nabla \beta Q_{\alpha \beta} E_\beta = \varepsilon_0 \varepsilon_{\alpha \beta} E_\beta + \xi_{\alpha \beta \gamma \delta} \nabla_\beta \nabla_\gamma E_\delta \\
B_\alpha \equiv \mu_0 H_\alpha + M_\alpha = \mu_0 \mu_{\alpha \beta} H_\beta + \chi_{\alpha \beta \gamma} \nabla_\beta E_\gamma
\]

Even more material parameters should be introduced for media comprising U-shaped split-ring resonators. Here a bi-anisotropy effect [2-5], i.e. induction of the electric dipole by the magnetic field, and the reciprocal effect, complement the effect of quadrupole polarisation of particles. As a result, the material equations in the index form contain 5 material parameters:

\[
D_\alpha = \varepsilon_0 \varepsilon_{\alpha \beta} E_\beta - \Psi_{\alpha \beta} E_\beta + \xi_{\alpha \beta \gamma \delta} \nabla_\beta \nabla_\gamma E_\delta \\
B_\alpha = \mu_0 \mu_{\alpha \beta} H_\beta + \Psi_{\alpha \beta} E_\beta + \chi_{\alpha \beta \gamma} \nabla_\beta E_\gamma
\]

Now let us try to find out which inclusion shapes offer artificial magnetism without higher multipoles. If U-shaped particles were modified so as to form a closed loop, both bi-anisotropy and quadrupole polarisation would vanish. A small closed loop has the uniform current distribution, and the induced electromotive force in it is independent of the direction of the wave propagation (it is equal to the negative time derivative of the applied magnetic flux). If the loop contains an open part, which is very small compared to the loop perimeter, the dependence of the induced magnetic moment on the propagation direction is also negligible. However, the bi-anisotropy remains, since the induced current distribution is not uniform and results in both electric and magnetic dipole moments of the loop. This bi-anisotropy of the array,
related to the open part of the loop, can be suppressed in two ways. The first way is to prepare the unit cell with two (four, six) Split Ring Resonators arranged so that the bi-anisotropy of the unit cell vanishes. However, this way is difficult to implement on the nanoscale.

Recently, there were some suggestions for possible ways towards artificial magnetism in the optical range without strong spatial dispersion, without high-order multipoles or bi-anisotropy. A suitable design is, for example, the four-split optical SRRs suggested in [22] and effective nanorings of plasmonic spheres [23]. In [23] an effective ring is formed by plasmonic nanospheres located at the corners of a regular polygon. The minimum number of nanospheres for which the higher multipoles can be (with a qualitative accuracy) neglected is four. In [22] each of four plasmonic scatterers forming the effective ring is a planar L-shaped nanoparticle. In [23] these four plasmonic scatterers are nanospheres. It is clear that in both these design solutions -- in spite of their geometrical differences -- the physical mechanism underlying the artificial magnetism is the same. Notice that the concentration of the effective rings should be very high in order to obtain a resonance of permeability, which would be strong enough for the permeability to attain negative values. Practically, the negative isotropic magnetism in a composite of such nanorings (randomly oriented or forming three mutually orthogonal arrays) would correspond to a physically not realisable concentration, as adjacent nanorings would have to intersect. Only an anisotropic structure, e.g. of parallel nanorings, would be able to show a resonance strong enough to achieve a negative value for the resonant component of the permeability tensor $\mu$ (orthogonal to the plane of the nanorings). A fully isotropic design that would show sufficiently strong resonances is based on core-shell magnetic nanoclusters [24]. This structure is shown in Fig. 6.

We conclude that the constitutive equations for nanostructured MTMs have to be carefully formulated and this is mandatory for a proper electromagnetic characterisation. In order to characterise bulk optically dense MTMs, the multipole polarisation and possible bi-anisotropy have to be estimated. If, and only if, these effects are negligible, one can describe the medium in terms of two material parameters, $\varepsilon$ and $\mu$.

REFERENCES
4.1.5 Advanced approaches to electromagnetic characterisation of metamaterials

**Advanced characterisation of metasurfaces**

In the literature one can find attempts to characterise metasurfaces by parameters which are different from those obtained by the Nicholson-Ross-Weir method. Papers [1, 2] were an attempt to combine the bulk averaging and surface averaging procedures for monolayer and bilayer gratings. In these papers we introduced a specific bulk averaging procedure for microscopic polarisation, which in fact described the effective electric and magnetic polarisation per unit area. As we understand now, the approach was physically controversial, and its application to boundary problems turned out to be successful only for non-resonant inclusions.

Works [3-5] were attempts to fit the reflection and transmission coefficients of a planar optically dense grid of resonant elements to coefficients achievable for a layer of a bulk resonant magneto-dielectric medium. Since parameters of bulk optically dense media with resonant particles should show Lorentzian resonance, the data were fitted to formulae

\[
\varepsilon = \varepsilon_h + \frac{A_\varepsilon \omega^2}{\omega^2 - \omega_r^2 - i\omega\gamma}, \quad \mu = 1 + \frac{A_\mu \omega^2}{\omega^2 - \omega_m^2 - i\omega\gamma},
\]

The thickness of the effective layer \(d\) was tuned in an attempt to relate \(d\) to the geometry of the grid (Note that this tuning is needed to account for the influences of the physical thickness of the sample/grid and the inclusion period). A complete fitting of \(\varepsilon\) and \(\mu\) obtained from the \(R\) and \(T\) coefficients to the Lorentz resonance by tuning all its parameters turned out to be impossible, and did not even result in an acceptable accuracy. The authors of [3-5], however, consider their results to be promising and hope that further development of this approach will lead to a more complete success. Inspecting Table 1 from work [3] (for a grid of microwave split-ring resonators embedded
into a 3-mm thick dielectric matrix) one can see that fitting the measured and simulated coefficients is successful (with an acceptable 10-15% accuracy) for the electric and magnetic resonant frequencies $\omega_e$, $\omega_m$ and for the magnitudes of electric and resonances $A_e$ and $A_m$. But fitting values were not presented for the damping frequencies $\gamma_e$ and $\gamma_m$ which, in our opinion, are parameters no less important for the material’s characterisation. The fitting procedure in these papers allows obtaining good fitting results for any 4 of 6 resonance parameters, whereas two other parameters cannot be fitted. The arbitrary choice of these 4 successful parameters clearly indicates that they do not give an adequate description of the structure being modelled.

In what concerns the interaction with plane waves, metasurfaces should and can be characterised by fully self-consistent parameters. In paper [6] it is suggested to use spatially-dispersive $\varepsilon$ and $\mu$ parameters for MTM layers with a few or only one inclusion layer across the meta-layer thickness. These parameters take into account the influence of polariton waves excited at the surfaces of the MTM layer by incident plane waves, and these parameters are applicable to the case when the spatial dispersion is weak. These $\varepsilon$ and $\mu$ result from a bulk averaging approach applied for electric and magnetic polarisations combined with the surface averaging approach for calculating electric and magnetic fields. The method developed in that paper implies also specially obtained additional boundary conditions (see also [7]). However, this method cannot serve for the experimental characterisation of MTM layers. These non-local $\varepsilon$ and $\mu$ can be calculated theoretically but cannot be extracted from $R$ and $T$.

Probably, a more adequate condensed description was suggested in works [8-10]. This method is applicable for the experimental characterisation of metasurfaces containing one resonant inclusion layer across the host medium layer. There are four tensor characteristic parameters in this case: electric and magnetic, TE and TM surface susceptibilities. For optically dense metasurfaces of separate scatterers, these four parameters do not depend on the angles of incidence, and the dependences for $R$ and $T$ for any angle can be explicitly found through them. However, a significant drawback of the approach suggested in [8-10] is that it does not take into account the presence of the host dielectric layer in which the inclusions are embedded. Since inclusions forming MTMs cannot be located in free space, this approach in its present variant is not suitable for the experimental characterisation of MTMs. The generalisation of this approach to a realistic case when the inclusions are incorporated in a dielectric matrix would lead to a significant complication of the method.

Many nanostructured metasurfaces support surface waves, e.g. surface plasmon polaritons. In some special cases it is possible to predict dispersive properties of metasurfaces using CMPs found from the $R$ and $T$ coefficients. If scattering inclusions forming the material (grid) are well isolated, they can be considered to be resonant dipoles and the dipole polarisabilities can be extracted from already retrieved surface susceptibilities [10]. Then one can study the eigenwaves in a planar array of dipole particles. This possibility has not yet been studied.

To our knowledge, at this time there is no general approach in the literature, which would be applicable to experimental characterisation of metasurfaces comprising 2-3 inclusion gratings across the layer. Notice that the approach suggested in [8-10] is also not applicable to a metasurface consisting of a solid nanolayer with holes: the surface susceptibilities do not give a condensed description of such structures as they are angle-dependent. The proper electromagnetic characterisation of these metasurfaces is still an unsolved problem.
Advanced characterisation of bulk magneto-dielectric metamaterials

The bulk MTMs discussed in the overview [11] showed no features of strong spatial dispersion in the whole resonance band, and the retrieved material parameters were independent on the number of unit cells across the layer. These MTMs may therefore be referred to as Bloch lattices. For Bloch lattices the advanced characterisation approach was started in [12-14] and continued by [11].

The homogenisation model [11] comprises the strict proof that bulk EMPs defined by formulæ (1) through the refraction index $n_{\text{eff}}$ and the wave impedance $Z_w$ are exactly equal to the parameters defined by formulæ through auxiliary field vectors $D$ and $B$. This proof is an important generalisation of the same result of the well-known quasi-static theory of lattices. To retrieve the CMPs $\varepsilon$ and $\mu$ from coefficients $R$ and $T$ in the dynamic theory [12, 13], it was suggested first to retrieve $n_{\text{eff}}$ and $Z_w$ in the usual way and second, using specially derived relations between $Z_w$ and $Z_B$, to find $Z_w$.

The application of local material parameters $\varepsilon$ and $\mu$ to boundary problems is not compatible with the representation of the whole MTM layer as a uniform layer consisting of an effective medium. Beyond the quasi-static limit (where the optical size of the averaging volume $V$ is by definition negligible) the bulk averaging approach cannot be used when there is a sharp boundary to the lattice as this causes inconsistencies in the averaging. When we calculate the averaged field at a point $A$, we integrate the microscopic field over the volume $V$ centred at point $A$. If point $A$ is close to a sharp boundary of the effective medium, the volume $V$ turns out to be located partially inside the medium, partially outside it, and the averaging procedure is strictly speaking not applicable.

An introduction of transition layers on both sides of the material layer could enable the use of local EMPs for MTM layers. Material parameters of these layers would need to be different from the local $\varepsilon$ and $\mu$. Transition layers were first suggested by P. Drude in order to resolve the same problem for natural liquid and crystal media in the visible frequency range. However, before the birth of MTMs the introduction of Drude layers was usually not necessary. For natural crystals the quasi-static homogenisation model (when the phase shift of the wave over the lattice period $a$ is negligible) gives a good accuracy. Therefore, the introduction of transition layers with thickness $a$ instead of the sharp boundary did not lead to any practical improvement for bulk layers of natural materials. Moreover, in natural media there are surface states which mask the effect of transition layers: so-called Tamm and Shockley states for solid bodies and molecular state related to the surface tension for liquids. However, the situation with MTMs is very different: here, physical surface states are often not significant whereas the contribution of transition layers into the reflected and transmitted fields is large.

A method of the extraction of local EMPs $\varepsilon$ and $\mu$ from the $R$ and $T$ coefficients of the layer was developed in [12, 13]. The retrieval of parameters of Drude transition layers for a MTM slab was done in [11]. These parameters are the effective refraction coefficient $n$ and effective wave impedance $Z_w$, and in the examples studied they also satisfied the locality requirements. Therefore, they are believed to be applicable to different angles of incidence on an MTM layer, if used together with bulk EMPs describing the internal part of the layer.
The use of local EMPs introduced for MTMs in work [12] together with parameters of transition layers [11] leads to a homogenisation model which has a serious advantage compared to the use of Bloch material parameters, even though there are certain complications. Local EMPs are applicable to any angle of incidence of plane waves and to boundary problems with spherical and cylindrical waves. Local EMPs are therefore CMPs, unlike Bloch EMPs.

Bloch EMPs are defined and retrieved for normal incidence and can only be used to predict the $R$ and $T$ coefficients of layers of different thickness for the same normal incidence. Of course, applying the NRW method, modified for angles of incidence different than normal incidence, one can retrieve from $R$ and $T$ the permittivity and permeability in the form of scalar functions of the incidence angles $\theta$ and $\phi$. These functions are however different for the TE and TM polarisations. One can call them $\varepsilon_{\text{TE}}(\theta, \phi)$ and $\mu_{\text{TM}}(\theta, \phi)$, as it was done in [15]. However, such functions have no clear physical meaning and are not useful for any other purpose than to calculate $R(\theta, \phi)$ and $T(\theta, \phi)$ from which they were derived. Therefore such parameters are, in our opinion, not very useful.

Publications [11-14] indicate potentially promising ways (the use of transition layers) to attain the proper electromagnetic characterisation procedures suitable for bulk magneto-dielectric MTM layers. These studies have shown that the retrieved bulk EMP meet the requirement of locality. However, additional research is still necessary to prove that parameters retrieved in these works give a good accuracy in predicting coefficients $R(\theta, \phi)$ and $T(\theta, \phi)$ for all angles of incidence at least for Bloch lattices.

Among unsolved problems we have to mention the characterisation of all metamaterials which are not Bloch Lattices and the extraction of the normal components of local tensors $\varepsilon$ and $\mu$ when MTMs are anisotropic, as these cannot be found studying the normal incidence of the plane wave.

REFERENCES

4.2 Measurements of inclusion geometry and chemical characterisation

Based on Wikipedia, the free encyclopedia http://en.wikipedia.org, February 2010

Introduction

Characterisation, when used in materials science, refers to the use of measuring and visualisation techniques to probe into the surface and internal structure. Several different advanced techniques can be used for the structural, chemical, and topological characterisation of the obtained nano-structures.

Analysis techniques are used to magnify the specimen in order to visualise its internal structure, and to gain knowledge as to the distribution of elements/inclusions within the specimen and their interactions. Magnification and internal visualisation are normally done in a type of microscope.

The metamaterial inclusions created in the EC projects are built up from nanometre size. To test the geometry and distribution in space of the inclusions, techniques are used that show contrast with respect to the matrix in which the inclusions are embedded. Light or other EM waves, sound, or moving particles, are forced to deviate from a straight trajectory by non-uniformities in the sample, and this is called scattering. These techniques are based on observing the scattered intensity of a beam hitting a sample as a function of incident and scattered angle, polarisation, and wavelength or energy. When the scattered radiation is analysed as a function of time, these techniques are able to register dynamic processes.

Below certain structural characterisation techniques often used by materials scientists will be presented.

Raman spectroscopy

Raman spectroscopy employs the Raman effect for materials analysis. The frequency of light scattered from a molecule may be changed up and down, based on the structural characteristics of the molecular bonds. A monochromatic light source (usually from a laser in the visible, near infrared, or near ultraviolet range) is required for illumination, and a spectrogram of the scattered light then shows the deviations caused by state changes in the molecule. In a gas, Raman scattering can occur due to a change in vibrational, rotational or electronic energy of a molecule. Chemists are concerned primarily with the vibrational Raman effect, but Raman spectroscopy is also used as a tool to detect high-frequency magnons (spinwaves) in one of the EC projects.

Brillouin light scattering spectroscopy (BLS)

Brillouin light scattering (BLS) similarly measures the energy loss of photons (usually at a convenient visible wavelength) reflected from or transmitted through a magnetic material. Brillouin spectroscopy is similar to the more widely known Raman scattering but probes a lower energy and has a higher energy resolution in order to be able to detect the meV energy of magnons. The frequency and the wave vector of the scattered photons are shifted by amounts equal to the frequency and the wave vector of the scattering magnons, which allows one to map the dispersion of the magnons. Because of the wave vector conservation in the magnon-photon interaction, the wavelength of spin waves that can be detected in extended systems is of the same order of magnitude as that of light.
Scanning electron microscopy (SEM)

Scanning electron microscope (SEM) is a type of electron microscopy that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample’s surface topography, composition and other properties such as electrical conductivity.

The types of signals produced by an SEM include secondary electrons, back-scattered electrons (BSE), characteristic X-rays, light (cathodo-luminescence), specimen current and transmitted electrons. Secondary electron detectors are common in all SEMs, but it is rare that a single machine would have detectors for all possible signals. The signals result from interactions of the electron beam with atoms at or near the surface of the sample. In the most common or standard detection mode, secondary electron imaging or SEI, the SEM can produce very high-resolution images of a sample surface, revealing details less than 1 to 5 nm in size. Due to the very narrow electron beam, SEM micrographs have a large depth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample. A wide range of magnifications is possible, from about 10 times (about equivalent to that of a powerful magnifying glass) to more than 500,000 times, about 250 times the magnification limit of the best light microscopes. Back-scattered electrons (BSE) are beam electrons that are reflected from the sample by elastic scattering. BSE are often used in analytical SEM along with the spectra made from the characteristic X-rays. Because the intensity of the BSE signal is strongly related to the atomic number (Z) of the specimen, BSE images can provide information about the distribution of different elements in the sample. For the same reason, BSE imaging can image colloidal gold immuno-labels of 5 or 10 nm diameter which would otherwise be difficult or impossible to detect in secondary electron images in biological specimens. Characteristic X-rays are emitted when the electron beam removes an inner shell electron from the sample, causing a higher energy electron to fill the shell and release energy. These characteristic X-rays are used to identify the composition and measure the abundance of elements in the sample.

Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) is a microscopy technique whereby a beam of electrons is transmitted through an ultra thin specimen, interacting with the specimen as it passes through. An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a CCD camera.

TEMs are capable of imaging at a significantly higher resolution than light microscopes, owing to the small de Broglie wavelength of electrons. This enables the instrument’s user to examine fine detail – even as small as a single column of atoms, which is tens of thousands times smaller than the smallest resolvable object in a light microscope.

At smaller magnifications TEM image contrast is due to absorption of electrons in the material, due to the thickness and composition of the material. At higher magnifications complex wave interactions modulate the intensity of the image, requiring expert analysis of observed images. Alternate modes of use allow for the TEM to observe modulations in chemical identity, crystal orientation, electronic structure and sample induced electron phase shift as well as the regular absorption based imaging.
Atomic Force Microscopy (AFM)

Atomic Force Microscopy (AFM) or scanning force microscopy (SFM) is a very high-resolution type of scanning probe microscopy, with demonstrated resolution of fractions of a nanometre, more than 1000 times better than the optical diffraction limit. The precursor to the AFM was the scanning tunneling microscope. The information is gathered by ‘feeling’ the surface with a mechanical probe.

The AFM consists of a cantilever with a sharp tip (probe) at its end that is used to scan the specimen surface. The cantilever is typically silicon or silicon nitride with a tip radius of curvature on the order of nanometres. When the tip is brought into proximity of a sample surface, forces between the tip and the sample lead to a deflection of the cantilever according to Hooke’s law. Depending on the situation, forces that are measured in AFM include mechanical contact force, van der Waals forces, capillary forces, chemical bonding, electrostatic forces, magnetic forces (see magnetic force microscope, MFM), Casimir forces, solvation forces, etc. As well as force, additional quantities may simultaneously be measured through the use of specialised types of probe (see scanning thermal microscopy, photothermal microspectroscopy, etc.). Typically, the deflection is measured using a laser spot reflected from the top surface of the cantilever into an array of photodiodes. Other methods that are used include optical interferometry, capacitive sensing or piezo-resistive AFM cantilevers.

The AFM can be operated in a number of modes, depending on the application. In general, possible imaging modes are divided into static (also called contact) modes and a variety of dynamic (or non-contact) modes where the cantilever is externally oscillated at or close to its fundamental resonance frequency or a harmonic. The oscillation amplitude, phase and resonance frequency are modified by tip-sample interaction forces; these changes in oscillation with respect to the external reference oscillation provide information about the sample’s characteristics.

Electron Energy Loss Spectroscopy (EELS)

Electron Energy Loss Spectroscopy (EELS) exposes a material to a beam of electrons with a known, narrow range of kinetic energies. Some of the electrons will undergo inelastic scattering, which means that they lose energy and have their paths slightly and randomly deflected. The amount of energy loss can be measured via an electron spectrometer and interpreted in terms of what caused the energy loss. Inelastic interactions include phonon excitations, inter and intra band transitions, plasmon excitations, inner shell ionisations, and Čerenkov radiation. The inner-shell ionisations are particularly useful for detecting the elemental components of a material.

With some care, and looking at a wide range of energy losses, one can determine the types of atoms, and the numbers of atoms of each type, being struck by the beam. The scattering angle (that is, the amount by which the electron’s path is deflected) can also be measured, giving information about the dispersion relation of whatever material excitation caused the inelastic scattering.

Very recently, one group in Max Planck Institute for Microstructure physics in Halle Germany proved that by using spin polarised electron energy loss spectroscopy (SPEELS), very high energy surface magnons can be exited. This technique allows people to probe, for the first time, magnons and their dispersion in an ultrathin magnetic system.
Scanning Near-field Optical Microscopy (SNOM)

Scanning Near-Field Optical Microscopy (SNOM) is a scanning probe microscopy technique for the optical investigation of nanostructures with a resolution below the diffraction limit. This technique is based on a probe with evanescent field which scans the surface of interest. There are two types of probes and SNOM: apertured and scattering (apertureless) SNOM (s-SNOM).

The apertured SNOM is based on using a tapered optical fiber coated with opaque metal which is brought in a close proximity of the sample. The opening of the optical fiber acts as a point source (illumination mode operation) or a detector (collection mode) being capable to interact with evanescent waves. The achievable resolution in practice is $\sim \lambda/10$ and it depends on the fiber aperture diameter, that is, how small signal can be detected.

In the s-SNOM, the probe is a nanosized scatterer. The near-field of the externally illuminated probe is modified by the sample so the scattered far-field carries the information of the sample’s local optical properties. The most important advantage of the s-SNOM is a better resolution determined only by the radius of curvature of the probe. Furthermore, enhanced near-fields of illuminated metallic probes are used in order to increase optical response enabling tip-enhanced microscopy as well as tip-enhanced spectroscopy (fluorescence and Raman spectroscopy).

Ellipsometry

Ellipsometry is an ‘indirect’ structural characterisation. It is a versatile and powerful optical technique for the investigation of the dielectric properties (complex refractive index or dielectric function) of thin films. As an optical technique, spectroscopic ellipsometry is non-destructive and contactless.

The name ‘ellipsometry’ stems from the fact that the most general state of polarisation is elliptic. Upon the analysis of the change of polarisation of light, which is reflected off a sample, ellipsometry can yield information about layers that are thinner than the wavelength of the probing light itself, even down to a single atomic layer. Ellipsometry can probe the complex refractive index or dielectric function tensor, which gives access to fundamental physical parameters and is related to a variety of sample properties, including morphology, crystal quality, chemical composition, or electrical conductivity. It is commonly used to characterise film thickness for single layers or complex multilayer stacks ranging from a tenths of a nanometer to several micrometers with an excellent accuracy.

For studies of anisotropic samples ellipsometric measurements and evaluations are often performed cooperatively with those of polarised transmission and reflection spectroscopy. Typically all measurements can be performed in the same experimental set-up.

Purity and monodispersity of proteins (Gel electrophoresis)

Gel electrophoresis is a technique used for the separation of deoxyribonucleic acid (DNA), ribonucleic acid (RNA), or protein molecules using an electric field applied to a gel matrix. The term ‘gel’ in this instance refers to the matrix used to contain, then separate the target molecules. ‘Electrophoresis’ refers to the electromotive force (EMF) that is used to move the molecules through the gel matrix. By placing the molecules in wells in the gel and applying an electric field, the molecules will be made to move through the matrix at different rates, determined largely by their mass when the charge to mass ratio ($Z$) of all species is uniform, toward the anode if negatively charged or toward the cathode if positively charged.
4.3 Measurement techniques for electromagnetic characterisation of nanostructured materials

It is clear from the theoretical chapters of this booklet devoted to the electromagnetic characterisation of nanostructured materials, that the main criterion for the choice of the measurement technique is the procedure for the retrieval of characteristic parameters from the measurement data. For this retrieval (post-processing), suitable software should be available. As stated in the theoretical chapters, adequate retrieval of characteristic parameters and corresponding software is not available for all types of nanostructured materials. Procedures are clearly established only for those nanostructured materials which are not referred to as metamaterials (MTMs). The problem of electromagnetic characterisation of different types of MTMs is one of the main challenges in modern applied electrodynamics.

Another criterion for the choice of the measurement technique is the adequate classification of the material as explained in Chapter 4.1. Below in Tables 2 and 3 is a list of most known measurement techniques for linear electromagnetic characterisation of nanostructured layers and films is given for both optical and radio frequency ranges. We did not include in these tables two-beam interferometric spectroscopy and holographic interferometry based on Michelson interferometers, since these techniques require a larger size of the sample (few mm and more) which is rarely available for nanostructured electromagnetic materials.

Recent developments include an experimental method implemented [3] with a supercontinuum light source and Fourier-transform interferometer. Broadband (1.1 to 1.7 μm) phase measurements are used to determine the dispersion relation of MTMs at normal incidence in terms of the complex wavenumber leading to an effective refractive index. The experimental setup is a Jamin–Lebedeff interferometer, modified for measurements in transmission and reflection under normal incidence. With this technique an accuracy of the refractive-index structures of about 4% in the real and imaginary parts can be obtained.

THz-Time Domain Spectroscopy (TDS) normally requires two measurements [4]: one reference waveform measured with the reference of known dielectric properties, and a second measurement through the sample. Because of the relatively clean separation in time between the main transmitted pulse and the first internal reflection, it becomes possible to keep only the first directly transmitted terahertz pulse. Comparing the ratio and phase change between the sample and reference, the real part and imaginary part of refractive index of studied sample can be obtained simultaneously. A detailed procedure to extract the negative refractive index of low-loss metamaterials is based on THz-TDS measurement. (something (i.e., a verb) is missing from this sentence?)

A microwave method [16] was proposed for permittivity measurements of thin dielectric materials. A simple expression is given to measure the complex permittivity of thin materials, using propagation constant measurements at two different frequencies. The materials do not need to fill the total aperture of the waveguide. The stated advantages are that: 1) it eliminates the requirement of precise knowledge of the thickness of thin samples, 2) it can be adapted to dispersive and non-dispersive materials by adjusting the degree of power series representation of the complex permittivity; and 3) its accuracy can be increased by improving the accuracy of permittivity measurements in conventional techniques that require complete sample filling of the waveguide aperture. The proposed method has been verified with complex permittivity measurements.

Femtosecond interferometric spectroscopy and other techniques used to retrieve non-linear parameters of materials are also not included in the tables.
## Techniques for Optical Range

<table>
<thead>
<tr>
<th>Techniques</th>
<th>Measuring Equipment</th>
<th>Direct Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free space techniques [10-12]</td>
<td>Receiving antenna + vector network analyzer</td>
<td>Complex S-parameters of the set-up between the input and output points</td>
</tr>
<tr>
<td>Waveguide techniques [13-16]</td>
<td>Receiving probe + vector network analyzer</td>
<td>Complex S-parameters of the set-up between the input and output points</td>
</tr>
<tr>
<td>Resonator techniques [17]</td>
<td>Receiving probe or receiving waveguide with probe + vector network analyzer</td>
<td>Complex S-parameters of the set-up between the input and output points</td>
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## Techniques for Radio Frequency Range

<table>
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<tr>
<th>Techniques</th>
<th>Measuring Equipment</th>
<th>Direct Results</th>
</tr>
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<tr>
<td>Free space techniques [10-12]</td>
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<td>Complex S-parameters of the set-up between the input and output points</td>
</tr>
</tbody>
</table>

## Table 2. The list of main measurement techniques for the optical range.

## Table 3. The list of measurement techniques for the radio frequency range.

## REFERENCES

4.4 Measurement techniques for magnetic and spin wave properties

The descriptions of techniques are taken from Wikipedia on 2/2/2010.

Magnetometer

A magnetometer is a scientific instrument used to measure the strength and/or direction of the magnetic field in the vicinity of the instrument. Magnetometers can be divided into two basic types:

- scalar magnetometers measure the total strength of the magnetic field to which they are subjected; and
- vector magnetometers have the capability to measure the component of the magnetic field in a particular direction, relative to the spatial orientation of the device.

The use of three orthogonal vector magnetometers allows the magnetic field strength, inclination and declination to be uniquely defined.

Superconducting quantum interference devices (SQUID)

Superconducting quantum interference devices (SQUID) are an example of a vector magnetometers are superconducting quantum interference devices (SQUIDs), which measure extremely small magnetic fields; they are very sensitive vector magnetometers, with noise levels as low as $3 \text{ fT-Hz}^{-0.5}$ in commercial instruments and $0.4 \text{ fT-Hz}^{-0.5}$ in experimental devices.

Vibrating sample magnetometer (VSM)

Vibrating sample magnetometers (VSM) measure magnetic properties. A sample is placed inside a uniform magnetic field to magnetise the sample. The sample is then physically vibrated sinusoidally, typically through the use of a piezoelectric material. Commercial systems use linear attenuators of some form and historically the development of these systems was done using modified audio speakers, though this approached was dropped due to the interference through the in-phase magnetic noise produced, as the magnetic flux through a nearby pickup coil varies sinusoidally. The induced voltage in the pickup coil is proportional to the sample’s magnetic moment, but does not depend on the strength of the applied magnetic field. In a typical setup, the induced voltage is measured through the use of a lock-in amplifier using the piezoelectric signal as its reference signal. By measuring in the field of an external electromagnet, it is possible to obtain the hysteresis curve of a material.

Magnetic force microscope (MFM)

Magnetic force microscope (MFM) is a variety of atomic force microscope, where a sharp magnetised tip is scanning the magnetic sample; the tip-sample magnetic interactions are detected and used to reconstruct the magnetic structure of the sample surface. Many kinds of magnetic interactions are measured by MFM, including magnetic dipole–dipole interaction. MFM scanning often uses non-contact AFM (NC-AFM) mode and e.g. domains can be detected.
Magneto-optic Kerr effect (MOKE)

Magneto-optic Kerr effect (MOKE) is a technique based on magneto-optic effects. It describes the changes of light reflected from magnetised media and e.g. the magnetic domain structure can be investigated. The light that is reflected from a magnetised surface can change in both polarisation and reflectivity. (The effect is identical to the Faraday effect, except that the magneto-optical Kerr effect is a measurement of the reflected light, while the Faraday effect is a measurement of the transmitted light.)

Time-resolved Scanning Kerr Microscopy (TRSKM)

Time-resolved Scanning Kerr Microscopy (TRSKM) can be applied to detect both static and dynamic (time resolved) scanning. It detects the change of its magnetisation due to the pumping of the sample by either picosecond pulses of magnetic field, or femtosecond optical pulses, or GHz frequency microwaves, while the relative time delay between the pump and the probe and/or the position of the sub-micrometer probe spot on the surface of the sample are varied. The TRSKM performs a 3D vectorial analysis of the time dependent magnetisation and is thus *phase sensitive*. It has spatial resolution down to 300 nm.

Spin wave measurements

Spin wave measurements or magnon spectrum measurements can be divided into four experimental methods of which two are discussed above: inelastic light scattering (Brillouin scattering, Raman scattering and inelastic X-ray scattering) and inelastic electron scattering (spin-resolved electron energy loss spectroscopy). The last technique requires large installations often at central facilities. E.g. the Advanced Light Source (ALS) in Berkeley CA has a full field soft X-ray microscope dedicated to various applications in modern nanoscience, such as nanomagnetic materials. XM-1 still holds the world record in spatial resolution down to 15nm and is able to combine high spatial resolution with a sub-100ps time resolution to study e.g. ultrafast spin dynamics.

Inelastic neutron scattering

Inelastic neutron scattering measures the energy loss of a beam of neutrons that excite a magnon, typically as a function of scattering vector (or equivalently momentum transfer), temperature and external magnetic field. Inelastic neutron scattering measurements can determine the dispersion curve for magnons just as they can for phonons. Important inelastic neutron scattering facilities are present at the ISIS neutron source in Oxfordshire, UK, the Institut Laue-Langevin in Grenoble, France, the High Flux Isotope Reactor at Oak Ridge National Laboratory in Tennessee, USA, and at the National Institute of Standards and Technology in Maryland, USA.

Spin-wave resonance (ferromagnetic resonance)

Spin-wave resonance (ferromagnetic resonance) measures the absorption of microwaves, incident on a magnetic material, by spin waves, typically as a function of angle, temperature and applied field. Ferromagnetic resonance is a convenient laboratory method for determining the effect of magnetocrystalline anisotropy on the dispersion of spin waves.
Vector Network Analyser ferromagnetic resonance (VNA-FMR)

Vector Network Analyser ferromagnetic resonance (VNA-FMR) is used to analyze the properties of electrical networks, especially those properties associated with the reflection and transmission of electrical signals known as scattering parameters (S-parameters).

Network analyzers are used mostly at high frequencies; operating frequencies can range from 9 kHz to 110 GHz. Special types of network analyzers can also cover lower frequency ranges down to 1 Hz. These network analyzers can be used for example for the stability analysis of open loops or for the measurement of audio and ultra sonic components.

The two main types of network analyzers are

- Scalar Network Analyzer (SNA) – measures amplitude properties only;
- Vector Network Analyzer (VNA) – measures both amplitude and phase properties.

Microstrip detectors

Microstrip detectors (essentially ‘near field’ microwave measurements) are a particle detector designed to consist of a large number of identical components laid out along one axis of a two-dimensional structure, generally by lithography. The idea is that several components will react to a single passing particle, allowing an accurate reconstruction of the particle’s track. Silicon microstrip detectors, in which the sensing mechanism is the production of electron-hole pairs in a 300-micrometre layer of silicon, with the electrons then being attracted by an electric field created by a pattern of inter-digitied anodes and cathodes on the surface of the silicon separated by $\text{SiO}_2$ insulator, are a common design.
Further information
Useful Links

The following brochures can be downloaded from the Industrial Technologies website:
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**ECONAM**

FP7-NMP-CSA-CA-218696

www.econam.metamorphose-vi.org

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<td>Coordinator</td>
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**MAGNONICS**

FP7-NMP-SMALL-2008-2228673

www.magnonics.org

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[www.metachem-fp7.eu](http://www.metachem-fp7.eu)

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Philippe Barois  
barois@cppp-bordeaux.cnrs.fr  
+33-5-56845669 |

### NANOGOLD
**FP7-NMP-SMALL-2008-228455**  
[http://nanogold.epfl.ch](http://nanogold.epfl.ch)

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01/08/2009 – 31/07/2012 |
| Coordinator | EPFL, CH  
Toralf SCHARF  
toralf.scharf@epfl.ch  
+41 32 7183200 |

### NIM_NIL
**FP7-NMP-SMALL-2008-228637**  
[www.nimnil.org](http://www.nimnil.org)

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| Coordinator | PROFACTOR GmbH, AT  
Iris Bergmair  
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Metamaterials control the flow of electromagnetic waves (e.g. light) via interactions with inclusions. Metamaterial designs realised with nanotechnology can really be viewed as ‘effectively continuous materials’!

An exchange workshop between materials scientists and electromagnetic engineers was held in Brussels on December 9-11, 2009.

The tutorial lectures are represented in this booklet.