Electromagnetics of perfect absorbers:

Part 1: 2D vs 3D geometry

Part 2: Composite materials filled with carbon nano- and micro-inclusions

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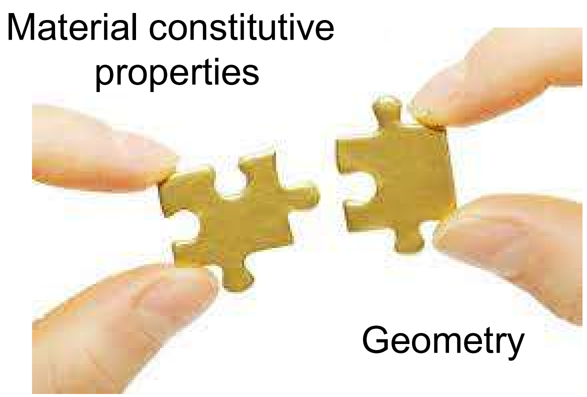


Joensuu - Cassino – Minsk, May 24-25, 2021

Complex permittivity

$$\varepsilon(\omega) = \varepsilon' + i\varepsilon''$$

$$\tan(\delta) = \frac{\varepsilon''}{\varepsilon'}$$

- ε’ is responsible to the Energy **storage** in the system
- ε” is responsible to the Energy **losses** in the system

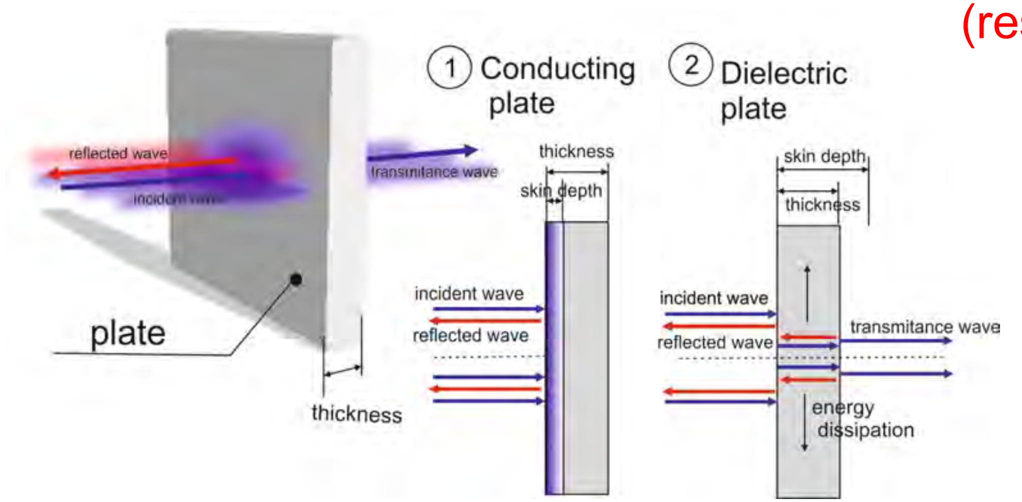
$$\sigma = \omega\varepsilon_0 \,\mathrm{Im}(\varepsilon) = 2\pi\nu\varepsilon_0 \,\mathrm{Im}(\varepsilon)$$

Absorption = losses = imaginary part of permittivity = conductivity

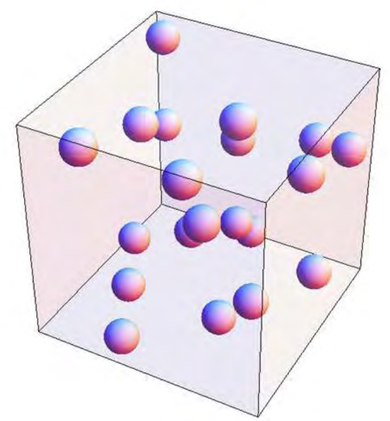
Classification of materials based on permittivity

$\frac{\varepsilon_r''}{\varepsilon_r'}$	Current conduction	Field propagation
0		perfect dielectric lossless medium
$\ll 1$	low-conductivity material poor conductor	low-loss medium good dielectric
≈ 1	lossy conducting material	lossy propagation medium
$\gg 1$	high-conductivity material good conductor	high-loss medium poor dielectric
∞	perfect conductor	

Losses……
…… Absorption of the electromagnetic radiation



Conductor + dielectric + geometry
(resonator, waveguides, etc) =
= wanted EM response

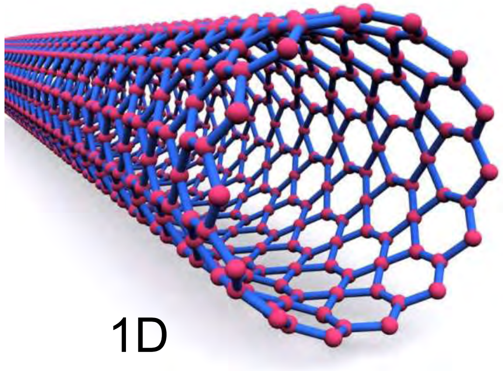


Material	Permitivity
Vacuum	1
Paper	1.4
Teflon	2
Epoxy resin	3
Concrete	4.5
Alumina ceramic	10
Water	80

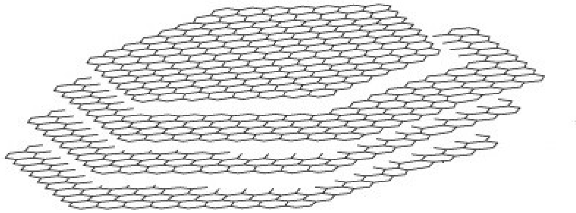
To tune the constitutive parameters of the bulk media we should **use mixtures!**

composites

Fillers used



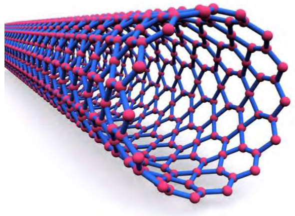
1D

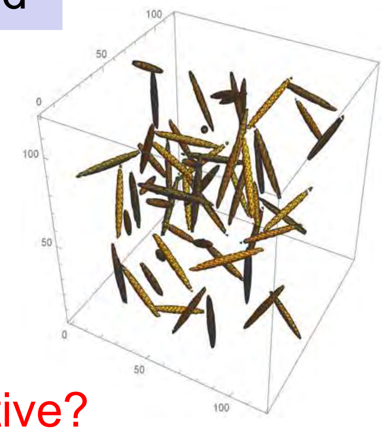


2D

Carbon black
Exfoliated graphite
Activated carbons…………..

High aspect ratio (length/diameter) → low percolation threshold





Same concentration

Nonconductive?
Conductive?
Reflective?
Absorptive?
Transparent?

What is wrong???

OUTLINE

1. WHAT IS IMPORTANT FOR COMPOSITE ELECTROMANGTIC RESPONSE? A NUMBER OF EXPERIENTAL EXAMPLES

2. Strategies of MODELING OF COMPOSITE ELECTROMANTIC PROPEORTES: BELOW PERCOLATION AND PERCOLATED COMPOSITES

3. 3D ARCHITECTURES MADE OF COMPOSITE MATERIALS (MATERIAL+GEOMETRY), what parameters (along with geometry) are important?

MOTIVATION:

Pay attention to the details: filler, matrix, fabrication, …..

Important issues

- **Frequency range**
  - ✓ Percolation threshold & behavior (low-frequency range only)
  - ✓ Frequency peculiarities of individual functional additive (vs its geometry) are visible in composites

1

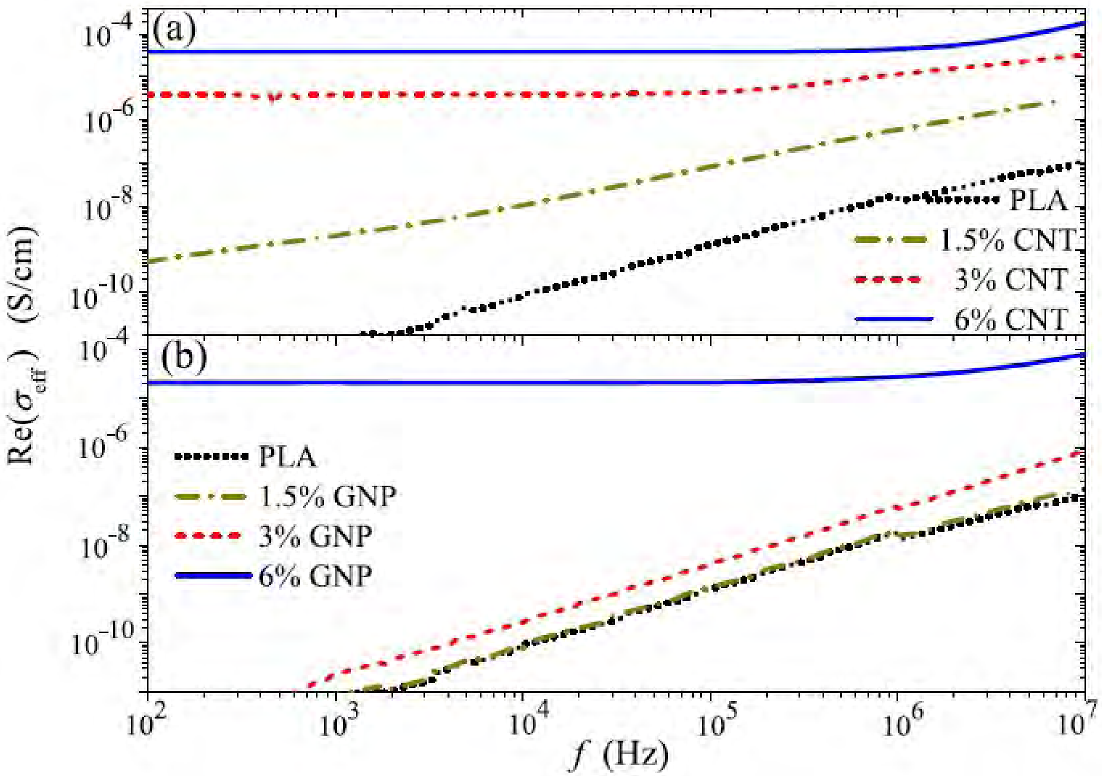
- **Matrix & Fabrication**
  - ✓ Matrix type, viscosity
  - ✓ Hardening, Solvent, Surfactant,
  - ✓ **Combination of Functional additives (bi-, many-fillers)**
  - ✓ **Filler concentration**
  - ✓ Functionalization, oxidation
  - ✓ Aggregation, agglomeration of fillers, dispersion state
  - ✓ Post processing treatment (e.g. thermal treatment, mechanical deformation, annealing, ionizing irradiation).

3

- **Individual functional additive**
  - ✓ type,
  - ✓ geometry,
  - ✓ perfectness,
  - ✓ ….

2

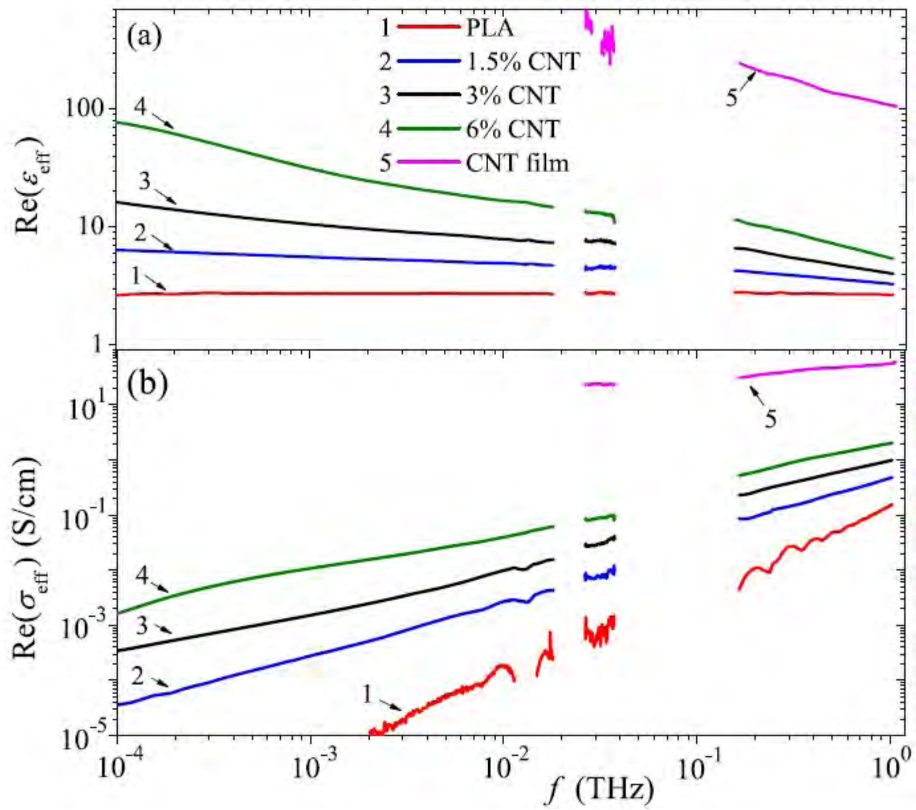
Percolation in low frequency range

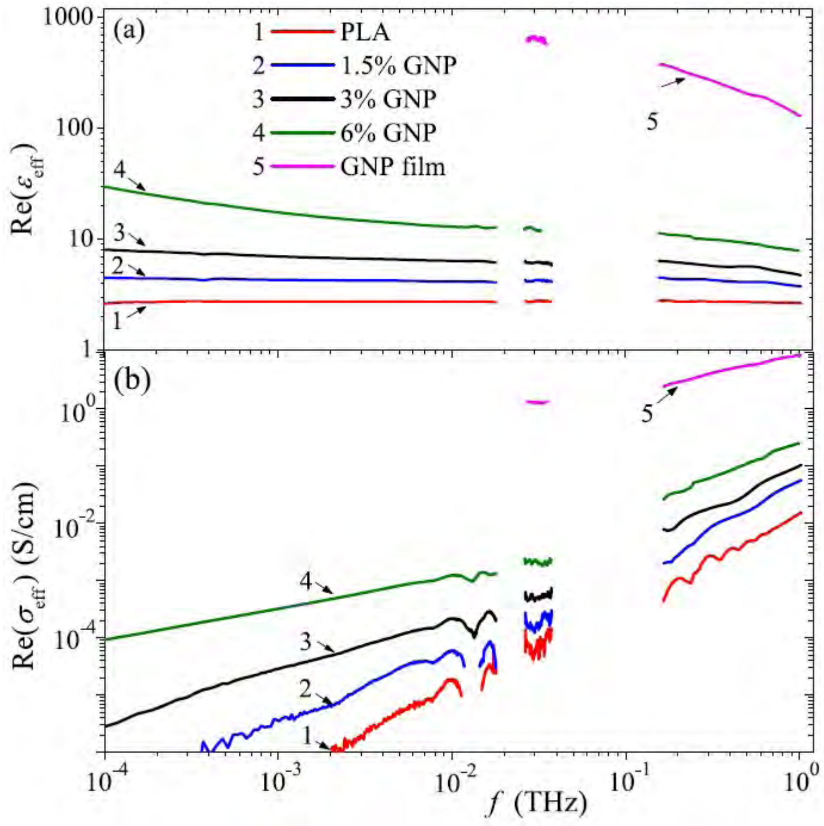


The percolation manifest itself as appearance of conductivity Plato only in DC and low-frequency range

M. V. Shuba, at al. // Mater. Res. Express. 2019

High frequency range: percolation ?





At high frequencies, there are no parameters to judge the percolation.
Fillers are coupled electromagnetically

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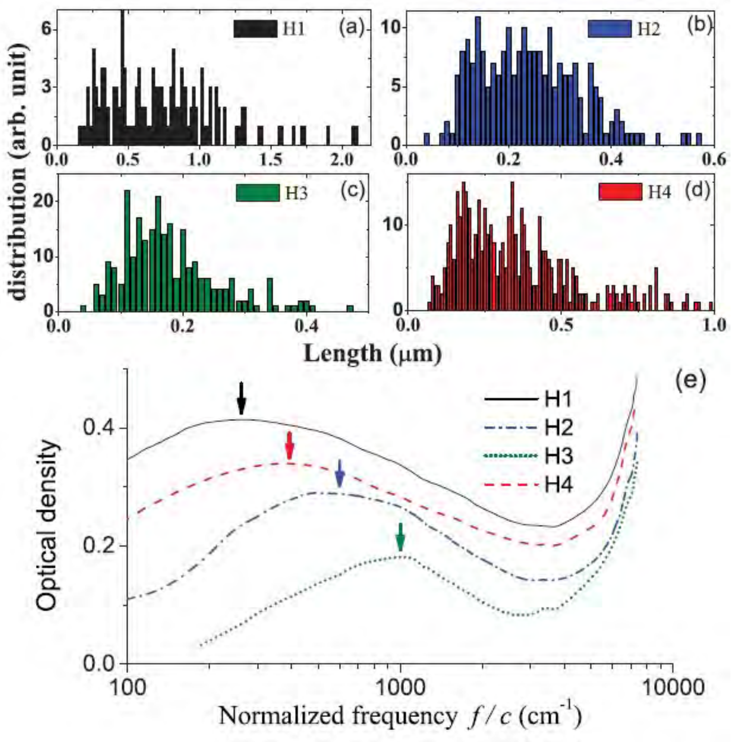
Resonant behavior of SWCNTs composites at certain frequencies

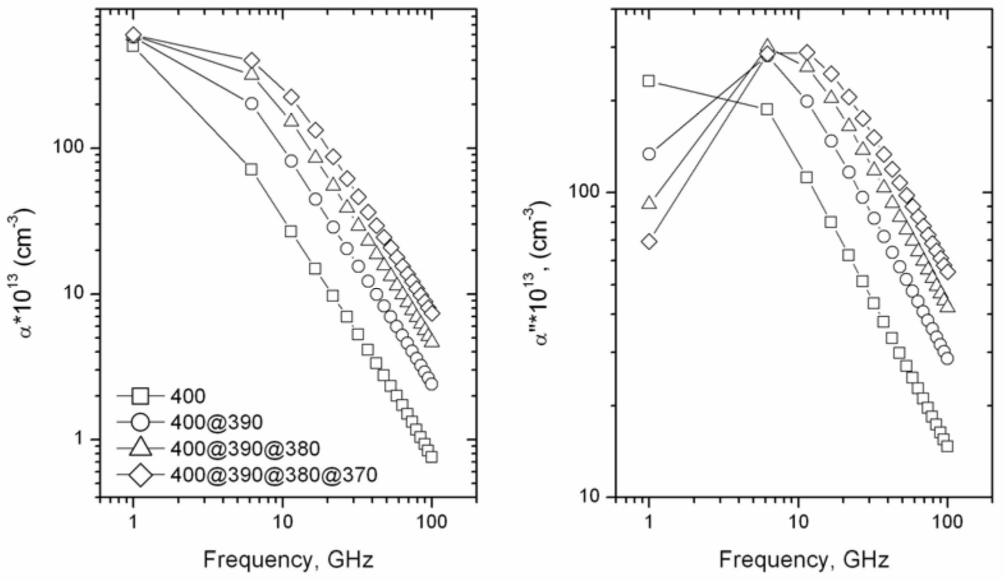


Antenna resonance related to the finite length of CNT manifests itself in THz frequencies (see lecture of Prof. Maksimenko).
The position of the absorption peak is dependent on the mean CNT length.

Electromagnetic screening of inner shells in MWCNTs

High-frequency polarizability of MWCNT, microwave range, modeling:

Reasonable nanotubes parameters – 10-20 mkm length, 30 nm diameter.



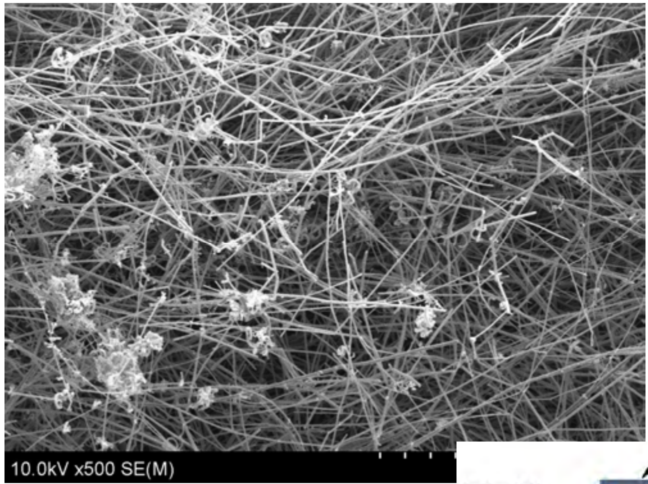
Dependence of MWCNT polarizability on the number of walls (screening effect in MWCNT)

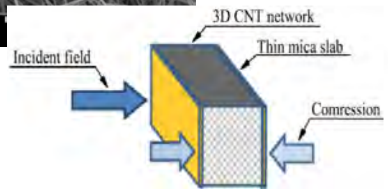
Number of walls in MWCNT might be very important!

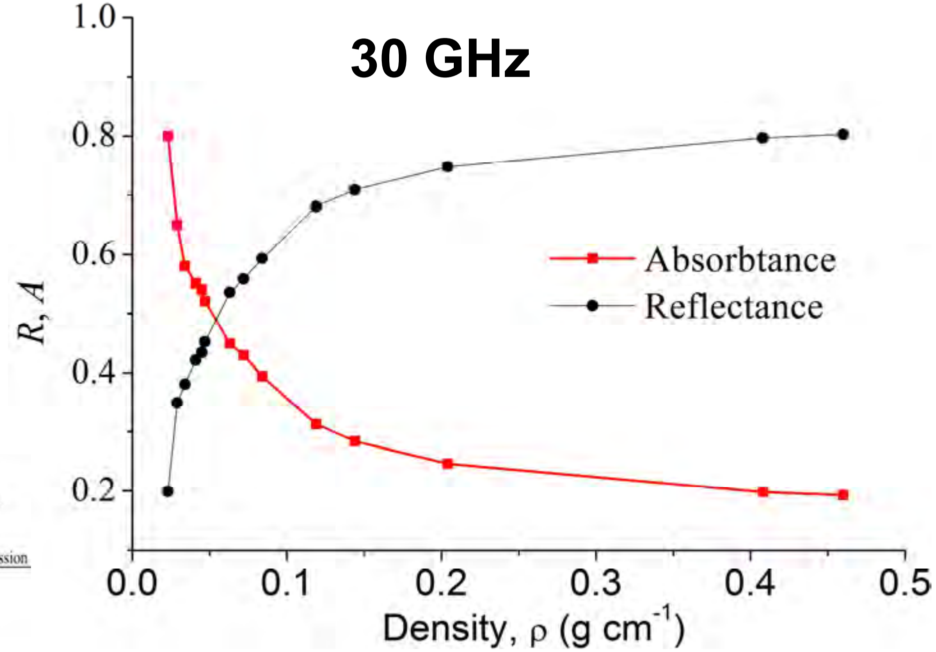
To use the same volume (weight) fraction of MWCNT effectively, remember about the frequency range to be addressed !

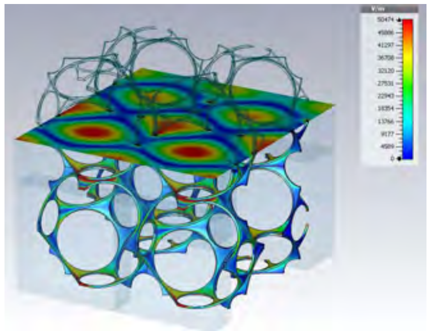
Strong electromagnetic screening of inner shells take place in MW range (only 4-5 outer metal walls, or 12-15 walls in total) take part in EM interaction in MW frequencies).

Sponge made of MWCNT in the microwave range









The density (inner structure) of the percolative network is importan t!!

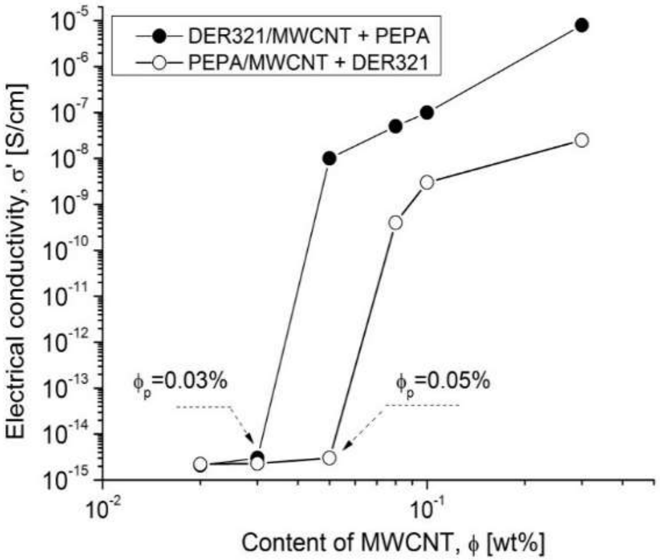
M.V. Shuba, et al Nanotechnology 29, 375202

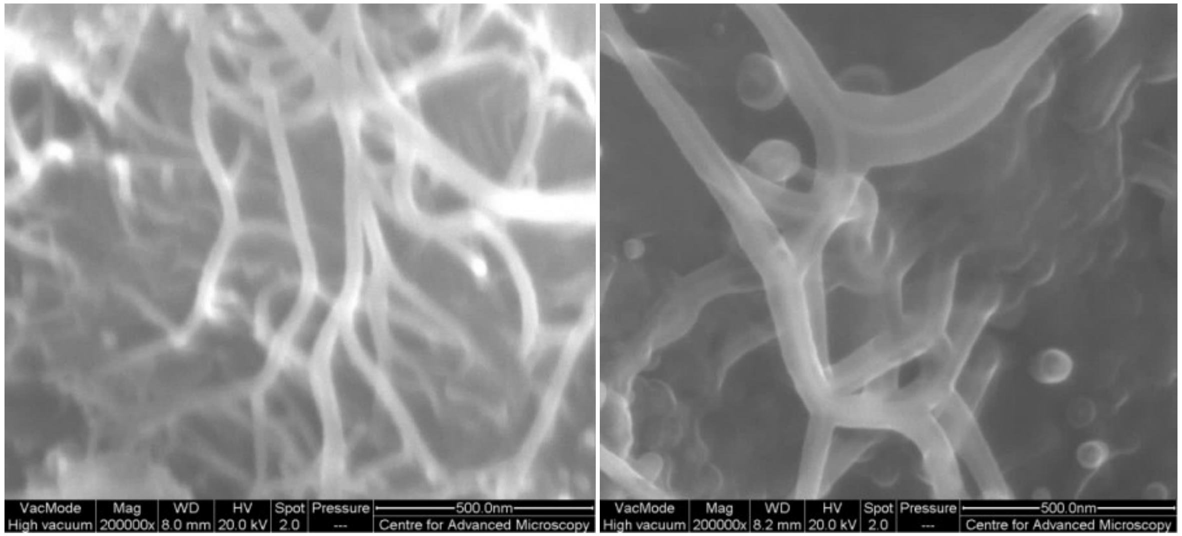
Fillers' lateral dimension, aspect ratio and estimated percolation thresholds

Filler type	Lateral size, μm	Aspect ratio	Percolation threshold, vol. %	Percolation threshold, wt. %
ACF	5	1.5	32.0	29
ACC	20	2	29.8	27
FG	15-44	6.1	17.1-25.3	27.3-38.2
MG	44-75	6.3	16.6-24.6	26.6-37.3
CG	100-200	6.5	16.2-24.0	26.1-36.5
EG	300-500	20	16-23	1-1.5
NG	500-750	10	10.8-16.3	18.1 -26.2
TG	10	100	18.1-26.2	2.1-3.2
CBH	100 nm	100		1.5-2.0
MWCNT	20	$0.5 * 10^3$		0.01
SWCNT	1	10^3		0.005

Conductivity / polarizability of the filler is important
But percolation threshold (geometry) is not less important !!
It affects all properties of the composite (mechanical, thermal….)

Polymer composites.
Effect of interfaces on Electrical Conductivity

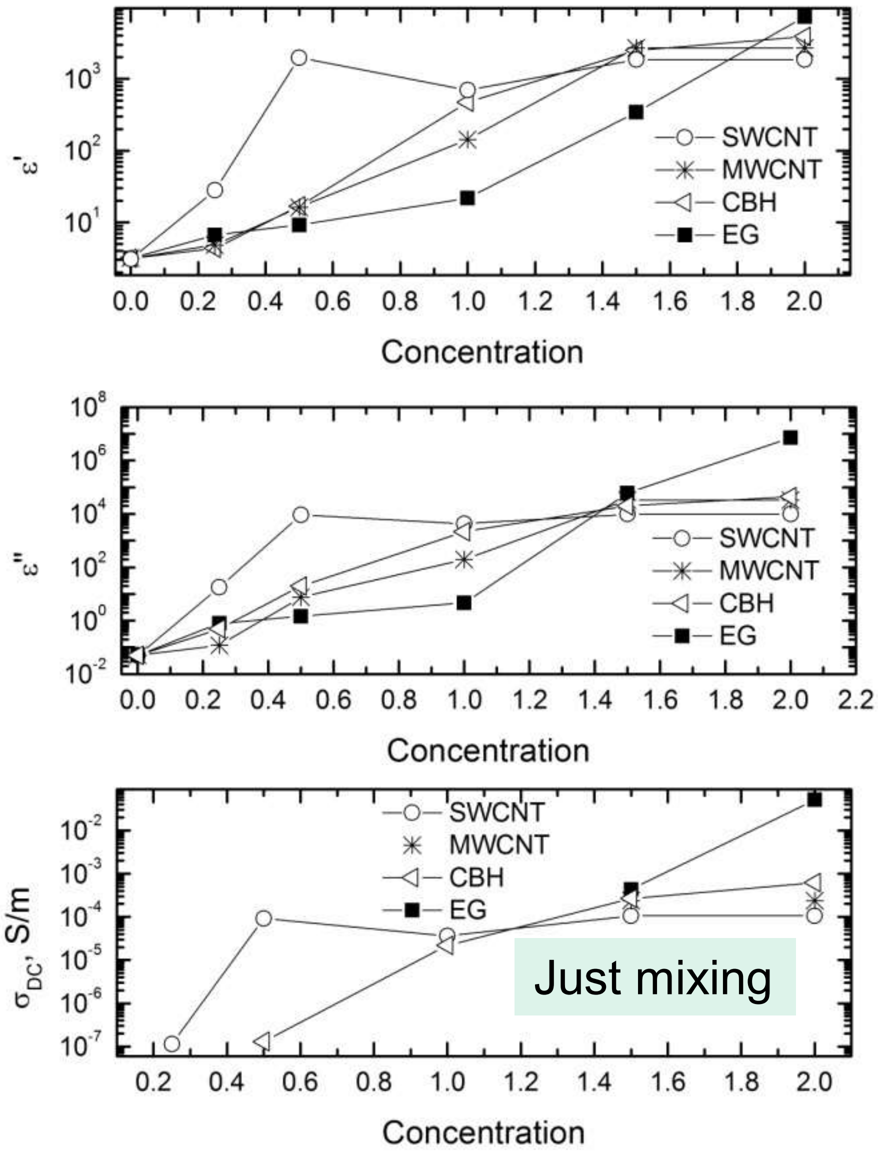




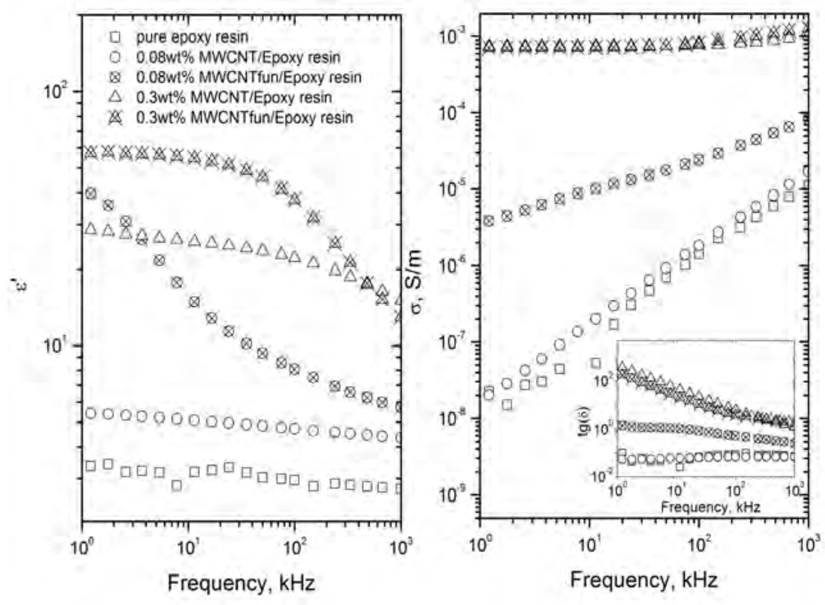
dc-Conductivity vs. nanotube content of epoxy nanocomposites containing epoxy-functionalized (*full symbols*) and amine-functionalized MWCNTs (*open symbols*).

SEM images of the cross-fracture of 0.3 wt.% epoxy composites: (a) amine-grafted ER/MWCNT-a, and (b) epoxy-grafted ER/MWCNT-e, at high magnification of 200 000x.

Low frequency range

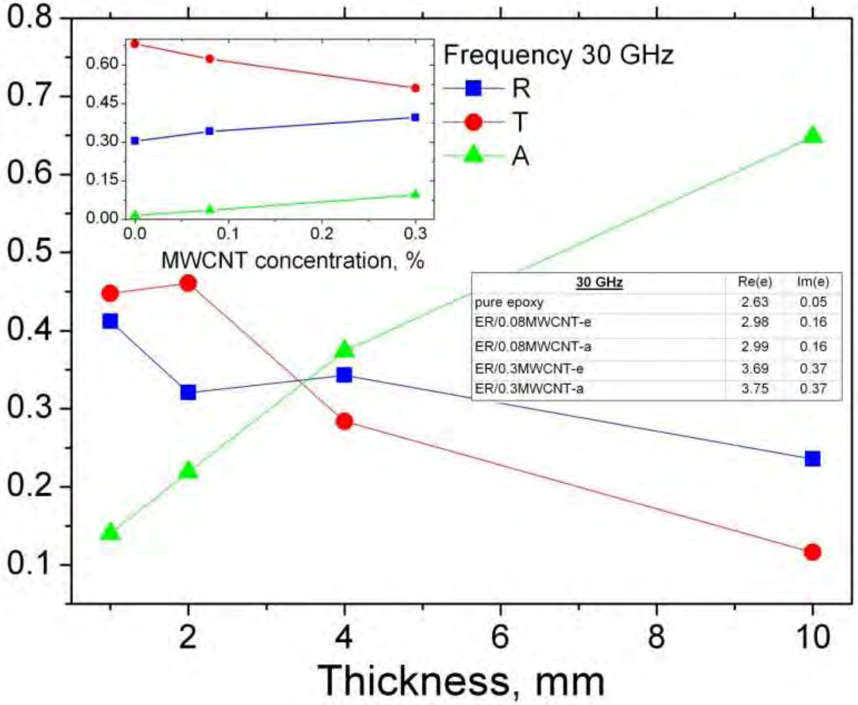


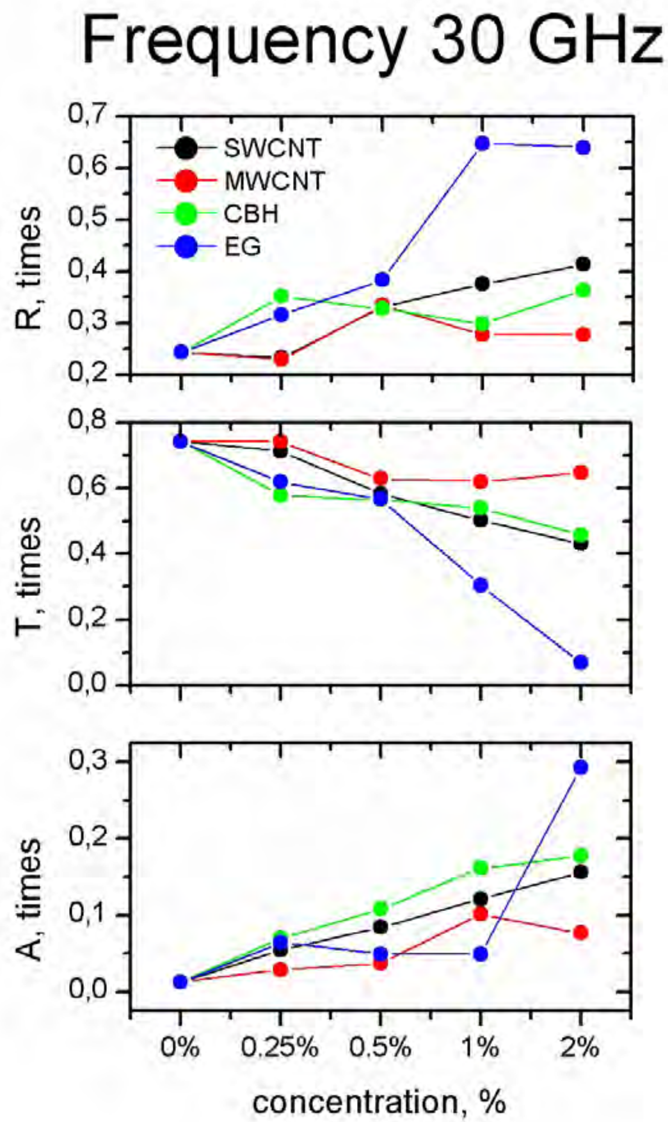
Just mixing



Sophisticated technique of composite fabrication

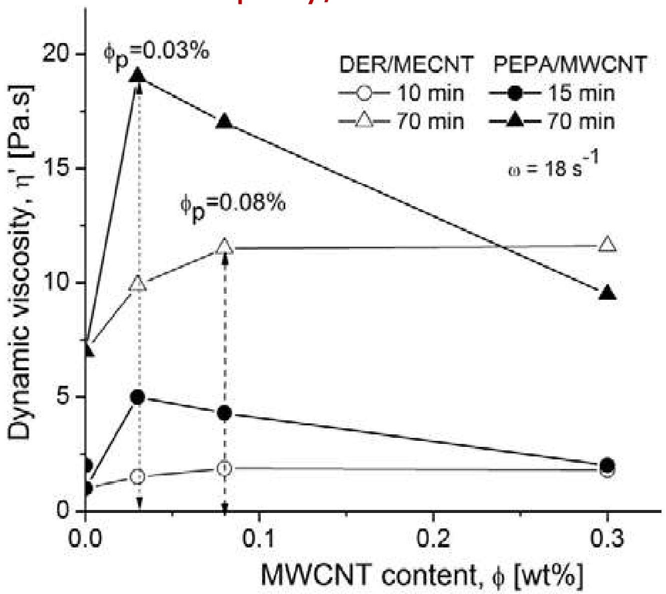
MWCNT, the same length, the same average number of walls, the same matrix, different composite fabrication techniques





Effect of Matrix Viscosity on Percolation Threshold of Nanocomposites

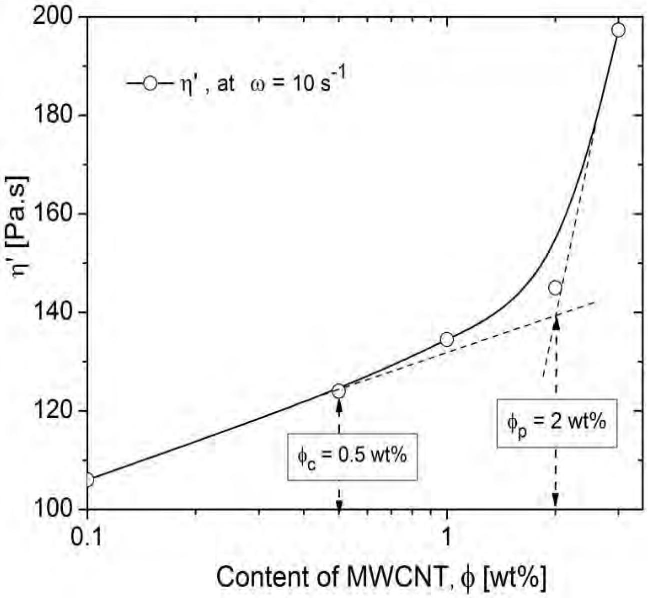
Epoxy/MWCNT



Rheological Percolation	
ER/MWCNT	0.03%
PP/MWCNT	2%

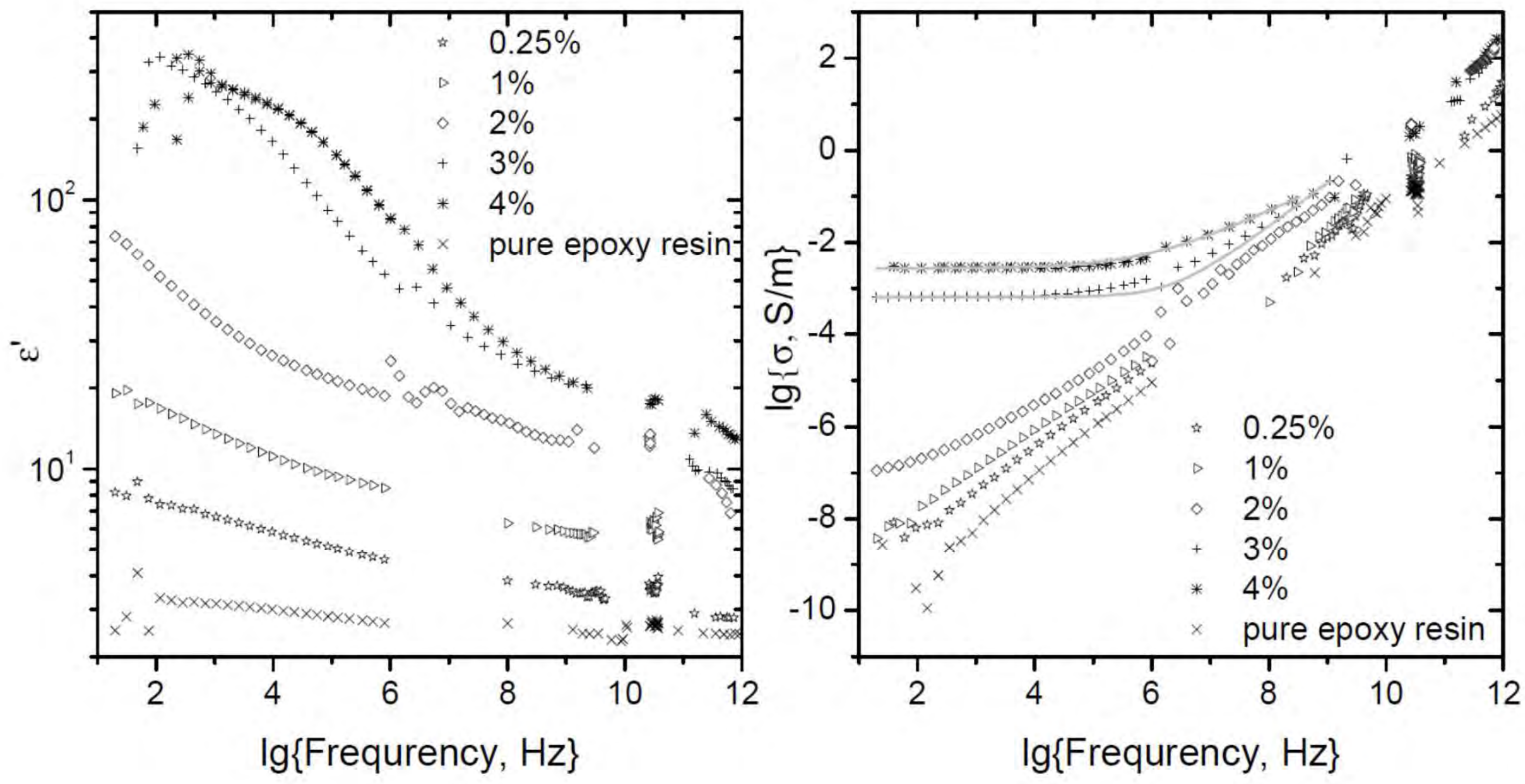
Electrical Percolation	
ER/MWCNT	0.03%
PP/MWCNT	3%

PP/MWCNT



- Low viscosity Epoxy resin matrix (η'=1.5 Pa.s) facilitates contacts between MWCNTs, resulting in very low rheological percolation threshold, φ~0.03 wt%.
- High viscosity Polypropylene matrix (η'=100 Pa.s) suppresses contacts between MWCNTs, resulting in higher values of the rheological percolation, φ=2 wt%.
- Rheological percolation coincides with Electrical percolation for the low viscosity ER/MWCNT systems. But, for more viscous PP/MWCNT systems, the electrical percolation threshold (3%) is slightly higher, than the rheological percolation (2%).

Dielectric properties of epoxy/GNP composites in wide frequency range (Hz – GHz – THz)



Real part of the effective permittivity (left) and conductivity (right) of epoxy resin and GNP/epoxy composites vs frequency for different concentrations in log-log scale.

Electromagnetic properties of epoxy/GNP composites in microwave range

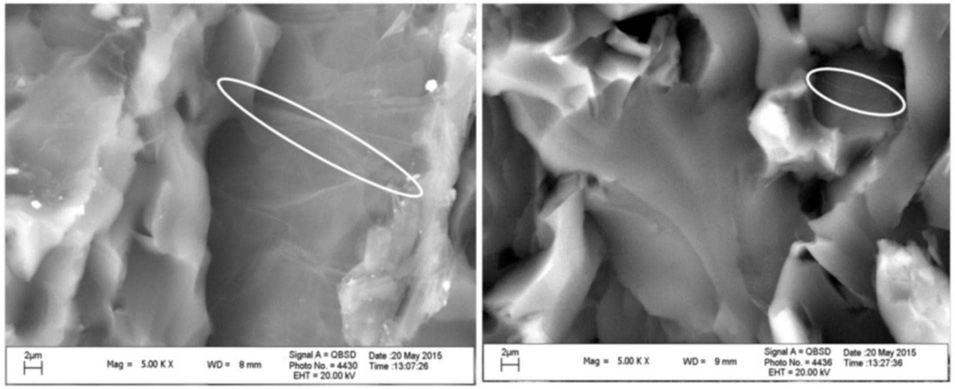
The annealing above the glass transition temperature of polymer was proved to be a simple but powerful process to improve significantly the electromagnetic properties of the GNP-based composites. Annealing lower substantially the percolation threshold, from 2.5 wt.% for as-produced samples to 1.4 wt.%.

Table 1: Shielding efficiency of 2 mm-thick composite layer at 30 GHz frequency

Sample	Reflectance, %	Transmittance, %	Absorbance, %
2%, annealed	57	15	28
4%	70	14	16

Annealing to glass transition temperature

SEM image of epoxy/GNP composites containing 2 wt% of GNP before (see large GNP clusters marked with white oval) and after annealing (see small GNP cluster).



Conclusions

Polymer properties

Fabrication method, dispersion state

individual filler properties vs frequency range

fillers functionalization, surface chemistry

????????????????

……..all are important for electromagnetic response of final composition

1000s of parameters have to be taken into account….
What to do?..... <u>MODELING</u>

1. **Effective medium theory** pertains to analytical modeling that describes the macroscopic properties of composite materials.

a) Clausius-Mossotti formula
b) Maxwell-Garnett model
c) Brugeman model

EMTs assume that the macroscopic system is homogeneous and predict the effective properties of a multiphase medium below the percolation threshold due to the absence of long-range correlations or critical fluctuations in the theory.

1. **Monte Carlo** simulation
2. **Equivalent circuit** technique

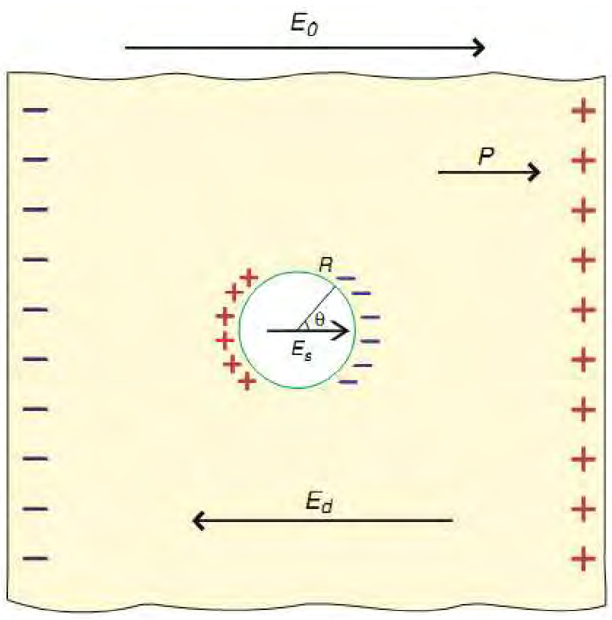
Can predict behavior of percolative system

The Lorentz sphere concept for calculating the local electric field E_L

Let us consider the case of a dense optical medium with molecular dipoles arranged in a cubic lattice. Lorentz pointed out that the field experienced by a molecule is not the macroscopically averaged field E but "local" field

$$E_L = E_0 + E_d + E_s + E_{near},$$

E0 is the external field, Ed is the depolarization field due to the polarization charges at the external surface of the medium, Ed=-P/ε0. Es is the depolarization field due to the polarization charges on the surface of the Lorentz sphere. Enear is the field induced by other dipoles lying withing the Lorentz sphere.



$$E_L = E + \frac{P}{3\varepsilon_0}.$$

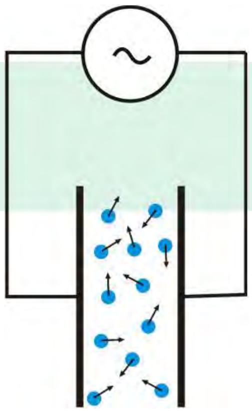
The field acting at an atom site in a cubic lattice is the macroscopic field E plus polarization of other atoms in the system.

Clausius-Mossotti formula

$$\frac{N\alpha}{3\varepsilon_0} = \frac{\varepsilon - 1}{\varepsilon + 2}$$

Clausius–Mossotti relation, which provides the essential link between the macroscopic observable – permittivity - and the microscopic parameter – polarizability.

Maxwell-Garnett model

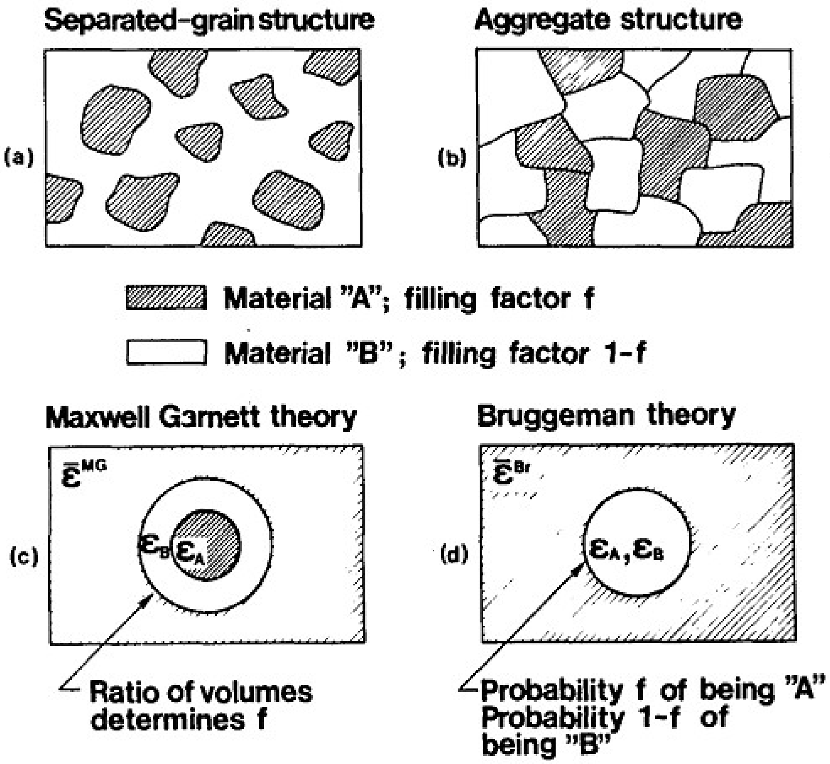


Now we will apply the Clausius–Mossotti relation to a metal-dielectric composite

$$\frac{N\alpha}{3\varepsilon_0\varepsilon_h} = \frac{\varepsilon - \varepsilon_h}{\varepsilon + 2\varepsilon_h}. \qquad \alpha = \frac{3\varepsilon_0\varepsilon_h f}{N}\frac{\varepsilon_1 - \varepsilon_h}{\varepsilon_1 + 2\varepsilon_h}, \qquad \frac{\varepsilon - \varepsilon_h}{\varepsilon + 2\varepsilon_h} = f\frac{\varepsilon_1 - \varepsilon_h}{\varepsilon_1 + 2\varepsilon_h}.$$

where f is the volume filling fraction of the ε_1 material in the composite.

Maxwell Garnett and Bruggeman theories



(a) and (b) depict two microstructures for heterogeneous two-phase media; (c) and (d) show the corresponding random unit cells used to derive the effective dielectric permeability within the Maxwell Garnett and Bruggeman theories.

Effective medium models for the optical properties of inhomogeneous materials, G. A. Niklasson, C. G. Granqvist, and 0. Hunderi / Vol. 20, No. 1 / APPLIED OPTIC 1981

$$\phi_2 = \left(\frac{\epsilon_1 - \epsilon^*}{\epsilon_1 - \epsilon_2}\right)\left(\frac{\epsilon_2}{\epsilon^*}\right)^W ,$$

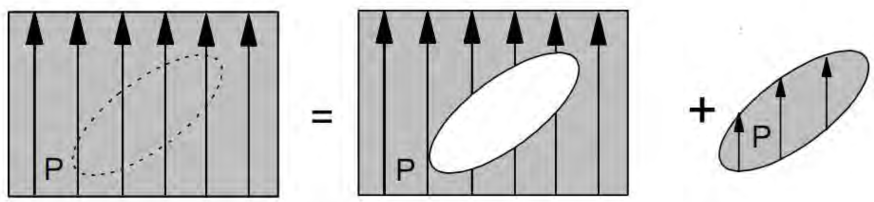
(Hanai-Bruggeman generalized)

ϵ^* = permittivity of the composite

ϕ_2: proportion of material 2 ($\phi_1 = 1 - \phi_2$)

The effective medium approach can also be used "in reverse." In nanocrystal research, it is a standard practice to calculate the permittivity of nanoparticles when the permittivity of the other component is known and that of the whole composite is measured. In such applications,
Bruggeman's EMT is preferred over MGT because singularities may arise in reversed MGT calculations when the fraction of nanoparticles is large or when the contrast in the permittivities of the two phases is significant.

The polarizability (ellipsoid is universal filler)



$$\alpha_i(\nu,\sigma) = \frac{4\pi abc}{3} \frac{\varepsilon_m(1 - \frac{i\sigma}{2\pi\nu\varepsilon_0} - \varepsilon_m)}{\varepsilon_m + N_i(1 - \frac{i\sigma}{2\pi\nu\varepsilon_0} - \varepsilon_m)},$$

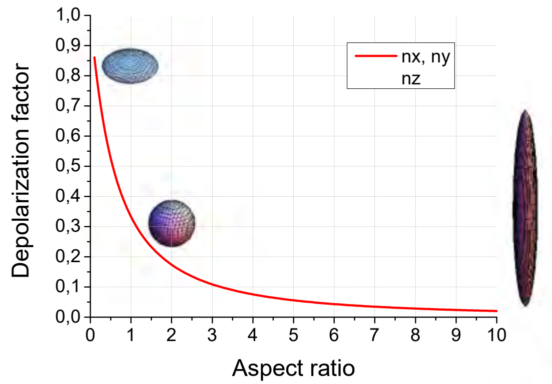
Sphere $\alpha_s = 4\pi R^3$

Disk (diameter much larger than thickness) $\alpha_d = 2D^3/3$

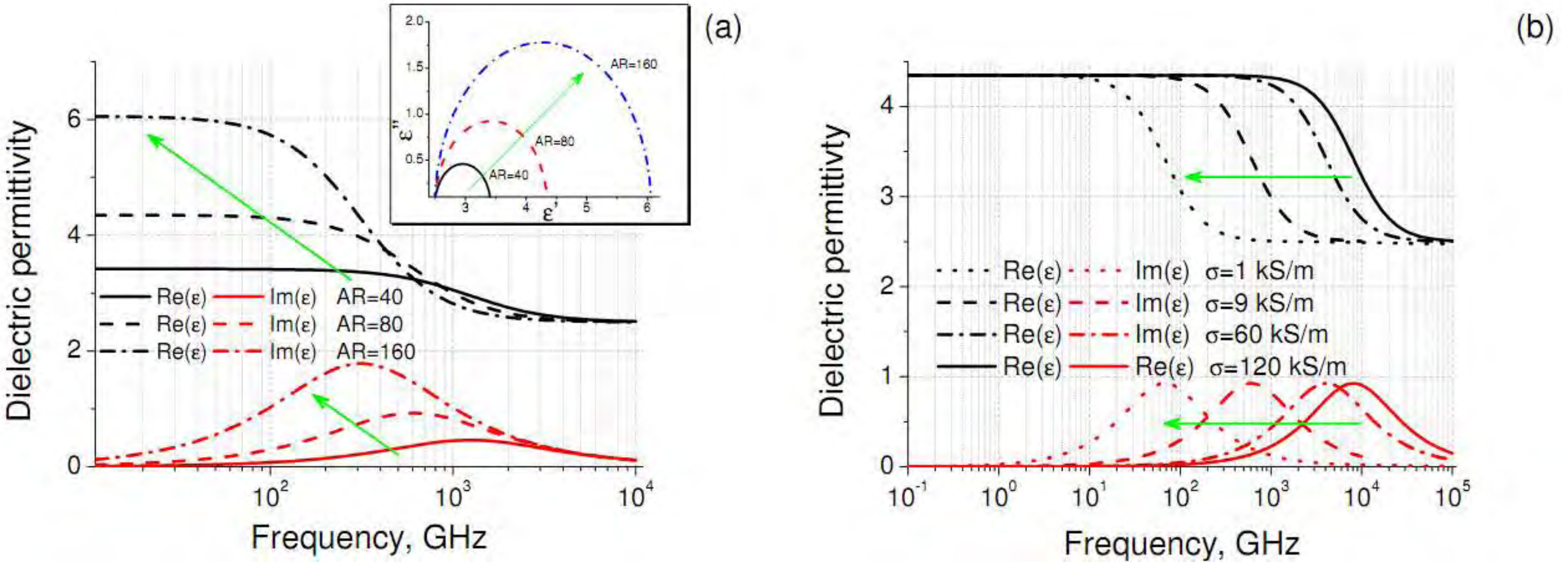
Needle (length much larger than radius)

$$\alpha_n = 4\pi L^3/(24(\ln[2L/R] - 5/3))$$

Maxwell Garnett EMA is expected to be valid at low volume fractions <<1, since it is assumed that the domains are spatially separated and electrostatic interaction between the chosen inclusions and all other neighbouring inclusions is neglected.



Composite modelling (MGA)

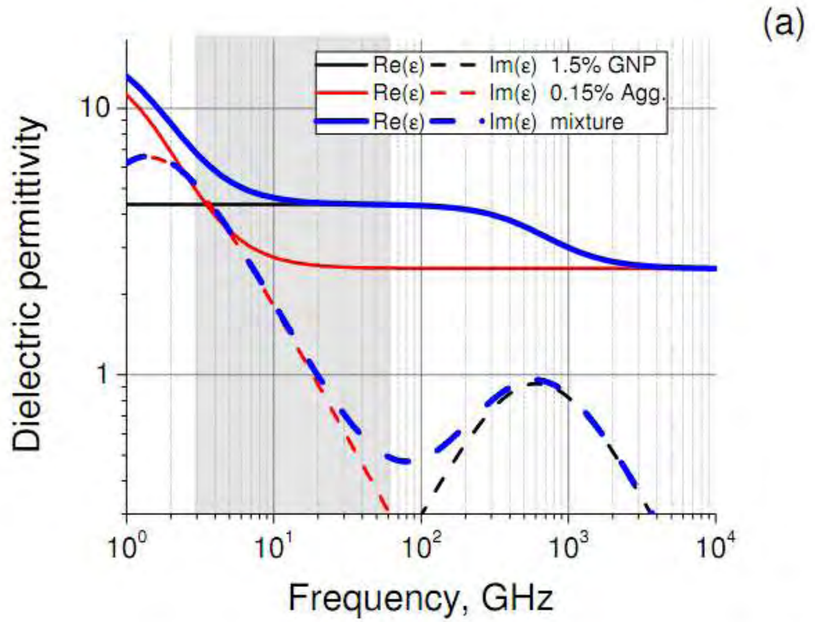


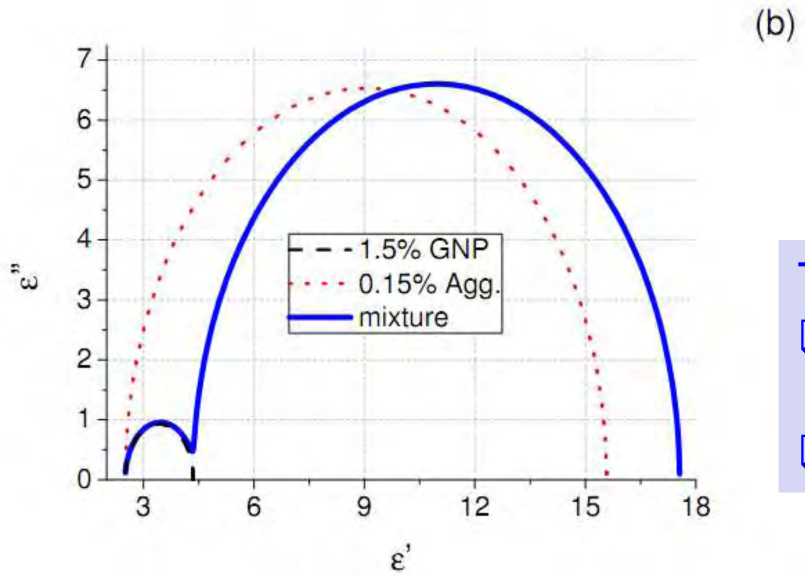
(a) Frequency dependence of dielectric permittivity of composite including 1.5 wt.% of particles with conductivity 9000 S/m and various aspect ratio (the green arrow show the growth of AR from 40 to 160), (inset: the identical curves in the Cole-Cole representation) (b) The same for composite with AR=80 and various conductivity (the green arrow shows the decrease of conductivity from 120 to 1 kS/m).

The task is to understand

- Whether the perfectness of the filler (GNP), i.e. its conductivity, is important for the EM response?
- Whether the lateral dimension of nanofiller (GNP) is importnat:? For which frequency ranges?

Effect of connected particles





(a) Frequency dependence of dielectric permittivity of composites containing 1.5 % GNP, 0.15% agglomerates (connected particles), and their mixture (b) the identical curves in the Cole-Cole representation

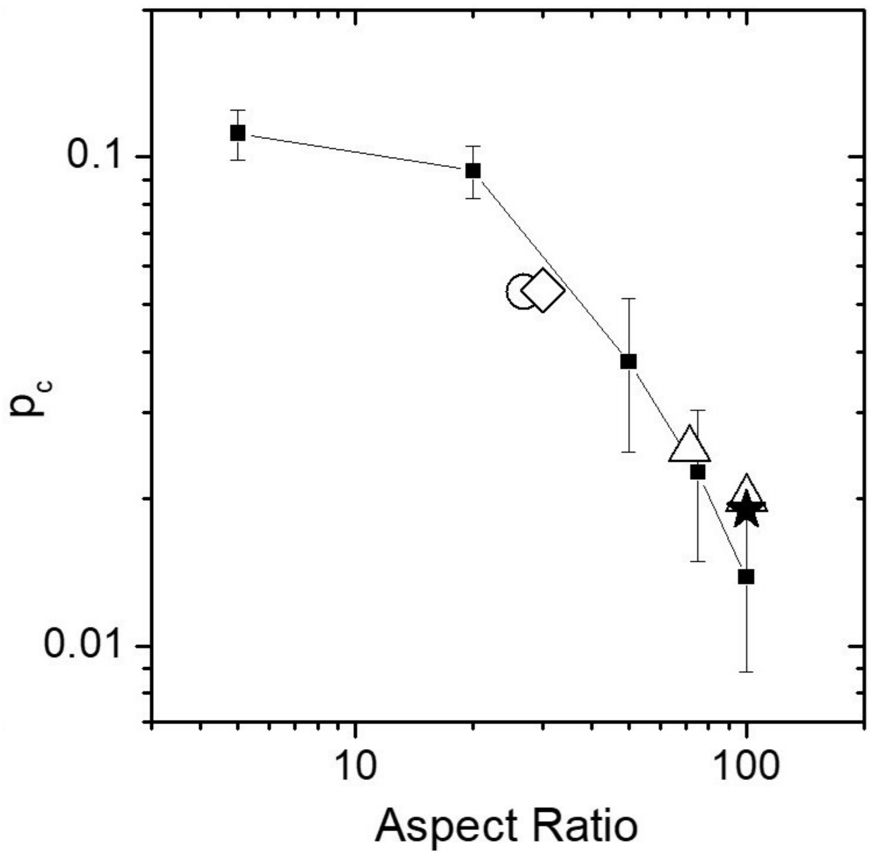
Agglomerates with diameter D=2a=2b macroscopic length =0.2 mm and conductivity =3000 S/m

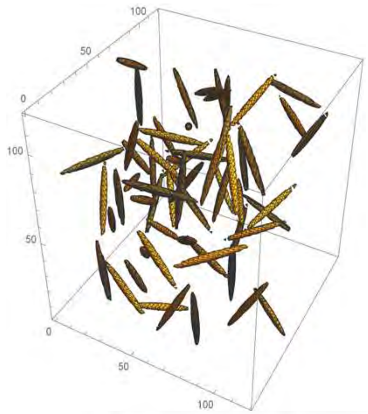
The task is to understand

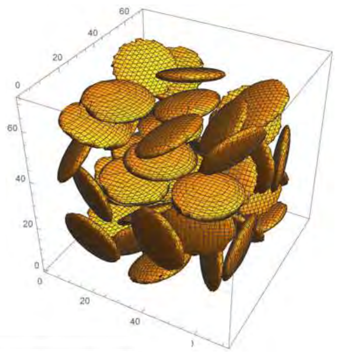
- ❑ Whether the agglomeration of the nanofiller (GNP) is important?
- ❑ For which frequency ranges?

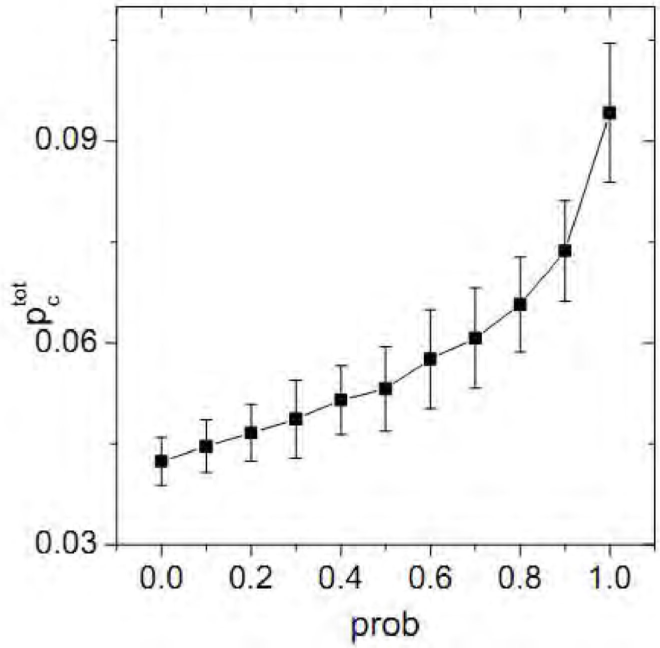
Model of the composite (Monte Carlo)

Monte Carlo experiments are a broad class of computational algorithms that rely on repeated random sampling to obtain numerical results. The underlying concept is to use randomness to solve problems that might be deterministic in principle.



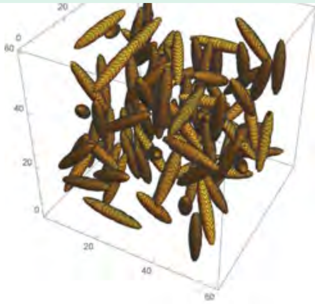




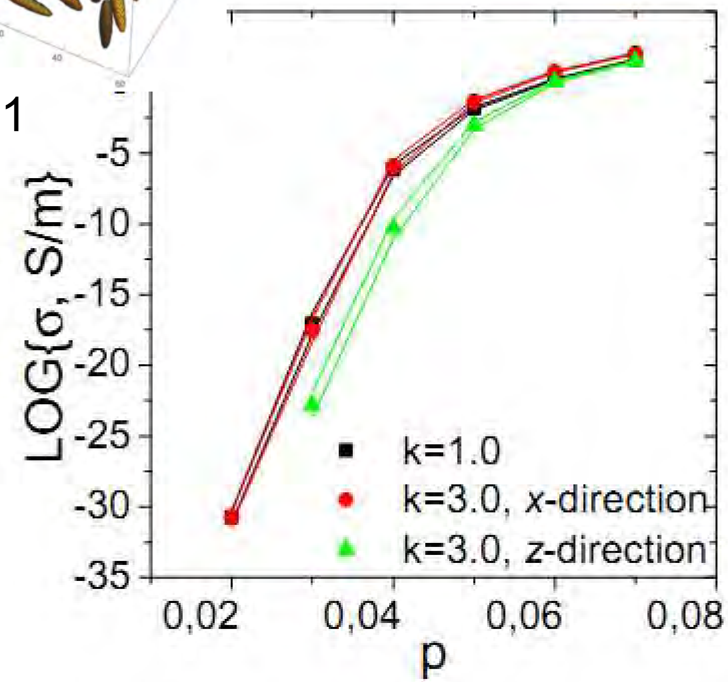


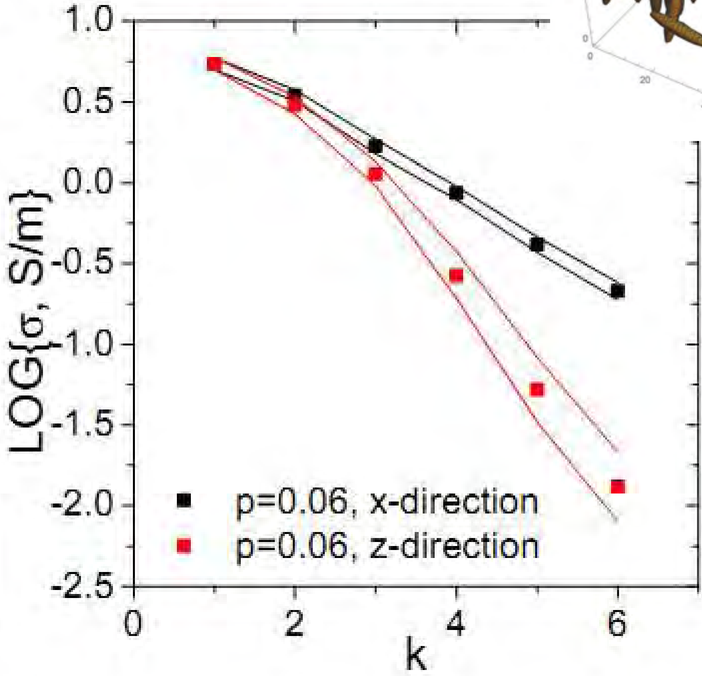
Dependence of the percolation concentration for hybrid composites of different composition

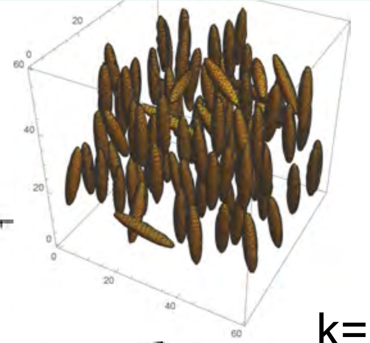
Partially oriented composites



k=1

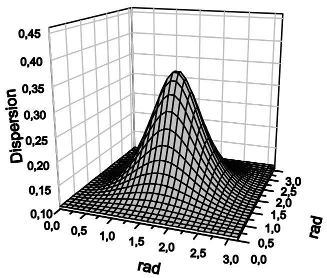






k=10

Conductivity dependence (a) on the concentration for the initial and deformed composite in different directions, and (b) on the deformation for the samples with 6 vol. % of the CNTs. Symbols stands for the mean values, and lines denote the 95 % confidence interval width.



A study of random resistor-capacitor-diode networks to assess the electromagnetic properties of carbon nanotube filled polymers

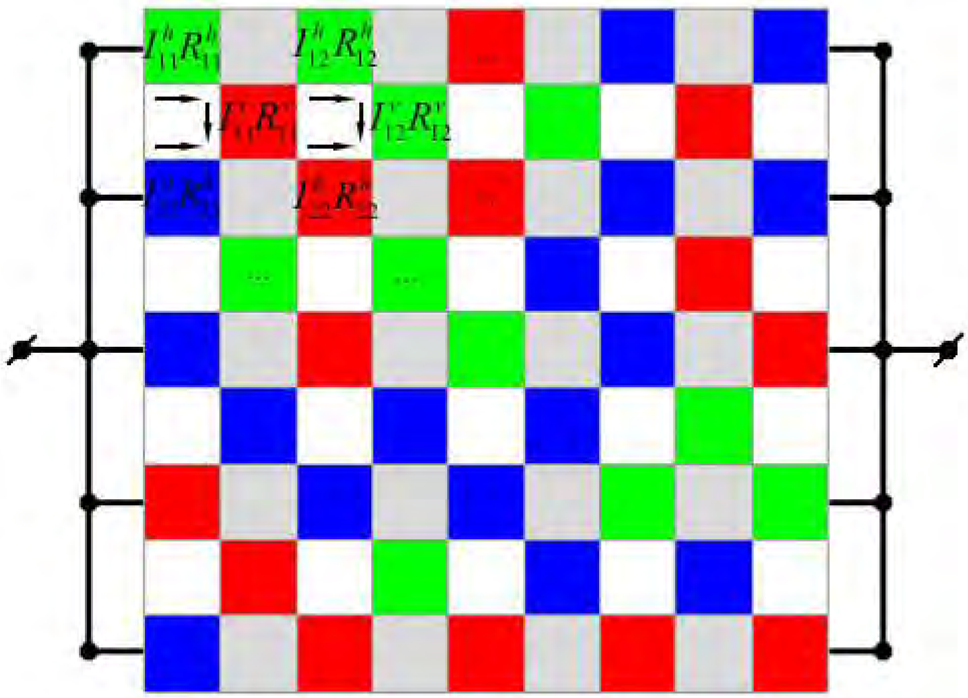
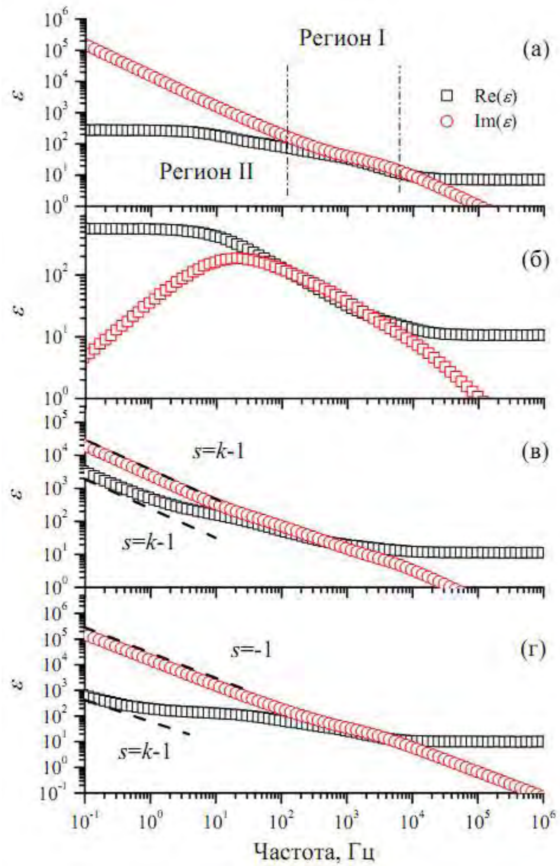


Illustration of an example ternary network (two dimensional square checkerboard) comprising a disordered mixture of resistors (shown in red), capacitors (shown in blue), and diodes (shown in green). Electrical contacts are shown in grey, while porosity is shown in white.

Physics underlying the EM response



Typical effective permittivity spectra of random RCD networks for different cases: (a) below D percolation and above R percolation, (b) below R and D percolations, (c) below R percolation and above D percolation, and (d) above R and D percolations.

Conclusions

Effective medium theories (below percolation)

percolation theories, MC simulations

equivalent electric circuits

electromagnetics of individual fillers

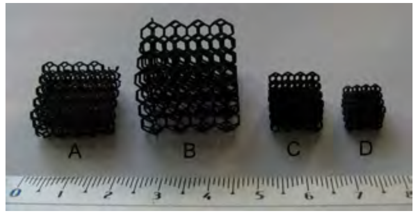
ab initio calculations

…..all could be used complementary to predict the EM response of composite

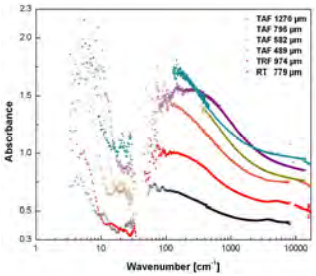
GEOMETRY: 3D printing

3D periodic lattices with conductive skeleton

i. <u>approach</u>: Fully carbon periodic lattice

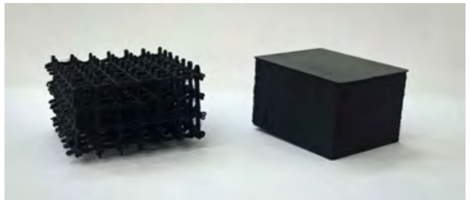


3D printing of photocurable resin → Carbonization → Fully carbon periodic lattice → High conductive glassy carbon skeleton



skeleton conductivity is 2 000 – 20 000 S/m

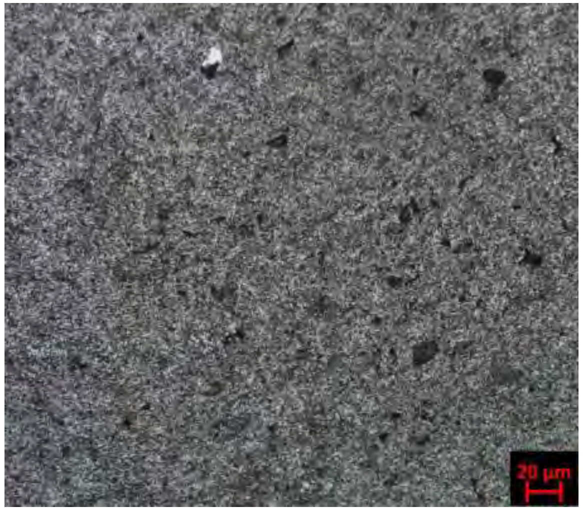
ii. <u>approach</u>: Composite based periodic lattice



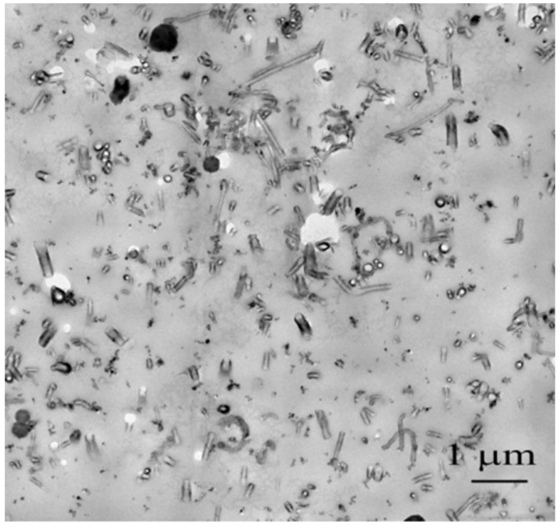
FDM 3D printing → Conductive filament = polymer / nano-carbon → Composite-based periodic lattice → Low conductive composite skeleton

skeleton conductivity is 0.1– 200 S/m

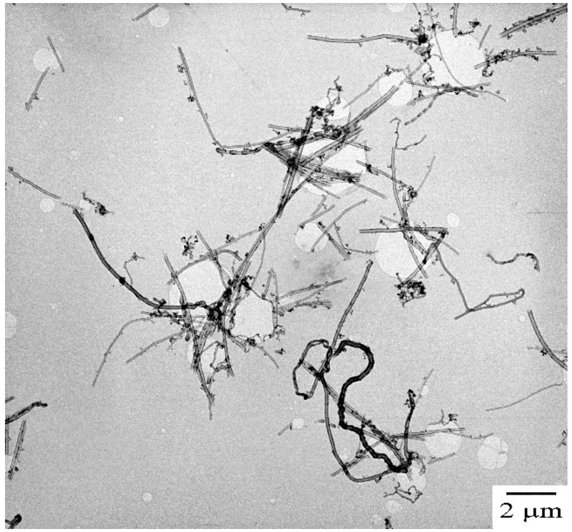
3D-printed filament



Cutted slice



Solution



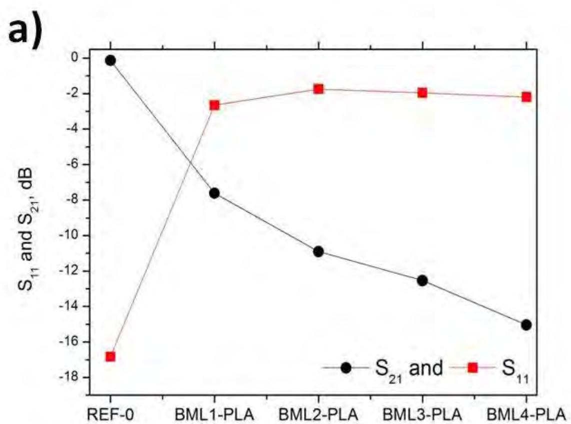
Cross sectional optical microscopy images in transmitted light through sections of 1 μm thickness of the 3DBM filament.

filament conductivity is 0.1– 200 S/m

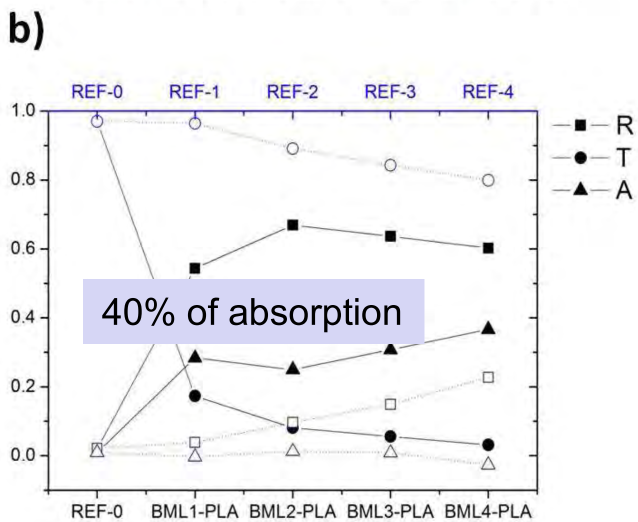
Whether the high conductivity of composite is always necessary???

A. Paddubskaya, et al, Electromagnetic and Thermal properties of 3D Printed Multilayered Nano-carbon / Poly(lactic) Acid Structures, Journal of Applied Physics **119**, 135102 (2016)

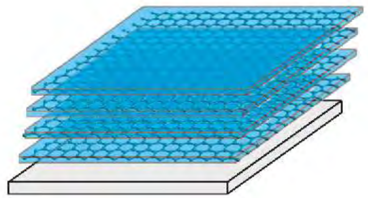
3D printed layered structures. Microwave probing



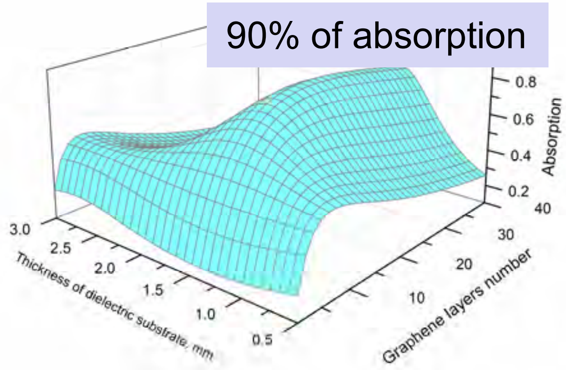
Thickness = 400 microns + substrate



Thickness = 400 nm + substrate



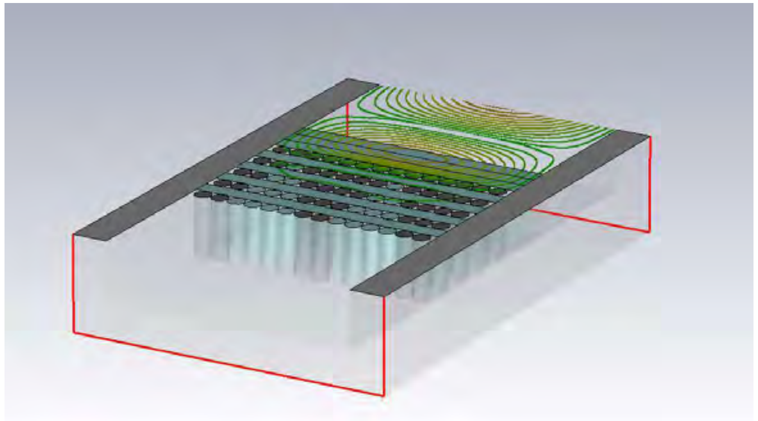
CVD graphene sandwich on the top of dielectric substrate, ¼ wavelength

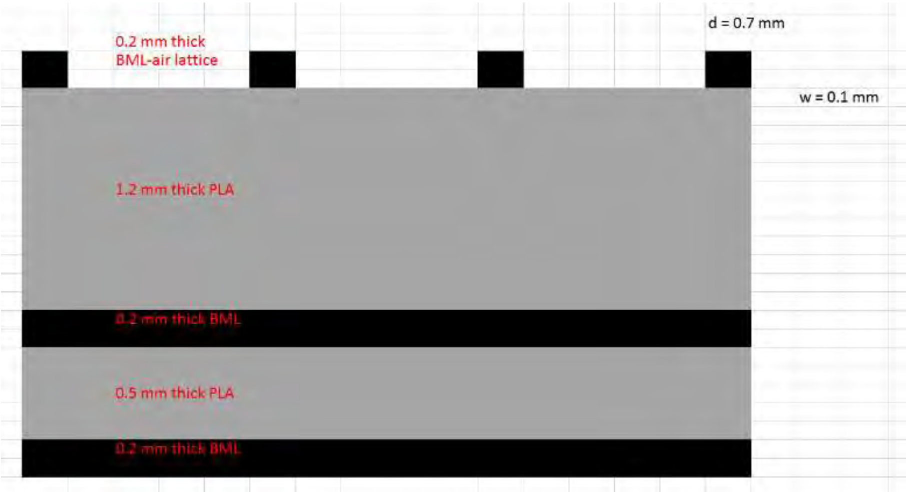


(a) Measured S-parameters of nano-carbon containing sandwich structures in dB at 30 GH. (b) Reflectance, absorbance, and transmittance reconstructed from the experimental data of reference samples (open symbols) and samples contacting 1-4 nano-carbon layers (solid symbols) at 30GHz.

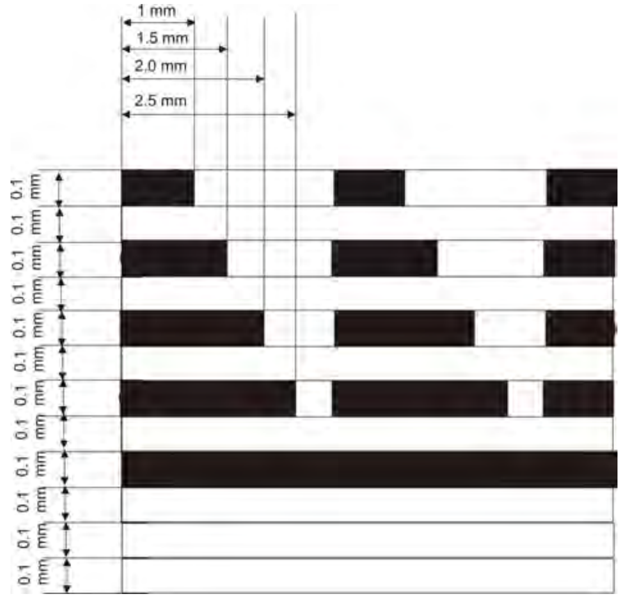
3D-printed sandwiches of sophisticated geometries

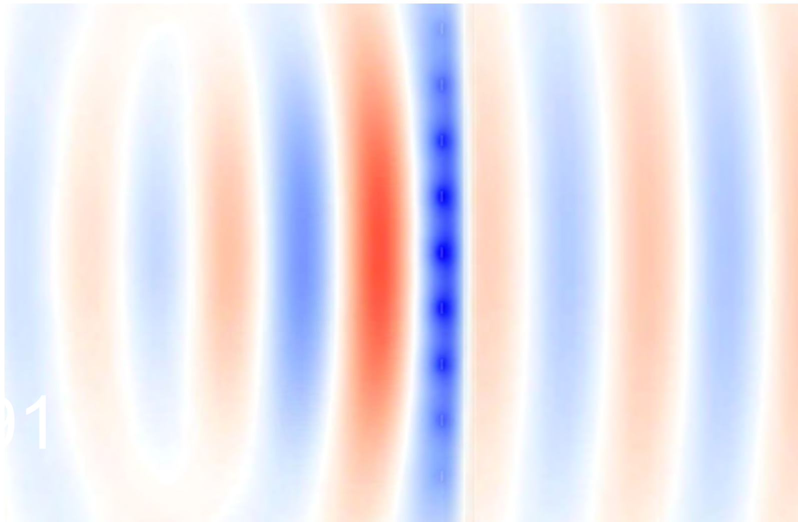
CST Studio calculations



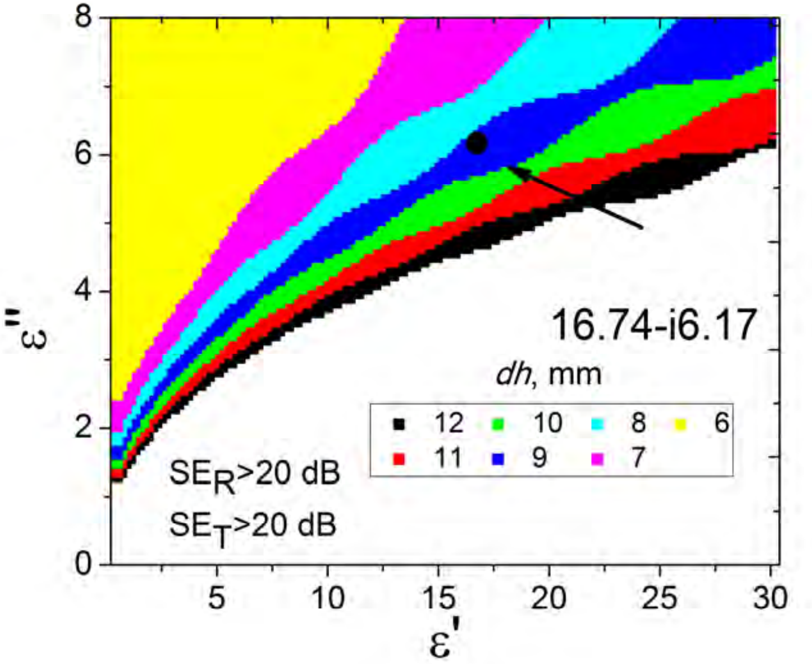


T=0, A=99%, R=1%

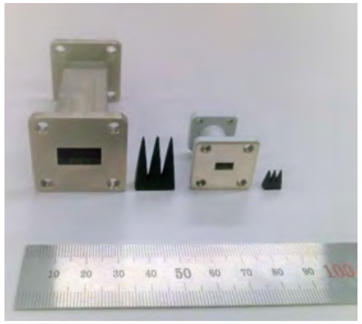


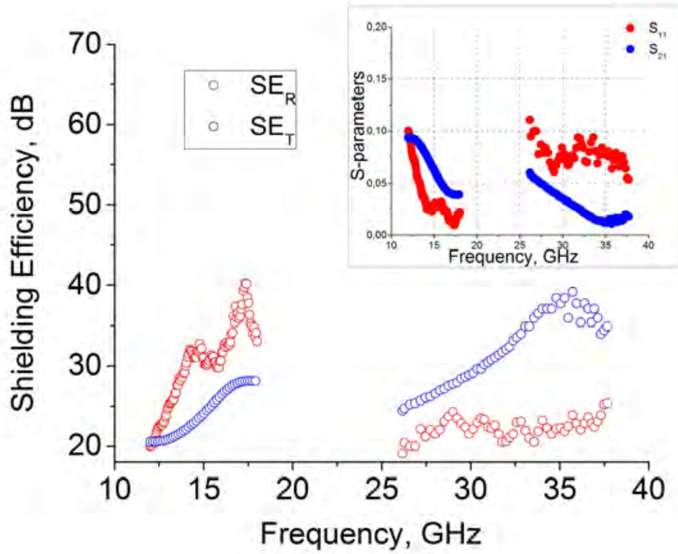


Optimal pyramid parameters determination



Effective shielding criteria as SE_T>20 dB and SE_R>20 dB (equivalent to the absorption of >99%).

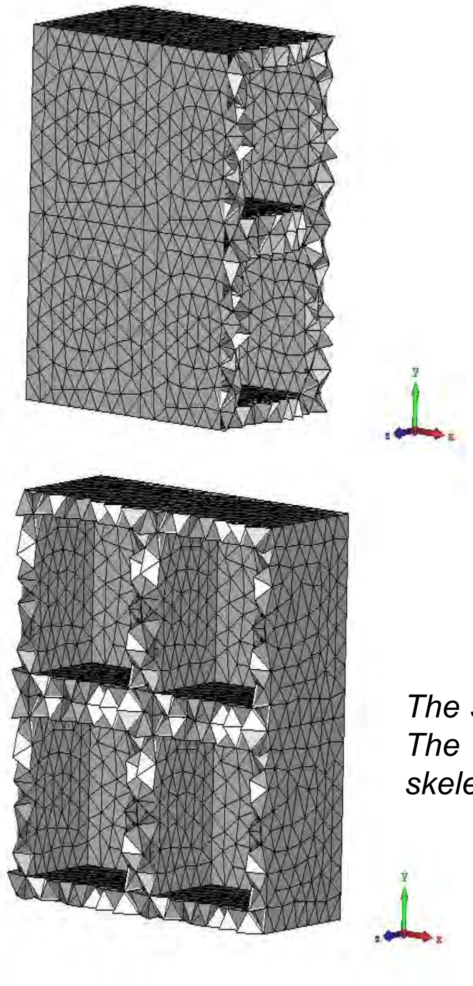


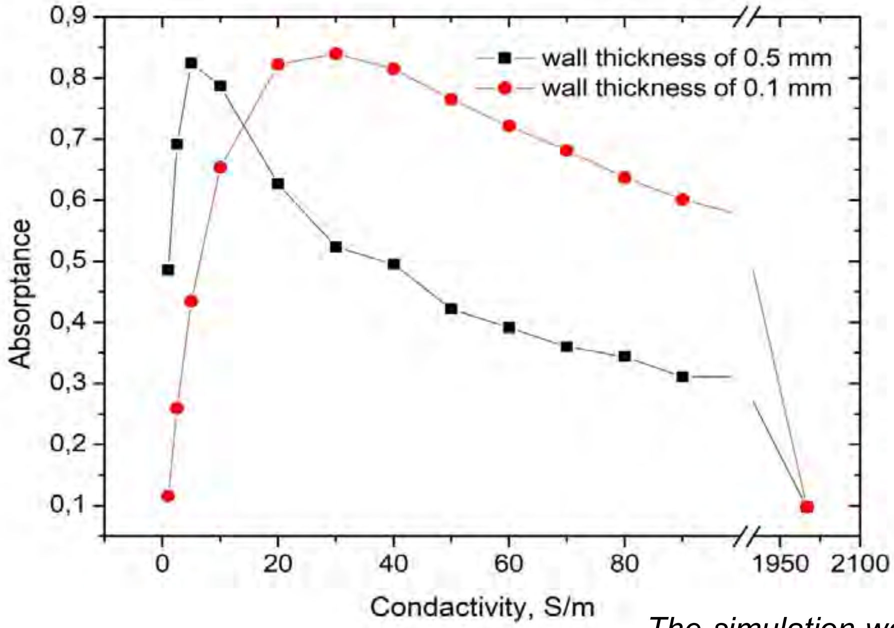


- ❑ The pyramid height d, required for the effective (20 dB) EMI shielding, presented as the dependence on the dielectric permittivity. Dot stands for the measured ε of used filament at frequency 30 GHz.
- ❑ The minimal pyramid's height dh, required for the effective shielding is 8–9 mm for the Ka-band. Similarly, dh=22 mm was evaluated for the Ku-band.

Close cells, … vs wall thickness

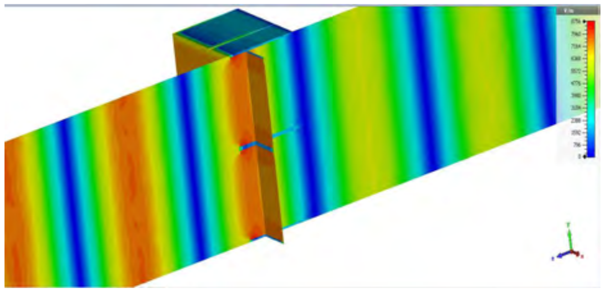
At relatively high conductivity the EM response are mainly determined by reflectance



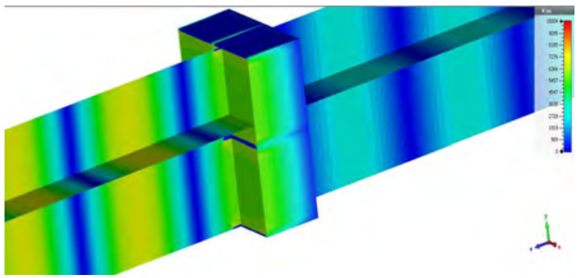


$1{*}1 * 2.5\ mm^3$

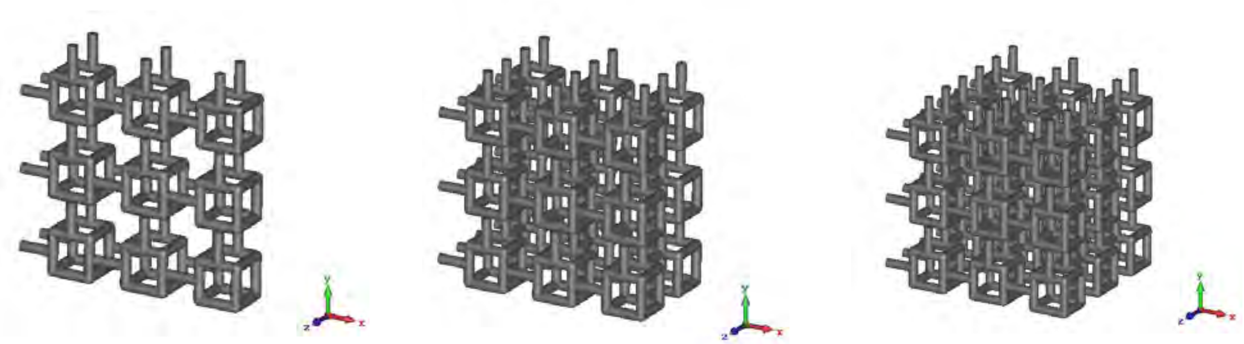
The simulation was made for 32GHz . The wall thickness is 0.1 mm and skeleton conductivity is 5S/m



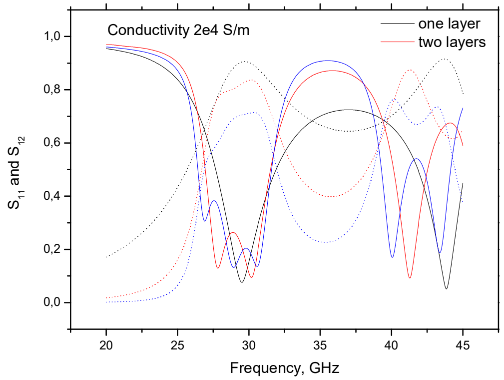
The simulation was made for 32GHz . The wall thickness is 0.1 mm and skeleton conductivity is 20 S/m



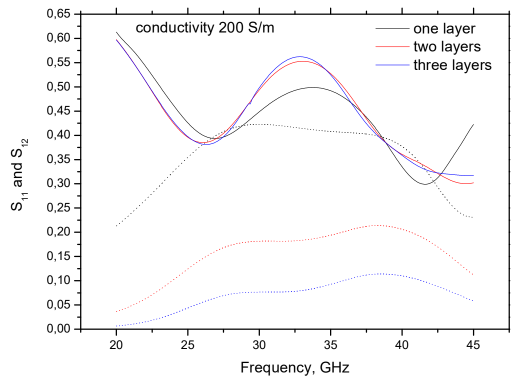
….vs number of layers



Conductivity 20 000 S/m

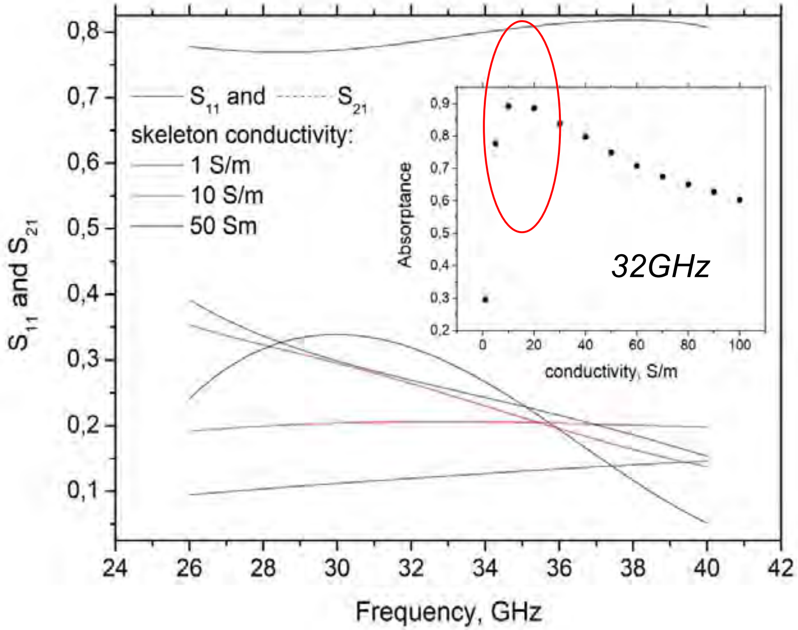


Conductivity 200 S/m



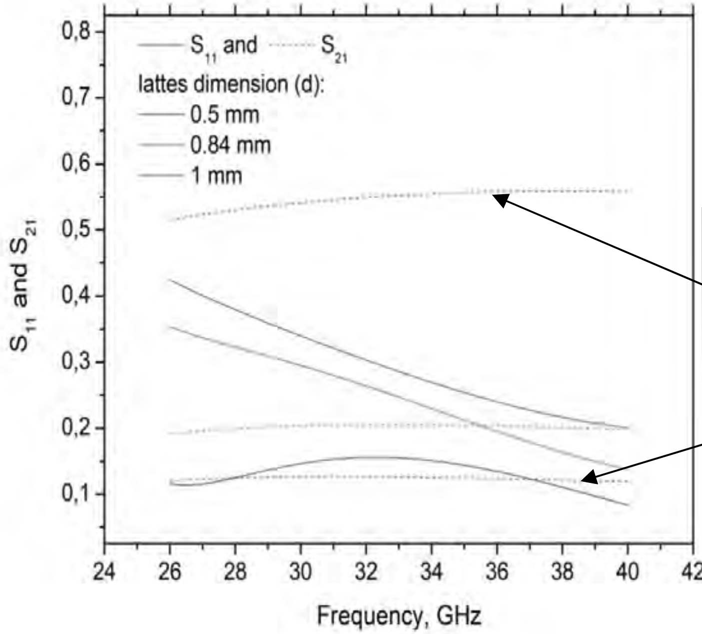
Frequency dependence of S_{11} and S_{12} parameters for a 3D structure based on one, two, or three layers of Gibson-Ashby cells as pictured in (a), and for two different values of backbone dc conductivity: (b) 20 000 S m^{-1}; and (c) 200 S m^{-1}. The following geometrical parameters were used in the calculation: L = 3mm, and d = 0.83 mm.

….vs the conductivity of 3D printed filament

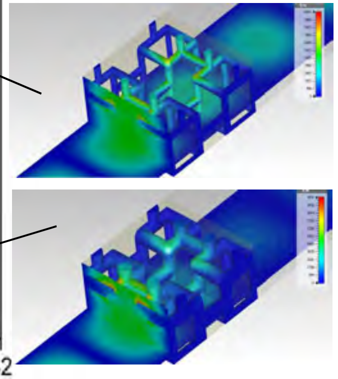


In the numerical calculation, the following parameters was used: d= 0.85 mm, L=2.4 mm, ε_h=1

….vs the dimensions of cubic lattice



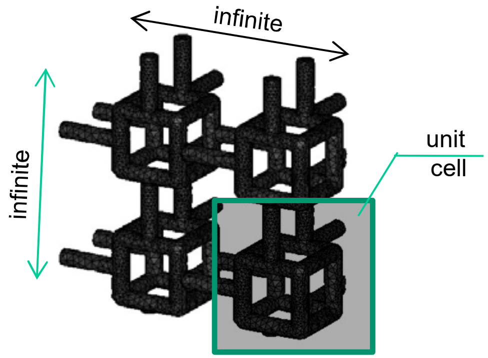
32GHz



In the numerical calculation, the following parameters was used: σ_{DC}= 10 S/m, L=2.4 mm, ε_h=1

✓*in the case of conductivity ~ 1-50 S/m the absorption of 3D-printed photonic crystal is more than 80%.*

✓*3D-printed photonic crystal can be used like almost perfect absorber*



Conclusions

ELECTROMANGTIC PARAMETERS OF COMPOSITE ARE IMPORTANT

EM PARAMETERS OF COMPOSITE COULD BE TUNED BY MANY FACTORS

GEOMETRY IS IMPORTANT

FOR ANY CONDUCTIVITY of the filament (composite) OPTIMAL GEOMETRY COULD BE FOUND: for resonant PERFECT ABSORPTION (the case of high conductivities) and for broadband high absorption (the case of incremental conductivities)

In collaboration

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תודה
Dankie
Спасибо
дзякуй
Takk
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Terima kasih
Grazie
Dziękujemy
Dėkojame
Ďakujeme
Vielen Dank
Paldies
Kiitos
Täname teid
谢谢
Thank You
Tak
感謝您
Obrigado
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감사합니다
Σας Ευχαριστούμ
ขอบคุณ
Bedankt
Děkujeme vám
ありがとうございます
Tack