Ensembles of plasmonic nanospheres at optical frequencies and a problem of negative index behavior

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Arrays of metallic nanoparticles support individual and collective plasmonic excitations that contribute to unusual phenomena like surface enhanced Raman scattering, anomalous transparency, negative index, and subwavelength resolution in various metamaterials. We have examined the electromagnetic response of dual Kron’s lattice and films containing up to three monolayers of metallic nanospheres. It appears that open cubic Kron’s lattice exhibits ‘soft’ electromagnetic response but no negative index behavior. The close-packed arrays behave similarly: there are plasmon resonances and very high transmission at certain wavelengths that are much larger than the separation between the particles, and a ‘soft’ magnetic response, with small but positive effective index of refraction. It would be interesting to check those predictions experimentally.

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I. INTRODUCTION

Media with strong dispersion of the refractive index may support backward waves, as is obvious from the following relation established by Lord Rayleigh in 1877:

\[ n_g = n - \frac{\lambda}{cn} \frac{dn}{d\lambda} \]  

(1)

where \( n_g \) is the group index for waves with wavelength \( \lambda \), phase velocity is \( v_p = c/n_g \), group velocity \( v = c/n \), where \( c \) is the light speed in vacuo. Hence, the group velocity may become negative in a system with large positive dispersion. The structures that support backward waves have been known since early 1900s and widely used in antenna and electronics technologies since 1950s. Media where the directions of phase and group velocities are opposite are known to produce negative refraction \( -1 \). It was noted in Ref. \( 1 \) that e.g. dispersion of light close to excitonic frequencies in solids can be negative. It is also true of artificial metamaterials with strong spatial dispersion, like photonic crystals \( 2 \), \( 3 \). Pafomov \( 4 \) and Veselago \( 5 \) showed that backward waves can propagate in isotropic medium with simultaneously negative permittivity \( \epsilon \) and permeability \( \mu \), exhibiting negative refraction, inverse Doppler and Vavilov-Cherenkov effects. Currently, such metamaterials are called negative index metamaterials (NIM). Veselago has noticed that a slab of NIM with thickness \( d \) would work as a flat lens. The lens could not produce an image of a distant object, since it cannot focus a parallel beam of light, but produces a replica of the object if it is placed less than distance \( d \) away from the nearest surface of the slab.

Recently, unusual properties of NIM systems attracted considerable attention followed first theoretical \( 6 \), \( 7 \) and then experimental \( 8 \) demonstration of feasibility of negative refraction by periodic metallic metamaterials like periodic wire meshes producing negative \( \epsilon \) \( 8 \) and split-ring resonators (SRR) giving negative \( \mu \) \( 7 \) in microwave region of incident radiation. Pendry has showed theoretically that ideal Veselago lens can produce sub-wavelength resolution (\emph{perfect lens}) \( 9 \). The effect appears because ideal NIM slab supports surface plasmon modes that are in resonance with incident radiation at any angles of incidence \( 10 \), \( 11 \). The incident field pumps those plasmon modes up and this lead to enhancement of evanescent waves reaching the surface on the image side of the slab further from the source. The induced displacement currents re-emit the light that reconstructs the image of the source without loss of resolution for features smaller than \( \lambda \). Similar effect involving surface plasmons is also responsible for extraordinary transmission in thin metallic hole arrays \( 12 \). This behavior is quite fragile, however, and limited by losses and spatial dispersion (metamaterials granularity) \( 10 \), \( 13 \), \( 14 \). Nevertheless, it has indeed been demonstrated experimentally by Lagarkov and Kissel that the NIM slab built with SRR interspersed with the wire mesh is able to resolve features \( \sim \lambda/6 \) in the source separated by for microwave radiation \( f = 1.7 \text{GHz} \) \( 15 \). Later on, the sub-wavelength resolution \( \sim \lambda/6 \) was demonstrated by N. Fang \textit{et al.} in the visible range using silver slab as a plasmonic medium \( 16 \). The silver slab is not a material with both permittivity and permeability negative (double negative), it only has \( \epsilon < 0 \) as any metal at frequencies below plasmon frequency, and \( \mu > 0 \), but the effect is still possible because the system is in quasistatic limit where the sign of permeability \( \mu \) drops out of the result for image intensity \( 9 \). Various papers describe metamaterials that show NIM-like response at far infrared frequencies \( 17 \) and, most interestingly, in near-optical and optical interval \( 18 \), \( 19 \), \( 20 \), \( 21 \), \( 22 \).

II. ELECTROMAGNETIC RESPONSE OF METALLIC NANOPARTICLE ASSEMBLIES

The metallic periodic systems like ‘fishnet’ structure \( 18 \) support an infinite set (bands) of electromagnetic (EM) waves, \( \omega = \omega_k^0 \), where \( k \) is the wavevector (quasi-momentum), \( n = 1, 2, \ldots \) the number of the band (Flo-
quen mode). At small wavevectors $k$ such a crystal can be characterized by effective permittivity $\varepsilon$ and permeability $\mu$. Because of strong dispersion, it is easy to find crystals where some of the higher bands (second or third) support backward waves corresponding to negative group velocity, see Refs. [2, 3]. If such a band exists alone in a particular (usually narrow) frequency range, the crystal would operate as a NIM at those frequencies. Eleftheriades et al. have considered recently a possibility of an isotropic 3D NIM crystals (3D transmission lines) that might support backward waves in the first band if made of lumped capacitors and inductances, Ref. [24], see Fig. 1a. This is directly follows from the 3D transmission line (TL) model suggested by Kron for Maxwell equations in isotropic space with positive permittivity and permeability, $\varepsilon, \mu > 0$. In the case of ‘positive’ medium the dispersion at small $k$-vectors is positive for the lowest energy band, where eigenfrequency $\omega = \omega_k$ is a growing function of $k$. It should become a decreasing function of $k$ after a dual transformation of the TL. Indeed, this is the standard passband-to-stopband transformation, where the dispersion remains exactly the same but a substitution $C \leftrightarrow L$ with obvious replacement $\omega \leftrightarrow \omega'$, which means that the group velocity for the dual band changes sign: $v_g = d\omega/dk > 0 \rightarrow v'_g(\omega') < 0$. The dual transformation does indeed result in negative dispersion in the doubly degenerate first band around the $\Gamma$ point [24]. However, the Kron TL lattice contains a few elements per unit cell and, as a consequence, there is another ‘spurious’ band present in the first Brillouin zone. The 3D TL crystal can be fairly well impedance matched to free space in $\sim$GHz range and it supports a backward wave. The ‘spurious’ band can couple to highly attenuated evanescent waves, but losses may be the limiting factor in subwavelength resolution experiment with dual Kron’s TL lattice rather than the coupling to the ‘spurious’ band [24].

It would be interesting to find an implementation of the dual Kron 3D transmission line model for NIM in visible range. With this in mind, Enegha et al. have speculated that Ag nanoparticles can play a role similar to lumped inductance at optical frequencies. One can try, for instance, substituting lumped inductances by Ag nanoparticles in the dual Kron lattice, hoping that the capacitive coupling between the particles would bring about the same band structure as in 3D TL [26], see Fig. 1b. The nanoparticle system in Fig. 1b is a poor representation of 3D TL system shown in Fig. 1a: although one does have both electric and magnetic response from metallic nanoparticles in ac field, they cannot be considered as lumped circuit elements. Indeed, the interaction between particles beyond nearest neighbors is likely important in open structures like Kron’s cubic lattice, in addition to their non-negligible self-capacitance. We have calculated the two cases: (i) lattice of Ag spheres in vacuo (dielectric constant of the matrix is unity, $n_m = 1$, and (ii) dielectric constant of the matrix is $n_m = 1.4$. The second case corresponds to experimentally accessible case of metallic spheres embedded in an organic matrix. We see from Fig. 1d that the realistic case of Ag spheres in the dielectric matrix the electromagnetic response of the system is ‘soft’ ($Re(n)$ is small) but positive. Correspondingly, the dual Kron’s lattice of Ag nanoparticles in vacuo shows only a weak negative index behavior, $Re(n) \approx -0.3$ but it is overwhelmed by losses, since $Im(n) \gg |Re(n)|$. It is likely, therefore, that the weak negative index behavior of Ag spheres in dual Kron’s lattice won’t be observable in sub-wavelength focusing experiments.

To get more insight into electromagnetic (EM) response of nanoparticle arrays, we have performed extensive Finite Difference Time Domain (FDTD) modeling [27] of dual Kron lattices (Fig. 1) and close packed layers of spherical Ag nanoparticles (Figs. 2-4). The dielectric constant of Ag was assumed to have a Drude form

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i\gamma)}, \quad (2)$$

with $\omega_p = 9.04$ eV, $\gamma = 0.02$ eV [28]. The bare Mie resonance of Ag nanoparticles would be at $\omega_M = \omega_p/\sqrt{3} = 5.22$ eV or wavelength $\lambda_M = 238$ nm [29]. The transmission characteristics of the slabs have been calculated by FDTD and then used to estimate the effective index of refraction $n$, permittivity $\varepsilon$ and permeability $\mu$ from complex scattering coefficients according to a standard procedure [30].

The calculated effective permittivity and permeability of the dual Kron’s lattice of Ag particles with radius $R = 100$nm show a series of sharp resonances, $Re(\varepsilon) < 0$ at $\lambda > 0.8\mu m$, and $Re(\mu)$ becomes negative at $\lambda < 1\mu m$. In the same region $Re(\varepsilon)$ is also negative, and we see that the material has a small negative index at $\lambda \approx 0.9\mu m$, where $Re(n) \approx -0.3$. However, the losses are very large there, $Im(n) \approx 1.7$, and this will likely preclude sub-wavelength resolution with the lens made with this metamaterial. Large losses seem to be quite general for systems of metallic nanoparticles [26] and may severely limit their use for the purpose of sub-wavelength resolution.

It is easily understood that the nanoparticles should be almost touching to increase capacitive coupling between them. To see this, we considered Kron’s lattice with Ag nanoparticles with radius $R = 300$nm with the gap of 300nm between them, embedded in a material with dielectric constant $\varepsilon_m = 6.5$. In this case the index remained positive at all wavelengths of interest, $Re(n) \approx 2.5$ at $\lambda = 1.2 - 3.2\mu m$, since the displacement current were ineffective in producing $Re(\mu) < 0$, and $Re(\varepsilon)$ only dipped below zero at a couple of very narrow intervals around resonant wavelengths. Since the volume fraction of the metal was quite small, the losses were minimal, typically $Im(n) < 0.3$. To get NIM behavior, one needs to sharply increase the metal fraction, but this immediately leads to prohibitively large losses, as described above.

We have also studied arrays of Ag nanospheres with radius $R = 30$nm close packed into one, two, and three monolayers, Figs. 2-4. Such systems can be prepared, for
Ag nanoparticles with radius \( R \) and lattice period \( a \). Particles themselves show some inductance (marked by the coil sign) and are capacitively coupled to each other, as schematically indicated in the graph (b). There is some resemblance to Kron’s lattice in vacuo and in matrix material with \( n \) nanoparticles (b). (d) Real and imaginary parts of index \( n \), for Kron’s lattice in vacuo and in matrix material with \( n_m = 1.4 \). Ag lattice in the matrix shows some ‘softness’ at \( \lambda \approx 0.9 \mu m \), whereas system in vacuo exhibits a weak negative index behavior with \( \text{Re}(n) \approx -0.3 \) but \( \text{Im}(n) \gg |\text{Re}(n)| \).

System with three layers of nanospheres packed in ABC sequence characteristic of face-centered cubic lattice (fcc) is interesting, because there is no ‘see-through’ channels in ABC stack. However, even in this case transmission exceeds 40% at the resonance, Fig. 4. We see from Figs. 2-4 that one to three monolayers of close packed metallic Ag nanospheres produce an extraordinary transmission in the vicinity of \( \lambda = 1.1 \mu m \), which is much larger than the radius of the spheres \( R \) and the lattice spacing \( a \). It is also much larger than the Mie resonant wavelength \( \lambda_M = 238 \text{ nm} \). Since in ABC trilayers there is no open “channels” for light to squeeze through the film, the explanation of unusual ‘transparent metal’ behavior lies in the fact that the incident light strongly couples to an array. Strong coupling of the incident light is obviously facilitated by periodic ‘roughness’ of the arrays, since the (quasi)momentum conservation is easier to meet. It would be interesting to see how surface plasmon polaritons are supported by arrays of nanoparticles, in other words, what kind of surface plasmon waveguiding is possible with arrays of nanoparticles considered in the present paper.

Importantly, electric field concentrates in the region where the spheres touch, especially when the centers of the spheres are oriented along a polarization of incident electric field, which looks analogous to corresponding electrostatic problem of two close metallic spheres. In fact, the local electric field enhancement exceeds a factor of \( \eta \sim 30 \), which would facilitate strong Raman signal if the species were positioned on the particles near the field peaks (Raman enhancement factor \( \eta^4 \approx 10^6 \)).

In terms of electromagnetic response, there is a clear topological difference between a monolayer and a few-layer systems. Indeed, at normal incidence the magnetic field in the incident wave cannot excite any displacement currents that would for a close loops, since the field does not ‘see’ any such loops. In AB and ABC layers there are three-membered loops in the fcc lattice that can produce such a magnetic response. As follows from the data
FIG. 2: (Top panel) Transmission $T$, reflection $R$, and absorption $A$ of a monolayer of closely packed nanospheres with radius $a = 30\text{nm}$. Note a very large transmission $T \approx 0.75$ at $\lambda = 1.1\mu m$, much larger than the period of the monolayer, $\lambda \gg a$. (Bottom panel) Permittivity $\varepsilon(a)$, permeability $\mu$, and the effective index $n$ of the monolayer of Ag nanoparticles.

in Figs. 3,4, we do see some ‘softness’ in magnetic response of the AB and ABC arrays in Re($\mu$) at $\lambda \lesssim 0.8\mu m$, Fig. 2b. At the same time, the index for the monolayer is positive and does not show any particular ‘softness’, cf. Fig. 2.

III. CONCLUSIONS

We have analyzed various arrays of metallic nanoparticles in search for an isotropic negative index behavior that was envisaged for dual Kron’s cubic lattice of lumped circuit elements (3D transmission line model)\cite{24}. In particular, we wanted to see if the assembl-
Re(n) ≈ 0.3 at λ ≈ 0.7μm. Although the arrays do not behave as negative index media, we see an intriguing behavior characteristic of a ‘transparent metal’. All those predictions would be very interesting to test experimentally.

FIG. 4: (Top panel) Transmission T, reflection R, and absorption A of a three (ABC packing sequence) layers of closely packed nanospheres with radius a = 30nm. (Bottom panel) The effective index n of the bi-layer of Ag nanoparticles. Although there is no ‘see-through’ channels in this structure, we still observe a large transmission at λ=1.1μm.

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