Plasmons in disordered nanoparticle chains: Localization and Transport

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Disorder-induced effects on plasmon coupling in chains of metallic nanoparticles are studied within a dipole model, by considering two types of disorder: fluctuations of the particles’ shapes and fluctuations of their positions. Typical localization effects are found both in the eigenmodes and in the transport behavior of the system, and an estimate of the localization length is made. It is argued that chains with deliberately introduced disorder constitute promising systems for studying localization effects of electromagnetic waves at optical frequencies under well controllable and manipulable conditions.

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I. INTRODUCTION

Disorder-induced localization was studied in detail for the wavefunctions of electrons by P. W. Anderson. This localization effect rests on the interference of multiply scattered waves. Therefore, a similar effect is also present for electromagnetic waves, with the difference that there is no interaction between the photons and, hence, localization does not have to compete against interaction effects. In general, in three dimensions Anderson-localization of waves is observable if the density of scatterers exceeds a critical value, as expressed by the Ioffe-Regel criterion: \( kl \lesssim 1 \), with \( k \) denoting the wavenumber, and \( l \) the mean free-path length. Hence, for electromagnetic waves in the visible spectrum (with \( k \) on the order of \( 10^7 \ \text{m}^{-1} \) the mean free-path length has to be on the order of a few nanometers. This can be achieved, for example, with semi-conductor powders.

In the present paper, localization of an electromagnetic excitation in disordered chains of metallic nanoparticles is studied. In the context of integrated optics and plasmonic waveguides, the response of nanoparticle chains without sizeable disorder to an optical excitation with a frequency close to the plasmon resonance frequency of a single chain member has already been investigated in detail both experimentally and theoretically. In these studies it has mostly been assumed that the nanoparticles are perfect spheres, and it has been shown that such ideal chains offer interesting perspectives for sub-wavelength waveguiding.

Recently, Alú and Engheta have made an important step by studying the effect of small random uncontrollable disorder on the guidance properties of such chains, within first order perturbation theory. These authors were able to quantify the resulting additional radiation losses for the guided mode. Here, a further step is taken by evaluating even strong disorder, and making the connection to localization physics.

In a wider context, localization of surface plasmons has already been reported experimentally for semicontinuous metal films, and studied theoretically, e.g., for randomly distributed metal particles. Also the celebrated surface enhanced Raman spectroscopy (SERS) is basically enabled by the formation of “hot spots” near a rough surface. These hot spots are regions with an extremely enhanced near-field, and result from the localization of surface plasmons.

The disordered nanoparticle chains studied in this contribution offer an alternative approach to such phenomena. When the individual nanoparticles are subjected to shape fluctuations, and randomly oriented, the polarization tensors of the chain elements have, in general, three distinct principal axes, which are not aligned within the chain. As will be shown by studying their optical properties, such chains exhibit typical signatures of localized modes, when excited at frequencies close to the plasmon-resonance frequency of a single particle. In contrast to systems with truly random disorder, such systems may allow one to introduce specifically engineered types of disorder, and therefore enable one to create hot spots at desired positions, and with predefined properties.

The model used to describe the optical properties of the chains is briefly introduced in Sec. II. In Sec. III numerical results for two types of disorder are shown and some concluding remarks are given in Sec. IV.

II. MODEL

The present theoretical study is based on a model of electromagnetic transport through a chain of metallic nanoparticles which regards
the chain as a linear array of point dipoles. This approximation is viable as long as the individual chain members are small compared to the relevant wavelengths, so that their optical response can be described in the quasi-static approximation. Moreover, it is required that the distance between the chain elements is large compared to their linear size, so that higher multipoles are negligible. Experiments conducted in this parameter regime are in good qualitative agreement with predictions made by this model. This dipole model was proposed in 2000 by Brongersma et al., and since then has been elaborated further in several studies. In particular, Weber and Ford pointed out that while in the parameter regime used, the quasi-static approximation is valid for the response of a single chain member, for the coupling of the particles the quasi-static model is not sufficient. Therefore, in the following always the standard field produced by an oscillating dipole $p e^{i\omega t}$ is used:

$$E = \frac{1}{4\pi\epsilon_0} \left\{ \frac{k^2}{r} (\hat{r} \times p) \times \hat{r} \right\} e^{ikr} + \left[ 3\hat{r}(\hat{r} \cdot p) - p \right] \left( \frac{1}{r^3} - \frac{ik}{r^2} \right) e^{ikr}$$

$$= \frac{1}{4\pi\epsilon_0} \left\{ p \left[ ik \frac{k^2}{r^2} - \frac{1}{r^3} + \frac{k^2}{r} \right] \right\} e^{ikr} + \hat{r}(\hat{r} \cdot p) \left[ 3 \frac{3ik}{r^3} - k^2 \right] e^{ikr},$$

with the vector $r$ pointing from the source to the observation point ($\hat{r}$ denotes the corresponding unit vector) and the wave-number $k = \omega/c$. The time-dependence is suppressed in Eq. (1) and in the following (always assuming a harmonic time-dependence $e^{i\omega t}$).

Assuming, to begin with, that all particles are spheres surrounded by vacuum, the dipole moment $p(r_j)$ induced in the $j$-th particle located at the position $r_j$ is related to the electric field $E(r_j)$ through its effective polarizability $\alpha_{\text{eff}}$:

$$p(r_j) = \epsilon_0 \alpha_{\text{eff}} E(r_j),$$

with the vacuum permittivity $\epsilon_0$. The effective polarizability, in its turn, is related to the quasi-static one $\alpha$ via:

$$\alpha_{\text{eff}} = \frac{\alpha}{1 - \frac{\omega_p^2}{\omega^2}},$$

with $k = \omega/c$ and $c$ denoting the vacuum speed of light. Here, the radiation damping is included within the Abraham-Lorentz approximation. Therefore, the model can be expected to be quantitatively correct as long as radiation damping is a small correction. Since the electric field at each chain site is the sum of the applied external field and the fields produced by all other dipoles, Eq. (2) describes a coupled system of equations for the moments at the sites.

When replacing the spheres by arbitrarily deformed particles their polarizabilities have to be described by tensors, instead of scalar polarizabilities $\alpha$ and $\alpha_{\text{eff}}$. Then the induced dipoles and the local electric fields are no longer parallel. Accordingly, the effective polarizabilities then are defined by diagonalizing that tensor, and using Eq. (3) for each diagonal element. The tensorial character of the polarizabilities implies that a decoupling of transversal and longitudinal modes is no longer possible in chains of randomly oriented, distorted particles. If a chain of ideal spheres is excited with a field polarized perpendicular to the chain-axis, symmetry requires that also all induced dipoles are oriented perpendicular to this axis (transversal mode); similarly a parallel excitation leads to dipoles oriented along the chain axis (longitudinal mode). While this categorization is very helpful for modeling the perfect chain and also enables one to derive some analytical results in this case, it is no longer valid for a disordered chain. Of course, the discrimination of transversal and longitudinal excitation remains meaningful.

This set of equations (2), augmented by tensorial polarizabilities for each particle, allows one to investigate the propagation of an optical excitation through a chain of disordered metallic nanoparticles in detail. In the present study mainly chains of randomly oriented ellipsoids are considered, and both eigenmodes and transport properties are calculated. As a second type of disorder also chains of perfect spheres but with variations of the particle positions is used.

III. NUMERICAL RESULTS

Let us start by investigating a chain of 50 ideal spheres, with a center-to-center distance of 80 nm and a sphere-radius of $a_0 = 25$ nm, assuming that the dielectric properties of the particles are described by the Drude model

$$\epsilon(\omega) = \epsilon_0 \left[ 1 - \frac{\omega_p^2}{\omega^2 + \omega \tau} \right],$$

with plasma frequency $\omega_p = 1.4 \cdot 10^{16}$ s$^{-1}$ and relaxation time $\tau = 1.27 \cdot 10^{-14}$ s, as appropriate for silver. In Fig. 1 an eigenmode of this
chain is depicted by plotting the induced dipole moments $|p_n| = |p(r_n)|$; this mode can be recognized as a standing wave\textsuperscript{11}. This changes drastically when one individual sphere in the chain center is replaced by an ellipsoid, here with semi-axes 0.98 $a_0$, 0.96 $a_0$, and 1.02 $a_0$, representing an isolated defect. As shown in Fig. 1\textsuperscript{11} this defect leads to the emergence of an exponentially localized mode, similar to the localization of electronic wavefunctions around isolated lattice defects.

Here, it should be mentioned that Anderson localization is not the appearance of a localized eigenmode in a system with one isolated defect, but, as already indicated by the title of the original work\textsuperscript{1}, the absence of diffusion in a system containing many defects. The collaborative effect of these defects leads to a breakdown of the diffusive transport and hence, a change in the transport characteristic from an algebraic behavior, typical for a diffusive transport, to an exponential one is a clear indicator for Anderson localization. Certainly, in the context of electromagnetic waves also absorption could lead to an exponential transport behavior and therefore, to make the connection between Anderson localization and the propagation of electromagnetic waves through a disordered medium it is important to ensure that the exponential decay is caused by the disorder and not by absorption processes.

For studying Anderson localization in chains of nanoparticle, the transport through 80-element chains of randomly oriented ellipsoids with normally distributed semi-axes is investigated, assuming a mean of $a_0$ and a standard deviation of $\sigma a_0$. In Fig. 2\textsuperscript{1} the results obtained when only the first particle is subjected to the incident field is plotted for $\sigma = 0.05$, and compared with the transport through a chain of spheres. Again the center-to-center distance was 80 nm and $a_0 = 25$ nm; here and in the following the results in the disordered cases are averaged over 1000 realizations.

Figure 1. (Color online) Extended, standing-wave like mode in a chain of 50 silver nanoparticles consisting of perfect spheres (dashed line with circles) compared to a localized eigenmode which emerges if one single sphere is replaced by an ellipsoid (solid line with crosses). The resonance frequency of this mode is $\omega = (1.0912 - 0.147296i) \omega_{spp}$, where $\omega_{spp} = \omega_p/\sqrt{3}$ is the resonance frequency of a sphere.

Figure 2. (Color online) Induced dipole moments in chains of 80 randomly oriented ellipsoids and ideal spheres, respectively, when the incident field is present only at the position of the first particle, possessing the frequency $\omega = \omega_{spp}$. In a) the external field is polarized perpendicular to the chain axis, whereas it is polarized parallel to this axis in b). The dashed line in a) shows that here the dipole moments decay almost exponentially in the transversely excited disordered chain.

In the case of transversal excitation shown in Fig. 2 a) the disorder obviously causes a substantial increase of the induced dipole moments as compared to the ideal chain; observe the logarithmic scale. Most significantly, the decay of the moments along the chain changes from algebraic to nearly exponential when disorder is introduced, as indicated by the dashed line. This is, as explained above, a genuine hallmark of disorder-induced localization. In contrast, for longitudinal excitation the disorder only leads to a marginal decrease of the induced dipole moments.

Crucial for the considerable effect of the disorder in the case of transversal excitation is that the disorder disturbed the symmetry of the system. Hence, the effect does not depend on the...
precise type of disorder, only the parallelism of the incident field and the induced moments has to be circumvented. The strong effect induced by this rotating of the dipoles results from the heavy direction-dependency of the dipole field (see Eq. (1)).

\[ r_{n}^{\text{dis}} = nde_{x} + a_{n}^{z}e_{z} \tag{6} \]

for all \( n \), the dot product of \( r_{n}^{\text{dis}} \) with the polarization of the incident field \((x, e_{z})\) vanishes, and the component of the field along \( r \) in Eq. (1) is zero. Therefore, the fields produced by the dipole moment in \( z \)-direction in the first particle, caused by the external field, are also polarized in \( z \)-direction at all positions \( r_{n}^{\text{dis}} \) (see Eq. (1)). Since, similar arguments hold for the fields produced by the dipole moments of all other chain members, all induced dipole moments are parallel to the incident field. Thus, a disorder described by Eq. (6) changes the induced moments only marginally, as demonstrated by the red crosses in Fig. 3. The same qualitative result is obtained if instead of non-zero \( a_{n}^{x} \), non-zero \( a_{n}^{y} \) or even non-zero \( a_{n}^{z} \) and non-zero \( a_{n}^{x} \) are used. But, if the positions are varied in \( z \)-direction

\[ r_{n}^{\text{dis}} = nde_{x} + a_{n}^{x}e_{x} \tag{7} \]

the dot products of \( r_{n}^{\text{dis}} \) with the polarization of the incident field vanish no longer and hence, in this case the induced dipole moments and the external field are in general not parallel. This results in a qualitative change of the transport behavior as exemplified by the gray circles in Fig. 3.

Naturally, the transport characteristics of the disordered chain depend on the strength of the particular kind of disorder, in addition to the center-to-center distances and to the optical properties of the nanoparticles. For studying the dependence of the distortion strength again chains of randomly oriented ellipsoids with normally distributed semi-axes with a mean of \( a_{0} \) and a standard deviation of \( \sigma a_{0} \) are used. In Fig. 4 the transport is depicted for different strengths \( \sigma a_{0} \), for the interesting case

Figure 3. (Color online) Induced dipole moments in chains of 80 spheres. In the ideal case the particles are arranged on a 1D linear chain with a center-to-center distance of 80 nm, while the disorder is introduced due to normally distributed variations of the particles’ positions (with a mean of 0 and a standard deviation of 5 nm). The positions are varied in all directions (disordered, see Eq. (4)), or only in one dimension (perpendicular (see Eq. (3)) or parallel (see Eq. (2)) to the incident field), respectively. The incident field is present again only at the position of the first particle, possessing the frequency \( \omega = \omega_{\text{pp}} \) and polarized perpendicular to the chain axis. For clarity in the 1D cases only the induced moments in every third particle are depicted.

This is demonstrated in Fig. 3 where the disorder is not introduced due to distortions of the elements’ shapes, but due to variations of the positions of the particles. If one assumes that the chain axis is oriented along the \( x \)-axis of the coordinate system used the sites of the ideal chain could be labeled by

\[ r_{n}^{\text{de}} = nde_{x} \tag{4} \]

with the center-to-center distance \( d \). The disorder is now introduced due to normally distributed deviations \( a_{n}^{x,y,z} \) from these ideal positions

\[ r_{n}^{\text{dis}} = nde_{x} + a_{n}^{x}e_{x} + a_{n}^{y}e_{y} + a_{n}^{z}e_{z} \tag{5} \]

In Fig. 3 the results for three cases of this type of disorder are depicted for a transversal excitation. In every case the mean of \( a_{n}^{x,y,z} \) was zero with a standard deviation of 5 nm and a site distance \( d \) of 80 nm. This disorder again leads to an exponential decay as demonstrated by the curve labeled disordered in Fig. 3. However, for this type of disorder it is easily possible to change the disorder such, that the induced dipole moments and the incident field remain parallel. Due to the structure of the dipole field (see Eq. (1)) a variation of the chain elements’ position perpendicular to the incident field does not affect the orientation of the induced dipoles. To clarify this, assume a polarization of the incident field in \( z \)-direction with the chain-axis again in the \( x \)-direction. Since, for a perfect sphere, the induced dipole moment and the field at the position of the sphere are parallel, all induced moments in the chain and the incident field are parallel if the fields at all chain sites are parallel to the external field. If now the positions of the particles are varied only perpendicular to the polarization of the external field, for example only in \( x \)-direction,
of transversal excitation. Here, the cross-over from an algebraic to the exponential decay is visible. In order to extract the dependence of the localization length $b$ on the distortion strength $\sigma$, the dipole moments in the middle part of the chain have been fitted to the expression

$$|p_n|^2 = a \exp(-n/b). \quad (8)$$

The results are shown in Fig. 4b). As expected, an increase of the disorder strength causes a decrease of the localization length, and hence a “stronger” localization. Since Anderson localization is caused by multiple scattered waves, the variation of the individual chain members should not be too large. After increasing the value of $\sigma$ to 0.2, for instance, one does no longer find an exponential decay of the induced dipole moments along the chain. For the randomly oriented ellipsoids this is due to the fact that the chain is excited with the resonance frequency of an undistorted chain member and that the distortion of the particles also affects the resonance frequencies; a too large distortion decreases significantly the scattering cross-section of the particle at the frequency used and thus decreases the effect of multiple scattered waves.

Perfect exponential localization would imply that for longer chains the induced dipole moments can drop substantially below those in ideal chains. Somewhat surprisingly, this does not seem to occur in the system studied here. Instead, in longer chains there appears to be a second cross-over after which the response of the disordered chain again approaches that of the ideal one. This is exemplified in Fig. 5 for a chain of 200 particles. Thus, there are at least two characteristic length scales: That which marks the onset of the fully developed exponential decay, and that which marks the return to the behavior of the ideal chain.

IV. CONCLUSIONS

In conclusion, chains of randomly or even deliberately distorted nanoparticles constitute novel experimentally accessible and theoretically tractable systems for studying localization effects of electromagnetic waves at optical frequencies. Utilizing these localization effects in combination with specific types of the engineered disorder offers the prospect of obtaining particularly high field enhancement for application purposes.

![Figure 4](image1.png)

Figure 4. (Color online) Dependence of the transport characteristics on the strength $\sigma$ of the distortion of the spheres, for transversal excitation. Panel a) shows the induced dipole moments for different values of $\sigma$, while panel b) depicts the dependence of the localization length $b$ (in numbers of particles, see Eq. 8) on $\sigma$, with numerical errors as indicated by the symbols. In all cases the frequency of excitation was $\omega = \omega_{spp}$.

![Figure 5](image2.png)

Figure 5. (Color online) As Fig. 4b), but for a chain of 200 particles. Note that the induced dipole moments in the disordered chain do not drop below those of the ideal one.

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For determining the eigenmodes, the set of equations (2) can be recast into matrix form $M(\omega)p = E_{\text{ext}}$ with $E_{\text{ext}}$ denoting the external electric fields present at the positions of the nanoparticles. The frequencies of the eigenmodes are given by the complex roots of $\text{det}(M) = 0$, and the corresponding eigenmodes by the nontrivial solutions of $Mp = 0$.