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LETTER TO THE EDITOR

Divergence of dipole sums and the nature of non-Lorentzian exponentially narrow resonances in one-dimensional periodic arrays of nanospheres

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Abstract

The origin and properties of non-Lorentzian spectral lines in linear chains of nanospheres are discussed. The lines are shown to be super-exponentially narrow with the characteristic width $\propto \exp[-C(h/a)^3]$ where C is a numerical constant, h the spacing between the nanospheres in the chain and a the sphere radius. The fine structure of these spectral lines is also investigated.

One-dimensional periodic chains (ODPCs) of metallic nanospheres have attracted significant recent attention due to their unusual optical properties. Although the general theoretical framework for analysing electromagnetic interactions in ODPCs was built a decade ago [1], recent dramatic advances in nanofabrication have reinvigorated interest in ODPCs, which, in turn, has led to several new results of high experimental relevance. In particular, radiatively non-decaying surface plasmons (SPs) in ODPC with possible applications to building novel lasers were discussed in [2]; unusual shifts of plasmon resonance frequencies were found in [3] and a dramatic narrowing of SP spectral lines was found in [4, 5] in finite chains of moderate length. In this letter I show that two of these phenomena (unusual shifts and narrowing of SP spectral lines) are directly related to a logarithmic divergence of dipole sums (electromagnetic eigenvalues)—a theoretical interpretation that has not been given so far. The SPs that can be excited as a result of this divergence possess highly unusual properties. In particular, the resonance line-shapes are essentially non-Lorentzian and are characterized by a vanishing integral weight. This is in a sharp contrast to spectral line broadening or narrowing due to change in the decay rate. Another consequence which has not been previously noted is that each narrow resonance is paired with an even more narrow spectral hole. An interesting new property discussed below is that the narrow collective SP resonances can be excited in ODPCs even when the distance between neighbouring spheres is much larger than the sphere diameters.

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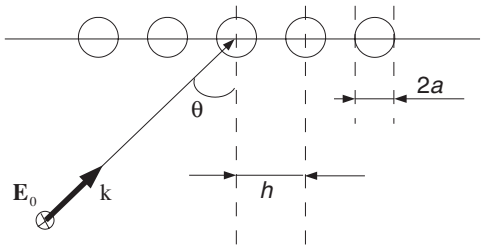

Figure 1. Sketch of the ODPC excitation by a linearly polarized plane wave.

However, the resonances become so narrow in this case that, unless one takes special care, it is extremely unlikely that they would be noticed in any numerical or experimental investigation.

We start with a brief summary of the underlying physics. The geometry of an ODPC excited by a plane wave of the form $\mathbf{E}_0 \exp(\mathrm{i}\mathbf{k}\cdot\mathbf{r})$ is illustrated in figure 1. Here the polarization vector $\mathbf{E}_0$ is perpendicular to the chain, the incidence angle is denoted by θ, lattice spacing by h and the sphere radius by a. Each sphere is assumed to be polarizable and characterized by the dipole polarizability α. We work in the approximation introduced by Doyle [6] in which each sphere is treated as an elementary dipole located at its centre but is characterized by non-quasi-static polarizability α which is calculated from the coefficient a_1 of the Mie theory [7]:

$$\alpha = \frac{3\mathrm{i}}{2k^3}\frac{m\psi_1(mka)\psi_1'(ka) - \psi_1(ka)\psi_1'(mka)}{m\psi_1(mka)\xi_1'(ka) - \xi_1(ka)\psi_1'(mka)}, \tag{1}$$

where $\psi_1(x)$ and $\xi_1(x)$ are the Riccati–Bessel functions, $m = \sqrt{\epsilon}$ is the complex refractive index of the spheres and $k = \omega/c = 2\pi/\lambda$ is the wave number of the incident wave. The above approximation allows one to include spheres which are not small compared to the incident wavelength λ while staying within the purely dipole theory. The higher multipole interactions of the spheres, as well as the input of higher multipoles to the optical cross sections, are ignored in this approximation. Note that the polarizability α defined by (1) is the *exact* dipole polarizability with respect to excitation by a plane wave, but not by secondary waves scattered by spheres in the chain. However, the dipole approximation was shown to be very accurate when h is the order of or larger than $2a$ (which is the case discussed below) by direct comparison with a converged T-matrix solution [4]. In general, it is known that short-range multipole interactions of orders higher than the first (dipole) do not play a significant role for transverse electromagnetic excitations of finite or infinite linear arrays of interacting spheres even when the spheres are in close proximity [8, 9]. Physically, one can argue that the short-range interaction is not important for transverse excitations because it does not lead to an electric current along the chain (in a sharp contrast to longitudinal excitations which are not discussed in this letter).

In the approximation formulated above, each sphere is characterized by a dipole moment which, in the case of the geometry shown in figure 1, is collinear with the polarization vector $\mathbf{E}_0$ and has the amplitude d_n, n being the index which labels spheres in the chain. The amplitudes d_n are coupled to the external field and to each other by the coupled-dipole equation [1]

$$d_n = \alpha\left[E_0\exp(\mathrm{i}kn\sin\theta) + \sum_{n'\neq n} W_{n-n'}(kh)d_{n'}\right]. \tag{2}$$

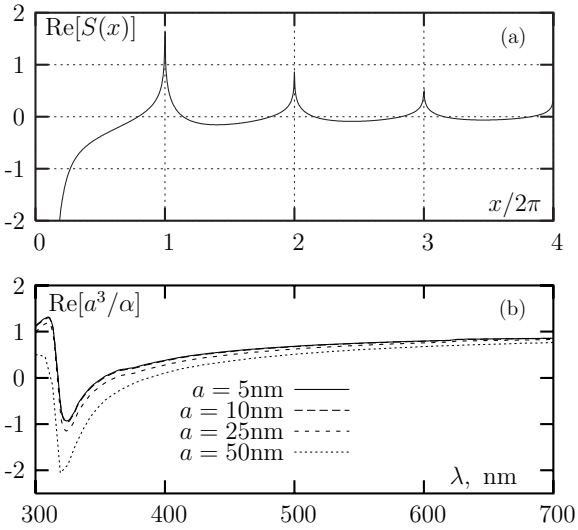

Figure 2. (a) Function Re $S(x)$ for $\theta = 0$. (b) Re(a^3/α) calculated for silver for different values of a; the curves $a = 5$ nm and $a = 10$ nm correspond to the quasi-static limit and are indistinguishable.

Here $W_{n-n'}$ is the dipole interaction term given by

$$W_n(x) = k^3 \left(\frac{x^{-1}}{|n|} + \frac{\mathrm{i}x^{-2}}{|n|^2} - \frac{x^{-3}}{|n|^3} \right) \exp(\mathrm{i}x|n|). \tag{3}$$

The coupled-dipole equation (2) is easily solved to yield

$$d_n = \frac{a^3 E_0 \exp(\mathrm{i}khn \sin\theta)}{a^3/\alpha - (ka)^3 S(kh)}, \tag{4}$$

where the dimensionless quantity $(ka)^3 S(kh)$ is the dipole sum that characterizes excitation of the SP with the wave number $q = k \sin\theta$. The function $S(x)$ is given by

$$S(x) = 2 \sum_{n>0} \left(\frac{1}{xn} + \frac{\mathrm{i}}{(xn)^2} - \frac{1}{(xn)^3} \right) \exp(\mathrm{i}nx) \cos(nx \sin\theta). \tag{5}$$

It can be seen that the above series diverges logarithmically when $(1 \pm \sin\theta)kh = 2\pi l, l$ being an integer. It is convenient to separate the sum into two parts: $S(x) = S_1(x) + S_2(x)$ where S_1 is given by

$$S_1(x) = 2 \sum_{n>0} \frac{\cos(nx)\cos(nx \sin\theta)}{nx} = -\frac{1}{2x} \ln[4(\cos x - \cos(x \sin\theta))^2] \tag{6}$$

and diverges when $\cos x = \cos(x \sin\theta)$ while $S_2(x)$ is the reminder of series (5) and converges for all values of parameters. For simplicity, we will assume everywhere below normal incidence ($\theta = 0$), which was also the case considered in [4]. Then the divergence takes place when $h = \lambda l$.

The specific extinction cross section per one sphere is given by [1]

$$\sigma_e = \mathrm{Im} \frac{4\pi k a^3}{a^3/\alpha - (ka)^3 S(kh)}. \tag{7}$$

Optical resonances occur when the real part of the denominator in the above expression vanishes. In figure 2(a) we plot Re $S(x)$ for $\theta = 0$. The sharp peaks in the plot correspond to

the points where Re S diverges. In figure 2(b) we also plot $\mathrm{Re}(a^3/\alpha)$ calculated according to (1) for silver. Interpolated experimental dielectric function from [10] was used in calculations. It can be seen that in an isolated sphere, the SP (Frohlich) resonance takes place in the interval 350 nm $< \lambda <$ 380 nm, depending on the value of a. The resonant wavelength is obtained from $\mathrm{Re}(a^3/\alpha) = 0$. Above the Frohlich resonance (at smaller wavelengths), the spectral variable $\mathrm{Re}(a^3/\alpha)$ becomes negative. (Here we ignore the region $\lambda <$ 320 nm where no resonance excitation can take place due to the strong interband absorption.) Therefore, in order to excite an SP in an interacting ODPC in this spectral region, the variable Re S must be also negative. As can be seen from figure 2(a), this happens for sufficiently small values of the parameter $x = kh$ and corresponds to the conventional blue shift of the transverse electromagnetic oscillations, which is well known and can be described by the quasi-static interaction [11]. However, below the Frohlich resonance (at larger wavelength), the spectral parameter $\mathrm{Re}(a^3/\alpha)$ is positive. Therefore, in order to excite an SP in this spectral region, the variable Re S must also be positive. Obviously, this requirement is fulfilled near the points of divergence of Re S. Thus, if h/λ is close to an integer, the transverse collective oscillations of the chain are shifted to the red from the Frohlich wavelength, in contrast to the usual case. Quite remarkably, the collective resonance can take place even if $a \ll h$ and $(ka)^3 \ll 1$. Indeed, no matter how small ka is, the resonant condition can always be satisfied sufficiently close to the point $\lambda = h/l$. Below, we focus on the first of these resonances, which corresponds to $\lambda \approx h$ and can be experimentally observed in metal ODPCs in the visible and IR spectral regions below the Frohlich frequency of an isolated sphere.

In figure 3(a) we plot the dimensionless extinction efficiency $Q_e = \sigma_e/4\pi ka^3$ for the following values of parameters: $a =$ 50 nm and $h =$ 500 nm. The sharp resonance corresponding to $\lambda \approx h$ is clearly visible. The curve is very close to that shown in figure 1(a) of [4]. In figure 3(b) the origin of the sharp resonance is illustrated. Namely, we see that in a very narrow spectral interval near $\lambda =$ 500 nm real parts of the two terms in the denominator of (7) cancel each other. From the analysis of figure 3(b), it is obvious that there should be, in fact, two closely spaced narrow resonances separated by a spectral hole. However, the first of the two resonances is suppressed due to radiative losses. The imaginary part of the denominator of (7) is plotted in figure 3(c). As was pointed out in [1], the imaginary part of $S(x)$ experiences a jump at $x = 2\pi$. However, no exact cancellation of the imaginary part of the denominator can take place. For the geometry considered here, it can be shown that $\mathrm{Im}[(ka)^3 S(kh)] > -5(ka)^3/12$ while $\mathrm{Im}(a^3/\alpha) < -2(ka)^3/3$, so that the imaginary part of the denominator is $\leqslant -(ka)^3/4$, with the equality taking place for nonabsorbing materials with $\mathrm{Im}\,\epsilon = 0$. Finally, in figure 3(d) the sharp resonance seen in figure 3(a) is completely resolved. The narrow spectral hole located exactly at $\lambda = h$ can also be seen in this figure.

Let us estimate the width and amplitude of the narrow resonances occurring due to the divergence of $S(x)$. We define the width of the resonance as the distance from the resonance wavelength λ_r, determined from the condition $\mathrm{Re}[a^3/\alpha(\lambda_r) - (2\pi a/\lambda_r)^3 S(2\pi h/\lambda_r)] = 0$ to the centre of the spectral hole at $\lambda = h$; thus, $\Delta\lambda = |\lambda_r - h|$. We estimate λ_r assuming that the dominant contribution to Re S comes from the logarithmically diverging term (6). We also assume that $\Delta\lambda \ll 2\pi$ and expand the argument of the cosine in (6) near the point $x = kh = 2\pi$, which leads to the following estimate:

$$\Delta\lambda \approx \frac{h}{2\pi} \exp\left[-\frac{C}{2(2\pi)^2}\left(\frac{h}{a}\right)^3\right], \tag{8}$$

where $C = \mathrm{Re}[a^3/\alpha(\lambda = h)]$ is a constant of the order of unity. For example, for $h =$ 500 nm, $C \approx 0.5$. Using $a =$ 50 nm, we obtain from (8) $\Delta\lambda \approx 0.14$ nm in agreement with figure 3(d). Thus, the width of the resonance is completely determined by the geometrical factors

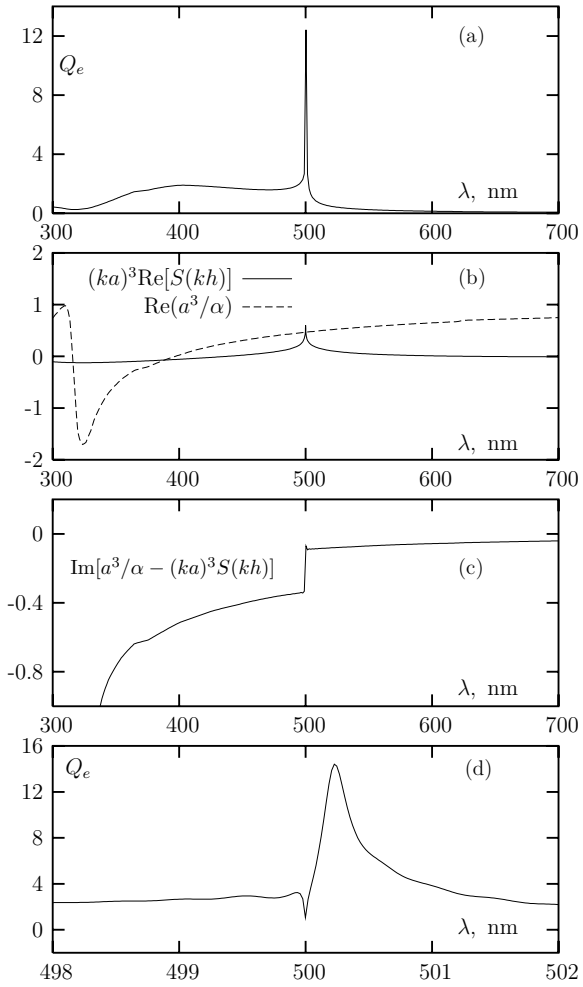

Figure 3. (a) Extinction efficiency Q_e for $h = 500$ nm and $a = 50$ nm. (b) Illustration of cancellation of the real part of the denominator in (7). (c) Spectral dependence of the imaginary part of the denominator. (d) The narrow resonance shown in the panel (a) fully resolved.

(the ratio h/a) and is not in any way controlled by relaxation. The latter, however, influences amplitude of the resonance. Indeed, the maximum value of Q_e in the peak is given by $-1/\mathrm{Im}[a^3/\alpha - (ka)^3 S(kh)]$. For the geometry considered here, it can be verified that this value cannot be greater than $(h/\pi a)^2$, which is the limit for nonabsorbing material. However, for strongly absorbing materials the amplitude of the resonance can become negligibly small.

Since the amplitude of the narrow resonances does not increase when the width decreases super-exponentially, it is impossible to effectively excite these resonances by a near-field probe. For example, consider the case when a single sphere (say, $n = 0$) is excited by a near-field microscope tip of small aperture. Then the coupled-dipole equation for the amplitudes d_n can be solved by Fourier transformation:

$$d_n = \int_{-\pi/h}^{\pi/h} \frac{a^3 E_0 \exp(\mathrm{i}qhn)}{a^3/\alpha - (ka)^3 \tilde{S}(kh, qh)} \frac{h\,\mathrm{d}q}{2\pi}, \tag{9}$$

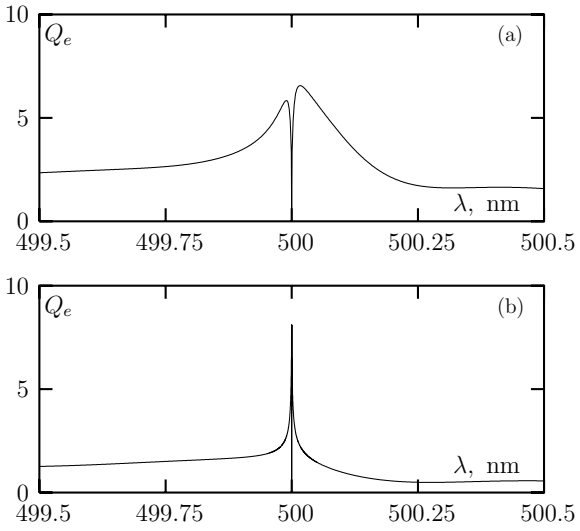

Figure 4. (a) Narrow resonances for $h = 500$ nm and $a = 45$ nm (a) and $a = 40$ nm (b).

where $\tilde{S}(kh, qh)$ is given by (5) in which $x \sin\theta$ in the argument of cosine must be formally substituted by qh and the variable x in the reminder of the formula substituted by kh. Function $\tilde{S}(kh, qh)$ diverges logarithmically when $\cos(kh) = \cos(qh)$; in particular, if $kh = 2\pi$ as in the examples considered above, the only point of divergence within the integration interval is $q = 0$. Similar to resonances in extinction spectra, this resonance is super-exponentially narrow in the SP wavenumber q, and its input into the above integral is negligible. We emphasize again that the resonances discussed here are essentially non-Lorentzian, and the conditions for applicability of the quasi-particle pole approximation, which under normal circumstances would properly describe coupling of the near-field probe to SPs, are severely violated.

The narrow resonance in figure 3(d) was obtained for $h = 500$ nm and $a = 50$ nm. We now show that narrow resonances also exist for smaller values of a and larger ratios h/a. To this end, we plot the extinction efficiency Q_e for $h = 500$ nm and $a = 45$ nm (figure 4(a)) and $a = 40$ nm (figure 4(b)). The dielectric function does not vary noticeably over the narrow spectral range shown in figure 4 and was therefore taken to be constant, $\epsilon = -8.5 + 0.76\mathrm{i}$, which corresponds to the experimental value at $\lambda = h = 500$ nm given in [10]. The narrow non-Lorentzian resonances are well manifested in figure 4. The central spectral hole is resolved to some degree in figure 4(a) but is shown only as a vertical line in figure 4(b). Obviously, it is impossible to resolve the spectral holes completely, since they do not have Lorentzian structure and are non-differentiable at the point $\lambda = h$. Note that the resonances shown in this figure are much more symmetrical with respect to the point $\lambda = 500$ nm than that shown in figure 3(d). This is due to the fact that with increasing the ratio h/a, the influence of radiative losses on the shape of resonance lines decreases. For even larger values of h/a, the resonances quickly become extremely narrow but do not disappear completely, at least in chains of sufficient length.

It is interesting to consider the possibility of narrow resonances in situations when the dipole approximation is not applicable, i.e., for spheres in close proximity. It can be shown that the resonances discussed in this letter do not disappear or get broadened when the full multipole interaction is taken into account. Furthermore, the spherical shape of the

particles is also not fundamental because the phenomenon discussed here originates due to long-range interaction in ODPCs while the higher multipole interaction is short range. This conclusion is in agreement with the numerical study of extinction spectra of periodic chains of cylindrical discs [5] which were shown to have sharp resonances similar to those found in chains of spheres. Generalization to two-dimensional arrays of particles is also possible. Two-dimensional periodically modulated structures have also attracted significant recent attention, with possible applications including random lasers [2], development of novel chemical and biological sensors [3] and the study of anomalous optical transmission through metal films [12].

To conclude this letter, we discuss several factors that contribute to broadening of the spectral lines discussed above. The most important factor is the finite length of a chain, since the divergence of the dipole sums is logarithmic. As was mentioned above, narrow resonances very close to those in infinite chains were obtained in [4] for $h/a = 10$ and only 50 spheres; however, observing more narrow resonances with $h/a > 10$ will require a substantially larger number of spheres. One possible solution to this problem is to place the ODPC into a circular optical fibre. Disorder is another important factor. Numerical simulations in finite chains (400 particles) [5] revealed that random uncorrelated displacements of particles with the amplitude of $\sim 0.1h$ do not noticeably change the resonance lineshape. This is an expected result for short-range disorder, i.e., the disorder with the correlation length of one or few lattice spacings. However, disorder with long-range correlations can result in much stronger changes in the resonance lineshapes. Further, the account of nonlocality of the dielectric response will not alter the nature of positive interference (synchronism) which results in the logarithmic divergences, and is not expected to broaden the narrow spectral lines. The two physical phenomena whose effects on the spectral lines discussed here are difficult to predict are the nonlinearity of the optical response (e.g., Kerr-type third-order nonlinearity) and quantum effects. These effects will be the subject of future work.

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