Anomalous Light Scattering by Small Particles

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Light scattering by a small spherical particle with a low dissipation rate is discussed based upon the Mie theory. It is shown that if close to the plasmon (polariton) resonance frequencies the radiative damping prevails over dissipative losses, sharp giant resonances with very unusual properties may be observed. In particular, the resonance extinction cross section increases with an increase in the order of the resonance (dipole, quadrupole, etc.); the characteristic values of electric and magnetic near fields for the scattered light are singular in the particle size, while energy circulation in the near field is rather complicated, so that the Poynting vector field includes singular points whose number, types, and positions are very sensitive to fine changes in the incident light frequency. The results may provide new opportunities for a giant, controlled, highly frequency-sensitive enhancement and variation of electromagnetic field at nanoscales.

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Light scattering by small particles is a fundamental problem of classical electrodynamics. It has attracted a great deal of attention from numerous researchers, starting from the pioneering publications of Lord Rayleigh [1]. Nowadays, interest in this problem is increasing incrementally owing both to its great academic importance and the vast variety of applications of the phenomenon in different disciplines [2]. Nonetheless, a certain very important particular case still requires careful inspection. Namely, though it is well known that *all* transverse [i.e., those excited at $\epsilon'_p(\omega) \neq 0$, where $\epsilon'_p(\omega)$ stands for real part of the particle dielectric permittivity and ω for the incident light frequency] electromagnetic modes of the particle have finite lifetimes because of radiative damping, see, e.g., [3], light scattering by small particles is considered generally in the limit when the radiative damping is overwhelmingly negligible relative to dissipative losses [4–6]. Meanwhile, a few publications devoted to study of the opposite limit [7–12] clearly show that light scattering in this case occurs in a very unusual manner. It motivated us to carry out a systematic study of the phenomenon presented in this Letter.

We consider light scattering by a spherical particle of radius a immersed in a transparent medium with refractive index $n_m = \sqrt{\epsilon_m}$, where the dielectric permittivity of the medium ϵ_m is purely real and positive. The size parameter $q = an_m\omega/c$ is supposed to be a small quantity. Here c is the speed of light in vacuum. The consideration is based upon the exact Mie solution of the macroscopic Maxwell equations with the usual continuity conditions at the particle surface [4]. It is implied that complex dielectric permittivity of the particle $\epsilon_p(\omega) = \epsilon'_p(\omega) + i\epsilon''_p(\omega)$ satisfies the condition $\epsilon'_p(\omega) < -1$, which allows excitation of the corresponding surface localized electromagnetic modes (SLEM), usually called surface plasmons (metals), or surface polaritons (dielectrics). At certain frequencies ω_ℓ excitation of SLEM becomes resonant. In what follows we focus on the case when $\epsilon''_p(\omega_\ell)$ is small and cutoff of the resonance scattering amplitude occurs because of the radiative damping.

It is shown that in this case light scattering by small particles exhibits features quite different from the conventional ones [4–6]. In particular, giant optical resonances with extremely narrow lines may be observed. At the resonance points the extinction (scattering) cross section $\sigma_{\mathrm{ext(sca)}}$ is determined by the corresponding single partial resonance mode and the value of $\sigma_{\mathrm{ext(sca)}}$ increases with an increase in ℓ; i.e., the cross section at the quadrupole resonance becomes greater than that at the dipole, etc. The characteristic values of both electric and magnetic fields inside the particle and in its vicinity (near field) are singular in q. Such a behavior is accompanied with rather complicated and unusual structure of energy flow flux density in the near field, which is very sensitive to changes of ω, so that in the vicinity of the resonances fine changes in ω result in global changes in the energy flow flux density configuration. Taking into account qualitative differences between all these peculiarities and the analogous features of the Rayleigh scattering we name the phenomenon *anomalous scattering*.

It should be stressed that the present study does not imply any revision of the Mie solution. We just consider the range of parameters of this solution which usually is not inspected, obtain certain approximations valid in this range and discuss physical consequences following from these approximations.

To begin with let us consider the extinction, scattering, and absorption cross sections. For these quantities the Mie solution yields the following expressions [4], where summation goes over the corresponding partial multipole cross sections:

$$\sigma_{\rm ext} \simeq \sum_{l=1}^{\infty} \sigma_{\rm ext}^{(l)}, \qquad \sigma_{\rm sca} = \sum_{l=1}^{\infty} \sigma_{\rm sca}^{(l)}, \qquad \sigma_{\rm abs} = \sigma_{\rm ext} - \sigma_{\rm sca}; \tag{1}$$

$$\sigma_{\rm ext}^{(l)} = \frac{2\pi}{k^2}(2l+1){\rm Re}(a_l + b_l), \tag{2}$$

$$\sigma_{\rm sca}^{(l)} = \frac{2\pi}{k^2}(2l+1)(|a_l|^2 + |b_l|^2). \tag{3}$$

Here $k = n_m\omega/c$. Regarding amplitudes a_l and b_l, for our purposes it is convenient to present them in the following form:

$$a_l = \frac{F_l^{(a)}(q,\epsilon)}{F_l^{(a)}(q,\epsilon) + iG_l^{(a)}(q,\epsilon)}, \tag{4}$$

where $\epsilon = \epsilon_p(\omega)/\epsilon_m(\omega)$. The expression for b_l follows from Eq. (4) with replacement $F_l^{(a)} \to F_l^{(b)}$; $G_l^{(a)} \to G_l^{(b)}$. Quantities $F_l^{(a,b)}$, $G_l^{(a,b)}$ are expressed in terms of the Bessel $[J_{l+1/2}(z)]$ and Neumann $[N_{l+1/2}(z)]$ functions, whose expansions in power series gives rise to the following formulas valid at small q:

$$F_l^{(a)}(q,\epsilon) \simeq q^{2l+1}\frac{l+1}{[(2l+1)!!]^2}(\epsilon - 1) + \ldots, \tag{5}$$

$$G_l^{(a)}(q,\epsilon) \simeq \frac{l}{2l+1}\left\{\epsilon + \frac{l+1}{l} - q^2\frac{\epsilon-1}{2} \times \left[\frac{\epsilon}{2l+3} + \frac{l+1}{l(2l-1)}\right] + \ldots\right\}, \tag{6}$$

where ellipsis denote omitted higher order in q terms. As for $F^{(b)}$ and $G^{(b)}$, the explicit expressions for these quantities are not required because of the estimate $|b_l| \sim q^{2l+3} \ll |a_l|$, which allows neglecting b_l relative to a_l at small q.

However, the conventional approach [4] corresponds to neglect of $F_l^{(a)}$ relative to $G_l^{(a)}$ either. Meanwhile omission of $F_l^{(a)}$ in the denominator of Eq. (4) is equivalent to neglect of the radiative damping. To show this note, at given q and $l = \ell$ the equation $G_\ell^{(a)}(q,\epsilon) = 0$ has purely real root $\epsilon_\ell = -\frac{1+\ell}{\ell} + O(q^2)$, see Eq. (6), which through dependence $\epsilon(\omega)$ defines the resonance frequencies ω_ℓ of the corresponding ℓth SLEM resonance ($\ell = 1, 2, 3\ldots$).

If $F_\ell^{(a)}$ in the denominators of Eq. (4) is neglected, $\sigma_{\rm sca}^{(\ell)}$ diverges at $\epsilon = \epsilon_\ell$. In contrast, according to the exact expression Eq. (4) $a_\ell = 1$ at $\epsilon = \epsilon_\ell$, which results in the following *finite* partial resonance cross sections [7]:

$$\sigma_{\rm ext}^{(\ell)} = \sigma_{\rm sca}^{(\ell)} = (2\ell+1)\frac{2\pi}{k^2}. \tag{7}$$

To make sure that the divergence cutoff does correspond to the radiative damping note that in the nondissipative limit with purely real ϵ and hence purely real $F_l^{(a)}$, $G_l^{(a)}$, see Eq. (5) and (6), in the leading (in small q) approximation $F_l^{(a)}$ in the denominator of Eq. (4) contributes to ϵ *imaginary* part of order $O(q^{2l+1})$, i.e., acts as $\epsilon''_{\rm eff}$ (effective ϵ''). On the other hand $\epsilon''_{\rm eff}$ related to the radiative losses may be estimated straightforwardly. The electromagnetic power dissipated in a unite volume is given by the expression $P = \frac{\omega}{4\pi}\epsilon''\overline{\mathbf{E}^2}$ [13]. Thus, if the radiative losses are described in terms of $\epsilon''_{\rm eff}$, we can write the following estimate for the the power scattered by the entire particle to the lth partial mode $\mathcal{P}^{(l)} \sim \omega\epsilon''_{\rm eff}a^3(\mathbf{E}_p^{(l)})^2$, where $\mathbf{E}_p^{(l)}$ stands for the characteristic value of electric field of the lth mode inside the particle (each of the modes makes additive contribution to the net power because cross-terms of the form $\mathbf{E}^{(l_1)}\mathbf{E}^{(l_2)}$ vanish owing to orthogonality of different modes). Far from the resonance frequencies ω_ℓ the Mie solution yields $\mathbf{E}_p^{(l)} \sim q^{l-1}\mathbf{E}_0$, where $\mathbf{E}_0$ is electric field of the incident light [4]. Finally we obtain $\mathcal{P}^{(l)} \sim \omega\epsilon''_{\rm eff}a^3q^{2(l-1)}(\mathbf{E}_0)^2$. On the other hand, the scattered power $\mathcal{P}_{\rm sca}^{(l)}$ is estimated as $c\sigma_{\rm sca}^{(l)}(\mathbf{E}_0)^2 \sim c|a_l|^2(\mathbf{E}_0)^2/(k^2) \sim cq^{2(2l+1)}(\mathbf{E}_0)^2/k^2$, see Eqs. (3)–(6). Equalizing $\mathcal{P}^{(l)}$ to $\mathcal{P}_{\rm sca}^{(l)}$ and bearing in mind that $ak = q$, $\omega = kc$ we eventually obtain $\epsilon''_{\rm eff} \sim q^{2l+1}$, which agrees with the contribution of $F_l^{(a)}$ to ϵ.

Note, being just a consequence of the nondissipative limit, Eq. (7) is valid at any q. However, at large q different resonance peaks are overlapped, which results in degradation of the resonances. On the contrary, at $q \ll 1$, while for a resonance frequency ω_ℓ the corresponding partial cross sections satisfy the condition $k^2\sigma_{\rm ext,sca}^{(\ell)}/2\pi = 2\ell + 1$, for other, nonresonant modes $k^2\sigma_{\rm ext,sca}^{(l)}/2\pi = O(q^{4l+2})$, see Eqs. (2), (3), (5), and (6). Thus, contribution of a single resonant mode to the net cross sections is much greater than that for the entire sum of the nonresonant modes. In other words $\sigma_{\rm ext} = \sigma_{\rm sca} \simeq 2\pi(2\ell+1)/k^2$ at $\omega = \omega_\ell$. Although formally the estimate is valid at $q \ll 1$, numerical calculations show that actually it is still good even at $q = 1$ (the corresponding error does not exceed a few per cents). It seems that validity beyond the formal applicability conditions is a general feature of the phenomenon, see below. Another consequence of the estimate is an increase in the net cross sections with an increase in the order of resonance. For example, the cross section at the quadrupole resonance is 5/3 of that at the dipole resonance, etc.

Taking $F^{(a)}$ at $\omega = \omega_\ell$ and the first term of expansion of $G^{(a)}$ in powers of $\delta\omega = \omega - \omega_\ell$ [we remind that $G^{(a)}(q, \epsilon(\omega_\ell)) = 0$] one obtains the usual Lorentz profile describing shape of the resonance peaks in the vicinity of ω_ℓ, see Eqs. (3), (5), and (6). The characteristic widths of the peaks are as follows:

$$\gamma_\ell = \frac{2q^{2\ell+1}(\ell+1)}{[\ell(2\ell-1)!!]^2(d\epsilon/d\omega)_\ell}, \tag{8}$$

where derivative $(d\epsilon/d\omega)_\ell$ is taken at $\omega = \omega_\ell$. Note the extremely sharp decrease in γ_ℓ with both decrease in q and increase in ℓ, see Fig. 1.

In reality, however, the line width cannot be smaller than the natural width γ related to dissipative losses. Thus, Eq. (8) is valid provided $\gamma_\ell \gg \gamma$, or in other terms $\epsilon''_{\rm eff}$ related to the radiative damping should be much greater

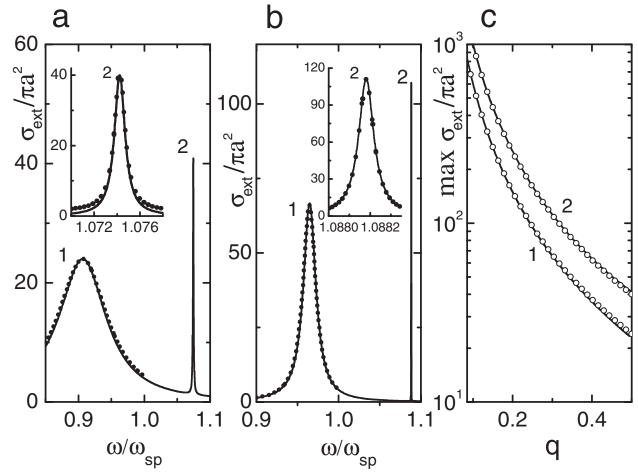

FIG. 1. Nondissipative limit for a spherical particle with radius a. Frequency dependence of the normalized extinction cross section $\sigma_{ext}/\pi a^2$ for $q = 0.5$ (a) and $q = 0.3$ (b); $\epsilon = 1 - \omega_0^2/\omega^2$, $\omega_{sp} = \omega_0/\sqrt{3}$ stands for frequency of the dipole resonance at $q \to 0$. Numerals indicate dipole (1) and quadrupole (2) resonance peaks. Insets show structure of the quadrupole resonance peaks. Solid lines represent calculations according to the exact Mie solution; dotted ones display the corresponding Lorenz profiles, see Eq. (8) and the paragraph above it. Note the different scales of axis on different panels. (c) Size dependence of the peak value of $\sigma_{ext}/\pi a^2$ for the resonances. Open circles show asymptotics $\sigma_{ext}/\pi a^2 \simeq 2(2\ell + 1)/q^2$ valid at $q \to 0$; see Eq. (7).

than ϵ'' related to actual dissipation. It gives rise to the applicability condition

$$\epsilon''(\omega_\ell) \ll \frac{q^{2\ell+1}}{\ell[(2\ell - 1)!!]^2}. \tag{9}$$

The condition is obviously violated (i.e., the Rayleigh scattering is restored) at $q \to 0$. So, to observe the anomalous scattering the particle should be small, but it should not be too small.

We stress that at $\epsilon''(\omega_\ell) \ll 1$ sharp resonances may take place at the conventional Rayleigh scattering too. However, at the Rayleigh scattering for small particles only the dipole resonance is pronounced—all higher order resonances are suppressed dramatically, while for the anomalous scattering this is not the case. There are also dramatic differences between the Rayleigh and anomalous scatterings in the near fields distributions, see below.

To observe the anomalous scattering at least the necessary condition $\epsilon''(\omega_\ell) \ll 1$ should be satisfied. On the other hand usually experiments are carried out with small particles of gold, silver, mercury and platinum [4–6]. For all these metals the condition $\epsilon''(\omega_\ell) \ll 1$ does not hold. A possible candidate for manifestation of the anomalous scattering may be an additively colored crystal of KCl with colloidal potassium particles as scatterers. A sketch of the corresponding experiment has been discussed in Ref. [7]. Another possible example is an aluminum particle in vacuum presented in Refs. [11,12]. For both the metals (K and Al) $\epsilon''(\omega_1) \approx 0.1$. Though the results for the colloidal particles obtained in Ref. [7] should be regarded as estimates, calculations in Refs. [11,12] are rather detailed based upon the actual experimental dependence $\epsilon(\omega)$ for aluminum [14] and rescaling of the effective collision frequency of free electrons due to the size effect. Nevertheless, the issue about experimental observation of the phenomenon requires much more attention and deserves separate consideration lying beyond the framework of the present Letter.

The most appealing manifestation of the anomalous scattering takes place in the near field. The key point is that the dramatic changes in both the modulus and phase of complex amplitude a_ℓ in the vicinity of SLEM resonances at the anomalous scattering relative to that at the conventional Rayleigh approximation brings about the corresponding dramatic changes in the near field structure. Certain discussion of peculiarities of the near field distribution, actually attributed to the anomalous scattering, has already been conducted in Refs. [8,10–12]. It occurs that actually the anomalous scattering affects the near field distribution up to relatively large dissipation rates. For example, while for a particle with $q = 0.3$ the anomalous scattering applicability condition reads $\epsilon'' \ll 0.03$, see Eq. (9) at $\ell = 1$; in reality the complete restoration of the Rayleigh scattering happens only at $\epsilon'' > 0.6$ [8]. For this reason, for the problem in question, special attention should be paid to the nondissipative case. On one hand such a case is the ultimate theoretical limit for the near field amplification caused by the anomalous scattering. On the other, as it just has been said, at finite dissipation the structure of the near field inherits peculiarities of this limit up to not so small values of ϵ''.

The complete description of the near-field structure requires too much space and will be presented elsewhere. Here we discuss just the configuration of the Poynting vector $\mathbf{S}(r, \theta, \varphi)$ at the vicinity of the dipole resonance for a particle with $q = 0.3$. It may be shown that for a plane incident wave propagating along the z axis with vector $\mathbf{E}$ lying in the xz plane all singular points of the field distribution are also lying in the same plane. Creation, motion, and annihilation of various singular points with changes in ϵ are shown in Fig. 2. For the given $q = 0.3$ the exact dipole resonance corresponds to $\epsilon = -2.223\ldots$. Note the global changes of the near field distribution at very small changes in ϵ. It is important that all the singular points are lying in the near field; i.e., all these field peculiarities have a characteristic scale smaller than the wavelength.

The next important feature of the anomalous scattering is the size dependence of the characteristic fields. Far from the resonance frequencies ω_ℓ the characteristic values of the partial electromagnetic modes in the near field and inside the particle are proportional to certain positive powers of q, i.e., vanish at $q \to 0$ [4]. In contrast, at $\omega = \omega_\ell$ the analogous estimates read as follows:

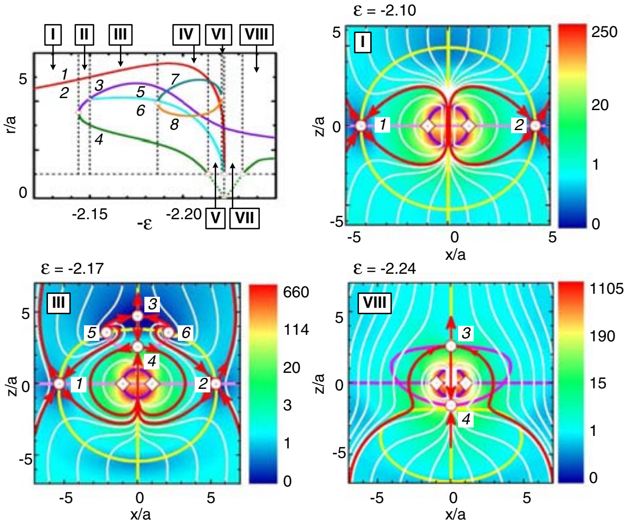

FIG. 2 (color online). Distances from the particle center to various singular points (marked with italic Arabic numerals) of the Poynting vector field as a function of $-\epsilon$ in the vicinity of the dipole resonance at $q = 0.3$ and the corresponding field distributions at several characteristic values of ϵ. Roman numerals designate regions with fixed topological structures of the field. Color density plots show values of modulus of the Poynting vector (log scale) normalized over its value for the incident light. Field lines are shown in white, separatrices in red, null-isoclines $S_\theta(r, \theta) = 0$ in yellow, $S_r(r, \theta) = 0$ in pink, the particle surface in violet, and singular points as open red circles. Note two optical vortices (Arabic numerals 5 and 6). Open red diamonds on the particle surface indicate centers of SLEMs. They correspond to centers of the "optical whirlpools" discussed in [10] at $\epsilon'' \neq 0$. However, our results show that the optical whirlpools exist even at $\epsilon'' = 0$; see, e.g., panel VIII.

$$\frac{{}^{(s,p)}E^{(\ell)}_{r,\theta,\varphi}}{E_0} = O(q^{-(\ell+2)}); \quad \frac{{}^{(s,p)}H^{(\ell)}_{\theta,\varphi}}{E_0} = O(q^{-(\ell+1)}), \quad (10)$$

i.e., ${}^{(s,p)}E^{(\ell)}_{r,\theta,\varphi}$ and ${}^{(s,p)}H^{(\ell)}_{\theta,\varphi}$ diverge at $q \to 0$. Only ${}^{(s,p)}H^{(\ell)}_r$ remain finite and vanish as $q^{\ell-1}$. Here subscripts indicate the correspondent field components in the spherical coordinate frame whose center coincides with that for the particle; superscripts (p) and (s) mean the fields inside the particle and the scattered ones in its vicinity, respectively.

It should be stressed that this singularity has nothing to do with the singular points in the near field distribution discussed above. The near field singularities occur at *finite* q at certain points of space owing to the coordinate dependence of the field. On the contrary, now the singularity happens at $q \to 0$ and affects the entire near field as a whole. Though at $\epsilon'' \neq 0$ the divergence of the fields at $q \to 0$, is stabilized; see Eq. (9) and the paragraph below it, the discussed size dependence may still give rise to very large enhancement of the fields achieved at small but finite q.

The results obtained may open new prospects for controlled giant, highly frequency-sensitive changes of electromagnetic field at nanoscales. Special attention should be paid also to cooperative phenomena in an ensemble of monodisperse particles.

Nonlinear effects are not discussed in the present Letter. Meanwhile there should be plenty of them. The simplest one is related to dependence of the resonance frequencies on amplitude of the SLEMs. Any (even rather weak) dependence of such a kind should result in broad hysteretic loops owing to the giant amplification of the amplitude at the resonance points. This and other nonlinear phenomena will be inspected in our further publications.

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