Metal nanoparticles with sharp corners: Universal properties of plasmon resonances

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Abstract - We predict the simultaneous occurrence of two fundamental phenomena for metal nanoparticles possessing sharp corners with variable curvature: First, the main dipolar plasmonic mode experiences a strong red shift with increasing corner curvature; for large values of the curvature, the resonant frequency is controlled by the apex angle of the corner. Second, the split-off plasmonic mode experiences a strong localization at the corners. Altogether, this paves the way for the tailoring of metal nanostructures providing a wavelength-selective excitation of localized plasmons and a strong near-field enhancement of linear and nonlinear optical phenomena.

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Introduction. – Plasmon excitations of metal nanoparticles, including 2D particles (nanowires), is a vast and hot research area. Potential applications of nano-plasmons span from nano-lasers (spasers) [1–3] to bio-sensors and sensors of single atoms and molecules [4,5]. It is highly important to apprehend the possibilities of the tailoring of plasmonic resonances and the extents of concentration of the light energy deeply on the sub-wavelength scale.

Analytical plasmonic solutions to Maxwell’s equations are available only for metal nanoparticles of simplest 2D and 3D shapes - like circular cylinder, sphere, and ellipsoid [6,7]. They include the optical permittivity of the metal \( \epsilon_M(\omega) = \epsilon'_M(\omega) + i\epsilon''_M(\omega) \), such that \( \epsilon'_M < 0 \) and \( \epsilon''_M \ll |\epsilon'_M| \), and give often strongly degenerated plasmonic resonances. In particular, all plasmonic excitations of a circular cylinder correspond to a single eigenfrequency given by \( \epsilon'_M(\omega) = -1 \).

Using direct numerical methods, serious efforts have been undertaken to ascertain the phenomenology of the plasmonic response of 2D and 3D particles of more complicated shapes [8–11]. The general outcome is that the deviations from the most symmetric shapes result in enriching plasmon spectrum and in the appearance of new red-shifted resonances.

Regardless of the plasmonic effects, the presence of sharp corners and tips is known to lead to the corner singularities, i.e., to a strong local enhancement of electromagnetic fields [12,13]. The impact of these important structural elements on the plasmonic properties of nanoparticles is practically unexplored. In numerical simulations, the sharp surface features are typically rounded to avoid numerical instabilities. In particular, non-rounded \( \pi/2 \)-corners lead to the divergence of numerical methods for \( \epsilon_M \rightarrow -3 \) [14]. Classical mathematical foundations of the plasmonic theory [15,16] concern sufficiently smooth (Lyapunov) surfaces. Only recently a serious attempt has been made to overcome this restriction [17].

Experimentally, the presence of sharp features of metal nanoparticles is far from exotic. Modern chemical methods for the production of such particles are able to provide almost atomically sharp edges in the crystallographic directions [18–20]. The synthesis of metal nanostars has allowed recently to strongly enhance the near fields at the plasmonic resonance [21].

In this letter, we predict and analyze the decisive impact of corners of metal nanoparticles on fundamental plasmonic properties. Both the spectrum and the spatial
structure of the plasmonic modes are strongly affected by the corners showing simple and universal features.

**Basics.** – We employ one of the most efficient approaches to the description of plasmonic resonances—the method of integral equations for the amplitude of the surface charge density $\sigma(r)$ [22,23]. Applicable to metallic particles possessing sufficiently smoothed surfaces in the quasi-static approximation, it treats the plasmonic eigenproblem as a geometric issue. The real resonant values of the optical permittivity $\varepsilon_j$ depend only on the shape of the particle, while the corresponding eigenfunctions $\sigma_j(r)$ are scaling invariant. The knowledge of the eigenmodes allows to determine the width of the resonance, the polarizability of the particle, near fields, etc., using a perturbation routine. The reduction of the dimension of the problem to be solved strongly enhances the capability of numerical methods.

In the 2D case, the eigenproblem to be solved reads:

$$\int_L K(r, r’) \sigma_j(r’) \, dl’ = \Lambda_j \sigma_j(r), \quad r, r’ \in L, \quad (1)$$

where the line $L$ is the boundary of the particle, $dl$ is the length element along $L$ and $\Lambda_j = (\varepsilon_j + 1)/(\varepsilon_j - 1)$ is the eigenvalue. The kernel $K$ is real and is given by

$$K(r, r’) = \frac{n \cdot (r - r’)}{\pi (r - r’)^2}, \quad (2)$$

where $n = n(r)$ is the unit vector of the external normal. Generally, eq. (1) gives an infinite sequence of the modes.

The integral eigenproblem for $\varepsilon_j$ and $\sigma_j(r)$ possesses important general features [23]. The total modal charge is zero, \( \int_L \sigma_j(r) \, dl = 0 \). Since the kernel is not symmetric, \( K(r, r’) \neq K(r’, r) \), the eigenproblem is not Hermitian. Thus, one has to employ additionally the eigenfunctions $\tau_j(r)$ of the adjoint problem with the transposed kernel \( K’(r, r’) \) and the orthogonality relation \( \int_L \sigma_j(r) \tau_{j’}(r) \, dl = 0 \) for $j \neq j’$. In the 2D case, the eigenvalues appear in twin pairs $\varepsilon_j, \varepsilon_j^{-1}$.

We specify the boundary line $L$ by the polar-angle dependence of the radius, $|r|(\varphi) = r(\varphi)$. To investigate the impact of corners, we employed different parametrizations of $r(\varphi)$ with variable corner-curvature radius $\rho_c$ and apex angle $\theta_a \leq \pi/2$. The simplest one is given by

$$r = \frac{r_0(\rho + 1)}{\sqrt{\cos^2 \varphi + a^2 \sin^2 \varphi} + \sqrt{a^2 \sin^2 \varphi + p^2 \cos^2 \varphi}}, \quad (3)$$

where $r_0 = r(0)$ is the large half-diameter, $a = \cot(\theta_a/2)$, and $1 \leq p < \infty$. It gives a smoothed rhombus with the sharp apex angle $\theta_a$ and the normalized corner curvature $\kappa_c = r_0/\rho_c = \cot^2(\theta_a/2)(p - 1 + p^{-1})$ growing linearly with $p$ for $p \gg 1$, see also fig. 1(a). The case $p = 1$ corresponds to an ellipse with the axes ratio of $a$. Another parametrization, illustrated by fig. 1(b), is a smoothed equilateral triangle ($\theta_a = \pi/3$) transferring to the circle for $\rho_c = r_0$. The kernel $K(r, r’) = r(\varphi), r(\varphi’)$, and $dr/d\varphi$; it peaks at the corners with $K(r_c, r_c) = 1/2\pi\rho_c$.

**Resonant permittivities.** – The solid lines in Fig. 2. show the dependences $\varepsilon_1(\kappa_c)$ for the lowest dipolar branch and several values of the apex angle $\theta_a$ of the rhombus on a semi-logarithmic scale. The starting values of $\varepsilon_1$ correspond to the known plasmonic solutions for the elliptic cross-section. The increase of the corner curvature $\kappa_c$ results in a strong decrease of the resonant permittivities (i.e., in strong red shifts of the resonant frequencies in accordance with the Drude-like dependences $\varepsilon_M(\omega)$) for all values of $\theta_a$. This decrease persists for $\kappa_c \gtrsim 10$, when the shape is already settled down and the increasing sharpness of the corners remains the only variable feature. The dotted line is plotted for the triangular parametrization, $\theta_a = \pi/3$. When $\kappa_c$ increases, it approaches quickly the solid line corresponding to a rhombus with the same $\theta_a$. For $\kappa_c \rightarrow 1$, the dotted line and the solid line for $\theta_a = \pi/2$ tend to 1: This is the limit of the circular cross-section with $\varepsilon_j = -1$. We have made sure also that different types
of smoothing with the same $\kappa_c$ give essentially the same results for $\kappa_c \gg 1$.

The dipolar branches $\varepsilon_j(\kappa_c)$ with $j \geq 2$ are well separated from the main dipolar branch $\varepsilon_1(\kappa_c)$ for $1 \ll \kappa_c \lesssim 10^3$, so that $|\varepsilon_1 - \varepsilon_{2,3}| \approx |\varepsilon_1 + 1|$. This makes the selective excitation of the main branch possible. At the same time, the vicinity of the point $\varepsilon = -1$ is always filled up with the spectrum.

The horizontal dashed lines in fig. 2 indicate the critical values $\varepsilon_c = 1 - 2\pi/\theta_0$, which correspond to non-integrable field singularities for a perfect single corner with the apex angle $\theta_0$ [13]. Obviously, the branch $\varepsilon_1(\kappa_c)$ cannot cross the corresponding horizontal line. At the same time, the tendency of approaching the critical values is clearly seen, especially for not very small values of $\theta_0$. This approaching strongly slows down with increasing $\kappa_c$ so that the distances $\varepsilon_1(\kappa_c, \theta_0) - \varepsilon_c(\theta_0)$ remain larger than (0.2–0.8) even for $\kappa_c \approx 10^3$, i.e., for non-realistic sub-atomically sharp corners. Realistic values of the normalized corner curvature $\kappa_c = r_0/\rho_c$ can hardly exceed $10^2$–$10^3$, see also the discussion part.

**Plasmonic eigenfunctions.** – Next, we analyze the impact of varying the corner curvature on the spatial structure of the eigenfunction $\sigma_1(\mathbf{r})$, representing the surface charge density for the lowest dipolar mode. When using the polar angle $\varphi$, it is practical to employ the angular charge density $\sigma_j(\varphi) = \sigma_j(\mathbf{r}(\varphi))d\varphi/d\varphi$, such that $\sigma_j(\varphi)d\varphi$ gives the charge differential. Owing to the non-Hermitian nature of the plasmonic eigenproblem, normalization of $\sigma_j(\varphi)$ is a matter of convenience. Our first choice is $\sigma_j(0) = 1$.

Consider the representative case of a rhombus with $\theta_0 = \pi/3$; it corresponds to the non-degenerate branch $\varepsilon_1(\kappa_c)$. The solid lines in fig. 3(a) show the dependence $\sigma_1(\varphi)$ for three values of $\kappa_c$. All the necessary properties of the spatial symmetry are fulfilled. The sharp corners $\varphi = 0$ and $\pi$ are charged, while the obtuse corners $\varphi = \pm \pi/2$ are uncharged. Importantly, the charge distributions sharply peak at $\varphi = 0$ and the angular half-width of the peak is about $\kappa_c^{-1}$. More precise, the FWHM of the peak is $\approx 2.5/\kappa_c$ for $\kappa_c \gg 1$. Outside the close vicinities of $\varphi = 0$ and $\pi$, the charge density $\sigma_1(\varphi)$ tends to zero for $\kappa_c \to \infty$. Thus, the localization of the surface charge at the sharp corners occurs with increasing corner curvature. Remarkably, the eigenfunction $\sigma_1(\varphi)$ changes its sign between the charged and uncharged corners, and the corresponding zero points move towards the charged corners with increasing $\kappa_c$. This feature is not dictated by the symmetry properties. The higher dipolar eigenmodes $\sigma_{2,3,\ldots}(\varphi)$ also show localization at the sharp corners; far from them they possess a more complicated oscillatory structure.

Being useful to exhibit the angular localization, the chosen normalization is inconvenient in other respects: The value of the localized charge decreases as $1/\kappa_c$, and the non-localized charge distributed outside the corner areas becomes hidden. It is useful to consider the function $\kappa_c\sigma_1(\varphi, \kappa_c)$ whose localized part is expected to look like the Dirac $\delta$-function.

Figure 3(b) shows in detail the negative tail of the function $\kappa_c\sigma_1(\varphi, \kappa_c)$ for the same rhombus ($\theta_0 = \pi/3$) and several large values of $\kappa_c$. The reduced angular interval $[0, \pi/2]$ is fully sufficient for our analysis owing to the symmetry properties. All shown curves are well outside the peak area, $\varphi \gg \kappa_c^{-1}$. We see that after a very sharp initial drop, the function $\kappa_c\sigma_1(\varphi, \kappa_c)$ changes its sign at the point $\varphi_0(\kappa_c)$, reaches a pronounced minimum at $\varphi_{\min}(\kappa_c)$, and grows then slowly up to the second zero point, $\pi/2$. Both characteristic angles, $\varphi_0(\kappa_c)$ and $\varphi_{\min}(\kappa_c)$, tend to 0 for $\kappa_c \to \infty$, while the minimum value of $\kappa_c\sigma_1(\varphi_{\min}, \kappa_c)$ decreases steadily with increasing $\kappa_c$. Far enough from the charged corner, all curves practically coincide with each other showing a universal regular behavior. Within the interval $[0, \pi/2]$, see fig. 3, the total positive (localized) charge, remains comparable with, but not equal to, the total negative (delocalized) charge. This occurs in the whole range of $\kappa_c$. Variation of the apex angle $\theta_0$ does not change this feature.

Thus, the dipolar eigenfunctions $\sigma_j(\varphi)$ possess comparable localized and delocalized components for $\kappa_c \gg 1$. The localized components show a complicated behavior in the limit $\kappa_c \to \infty$. It cannot be described by the singular function $\delta(\varphi)$ alone. The dip in fig. 3(b), which grows steadily in the amplitude and approaches zero, must be responsible for an additional singular contribution. The slowness of the transition to the limit $\kappa_c \to \infty$ for $\sigma_1(\varphi, \kappa_c)$ correlates with that for $\varepsilon_1(\kappa_c)$.

**Observable properties.** – What is the impact of the charge localization on the observable characteristics of the 2D particles, such as the polarizability and the near-field enhancement? First, we determine the surface charge density $\sigma(\mathbf{r})$ induced by an external light electric field of the amplitude $E_0$. Expanding $\sigma$ by the eigenfunctions $\sigma_j$ and using the orthogonality relation $\langle \sigma_j \sigma_j' \rangle \propto \delta_{jj'}$, where $\langle \cdots \rangle$ means the integration along $L$, one can calculate the expansion coefficients [23]. As a function of the light frequency $\omega$, the $j$-th coefficient is proportional to the factor $|\varepsilon_j - \varepsilon_M(\omega)|^{-1}$; it peaks sharply at the eigenfrequency $\omega_j$ such that $\varepsilon'_M(\omega_j) = \varepsilon_j$ provided that
Fig. 4: (Colour on-line) (a) The product \(\xi(0)\xi'_{\text{M}}\) vs. the normalized corner curvature for the rhombus with different values of \(\theta_a\); the dotted line is a linear fit. (b) The ratio \(\xi(\delta r)/\xi(0)\) vs. \(\delta r/\rho_c\) for \(\theta_a = \pi/3\); the dotted line, \((1+\delta r/\rho_c)^{-3}\), is a Coulomb fit.

\[\varepsilon_{\text{M}}' = \left|\varepsilon_{\text{f}}\right|\]. As the lowest value \(\varepsilon(\kappa_c)\) is well separated from higher eigenvalues, we restrict ourselves to a single resonant term. In this case we have

\[
\sigma(r) = \frac{i(1-\varepsilon^2)}{4\pi\varepsilon_{\text{M}}'} \times \left(\frac{\tau_1(\mathbf{E}_0 \cdot \mathbf{n})}{\tau_1\sigma_1}\right) \times \sigma_1(r). \tag{4}
\]

The right-hand side does not depend on the choice of the normalization of \(\sigma_1(r)\) and \(\tau_1(r)\). With these eigenfunctions known, one can calculate any linear characteristic of the plasmon resonance, including the dipole moment, polarizability, polarization properties, extinction cross-section, and near fields. A similar procedure is applicable to the normalizations of \(1/\varepsilon\).

Consider now the upper limit of the corner curvature parameter \(\kappa_c = r_0/\rho_c\). The value of \(\rho_{\text{c,n}}\), compatible with the notion of bulk optical permittivity, is \(\sim 1\) nm [24]; smaller values cause additional losses. The size \(r_0\) has to be considerably smaller than the light wavelength to avoid the retardation effects [7]. Most probably, the latter restriction is not severe — owing to the charge localization at the corners, there should not be strong modification of our theory for \(r_0 = \lambda\). We can expect thus that \(\kappa_{\text{c,n}}\) is of practical interest.

While the values \(\kappa_c \gg 10^3\) are of no practical importance, the law describing the behavior of \(\varepsilon(\kappa_c)\) for \(\log \kappa_c \to \infty\) is of principal interest. Hopefully, this law can be established using the method of [17].

Conclusions. — We have shown that the apex angle \(\theta_a\) and the normalized corner curvature \(\kappa_c\) control the lowest plasmonic resonances for single 2D metal nanoparticles possessing sharp corners, \(\kappa_c \gg 1\). Under fairly weak restrictions, the full shape of the particle is of minor importance in this case. Being practically unattainable, the perfect-corner limit \(\kappa_c \to \infty\) sets, nevertheless, significant restrictions on the plasmonic frequencies. The lowest resonant frequency of the dipolar mode is strongly separated from the other frequencies, and the separation grows with decreasing \(\theta_a\). The corresponding plasmonic eigenfunction experiences progressive localization at the sharp corners with increasing \(\kappa_c\). Altogether, it makes the selective resonant excitation of the localized states possible providing efficient and controllable near-field enhancement.
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