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Localized plasmons in conductive nanoparticles: surface plasmon resonance method

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Localized plasmons in small metallic and conductive particles are considered on the basis of the classical electrodynamic approach and an approximate approach based on the surface plasmon resonance method. The results based on the quasi-static integral equation for the surface charge density are also presented. Approximate analytical results for resonant frequencies are presented. It is shown that the approximate approach gives good accuracy in the case of small particles with sizes of the order of several nm.

Keywords: localized plasmons, surface conductivity, graphene, fullerenes, integral equations.

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Introduction

Metallic and conducting nanoparticles (specifically, gold ones), fullerenes, and carbon nanotubes (CNTs) are used widely in medicine, medical physics, and physics in general as objects for interaction with laser beams [1–5]. Conducting nanoparticles (nanoclusters) resemble a molecule containing a multitude of atoms that share conduction electrons [5–8]. The size (radius) of such clusters may vary from one nanometer (fullerenes C28 and C60) to tens and even hundreds of nanometers. Atoms in such clusters may be located on their surface (fullerenes, CNTs, graphene) or in the bulk (metallic nanoparticles). A rigorous approach to solving the problem of interaction of particles with sizes on the order of 1 nm (meta-atoms) with an electromagnetic wave (photoionization) requires solving a quantum problem with the wave vector potential introduced into the Hamiltonian. However, the classical approach is sufficient to examine excitations with frequencies that do not exceed optical ones. This approach is quite accurate for conducting particles with sizes on the order of 10 nm and larger ones (e.g., gold nanoparticles), since the frequencies of the resulting localized plasmons (LPs) fall within the optical range [1–3]. In the case of metallic spherical particles and particles in the form of a rectangular parallelepiped, the simplest problem is reduced to the problem of an electron in a quantum box of the corresponding shape. The wave function and energy for a cubic box with infinitely high walls are

$$\psi(\mathbf{r}) = A\sin(n_x\pi x/a)\sin(n_y\pi y/a)\sin(n_z\pi z/a),$$

$$E_{n_x n_y n_z} = \pi^2\hbar^2(n_x^2 + n_y^2 + n_z^2)/(2m_e a^2).$$

Adjusted for a finite wall height on the order of several electronvolts, the levels decrease slightly. The energies of the lowest levels at $a = 10$ nm are $\pi^2\hbar^2/(2m_e a^2) = 0.003$ eV (on the order of $k_B T$ at room temperature); i.e., they correspond to frequencies of the infrared (IR) range. Thermal fluctuations induce overlapping in the line spectrum, and a quantum box of this kind may be regarded as a particle with a continuous spectrum of electrons from conduction band zero to the Fermi energy; i.e., the methods of plasmonics may be used to calculate the oscillation spectrum. The level energies in particles with a size on the order of one nanometer are two orders of magnitude higher and correspond to the soft ultraviolet (UV) range. The quantum approach is relevant here. Fullerenes, CNTs, and graphene fragments may be characterized as conducting shells [9]. Owing to the small size of fullerenes (approximately 1 nm), their resonant frequencies lie in the UV range. At these quantum energies, the bonds of –electrons with carbon atoms are disrupted, and the common model of conductivity becomes inapplicable to graphene [10] and fullerene. The plasma shell model should be used instead [9]. The number of atoms may vary from several tens (fullerenes C28 and C60) to hundreds of thousands ($3.56 \cdot 10^5$ for a copper nanoparticle with radius $r = 10$ nm). The considered nanoclusters support LPs (resonant electromagnetic oscillations with complex resonant frequencies [1–8]). It is often needed to match the natural resonant frequencies of these particles with the frequencies of excitation lasers. The rate of decay of free oscillations in LPs excited by a short laser pulse is inversely proportional to the quality factor. Nanoparticles with plasmons may also be used as meta-atoms in photonic (electromagnetic) crystals.

The classical Mie solution is applicable to the problem of excitation of both metallic and dielectric spherical particles. In the case of fullerenes, an approach based on the introduction of shell conductivity was examined in [9]. In addition to approaches relying on classical electrodynamics, quantum

chemistry methods, which serve as a basis for calculations in standard software packages such as Gaussian 9, are often used.

In the present study, the surface plasmon resonance (SPR) method, wherein volume resonance emerges as a superimposition of resonance conditions onto the motion of a surface plasmon (SP) along the surface of a particle, is used. Conditions of a phase incursion divisible by 2π along closed SP trajectories and resonance conditions in motion along open trajectories (e.g., vanishing of current at the ends of a CNT) are possible. Since resonances often arise near the SPR frequency, where an SP is decelerated strongly, the obtained results correspond closely to the quasi-static approach to determining the LP frequencies [1–3], and the field itself is quasi-static in nature. It is demonstrated below that the SPR-based approach yields frequencies that also agree closely with the exact solution in the case of a significant SP deceleration. In metals, it is typically observed near the SPR frequency: $\omega)_{spr} = \sqrt{\omega_p^2/(\varepsilon_L + 1) - \omega_{co}^2} \approx \omega_p/\sqrt{\varepsilon_L + 1}$. The plasma frequency and the lattice permittivity for silver are $\omega_p = 1.57 \cdot 1)^{16}$ Hz and $\varepsilon_L \approx 10$; thus, $\omega_{spr} = 47 \cdot 10^{15}$ Hz, and the wavelength is 400 nm. The permittivity of metal is written as $\varepsilon(\omega) = \varepsilon_L - \omega_p^2/(\omega^2 - i\omega\omega_c)$, where $\omega_p^2 = e^2 N_e/(m_e\varepsilon_0)$ is the plasma frequency squared. Note that the Lorentz term starts to depend on frequency at the polarization frequencies of the crystal lattice (normally in the UV range), but it also includes interband transitions [2] at somewhat lower frequencies. Copper has $\omega_p = 1.785 \cdot 10^{16}$ Hz and $\varepsilon_L \approx 20$, and we obtain $\omega_{spr} = 3.7 \cdot 10^{15}$ Hz and a wavelength of 486 nm. The LP frequencies are slightly lower than the SPR frequencies, and losses contribute to a reduction in the SPR frequency. The LP frequencies depend on permittivity of the ambient medium of particles (e.g., a transparent liquid). Collision frequencies ω_c for small particles (significantly smaller than electron mean range λ_e) are usually higher than the frequencies for bulk materials. In this case, scattering is induced mostly by collisions with the shell. In the quasi-static approach ($\nabla \cdot \mathbf{E} = 0$), bulk transverse plasmons with dispersion $\omega = \sqrt{\omega_{spr}^2 + k_0^2 c^2}$ and bulk longitudinal plasmons with dispersion $\varepsilon(\omega, \mathbf{k}) = 0$ are found in particles [2]. The spatial dispersion is essential for such plasmons, and they are not considered here.

Since the SPR-based approach is fairly simple to implement and yields simple analytical equations, it holds promise for the study of particles of a complex arbitrary shape. However, the shape of their closed surface should allow one to isolate three closed paths on the surface in different planes. Spherical, ellipsoidal, cylindrical, dumbbell-shaped, and torus-shaped particles (as well as a number of other particle types) fit this definition. Of interest are both the problem of excitation by a given field $\mathbf{E}_{in}(\mathbf{r}) = \mathbf{E}_0 \exp(-i\mathbf{kr})$ with time dependence $\exp(i\omega t)$ and the problem of free (natural) oscillations, where complex frequencies $\omega_m = \omega_m' + i\omega_m''$ are sought. The typical quality factors of such oscillations are low. The second problem is considered in the present study.

Electrodynamic formulation of the problem

The vector potential of a scattered or intrinsic field has the form

$$\mathbf{A}(bfr) \int\limits_V G(\mathbf{r} - \mathbf{r}', k_0)\mathbf{J}(\mathbf{r}')d^3r', \tag{1}$$

where Green's function (GF) $G(\mathbf{r}, k_0) = 4\pi|\mathbf{r}| \exp(-ik_0|\mathbf{r}|)$, $k_0 = \omega/c$ — wavenumber, $\mathbf{r}'$ — source point, and $\mathbf{r}$ — observation point. The fields from (1) are expressed as

$$E(\mathbf{r}) = E_{in}(\mathbf{r}) + (ik_0)^{-1}\eta_0 \left(k_0^2\mathbf{A}(\mathbf{r}) + \nabla \otimes \nabla\mathbf{A}(\mathbf{r})\right), \tag{2}$$

$$\mathbf{H}(\mathbf{r}) = \mathbf{H}_{in}(\mathbf{r}) + \nabla \times \mathbf{A}(\mathbf{r}), \tag{3}$$

where $\eta_0 = \sqrt{\mu_0/\varepsilon_0}$ and excitation fields are introduced. Polarization current density $\mathbf{Jr} = i\omega\varepsilon_0(\varepsilon(\mathbf{r}) - 1)\mathbf{E}(\mathbf{r})$ within particle volume V is found in (1). These equations allow one to formulate several types of volume integral equations (IEs) and integro-differential equations (IDEs) both for scattering problems and for problems of free (natural) oscillations in arbitrary nanoparticles [11]. In the present study, we examine free oscillations in homogeneous metallic nanoparticles, which are characterized by Drude–Lorentz permittivity $\varepsilon(\omega) = \varepsilon_L(\omega) - \omega_p^2/(\omega^2 - i\omega\omega_c)$, and carbon nanoclusters. Lorentz term ε_L may be considered to be constant and positive in the IR and optical ranges. Specifically, silver has $\varepsilon_L = 9.3$, plasma frequency (PF) $\omega_p = 1.57 \cdot 10^{16}$ Hz, and collision frequency (CF) $\omega_c = 3.46 \cdot 10^{13}$ Hz. Thus, the DC conductivity of silver is $\sigma_0 = \omega_p^2\varepsilon_0/\omega_c = 6.29 \cdot 10^7$, and real permittivity component $\varepsilon'(\omega) = 0$ at frequency $\omega = 5.148 \cdot 10^{15}$Hz. It is often assumed below that the CF is zero (i.e., dissipation is neglected, and only the radiation losses are taken into account). In the case of fullerenes and CNTs, integral (1) should be considered as an integral over their surface of surface current density $\mathbf{j}(\omega) = \sigma(\omega)\mathbf{E}_\tau(\omega)$. Specific (volume) conductivity $i\omega\varepsilon_0(\varepsilon(\mathbf{r}) - 1)$ should then be substituted with surface conductivity σ, which implies the introduction of an IE for surface electric field $\mathbf{E}_\tau(\omega)$ or surface current density $\mathbf{j}(\omega)$. The use of IEs and IDEs leads to rather complex and implicit algorithms.

In what follows, we compare a rigorous approach involving the use of Eq. (1) with IEs and IDEs to an approximate approach based on the examination of an SP with SPR. The quasi-static approach [2,3] and the results obtained this way are also considered. The SPR approximation allows one to obtain simple explicit formulae for resonant frequencies. An approximate approach for conducting shells may be constructed based on the equations for surface E-plasmons $k_s = k_0\sqrt{1 - 4/\varsigma^2(\omega)}$ and H-plasmons $k_s = k_0\sqrt{1 - \xi^2(\omega)/4}$, where $\xi(\omega) = \sigma(\omega)\sqrt{\mu_e/\varepsilon_0}$ is the normalized surface conductivity of the shell [12]. If a metal

particle is positioned in a dielectric, the Zenneck dispersion relation (DR) [2,13] for a transverse E-plasmon yields SP propagation constant $k_s = k_0\sqrt{\varepsilon(\omega)\varepsilon_d(\omega)/[\varepsilon(\omega)+\varepsilon_d(\omega)]}$. Here, $\varepsilon_d(\omega)$ is the permittivity of the dielectric material. An E-plasmon is an electromagnetic wave without a magnetic field component along the direction of its propagation. An H-plasmon is an electromagnetic wave without an electric field component along the direction of its propagation. Note that an H-plasmon for a bulk particle may exist only if it has magnetic properties. The given DRs are strictly valid at sufficiently large curvature radii (for flat conducting surfaces, such as graphene) and for a two-dimensional electron gas (2DEG). However, with strong deceleration, they may also be used for small particles. Next, we introduce propagation constants k_s along a certain closed arc s with perimeter L_s on the surface of a particle or an open line (in the case of particles in the form of nanowires). By virtue of closedness, we obtain equations $k_s l_s = 2k\pi$, $k = 1, 2, \ldots$, or $\omega\sqrt{1-4/\xi^2(\omega)} = 2k\pi C/L_s$, $\omega\sqrt{1-\xi^2(\omega)/4} = 2k\pi C/L_s$, $k = 1, 2, \ldots$. They are the ones setting the resonance conditions. Fullerene C60 thus has $L_s = 2.25$ nm; i.e., even with deceleration factors on the order of 100, the minimum possible frequencies lie in the UV range where normal surface conductivity becomes irrelevant. At UV frequencies with quanta energies greater than 3 eV, all carbon atoms are ionized. Therefore, when a fullerene shell is exposed to hard UV radiation, it may be regarded as plasma in which each atom gives up one, four, or even all six electrons. Such a shell is characterized as a 2DEG [9]. Lower-frequency spectra correspond to fullerenes with larger radii and greater numbers of atoms. The normalized surface conductivity for a sphere with radius r, surface area $S = 4\pi r^2$, and surface density of carbon atoms $n_S = 3.82\cdot 10^{19}\,\mathrm{m}^{-2}$ is $\xi = ik_0 t(1-\omega_p^2/(\omega^2 - i\omega\omega_c))$. Here, $\omega_p^2 = e^2 n_S/(\varepsilon_0 m_e t)$, where t is the shell thickness that is on the order of 0.1 nm (the size of an atom). The exact thickness of a graphene sheet is $t = 0.34$ nm (the distance between graphene sheets in alpha graphite). In the $\omega \sim \omega = 1.2\cdot 10^{16}$ Hz plasmonics region, the conductivity is low: $xi \approx -i\omega(t/c)(\omega_p^2/\omega_2) \sim -i0.3\cdot 10^{-2}$, therefore, the deceleration factor $n = \sqrt{1-4/\xi^2(\omega)}$ of plasmons does not exceed 600, and resonant frequencies may fall within the UV range.

Quasi-static formulae

Quasi-static solutions of Maxwell's equations correspond to localized plasmons; i.e., it is assumed below that $k_0 r = \omega r/c \ll 1$, where r is a certain characteristic particle size. It is convenient to introduce frequency $\omega_r = c/r$, which corresponds to the inverse time of light travel over distance r, and characteristic frequencies $\omega_0 = \omega_p/\sqrt{\varepsilon_L}$, $\tilde{\omega}_p = \omega_p/\sqrt{\varepsilon_L+1}$ of volume $\varepsilon(\omega_0) = 0$ and surface $\varepsilon(\tilde{\omega}_p) = -1$ plasmon resonances, respectively. Frequencies ω_0 and $\tilde{\omega}_p$ are close, and all resonances are grouped around them. The formulae may be written with either of these two frequencies. Dissipation is neglected here. If it is taken into account, we obtain

$$\omega_0 = \sqrt{\omega_p^2/\varepsilon_L - \omega_c^2} \approx \omega_p/\sqrt{\varepsilon_L} - \omega_c^2\sqrt{\varepsilon_L}/(2\omega_p),$$

which implies that these frequencies become slightly lower. At a radius of 1 nm, $\omega_r = 3\cdot 10^{17}$ Hz; metallic particles with radius $r < 10$ nm always have $\omega_p/\omega_r < 1$. Low-frequency plasmons for CNTs correspond to their lengths L, since their radii are significantly smaller: $r \ll L$. Approximate values of these frequencies are determined from equation $k_0 L\sqrt{1-4/\xi^2(\omega)} = m\pi$, $m = 1, 2, \ldots$ and may fall within the IR range (or even the terahertz range if CNTs are sufficiently long).

The quasi-static equation for a dielectric body is written as $\mathbf{E}(\mathbf{r}) = -\nabla\varphi(\mathbf{r})$, $\varphi(\mathbf{r}) = -\nabla\mathbf{A}(\mathbf{r})$, with $k_0^2\mathbf{A}(\mathbf{r})$ in (2) considered negligible compared to $\nabla\otimes\nabla\mathbf{A}(\mathbf{r})$. Since $\nabla G(\mathbf{r}-\mathbf{r}') = -\nabla' G(\mathbf{r}-\mathbf{r}')$, the action of operator ∇ on $\mathbf{A}(\mathbf{r})$ in (1) results in a volume integral of $G(\mathbf{r}-\mathbf{r}')\nabla'\mathbf{J}(\mathbf{r}')$ plus a surface integral of vector flux — $G(\mathbf{r}-\mathbf{r}')\mathbf{J}(\mathbf{r}')$. This integral on the surface is zero, since $\boldsymbol{\nu}(\mathbf{r})\cdot\mathbf{J}(\mathbf{r}) = 0$. By virtue of the law of conservation of charge, we obtain $\nabla'\mathbf{J}(\mathbf{r}') = -i\omega\varsigma(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')$, where $\varsigma(\mathbf{r})$ is the surface charge density and point $\mathbf{r}$ belongs to the surface. Indeed, there are no volume charges for a homogeneous particle. Therefore, the equation for the normal field component on the surface is

$$\begin{aligned}\boldsymbol{\nu}(\mathbf{r})\mathbf{E}(\mathbf{r}) &= -\nabla\varphi(\mathbf{r})\\ &= -\frac{1}{\varepsilon_0}\oint \boldsymbol{\nu}(\mathbf{r})\nabla G(\mathbf{r}-\mathbf{r}')\varsigma(\mathbf{r}')dr'^2. \qquad (4)\end{aligned}$$

This component E_V in (4) is defined as the double layer potential and undergoes a jump when the observation point crosses the surface (the particle boundary). Denoting the integral in (4) as I, we obtain $\varepsilon_0 E_V^+ = \varepsilon_0 I + \varsigma/2$ and $\varepsilon_0 E_V^- = \varepsilon_0 I - \varsigma/2$. Defining the jump, we find $\varsigma = 2\varepsilon_0 I(\varepsilon-1)/(1+\varepsilon)$. Thus, the quasi-static problem may be formulated based on the quasi-static IE for surface charge density $\varsigma(\mathbf{r})$ [2,3]:

$$\varsigma(\mathbf{r}) = 2\frac{1-\varepsilon}{1+\varepsilon}\oint_S \boldsymbol{\nu}(\mathbf{r})\nabla G(\mathbf{r}-\mathbf{r}', k_0)\varsigma(\mathbf{r}')d^2r'. \qquad (5)$$

Equation (5) characterizes a quasi-stationary LP surface charge distribution [2,3]. Its frequency dependence is specified by dependence $\varepsilon(\omega)$. A jump in the normal component of the electric field strength is observed in transition through the particle surface: $E_V(\mathbf{r}+0) = \varepsilon E_V(\mathbf{r}-\mathbf{0})$. Since the surface charge density is related to the field strength as $\varsigma(\mathbf{r}) = \varepsilon_0(1-1/\varepsilon)E_V(\mathbf{r}+0)$, an IE may also be formulated for it. Condition $\varepsilon \approx -1$ is typical for plasmonics, and the integral at frequency $\tilde{\omega}_p$ should then be close to zero for a non-zero charge distribution to exist. Equation (5) allows one to find the frequencies of quasi-static resonance.

Let us consider a spherical particle. The GF at $r > r'$ in a spherical coordinate system is written as [14]

$$G(\mathbf{r}-\mathbf{r}', k_0) = \frac{k_0}{4\pi i}\sum_{n=0}^{\infty}(2n+1)P_n(\cos(\gamma)) \times \psi_n(k_0 r')\xi_n^{(2)}(k_0 r),$$

$$\partial_r G(\mathbf{r}-\mathbf{r}', k_0) = \frac{k_0}{4\pi i}\sum_{n=0}^{\infty}(2n+1) \times P_n(\cos(\gamma))\psi_n(k_0 r')\partial_r\xi_n^{(2)}(k_0 r),$$

$$P_n(\cos(\gamma)) = \cos(\theta)\cos(\theta') + \sin(\theta)\sin(\theta')\cos(\varphi-\varphi').$$

Taking the distribution of surface charge density $\varsigma_{nm}(\mathbf{r}) = P_n^m(\theta)\exp(-im\varphi)$, we see that this function satisfies IE (5). Indeed, performing integration with expansion of Legendre polynomials in associated Legendre functions, we obtain

$$1 = \frac{1-\varepsilon}{1+\varepsilon}\frac{-2ik_0 r^2}{2n+1}\psi_n(k_0 r')\partial_r\xi_n^{(2)}(k_0 r).$$

This is the equation for resonant frequencies. It can be seen that they are also degenerate in m. This yields the following expression for permittivity: $\varepsilon = -(1-\alpha_n)/(1+\alpha_n)$ (or $\varepsilon = -1+2\alpha_n/(1+\alpha_n)$). Here,

$$\alpha_n = -2i(k_0 r^2/(2n+1))\psi_n(k_0 r')\partial_r\xi_n^{(2)}(k_0 r). \quad (6)$$

Thus, spectral frequencies (6) condense towards SPR frequency $\tilde{\omega}_p$.

The LP spectrum [2,3] for metallic spherical particles with permittivity $\varepsilon(\omega) = \varepsilon_L - \omega_p^2/\omega^2$ is characterized well by quasi-static formula

$$\omega_n = \omega_p/\sqrt{\varepsilon_L + 1 + 1/n - 4k_0 r/5}, \quad n = 1, 2, \ldots. \quad (7)$$

The expression in terms of $\tilde{\omega}_p$ and ω_r is

$$\omega_n \approx \tilde{\omega}_p\left(1 - \frac{1/n - 4(\tilde{\omega}_{p/\omega_r})/5}{2(\varepsilon_L+1)}\right), \quad (8)$$

i.e., the frequencies condense to $\tilde{\omega}_p$, and relation (8) is close to (6) at high n. To introduce dissipation, one needs to perform substitution $\omega_m \to \omega_m + i\omega_c$. It is evident that approximate solutions lead to condition $\varepsilon(\omega) \approx -1$, which translates into $\omega_m \approx \tilde{\omega}_p$. Metals have $\tilde{\omega}_p \sim \omega_p/3$; i.e., this is the optical range.

The approximate frequencies of a metallic sphere in vacuum may also be found by examining the SP motion along a circle of the maximum cross section under the assumption that the propagation constant is characterized by the Zenneck dispersion relation: $k_\varphi = k_0\sqrt{\varepsilon(\omega)/\varepsilon/\omega) + 1}$ [2,13]. With resonance condition $2\pi r k_\varphi = 2m\pi$ imposed, we find deceleration $\sqrt{\varepsilon(\omega_m)/(\varepsilon(\omega_m)+1)} = \alpha_m = m\omega_r/\omega_m$. Since there are three mutually perpendicular maximum cross sections of the sphere, we have three SP polarizations with the same frequencies (i.e., degeneracy). The value of α_m is large here, so the ratio is fulfilled at $\varepsilon(\omega_m) = -1 - 1/(\alpha_m^2 - 1) \approx -1$ or at $\omega_m = \tilde{\omega}_p/\sqrt{1 + 1/(\alpha_m^2-1)/(\varepsilon_L+1)}$. On the right-hand side of this implicit equation, we substitute ω_m with $\tilde{\omega}_p$:

$$\omega_m \approx \tilde{\omega}_p - \frac{\tilde{\omega}_p}{2(\varepsilon_L+1)(m\omega_r/\tilde{\omega}_p)^2}. \quad (9)$$

One may also write

$$\omega_m = \omega_0\Big/\sqrt{1 + \frac{1}{\varepsilon_L\left[1-(m\omega_r/\omega_m)^{-2}\right]}},$$

$$\omega_m \approx \tilde{\omega}_p\Big/\sqrt{1 + \frac{1}{(\varepsilon_L+1)(m\omega_r/\tilde{\omega}_p)^2}},$$

which agrees with (9). Thus, dependence (9) is close to (7), and the spectral frequencies also condense toward $\tilde{\omega}_p$.

Let us consider a cylindrical particle with height h and radius R. The Green's function in a cylindrical system [14] takes the form

$$G = \frac{1}{4\pi i}\sum_{m=-\infty}^{\infty}\exp(-im(\varphi-\varphi')) \int_0^{\infty}\frac{\exp\left(-\sqrt{\kappa^2-k_0^2}|z-z'|\right)J_m(\kappa\rho)J_m(\kappa\rho')}{\sqrt{\kappa^2-k_0^2}}\kappa d\kappa. \quad (10)$$

If the height is small, $h \ll R$, one may neglect the charge on the side surface and consider only the component $E_{zn} = J\left(\rho k_0\sqrt{\varepsilon}\right)\exp(-in\varphi)$. It satisfies the two-dimensional Helmholtz equation with $\partial_z = 0$. Accordingly, $\varsigma_n(\mathbf{r}) = \varepsilon_0(\varepsilon-1)J_n\left(\rho k_0\sqrt{e}\right)\exp(-in\varphi)$. When (10) is differentiated with respect to z, the following factor emerges: $-i\sqrt{k_0^2-\kappa^2}\,\mathrm{sgn}(z-z')$. We form a functional from (5) by multiplying it by $\varsigma_n(\mathbf{r})$ and integrating over the volume. Since integral

$$I(\kappa) = -i\int_{-h/2}^{h/2}\int_{-h/2}^{h/2}\mathrm{sgn}(z-z')\exp\left(-\sqrt{k^2-k_0^2}|z-z'|\right)dz\,dz'$$

is fairly easy to calculate, further details are omitted here. The integration over angle yields $2\pi\delta_{nm}$; i.e., the sum vanishes. The result is characteristic equation

$$\frac{2(1-\varepsilon)\int_0^{\infty}\int_0^{R}\int_0^{R}I(\kappa)J_n(\kappa\rho)J_n(\kappa\rho')\rho\rho' d\rho d\rho'\kappa d\kappa}{(1+\varepsilon)h\int_0^{R}J_n^2\left(\rho k_0\sqrt{e}\right)\rho dr} = 1. \quad (11)$$

It is approximate, and its accuracy is inversely proportional to height. Rewriting it as $(1-\varepsilon)/(1+\varepsilon) = \alpha_n^2$, we find the resonant frequencies for large α_n^2 values. At large n, the Bessel functions in the numerator of (11)

oscillate and the double integral is small; i.e., α_n^2 is large. It is somewhat more difficult to obtain approximations with account for field variations with height. In the other extreme case $h \gg R$, one may take component $E_{\rho nk} = J_k(\rho k_0\sqrt{\varepsilon})\exp(-ik\varphi)\cos(n\pi z/h)$ only. Let us define

$$\tilde{I}_n(\kappa) = \int_{-h/2}^{h/2}\int_{-h/2}^{h/2} \cos^2(n\pi z/h) \times \exp\left(-\sqrt{\kappa^2 - k_0^2}|z - z'|\right) dz\,dz'.$$

The characteristic equation then takes the form

$$\frac{2(1-\varepsilon)\int_0^\infty\int_0^R\int_0^R \frac{I_n(\kappa)J_k'(\kappa\rho)J_k(\kappa\rho')}{\sqrt{\kappa^2-k_0^2}}\rho\rho' d\rho d\rho'\kappa^2 d\kappa}{\left(1+\frac{(-1)^n}{2n\pi}\right)(1+\varepsilon)h\int_0^R J_k^2\left(\rho k_0\sqrt{\varepsilon}\right)\rho d\rho} = 1. \quad (12)$$

The first few resonant LP frequencies are determined approximately from equation $\sqrt{\varepsilon(\omega_m)/(\varepsilon(\omega_m)+1)} = \alpha_m = mc/(\omega_m R)$; i.e., they are characterized by formula (9) with substitution $r \to R$. At large radii, α_m may assume a moderate value (possibly on the order of unity). This corresponds to a large permittivity $\varepsilon(\omega_m)$ magnitude, which is typical of a low resonant frequency and small indices m. In this case, $\omega_m = m(1 + 1/(2\varepsilon(\omega_m)))c/R$. Let us assume, e.g., that $m = 1$ and $R = 600$ nm. Then $c/R = 5\cdot 10^{14}$ Hz and $\varepsilon = -347.4 - 59i$. Taking $\omega_1 = 5\cdot 10^{14}$ Hz as a first approximation, we find $\omega_1 = 5\cdot 10^{14}(1 - 0.0014 + 0.00024i)$ Hz. This is an IR LP. An increase in m again leads to large α_m, and the spectrum condenses around the plasmon resonance frequency. The losses are low here, since an LP is formed as a resonance of an SP that travels almost at the speed of light and features low losses. The examined particle has another characteristic size $L_s = 4R + 2h$. It may be greater than $2\pi R$, and the first resonant frequencies may be even lower if the $\Omega_m = mc/L_s$ frequency lies in the IR range. To verify this, we write down the resonance condition denoting $\Omega_m = mc/L_s$:

$$\omega_m = \Omega_m\sqrt{1 + [\varepsilon_L - (\omega_p/\omega_m)^2]^{-1}}.$$

If $\omega_p\Omega_m \gg \varepsilon_L$, $\omega_m \approx \Omega_m$. If $\varepsilon_L - (\omega_p/\omega_n)^2 \approx -1$, the square root becomes small, and $\omega_m \approx \tilde{\omega}_p \ll \Omega_m$. Index m is azimuthal for a cylinder with an LP along the circumference. In the case of a plasmon along the diameters and generating lines, this index characterizes radial axial dependences of the fields. Radiation losses are expected to be low at large radii. Let us also consider a cylindrical metallic particle of height h and radius R with two hemispheres with radius R at the ends. The lower LP frequencies of such a capsule may be characterized approximately by equation $\omega_m\sqrt{\varepsilon/(\varepsilon+1)} = \alpha_m = \Omega_m/\omega_m$, $\Omega_m = mc/(R + h/\pi)$. It is the same as (9) if substitution $m\omega_r \to \Omega_m$ is performed. However, modes (9) with substitution $r \to R$ are also possible for this particle.

Rigorous formulae

A rigorous problem for an arbitrary bulk particle may be formulated based on an IE or an IDE [11]. The problem has an analytical solution for a spherical surface. In the case of excitation of a sphere by a plane wave, this is the Mie solution. Using Debye potentials and stitching the fields when modeling a particle with a conducting shell, one may easily obtain the equations for surface LPs in fullerenes for E- and H-modes:

$$\xi\partial_x\psi_n^-(\chi_0) = i\left[f_n\psi_n^+(\chi_0) - \varepsilon\psi_n^-(\chi_0)\right], \quad (13)$$

$$\xi\psi_n^-(\chi_0) = i\left[g_n\partial_y\psi_n^+(\chi_0) - \partial_x\psi_n^-(\chi_0)\right]. \quad (14)$$

Here, $\xi = \sigma\eta_0$, $\chi_0 = k_0 r_0$, r_0 is the particle radius, $\psi_n^-(x) = \sqrt{\pi x/2}J_{n+1/2}(x)$ are Riccati–Bessel functions, $\psi_n^+(x) = \sqrt{\pi x/2}H_{n+1/2}^{(2)}(x)$ are Riccati–Hankel functions, and the coefficients are

$$f_n = \frac{\partial_r\psi_n^-(\chi_0)}{\partial_r\psi_n^+(\chi_0)} = \varepsilon^{1/4}\frac{\chi_0 J_{n-1/2}(\chi_0) - nJ_{n+1/2}(\chi_0)}{\chi_0 H_{n-1/2}^{(2)}(\chi_0) - nH_{n+1/2}^{(2)}(\chi_0)}, \quad (15)$$

$$g_n = \frac{\psi_n^-(\chi_0)}{\psi_n^+(\chi_0)} = \varepsilon^{1/4}\frac{J_{n+1/2}(\chi_0)}{H_{n+1/2}^{(2)}(\chi_0)}. \quad (16)$$

This approach was used in [9] to examine LPs in fullerenes and diffraction off them. Free oscillations for the E_{nm} and H_{nm} modes of spherical particles are characterized [15] by equations

$$\frac{n}{k_0 r}(\varepsilon - 1) + \frac{J_{n-1/2}(k_0 r\sqrt{\varepsilon})}{J_{n+1/2}(k_0 r\sqrt{\varepsilon})} = \sqrt{\varepsilon}\frac{H_{n-1/2}^{(2)}(k_0 r)}{H_{n+1/2}^{(2)}(k_0 r)}, \quad (17)$$

$$\frac{J_{n-1/2}(k_0 r\sqrt{\varepsilon})}{J_{n+1/2}(k_0 r\sqrt{\varepsilon})} = \frac{H_{n-1/2}^{(2)}(k_0 r)}{\sqrt{\varepsilon}H_{n+1/2}^{(2)}(k_0 r)}. \quad (18)$$

Here, $n = 1, 2, \ldots$ is the meridional index corresponding to dependence $P_n^m(\theta)$, and degeneracy with respect to azimuthal index m with dependence $\exp(-im\varphi)$ is observed. Equations (17) and (18) for $n = 1$ may be written as

$$\frac{\sin(k_0 r\sqrt{\varepsilon})}{\sin(k_0 r\sqrt{\varepsilon})/(k_0 r\sqrt{\varepsilon}) - \cos(k_0 r\sqrt{\varepsilon})} = \frac{\sqrt{\varepsilon}k_0 r}{1 + i(k_0 r)} + \frac{1-\varepsilon}{k_0 r} = \alpha, \quad (19)$$

$$\sqrt{\varepsilon}\frac{\sin(k_0 r\sqrt{\varepsilon})}{\sin(k_0 r\sqrt{\varepsilon})/(k_0 r/\sqrt{\varepsilon}) - \cos(k_0 r\sqrt{\varepsilon})} = \frac{k_0 r}{1 + i(k_0 r)} = \beta, \quad (20)$$

or as $\tan(k_0 r\sqrt{\varepsilon})(1-\alpha/(k_0 r\sqrt{\varepsilon})) = -\alpha$ and $\tan(k_0 r\sqrt{\varepsilon})(1-\beta/(k_0 r\varepsilon)) = -\beta/\sqrt{\varepsilon}$. The first relation takes the form $\tan(k_0 r\sqrt{\varepsilon}) \approx \alpha(k_0 r)^3\varepsilon/3$ at $|k_0 r\sqrt{\varepsilon}| \ll 1$ and is fulfilled exactly at $\varepsilon = 0$. Let us rewrite the second equation in the form $\sqrt{\varepsilon}\tan(k_0 r\sqrt{\varepsilon}) = \beta\lfloor(k_0 r\sqrt{\varepsilon})/(k_0 r\sqrt{\varepsilon}) - 1\rfloor$. It is also fulfilled exactly at $\varepsilon = 0$; i.e,. both equations have a degenerate solution $\omega = \omega_0$. These equations do not provide radiation losses. Taking ohmic losses into account, one may write $\omega = \omega_0 + i\omega_c$. A more accurate resonant frequency for (20) with dissipation is

$$\omega_1' = \mathrm{Re}(\omega_1)$$

$$= \omega_0\sqrt{1+\frac{\omega_c}{3\omega_0}\left(3-\frac{(k_0 r)^4}{1+(k_0 r)^2}\right) - \frac{\omega_c^2}{3\omega_0^2}\left(3-\frac{(k_0 r)^3}{1+(k_0 r)^2}\right)}.$$

Here, $k_0 r = \omega_0/\omega_r$ is fairly small; therefore, $\omega_1' \approx \omega_0 + \omega_c/2$. Likewise, we obtain $\varepsilon - (k_0 r)^2\varepsilon^2/9 = 0$ by revising the root in (19). Since the contribution of the second term here is small compared to that of the first, it is sufficient to set the real part of permittivity to zero: $\varepsilon_L - \omega_p^2/(\omega^2+\omega_c^2) = 0$, which yields $\omega' = \omega_0\sqrt{1-\omega_c^2/\omega_0^2} = \omega_0 - \omega_c^2/(2\omega_0)$; i.e., dissipation lifts degeneracy. The next $n = 2$ modes may be called quadrupole ones. Their resonant frequencies without dissipation also satisfy the $\varepsilon = 0$ condition, but differ slightly from ω_0 due to dissipation. Using the expansions of cylindrical functions in (17) and (18), one may demonstrate that the LP spectra condense towards frequency ω_0.

We used the Zenneck dispersion relation obtained for a flat surface to derive some of the formulae for complex particles. Naturally, this is an approximation. However, it yields resonant frequencies for small particles in the SPR region that agree well with the results obtained using other methods (including the exact results for spherical particles). Approximate resonant frequencies in the IR range, where SPs are decelerated slightly, may be less accurate. In any case, such plasmons moving along curved surfaces may emit energy, shifting the resonant frequency and reducing the quality factor. In the case of IR laser excitation, a low quality factor is not a critical parameter. It is preferable to verify the obtained results against rigorous formulae. Let us consider symmetric mode E_{0n} of a metallic cylinder with the electrical field in it assuming the form $E_z = E_0 J_0(\rho\sqrt{k_0^2\varepsilon - k_{zn}^2})\cos(k_{zn} z)$, $E_\rho = ik_z E_0 J_1(\rho\sqrt{k_0^2\varepsilon - k_{zn}^2})\cos(k_z z)/\sqrt{k_0^2\varepsilon - k_{zn}^2}$, $E_\varphi = 0$ where $k_{zn} = n\pi/h$. Inside, it satisfies the Helmholtz wave equation. Note that the field completely penetrates a particle smaller in size than the skin layer, and the complex nature of permittivity should be taken into account in this case. A different solution satisfying the Helmholtz equation at $\varepsilon = 1$ and the radiation condition needs to be constructed outside the cavity. There are no tangential electric field components at the boundary of the cylinder. This mode also has$H_\rho = 0$ and $H_z = 0$. The magnetic field has a single component. It takes the following form inside the cavity:

$$H_\varphi = -i\omega\varepsilon_0\varepsilon E_0 J_1(\rho\sqrt{k_0^2\varepsilon - k_{zn}^2})\cos(k_z z)/\sqrt{k_0^2\varepsilon - k_{zn}^2}. \quad (21)$$

Thus, our task is to find this component outside the cavity and stitch it with (21). It has $H_\varphi = \partial_z A_\rho - \partial_\rho A_z$. We define the components of the vector potential in terms of polarization current densities $J_\rho(\mathbf{r}) = i\omega\varepsilon_0(\varepsilon-1)E_\rho(\mathbf{r})$, $J_z(\mathbf{r}) = i\omega\varepsilon_0(\varepsilon-1)E_z(\mathbf{r})$ as

$$A_\rho = i\omega\varepsilon_0(\varepsilon-1)\int_V \cos(\varphi-\varphi')G(\mathbf{r}-\mathbf{r}')E_\rho(\mathbf{r}')d^3r',$$

$$A_z = i\omega\varepsilon_0(\varepsilon-1)\int_V G(\mathbf{r}-\mathbf{r}')E_z(\mathbf{r}')d^3r'.$$

Azimuthally symmetric GF (10) takes the following form in a cylindrical system:

$$G = \frac{1}{4\pi}\int_0^\infty \frac{\exp\left(-\sqrt{\kappa^2-k_0^2}|z-z'|\right)J_0(\kappa\rho)J_0(\kappa\rho')}{\sqrt{\kappa^2-k_0^2}}\kappa d\kappa.$$

We thus obtain

$$A_\rho(\rho, z) = -\frac{k_{zn}\omega\varepsilon_0(\varepsilon-1)}{4\pi\sqrt{k_0^2\varepsilon - k_{zn}^2}}E_0 I_\rho(\rho, z),$$

$$A_z(\rho, z) = \frac{i\omega\varepsilon_0(\varepsilon-1)}{4\pi}E_0 I_z(\rho, z),$$

where the following integrals were introduced:

$$I_\rho(\rho, z) =$$

$$= \int_0^\infty\int_0^{2\pi}\int_{-h/2}^{h/2}\int_0^R \frac{\rho'\cos(\varphi-\varphi')J_0(\kappa\rho)J_0(\kappa\rho')J_1(\rho\sqrt{k_0^2\varepsilon-k_{zn}^2})}{\chi}$$

$$\times\exp(-\chi|z-z'|)\cos(k_{zn}z')\kappa d\kappa d^3r',$$

$$I_z(\rho, z) = \int_0^\infty\int_0^{2\pi}\int_{-h/2}^{h/2}\int_0^R \frac{\rho' J_0(\kappa\rho)J_0(\kappa\rho')J_0(\rho\sqrt{k_0^2\varepsilon-k_{zn}^2})}{\chi}$$

$$\times\exp(-\chi|z-z'|)\cos(k_{zn}z')\kappa d\kappa d^3r'.$$

Here, $\chi = \sqrt{\kappa^2-k_0^2}$, $\sqrt{k_0^2-\kappa^2} = -i\chi$. The first integral is angle-independent and equal to zero. Indeed, we find $\sin(-\varphi) - \sin(2\pi-\varphi) = 0$ by integrating in φ'. In the second integral, integration over angle yields 2π. Integration in z' in I_z results in factor

$$I_n(\chi, z) = 2\frac{\begin{array}{c}\chi\cos(k_{zn}z) + \exp(-h\chi/2)\cosh(\chi z)\\ \times(n\pi/h\sin(n\pi/2) - \chi\cos(n\pi/2))\end{array}}{\chi^2+k_{zn}^2}.$$

Therefore, derivative $\partial_\rho I_z(\rho, z)$ is written as

$$I'_z(\rho, z) = -2\pi \int_0^\infty \int_0^R \frac{\rho' J_1(\kappa\rho) J_0(\kappa\rho') J_0(\rho'\sqrt{k_0^2\varepsilon - k_{zn}^2})}{\chi} \times I_n(\chi, z)\kappa^2 \rho' d\rho' d\kappa.$$

Integrating in ρ', we apply the mean value theorem, taking $\rho' J_0(\rho'\sqrt{k_0^2\varepsilon - k_{zn}^2})$ at midpoint $\rho' = R/2$. The result is

$$I'_z(\rho, z) = \pi R I_0(R\sqrt{k_{zn}^2 - k_0^2\varepsilon}/2) \times \int_0^\infty \frac{J_1(\kappa\rho)(J_0(\kappa R) - 1)}{\chi} \kappa I_n(\chi, z) d\kappa. \quad (22)$$

The integral should be calculated numerically by dividing the domain of integration in κ into two regions: $0 < \kappa < k_0$ and $k_0 < \kappa < \infty$ with κ substituted with χ. Since the real part of permittivity for an LP is close to zero, we introduced a modified Bessel function. The external magnetic field at $\rho = R$ is

$$H_\varphi(R, z) = \frac{i\omega\varepsilon_0(\varepsilon - 1)}{4} E_0 R I_0(R\sqrt{k_{zn}^2 - k_0^2\varepsilon}/2) \times \int_0^\infty I_n(z, k_0, \chi) \frac{J_1(\kappa R)(1 - J_0(\kappa R/2))}{\chi} I_n(\chi)\kappa d\kappa. \quad (23)$$

We equate it to component (21) at $\rho = R$. In this case, we multiply the equality by $\cos(n\pi z/h)$ and integrate it in z along the interface. The integration result is

$$\tilde{I}_n(k_0, \chi) = \int_{-h/2}^{h/2} I_n(\chi, z)\cos(k_{zn} z) dz = \frac{h\chi}{\chi^2 + k_{zn}^2} + \frac{\left(k_{zn}\sin\left(\frac{n\pi}{2}\right) - \chi\cos\left(\frac{n\pi}{2}\right)\right)\left[k_{zn}\sin\left(\frac{n\pi}{2}\right) \times (1 + \exp(-h\chi)) + \chi\cos\left(\frac{n\pi}{2}\right)(1 - \exp(-h\chi))\right]}{\chi^2 + k_{zn}^2}.$$

At large χ, this integral decreases as $1/\chi$. The end result is

$$\frac{1 - \varepsilon}{\varepsilon} = \alpha_n(\omega) = \frac{2(h/R) I_1(R\sqrt{k_{zn}^2 - k_0^2\varepsilon})}{\sqrt{k_{zn}^2 - k_0^2\varepsilon} I_0(R\sqrt{k_{zm}^2 - k_0^2\varepsilon}/2)} \times \int_0^\infty \tilde{I}_n(k_0, \chi) \frac{J_1(\kappa R)(1 - J_0(\kappa R/2))}{\sqrt{\kappa^2 - k_0^2}} \kappa d\kappa. \quad (24)$$

Quantity α_n in this equation is complex, large in magnitude, and has a small imaginary part. Thus, $\varepsilon \approx 0$, and frequencies $\omega_n = \omega_0/\sqrt{1 - [(\alpha_n(\omega_0) + 1)\varepsilon_L]^{-1}}$. The iteration method is well-suited for finding the complex roots of (24). The initial approximation was $\omega = \omega_0$. The results are listed in the table. Note also that exact Eqs. (15) and (16) also allow one to formulate iterative algorithms for root refinement. Specifically, the following is derived from Eq. (16) at $n = 1$ with three terms in the tangent expansion taken into account:

$$\varepsilon = \frac{2(k_0 r)^4 \varepsilon^2/15}{1 + i(k_0 r) - (k_0 r)^2/3} = \alpha_1.$$

The initial approximation should be taken from the $\varepsilon' = 0$ condition; i.e., $\omega_1 = \sqrt{\omega_p^2/\varepsilon_L - \omega_c^2}$. Having a non-zero complex permittivity, one may perform the first iteration. Since the value of $\alpha_1(\omega_1)$ is very small, one iteration is sufficient.

Real parts of circular frequencies (in THz) of a silver cylindrical resonator with $R = 4$ nm determined using formulae (24), (11), and (9)

n	$h = 6$ nm		
	(24)	(11)	(9)
1	5137.128	4890.883	4891.887
2	5138.009	4891.915	4891.926
3	5138.213	4891.929	4891.933
4	5138.232	4891.933	4891.936
n	$h = 12$ nm		
1	5138.078	4891.729	4891.832
2	5138.959	4891.887	4891.912
3	5139.164	4891.916	4891.927
4	5139.183	4891.926	4891.932

Localized plasmons in long nanoparticles

Long nanoparticles are those with their length satisfying relation $L \sim \lambda$ and small transverse dimensions: $k_0 r \ll 1$. Such particles may be regarded as nanoantennas. This is typical of nanowires, long CNTs, and graphene nanoribbons. A rigorous approach requires solving IEs in this case. With small transverse dimensions, they are reduced to Gallen- and Pocklington-type equations and their modifications [16]. In addition to these, resonances associated with transverse dimensions are also possible. By virtue of a significant length, the longitudinal current density component may be considered to be independent of transverse coordinates and taken in the form $J_n = \sin(n\pi z/L)$, $n = 1, 2, \ldots$, i.e., one may assume that it vanishes at the ends. This component produces volume charge density $\rho_V(\omega) = i(n\pi/L)/\cos(n\pi z/L)/\omega$ within a particle. Overall

component E_z within a particle is given by

$$E_z(\omega, z) = \frac{\sin(n\pi z/L)}{i\omega\varepsilon_0(\varepsilon(\omega)-1)}$$

$$= \frac{1}{i\omega\varepsilon_0}\int_0^L \left[k_0^2 K(\omega, z-z')\sin(n\pi z'/L)\right.$$

$$\left. + \frac{(n\pi/L)\partial_z K(\omega, z-z')}{\omega}\cos(n\pi z/L)\right]dz', \qquad (25)$$

where kernel

$$K(\omega, \rho, z-z')$$

$$= R\int_0^\infty \frac{J_0(\kappa\rho)J_1(\kappa R)\exp(-\sqrt{\kappa^2-k_0^2}|z-z'|)}{2\sqrt{\kappa^2-k_0^2}}d\kappa.$$

We consider this equation within a particle under the assumption that the left-hand side does not depend on ρ. Multiplying by ρ and integrating, we obtain the same equation with kernel

$$\tilde{K}(\omega, z-z') = \frac{1}{R}\int_0^\infty \frac{J_1^2(\kappa R)\exp(-\sqrt{\kappa^2-k_0^2}|z-z'|)}{\kappa\sqrt{\kappa^2-k_0^2}}d\kappa.$$

Multiplying (25) by $\sin(n\pi z/L)$ and integrating in z, we find characteristic equation

$$\frac{1-(-1)^n}{(n\pi z/L)(\varepsilon(\omega)-1)} = \int_0^L\int_0^L \sin(n\pi z/L)$$

$$\times\left[k_0^2\tilde{K}(\omega, z-z')\sin(n\pi z'/L)\right.$$

$$\left. + \frac{(n\pi/L)\tilde{K}(\omega, z-z')}{\omega}\cos(n\pi z/L)\right]dz'dz.$$

The left-hand side vanishes at even indices. The right-hand side may be simplified via integration by parts:

$$\int_0^L \tilde{K}(\omega, z-z')\cos(n\pi z/L)dz'$$

$$= \tilde{K}(\omega, z-z')((-1)^n-1)$$

$$+ (n\pi z/L)\int_0^L \tilde{K}(\omega, z-z')\sin(n\pi z/L)dz'.$$

Integrals over the coordinate are taken analytically, and a convergent spectral integral remains. It is convenient to find complex roots using the iteration method. As above, the initial approximations for it may be derived from the $k_0\sqrt{\varepsilon/(\varepsilon+1)} = n\pi/L$ conditions. This equation is rather approximate, since it does not take wire curvature into account. A rigorous approach requires solving the Sommerfeld equation for a wave along a wire [17] rather than the Zenneck equation. In the case of a Sommerfeld wave inside a wire, the only component of the Hertz electric vector may be expressed through the Bessel function as $\Pi_z = AJ_0(\sqrt{\varepsilon k_z^2 - k_z^2})\exp(-ik_z z)$, while the outside component may be expressed through the Macdonald function: $\Pi_z = BK_0(\rho\sqrt{k_z^2-k_z^2})\exp(-ik_z z)$. Stitching the fields, we find

$$\varepsilon = \alpha = -\frac{\sqrt{k_0^2\varepsilon - k_z^2}}{\sqrt{k_z^2-k_0^2}}\frac{J_0(R\sqrt{k_0^2\varepsilon-k_z^2})K_1(R\sqrt{k_z^2-k_0^2})}{K_0(R\sqrt{k_z^2-k_0^2})J_1(R\sqrt{k_0^2\varepsilon-k_z^2})}. \qquad (26)$$

With a short wire length and $k_z = n\pi/L$, we find the resonant frequencies under condition $\varepsilon \approx 0$. The value of

$$\alpha \approx -\frac{(n\pi/L)}{\sqrt{(n\pi/L)^2-k_0^2}}\frac{I_0(R\sqrt{(n\pi/L)^2})K_1(R\sqrt{(n\pi/L)^2-k_0^2})}{K_0\sqrt{(n\pi/L)^2-k_0^2}k_0^2 I_1(n\pi R/L)}$$

should be small in this case. At frequencies significantly lower than the optical ones, the velocity of a Sommerfeld wave in a wire is slightly slower than the speed of light. The permittivity is complex and large in magnitude at these frequencies. In this case, resonance condition $k_0 = n\pi/L$ is quite accurate at small indices and large lengths, and the resonant frequencies are low. Equation (26) is inconvenient. At $R \to \infty$, it transforms into the Zenneck equation, which is easier to use as an initial approximation.

Equations for an LP in a CNT are formulated in the same way as in a nanowire, the only difference being that surface current density $j_z = \sin(n\pi z/L)$ is specified. It produces surface charge density $\rho_s(\omega) = i(n\pi/L)\cos(n\pi z/L)/\omega$. Volume integrals are then replaced by surface ones, since all quantities contain delta function $\delta(\rho - R)$. Equation (25) takes the form

$$E_z(\omega, z) = \frac{\sin(n\pi z/L)}{\sigma_{zz}(\omega)}$$

$$= \frac{1}{i\omega\varepsilon_0}\int_0^L \left[k_0^2\bar{K}(\omega, z-z')\sin(n\pi z'/L)\right.$$

$$\left. + \frac{(n\pi/L)\partial_z\bar{K}(\omega, z-z')}{\omega}\cos(n\pi z/L)\right]dz'$$

with kernel

$$\bar{K}(\omega, z-z')$$

$$= R\int_0^\infty \frac{J_0(\kappa R)J_0(\kappa R)\exp(-\sqrt{\kappa^2-k_0^2}|z-z'|)}{2\sqrt{\kappa^2-k_0^2}}\kappa d\kappa.$$

Dynamic CNT conductivity $\sigma_{zz}(\omega)$ was determined in [18]. An approximate solution for an E-plasmon is

derived from condition $k_z = n\pi/L = k_0\sqrt{1-4(\eta_0\sigma_{zz}(\omega))^2}$. It also corresponds to the large-radius approximation. In order to obtain the dispersion relation in an infinite CNT, we write the current density as $J_z = \exp(-ik_z z)\delta(\rho - R)$ and find the field component for it:

$$E_z(R,z) = \frac{\exp(-ik_z z)}{2\pi i\omega\varepsilon_0}\int\limits_0^\infty (k_0^2 - k_z^2)\,\frac{J_0(\kappa R)J_0(\kappa R)}{\kappa^2 + k_z^2 - k_0^2}\,\kappa d\kappa$$

$$= \frac{\exp(-ik_z z)}{\sigma_{zz}}. \tag{27}$$

Integral (27) exists, since quantity k_0 is complex. Reducing by the exponential factor, we obtain equation

$$k_z^2 = k_0^2 - \frac{2\pi k_0}{\eta_0\sigma_{zz}(\omega)\int\limits_0^\infty \frac{J_0(\kappa R)J_0(\kappa R)}{\kappa^2 + k_z^2 - k_0^2}\,\kappa d\kappa}. \tag{28}$$

It is analogous to the equation for a surface E-plasmon along a graphene plane. One may write $J_z = \sin(n\pi z/L)\delta(x)$ for a graphene nanoribbon of small width W and length L. Owing to the smallness of width, we neglect the dependence on y and the J_y component. We thus obtain

$$W\,\frac{2\pi\omega\varepsilon_0\lfloor(-1)^n - 1\rfloor}{\sigma(\omega)(n\pi/L)} =$$

$$= \int\limits_0^\infty d\kappa \int\limits_0^{\pi/2} d\varphi \int\limits_0^L\int\limits_0^L \sin(n\pi z/L)\,\frac{\sin^2(\kappa\sin(\varphi)W/2)}{(k_y W)^2}$$

$$\times\,\frac{\exp(-i\sqrt{k_0^2 - \kappa^2}|z - z'|)}{\sqrt{k_0^2 - \kappa^2}}\,\sin(n\pi z'/L)\kappa^3 dz' dz.$$

Here, we switched to a polar coordinate system in integration. The integral over angle is calculated using the mean value theorem with midpoint $\varphi = \pi/4$, which yields factor $\pi\sin^3(\kappa\pi W/8)/2$. The integrals over coordinates z and z' are calculated explicitly. Thus, the right-hand side is represented by a convergent spectral integral.

Discussion and conclusions

It is demonstrated that the SPR method is a fine approximation for calculating LP resonances. This is attributable to the quasi-static nature of these resonances. Macroscopic parameters for nanoparticles were used throughout analysis. The macroscopic polarizability of a nanocluster may differ significantly from the value for a bulk sample (where atoms are arranged periodically) due mostly to the influence of boundaries and changes in the internal field. This should be taken into account in refining the formulae. Quantum-mechanical methods with the excitation of the cluster by the field of a plane monochromatic wave taken into account need to be used to find an exact solution to the problem. Such problems often turn out to be difficult to solve even in approximations. The presence of boundaries and free electrons leads to a significant change in the collision frequency. Problems associated with dimensional quantization and ballistic transport arise in the case of nanoclusters characterized by conductivity. Particles involved in conduction move at the Fermi velocity; i.e., they are characterized by de Broglie wavelength $\Delta = 2\pi\eta/(m_e v_f)$. Particles with lower energies are not involved in directional motion. In the case of a large mean range of an electron $\lambda_e \gg L$ and longitudinal motion, $n = 2L/\Delta$ levels corresponding to it arise. In addition, we have $m = 2W/\Delta$ levels corresponding to the transverse dimension. These latter levels for a long nanoribbon correspond to the number of longitudinal modes of conductivity, which is quantized. In practice, such a quantum well (nanoribbon) requires solving Schrödinger equations with a potential corresponding to the electromagnetic field. If this ribbon (e.g., a metallic one) also has thickness t, a three-dimensional object (a quantum box with approximately $8LWt/\Delta^3$ levels) emerges. These levels correspond to conduction electrons. The model of infinitely high walls with wave function $\psi = \sin(n\pi z/L)\sin(m\pi y/W)\sin(k\pi x/t)$ yields a known result for levels $E_{nmk} = 2m_e(n^2/L^2 + m^2/W^2 + k^2/t^2)/\eta^2$, but it does not provide any data on the transition frequencies. If the potential with account for all the atoms or the approximate potential for conduction electrons (for which the single-particle Schrödinger equation may be solved) in this box is known, the energy levels and the transition frequencies may be determined. The polarizability of such a meta-atom (quantum dot) in the field of a plane wave of the optical range may be determined by the perturbation method. The large number of atoms in a quantum dot offers hope that a macroscopic permittivity will provide a correct qualitative result.

Let us examine the example of a meta-atom in the form of a graphene region with dimensions L and W. The surface conductivity of graphene derived from linear dispersion (for electrons and holes in the vicinity of Dirac points) without regard to interband transitions is actually given by the Drude formula [10]:

$$\sigma(\omega,\mu,\omega_c,T) = \frac{\sigma_{\text{intra}}(0)}{1 + i\omega/\omega_c}, \tag{29}$$

$$\sigma_{\text{intra}}(0) = \sigma_0 = \frac{e^2 k_B T}{\pi\eta^2\omega_c}\,\ln\left(2\left[1 + \cosh\left(\frac{\mu_c}{k_B T}\right)\right]\right). \tag{30}$$

Here, μ_c is the electrochemical potential and T is temperature. Since, according to Drude, the DC value is $\sigma(0) = \sigma_0 = en_s\mu_F$, we determine surface concentration of conduction electrons and holes $n_s = \sigma_0/(ev_F)$ from (30). The mean range in graphene is rather large (on the order of a micrometer). If a cluster is significantly smaller in size, collisions may be neglected. Conductivity (29) is diffusion in nature. If the phonon dispersion in graphene is known, one may determine DC ballistic conductivity $g_B(0)$. The high-frequency ballistic conductivity is then obtained

by inserting $g_{\mathrm{B}}(0)$ instead of $\sigma_{\mathrm{intra}}(0)$ into (29). Since the collision frequency is fairly low, $g_{\mathrm{B}}(\omega) = -i\omega_c g_{\mathrm{B}}(0)/\omega$. This corresponds to the fact that the contribution to conductivity decreases with increasing frequency due to the oscillatory nature and the reduction in oscillation amplitude (the range decreases with decreasing period). The kinetic inductance, which takes the form $L_K = m_e v_F L/(W\sigma_0 e)$ for current directed along the large dimension in a 2DEG of this kind, then plays a significant role. It contributes to surface conductivity $\sigma(\omega) = g_B(\omega) + 1/(i\omega L_K)$. Writing down the resonance condition, we obtain $\omega_n = \sqrt{\Omega_n^2 - 4/(\omega_c \eta_0 g_{\mathrm{B}}(0) + (W/L)\eta_0\sigma_0 e/(m_e v_F))^2}$. Here, $\Omega_n = n\pi c/L$. Only low frequencies where the formulae remain valid should be considered, since the imaginary part of conductivity becomes small compared to the real one in the optical range. Transverse resonances are obtained by substituting $L \leftrightarrow W$.

As for the Drude–Lorentz formula for the permittivity of a metal, it is quite accurate in the IR and lower-frequency ranges. In the case of optical LPs, it is advisable to take several Lorentz terms in it to approximate experimental permittivities of metals. Specifically, $\varepsilon'(\omega)$ for silver goes through zero three times, and a single ε_L value is clearly insufficient. A complex frequency dependence of permittivity leads to implicit and cumbersome formulae. The resonant frequencies for them should be determined iteratively; two iterations are sufficient in most cases. As for the introduction of one constant ε_L into the given formulae, the corresponding error is no greater than a few percent, as is the error of the quasi-static formulae themselves. It should be noted that the use of strict formulae leads to a spectrum that condenses toward frequency $\omega_0 = \omega_p/\sqrt{\varepsilon_L}$, while the quasi-static approach and the SPR method yield frequency $\tilde{\omega}_p = \omega_p/\sqrt{\varepsilon_L + 1}$. Note also that particles are often examined in a certain transparent medium with permittivity $\tilde{\varepsilon}$. In this case, all the results are obtained by performing substitutions $k_0 \to k_0\sqrt{\tilde{\varepsilon}}$ and $\varepsilon_L \to \varepsilon_L - \tilde{\varepsilon}$.

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Conflict of interest

The author declares that he has no conflict of interest.

References

[1] L.A. Dymkan, V.A. Bogatyrev, S.Yu. Shchegolev, N.G. Khlebtsov. *Zolotye nanochastitsy: sintez, svoistva, biomeditsinskoe primenenie* (Nauka, M., 2008) (in Russian).
[2] V.V. Klimov. *Nanoplazmonika* (Fizmatlit, M., 2009) (in Russian).
[3] V.V. Klimov. Phys.-Usp., **51** (8), 839 (2008).
[4] A.V. Eletskii. Phys. Usp., **40**, 899–924 (1997). DOI: 10.1070/PU1997v040n09ABEH000282.
[5] L. Novotny, B. Hecht. *Principles of Nano-Optics* (Cambridge University Press, 2006).
[6] Yu.I. Petrov. *Fizika malykh chastits* (Nauka, M., 1982) (in Russian).
[7] S.G. Rodrigo. *Optical Properties of Nanostructured Metallic Systems* (Springer, Heidelberg, Dordrecht, London, New York, 2012).
[8] C.F. Bohren, D.R. Huffman. *Absorption and Scattering of Light by Small Particles* (Wiley, New York, 1983).
[9] M.V. Davidovich. Kvantovaya Elektron., **49** (9), 868–877 (2019). DOI: 10.1070/QEL16950
[10] G.W. Hanson. J. Appl. Phys., **103**, 064302–8 (2008). DOI: 10.1063/1.2891452
[11] M.V. Davidovich. Opt. Spetrosk., **130** (10), 1520–1542 (2022). DOI: 10.21883/EOS.2022.10.54863.3231-22
[12] M.V. Davidovich. Zh. Tekh. Fiz., **94** (3), 385–399 (2024). DOI: 10.61011/JTF.2024.03.57376.312-23
[13] J. Zenneck. Ann. der Physik, **23**, 846–866 (1907).
[14] G.T. Markov, A.F. Chaplin. *Vozbuzhdenie elektromagnitnykh voln* (Radio i Svyaz', M., 1983) (in Russian).
[15] M. Gastine, L. Courtois, J.L. Dormann. IEEE Trans., **MTT-15** (12), 694–700 (1967).
[16] M.V. Davidovichg. Techn. Phys., 67(10), 468–486 (2022). DOI: 10.1134/S106378422207012X.
[17] L.A. Vainshtein. *Elektromagnitnye volny* (Radio i Svyaz', M., 1988) (in Russian).
[18] G.Y. Slepyan, S.A. Maksimenko, A. Lakhtakia, O.M. Yevtushenko, A.V. Gusakov. Phys. Rev. B, **57**, 9485–9497 (1998). DOI: 10.1103/PhysRevB.57

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