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Localized plasmons in nanoparticles: calculation methods

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Received December 16, 2024
Revised December 16, 2024
Accepted December 16, 2024

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.

DOI: 10.61011/TP.2025.05.61117.438-24

Introduction

Localized plasmons (LP) — electromagnetic oscillations of electron plasma of small metallic and semiconductor particles localized in their small volumes. Such particles are called nanoclusters, quantum dots, meta-atoms, and quantum boxes when the dimensions of such a „box" become on the order of tens of nanometers or less. Since plasma particles motion is limited in three directions, such objects are called zero-dimensional (0D), in contrast to 1D-objects — quantum threads or wires, 2D-objects — two-dimensional electron gas (2DEG), e.g., in the form of graphene, thin conducting films and etc., as well as 3D-macro-objects. However, if the quantum wire is limited in length it also may be considered as LP carrier. Example — carbon nano-tube (CNT) of finite length, graphene fragments limited in two directions and etc. LP are widely used in medicine, medical physics and physics in general for the purposes of interaction with laser beams, e.g., LP in gold particles, fullerenes and CNT [1–5]. Conducting nanoparticles (nanoclusters) resemble a molecule containing a multitude of atoms that share conduction electrons [5–8]. The characteristic size (radius) of such clusters may vary from one 1 nm (fullerenes C28, 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 of 1 nm (meta-atoms) with an electromagnetic wave (photoionization) requires solving a quantum problem for Schrödinger equation (SE) with the wave vector-potential introduced into the Hamiltonian. However, the classical approach is quite 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 (e.g., gold nanoparticles), since the frequencies of the resulting localized plasmons (LPs) fall within the optical range [1–3] in the domain of surface plasmonic resonance (SPR). Fullerenes and CNTs may be characterized as conducting shells. The number of atoms may vary from several tens (fullerenes C20, C28, C60) to hundreds of thousands ($3.56 \cdot 10^5$ for a copper nanoparticle with radius $r = 10$ nm). The considered nanoclusters support LP — oscillations with complex resonant frequencies [1–8]. It is usually necessary to pair the resonant frequencies of these particles with the frequencies of lasers, so their determination is necessary. The rate of oscillations decay in LPs excited by a short laser pulse is inversely proportional to the Q-factor. The classical Mie solution is applicable to the problem of excitation of both dielectric and metallic particles. In case of fullerenes, an approach based on the introduction of shell conductivity was examined in [9]. In addition to approaches relying on electrodynamics, quantum chemistry methods, which serve as the basis for conventional software packages like Gaussian 9 are often used. Using such methods, it is possible to obtain a spectrum of low-frequency oscillations and excitations of the cluster lattice.

1. Quantum analysis

If we consider the parallelepiped particlea_x, a_y, a_z as an infinitely deep 3D quantum box (QB), or quantum well (QW) we'll obtain the wave function (WF)

$$\psi_{n_x n_y n_z} = A_{n_x n_y n_z} \sin(n_x \pi x / a_x) \sin(n_y \pi y / a_y) \sin(n_z \pi z / a_z)$$

and energy levels

$$E_{n_x n_y n_z} = (\hbar \pi)^2 \left[(n_x / a_x)^2 + (n_y / a_y)^2 + (n_z / a_z)^2 \right] / 2m_e. \quad (1)$$

Here m_e — is the mass of an electron. In the cubic QB with a size of 1 nm, we obtain minimal energy of 0.37 eV and approximately the same distances between the lower levels. With the size of 4 nm the energy level will be 0.023 eV, i.e. is already less than $k_B T$ at room temperature.

In such a QB with finite walls height (of the order of work function (WF) from metal) there are a lot of levels and they are dissolved because of thermal fluctuations, thus, forming the conduction band (CB) from zero CB to Fermi energy (FE). In this case, and for large sizes, the classical approach can be used. In [2] the criteria of its use is designated as a cluster with several dozens of atoms. It may be considered as quite strict. However, with already 1000 atoms (the cluster of size 1 nm) the actual distance of 0.1 eV between the levels for metals with WF 3–5 eV, i.e. this size may be considered a limit where conventional approach may still be used. In the cluster with a size of 10 nm the number of atoms is already 10^6. So, for the 1D quantum well 13.7 eV deep and$t = 0.34$ nm thick (2DEG in graphene) we obtain two levels from the strict equation [10] $E_1 = 1.77$ eV and $E_2 = 6.7$ eV instead of 3.466 eV and 13.86 eV for an infinitely deep QW. Therefore, the estimates like (1) are exceeded. As an example of quantum transition let's consider a spherical QB of the radius of r_0 with $V(r) = 0$, $r > r_0$ and $V(r) = -V_0$, $r < r_0$. Here, the energy is counted from the free state of the electron. The characteristic equation for the lower energy with zero angular momentum ($l = 0$) is expressed as [10]:

$$\cot\left(r_0\sqrt{2m_e(V_0 - |E|)}/\hbar\right) = -\sqrt{|E|/(V_0 - |E|)}, \qquad (2)$$

whereas these levels occur when the depth of the QB is larger than minimal $V_0 > V_{\min} = (\pi\hbar/r_0)^2/(8m_e)$. With a depth of 4.7 eV (silver ball) its radius shall meet the condition $r_0 > \pi\hbar/\sqrt{(8m_e V_{\min})} = 0.141$ nm. In smaller particle at this potential the levels do not occur. This means that such a particle should be considered as a fully quantum object, i.e. consider electrons in the field of all atoms, and the approximation of QB is not applicable. In this case, proportional $-Ze^2/|\mathbf{r} - \mathbf{r}_m|$ potentials of individual atoms with coordinates $\mathbf{r}_m$ arise, and the problem becomes purely quantum. Such problems definitely cannot be solved [10]. A convenient approach to solve them is the density functional theory [11]. It may account for all the contributions to kinetic and potential energies associated with the distribution of electrons with a given density, as well as energy levels and ionization potential (work function). We are considering quantum models to determine the boundary when the classical approach can be applied. There are many levels in a larger particle with a size of 1 nm or more, and it can be considered as a QB, or even conventionally as a volume with an electron plasma and a dielectric permittivity (DP) $\varepsilon(\omega) = \varepsilon_L(\omega) - \omega_P^2/(\omega^2 - i\omega\omega_e)$. Here, the first term is Lorentz term, and the second one corresponds to Drude electronic susceptibility. In general, if the orbital moment ($l \neq 0$) is present the Schrödinger equation for the radial portion of the wave function is expressed as [12,13]:

$$\partial_{rr}^2 R + 2\partial_r R/r + \left[2m_e(E + V_0)/\hbar^2 - l(l+1)/r^2\right]R = 0, \qquad (3)$$

where beyond QW $V_0 = 0$. By designating $\kappa_0 = \sqrt{2m_e(V_0 - |E|)}/\hbar$ and $\kappa = i\sqrt{2m_e|E|}/\hbar$, as well as introducing spherical Bessel functions

$$\psi_m(kr) = \sqrt{\pi/(2kr)}\, J_{m+1/2}(kr),$$

$$\xi_m^{(2)}(kr) = \sqrt{\pi/(2kr)}\, H_{m+1/2}^{(2)}(kr),$$

for equation (3) we have: $R = A\psi(\kappa_0 r)$ inside and $R = B\xi_l(|\kappa|r)$ outside of QW. From here $A\psi_l(\kappa_0 r_0) = B\xi_l(i\kappa r_0)$ and $A\kappa_0\psi_l'(\kappa_0 r_0) = Bi|\kappa|\xi_l'(i|\kappa|r_0)$, i.e. we have a characteristic equation for determination of levels

$$\frac{\kappa_0\psi_l'(\kappa_0 r_0)}{\psi_l(\kappa_0 r_0)} = i\,\frac{|\kappa|\xi_l'(i|\kappa|r_0)}{\xi_l(i|\kappa|r_0)}, \qquad (4)$$

where the second order spherical functions ξ_l are expressed via Macdonald functions. Levels for (4) do not depend on the quantum number l (degenerated). $l = 0$ and equation (2) correspond to the minimal negative level. Let's consider a metal particle in the form of a cylinder with a radius of r_0 and height h. The SE will be written as follows

$$\left|2m_e(E - V_0)/\hbar^2 + \rho^{-1}\partial_\rho + \partial_{\rho\rho}^2 + \rho^{-2}\partial_{\varphi\varphi}^2 + \partial_m^2\right|\psi(\rho, \varphi, z) = 0. \qquad (5)$$

We seek the solution inside in the form

$$\psi_m(\rho, \varphi, z) = R(\rho)H(z)\exp(im\varphi).$$

The method of variables separation gives

$$\left[\left(2m_e(E - V_0)/\hbar^2 - m^2\rho^{-2}\right)R(\rho) + \rho^{-1}R'(\rho) + R''(\rho)\right]/R(\rho) = -\frac{H''(z)}{H(z)} = \chi_0^2.$$

Its solution has the form

$$H(z) = A_n\cos(n\pi z/h) + B_n\sin(n\pi z/h),$$

$$\lambda_{0n} = h/(\pi n), \quad R_{mn}(\rho) = C_{mn}\, J_m(\kappa_n\rho).$$

It is classified as even and odd over z. Neumann function was rejected because of its singularity. Even WF has the form

$$\psi(\rho, \varphi, z) = A_m C_{mn}\, J_m(\kappa_n\rho)\cos(n\pi z/h)\exp(im\varphi),$$

$$\kappa_n = \sqrt{2m_e(E - V_0)/\hbar^2 - (n\pi/h)^2}.$$

However, it cannot be coupled with the WF in the external domain, since the separation of variables can no longer be used there, and the problem of such QW problem has no analytical solution. From SE the function follows to determine the energy:

$$E = -\frac{\int \Psi^*(r)(V_0 + \hbar^2\nabla^2/2m_e)\Psi(r)d^3r}{\int \Psi^*(r)\Psi(r)d^3r}. \qquad (6)$$

It defines the exact levels. There it should be integrated with the exact WF across the entire space. WF is exponentially-decreasing when removing from the QW. We will make a small mistake if we take its value in the well instead of the exact WF. This value can be expanded in the found

functions. For example, for the even WF we have an expansion

$$\Psi(r) = \sum_{m,n} A_n C_{mn} J_m(\kappa_n \rho) \cos(n\pi z/h) \exp(im\varphi). \quad (7)$$

Substituting it in (6) and equating the derivatives with respect to unknown coefficients to zero, we obtain a characteristic equation in the form of a determinant equal to zero, from which we can find all negative energy levels corresponding to the even WF. Just as for a spherical particle, there is a criterion here: to apply the classical approach: r_0 and h shall be more than 1 nm. As a result, when using six basic functions in (7) for a silver particle with $r_0 = h/2 = 1$ nm, we obtain the value $E_1 = -0.186$ eV.

The quantum solution of the problem allows us to obtain energy levels E_n. When an electromagnetic field is applied to a particle, due to its smallness, the spatial distribution of the field on the particle can be neglected and taken as $\mathbf{E} = \mathbf{E}_0 \exp(i\omega\mathbf{t})$. The field is not strictly harmonic (it has a spectrum near frequency ω), i.e. begins to act at a certain moment of time $t = t_0$ and ends at the moment T. In addition, thermal and other fields act on the particle, so spontaneous transitions can occur for an excited oscillation. To determine the probability of levels population at the moment of time T, the perturbation theory [10,12] is used, for which it is necessary to calculate the matrix elements of quantum mechanics perturbations [10,12]. All possible allowed transitions determine the spectrum of frequencies (vibrations) of the particle.

2. Classic analysis — problem formulation based on electrodynamics

In classical approach, of interest are both, the problem of excitation by a given field $\mathbf{E}_{in}(\mathbf{r}) = \mathbf{E}_0 \exp(i\omega t - i\mathbf{kr})$ with time dependence $\exp(i\omega t)$ and the problem of natural oscillations, where complex frequencies $\omega_m = \omega'_m + i\omega''_m$ are sought. The second problem is considered in the present study. The typical quality factors $Q_m = \omega'_m/(2\omega''_m)$ of such oscillations are low. In excitation problem for small sizes the dependence $\exp(-i\mathbf{kr})$ can also be neglected. However, the particle can be quite large, or it can be located in a dense medium where the wave vector $\mathbf{k}$ to modulo is significantly larger than $k_0 = \omega/c$. Based on solving the excitation problem, it is possible to calculate the dipole moment of a particle and the polarization of a unit volume with such particles, i.e., the effective DP. In principle, it depends both on the frequency and on $\mathbf{k}$, as well as the shape of the particle, i.e. is tensor and determines the spatial dispersion. For a dense medium consisting of such particles when determining DP it is required to account for the internal field [14].

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

$$\mathbf{A}(\mathbf{r}) = \int_V G(\mathbf{r} - \mathbf{r}', k_0)\mathbf{J}(\mathbf{r}')d^3r', \quad (8)$$

where Green's function (GF) is denoted $G(\mathbf{r}, k_0) = (4\pi|\mathbf{r}|)^{-1} \exp(-ik_0|\mathbf{r}|)$. The fields from (8) are expressed as

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}_{in}(\mathbf{r}) + (ik_0)^{-1}\eta_0\left(k_0^2\mathbf{A}(\mathbf{r}) + \nabla \otimes \nabla\mathbf{A}(\mathbf{r})\right), \quad (9)$$

$$\mathbf{H}(\mathbf{r}) = \mathbf{H}_{in}(\mathbf{r}) + \nabla \times \mathbf{A}(\mathbf{r}), \quad (10)$$

where $\eta_0 = \sqrt{\mu_0/\varepsilon_0}$ and excitation fields are introduced. Polarization current density $\mathbf{J}(\mathbf{r}) = i\omega\varepsilon_0\left(\varepsilon(\mathbf{r})-1\right)\mathbf{E}(\mathbf{r})$ within particle volume V is included in (8). These equations allow formulating 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 [15]. In the present study, we examine free oscillations in homogeneous metallic nanoparticles, which are characterized by DP as Drude–Lorentz $\varepsilon(\omega) = \varepsilon_L(\omega) - \omega_P^2/(\omega^2 - i\omega\omega_c)$, as well as by carbon nanoclusters. Lorentz term ε_L may be considered to be constant and positive in the IR and optical ranges. Thus, for silver $\varepsilon_L = 9.3$, plasmon frequency (PF) $\omega_P = 1.57 \cdot 10^{16}$, and collision frequency (CF) $\omega_c = 3.46 \cdot 10^{13}$ Hz. Accordingly, 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 of $\omega = 5.148 \cdot 10^{15}$ 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 (8) 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 $i\omega\varepsilon_0\left(\varepsilon(\mathbf{r}-1)\right)$ 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 this paper, we compare the rigorous approach based on equation (8) with IEs and IDEs to an approximate approach based on the examination of surface plasmons (SP) with SPR. The frequency of SPR is defined as $\omega_{spr} = \sqrt{\omega_P^2/(1+\varepsilon_L) - \omega_c^2/4}$ and at low CF ω_c is equal $\omega_{spr} = \tilde{\omega}_P = \omega_P/\sqrt{1+\varepsilon_L}$. Such approximation allows obtaining simple explicit formulae for resonant frequencies. The approximate approach for conducting shells may be constructed based on the equations for surface E-plasmons $k_s = k_0\sqrt{1-4/\xi^2(\omega)}$ and H-plasmons $k_s = k_0\sqrt{1-\xi^2(\omega)/4}$, where $\xi(\omega) = \sigma(\omega)\sqrt{\mu_0/\varepsilon_0}$ is the normalized surface conductivity of the shell [16]. These equations are strictly valid for sufficiently large radii of curvature (for flat conductive surfaces such as graphene). Next, we introduce propagation constants k_s along a certain closed arc s with perimeter L_s on the surface. Because of closeness we obtain the equations $k_s L_s = 2k\pi$, $k = 1, 2, \ldots$, or $\omega\sqrt{1-4/\xi^2(\omega)} = 2k\pi c/L_s$, $\omega\sqrt{1-\xi^2(\omega)/4} = 2k\pi c/L_x$, $k = 1, 2, \ldots$. 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. However, 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 laser, it may be regarded as plasma in which each atom gives up 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. At a radius r the spheres with a surface $S = 4\pi r^2$ for the surface density of atoms of carbon $n_S = 3.82 \cdot 10^{19}\,\mathrm{m}^{-2}$ and have normalized surface conductivity $\xi = ik_0t\big(1-\omega_P^2/(\omega^2-i\omega\omega_c)\big)$. Here $\omega_P^2 = e^2 n_S/(\varepsilon_0 m_e t)$, where t — thickness of the shell of 0.1 nm (of the order of atom size). For graphene, we can take $t = 0.34\,\mathrm{nm}$ — the distance between graphene layers in alpha graphite, i.e. the approximate size of the electron shell for πelectrons. In $\omega \sim \omega_P = 1.2 \cdot 10^{16}$ plasmon region, the conductivity is low: $\xi \approx -i\omega(t/c)(\omega_P^2/\omega^2) \sim -i03 \cdot 10^{-2}$, therefore, maximal deceleration of plasmons $n = \sqrt{1-4/\xi^2(\omega)}$ is no more than 600, i.e. resonant frequencies lie in UV-band.

3. Quasi-static formulae

Quasi-static solutions of Maxwell's equations correspond to the 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. For further information, it is convenient to introduce frequency $\omega_r = c/r$, corresponding to the reverse time of the light passing the distance r, as well as characteristic frequencies $\omega_0 = \omega_P/\sqrt{\varepsilon_L}$, $\tilde{\omega}_P = \omega_P/\sqrt{\varepsilon_L+1}$, respectively, volumetric $\varepsilon(\omega_0) = 0$ and surface $\varepsilon(\tilde{\omega}_P) = -1$ plasmon resonances. 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

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

and

$$\tilde{\omega}_P \approx \omega_P/\sqrt{\varepsilon_L+1} - \omega_c^2\sqrt{\varepsilon_L+1}/(2\omega_P),$$

which implies that these frequencies become slightly lower. At a radius of 1 nm, $\omega_r = 3 \cdot 10^{17}\,\mathrm{Hz}$ and for metallic particles with radius $r < 10\,\mathrm{nm}$ we 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). These are low-Q oscillations.

The quasi-static equation for a dielectric body is written as $\mathbf{E}(\mathbf{r}) = -\nabla\varphi(\mathbf{r})$, $\varphi(\mathbf{r}) = -\nabla\mathbf{A}(\mathbf{r})$, neglecting (2) $k_0^2\mathbf{A}(\mathbf{r})$ 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$-G(\mathbf{r}-\mathbf{r}')\,\mathbf{J}(\mathbf{r}')$. On the surface $\mathbf{v}(\mathbf{r})\,\mathbf{J}(\mathbf{r}) = 0$ and surface integral is equal to zero. By virtue of the law of conservation of charge, we obtain $\nabla'\,\mathbf{J}(\mathbf{r}') = -i\omega\xi(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')$, where $\xi(\mathbf{r})$ is the surface charge density and point $\mathbf{r}$ belongs to the surface. Indeed, in a particle with a homogeneous DP, there are no volume charges in a homogeneous particle. Therefore, the equation for the normal field component on the surface is

$$\boldsymbol{\nu}(\mathbf{r})\mathbf{E}(\mathbf{r}) = -\nabla\varphi(\mathbf{r}) = -\frac{1}{\varepsilon_0}\oint_S \boldsymbol{\nu}(\mathbf{r})\nabla G(\mathbf{r}-\mathbf{r}')\xi(\mathbf{r}')dr'^2. \tag{11}$$

This componentE_ν in (11) is defined as the double layer potential and undergoes a jump $E_\nu^+/E_\nu^- = \varepsilon$ when the observation point crosses the surface — the particle boundary. Denoting in (11) the integral as I, we have $\varepsilon_0 E_\nu^+ = \varepsilon_0 I + \xi/2$ and $\varepsilon_0 E_\nu^- = \varepsilon_0 I - \xi/2$. Defining the jump, we find $\xi = 2\varepsilon_0 I(\varepsilon-1)/(1+\varepsilon)$. Thus, the quasi-static problem may be formulated based on the quasi-static IE for surface charge density $\xi(\mathbf{r})$ [2,3]:

$$\xi(\mathbf{r}) = 2\,\frac{1-\varepsilon}{1+\varepsilon}\oint_S \boldsymbol{\nu}(\mathbf{r})\nabla G(\mathbf{r}-\mathbf{r}', k_0)\xi(\mathbf{r}')d^2r'. \tag{12}$$

Equation (12) characterizes a quasi-stationary LP surface charge distribution [2,3]. Its frequency dependence is characterized by dependence $\varepsilon(\omega)$. A jump in the normal component of the electric field strength is observed in transition through the particle's boundary: $E_\nu(\mathbf{r}+0) = \varepsilon E_\nu(\mathbf{r}-0)$. Since the surface charge density is related to the field strength as: $\xi(\mathbf{r}) = \varepsilon_0(1-1/\varepsilon)E_\nu(\mathbf{r}+0)$, IE may also be formulated and relative to 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 (12) 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 [13]

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

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

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

Taking the distribution of surface charge density $\xi_{nm}(\mathbf{r}) = P_n^m(\theta)\exp(-im\varphi)$, we see that this function satisfies IE (12). Indeed, performing integration with expansion of Legendre polynomials in associated Legendre functions, we obtain

$$\int_0^{2\pi} P_n\big(\cos(\gamma)\big)\exp(-im\varphi')d\varphi' = 2\pi\exp(-im\varphi)\,\frac{(n-m)!}{(n+m)!} \times P_n^m\big(\cos(\theta)\big)P_n^m\big(\cos(\theta')\big),$$

and then after integration over θ' we'll find

$$1 = \frac{1-\varepsilon}{1+\varepsilon}\,\frac{-2ik_0r^2}{2n+1}\,\psi_n(k_0r')\partial_r\xi_n^{(2)}(k_0r).$$

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, $\alpha_n = -2i\big(k_0r^2/(2n+1)\big)\psi_n(k_0r')\partial_r\xi_n^{(2)}(k_0r)$ is a complex value. By expressing the functions ψ_n and $\xi_n^{(2)}$ through Bessel $J_{n+1/2}(k_0r)$ and Hankel $H^{(2)}_{n+1/2}(k_0r)$ functions, as well as using the asymptotic formulae for low arguments we'll find in the first order $\alpha_n = -2\pi(n+1)/(2n+1)^2$. We have $\alpha_1 = -4\pi/9$, and at large indices $\alpha_n = -\pi/(2n)$. Now resonance frequencies are expressed as

$$\omega_n = \tilde{\omega}_P\sqrt{\frac{1}{1-2\alpha_n/[(\varepsilon_L+1)(1+\alpha_n)]} + i\,\frac{\omega_n\omega_c}{\tilde{\omega}_P^2}}$$

$$\approx \tilde{\omega}_P\sqrt{1+\frac{2\alpha_n}{(\varepsilon_L+1)(1+\alpha_n)} + i\,\frac{\omega_n\omega_c}{\tilde{\omega}_P^2}}. \qquad (13)$$

Thus, the frequencies of the spectrum (13) condense to the frequency of the surface plasmon resonance $\tilde{\omega}_P$.

For metallic spherical particles with DP of $\varepsilon(\omega) = \varepsilon_L - \omega_P^2/\omega^2$ the spectrum of localized plasmons is properly delineated by the quasistatic formula [2,3]

$$\omega_n = \omega_P/\sqrt{\varepsilon_L + 1 + 1/n - 4k_0r/5},\ \ n = 1, 2, \ldots. \qquad (14)$$

Expressed as $\tilde{\omega}_P$ and ω_r, we have

$$\omega_n \approx \tilde{\omega}_P\left(1 - \frac{1/n - 4(\tilde{\omega}_P/\omega_r)/5}{2(\varepsilon_L+1)}\right), \qquad (15)$$

i.e. the frequency spectra become dense to the frequency$\tilde{\omega}_P$, and at higher n the frequency (15) is close to (13). To allow for dissipation, it is required to perform substitution $\omega_m \to \omega_m + i\omega_c$. It is evident that approximate solutions lead to condition $\varepsilon(\omega) \approx -1$, i.e. $\omega_m \approx \tilde{\omega}_P$. For metals $\tilde{\omega}_P \sim \omega_P/3$, i.e. this is an optical range.

The frequencies of a metal ball can also be found approximately by considering the motion of the plasmon along the equatorial or meridional circles of the ball, assuming that the propagation constant is described by Zenneck dispersion equation (DE) $k_\varphi = k_\theta = k_0\sqrt{\varepsilon(\omega)/\big(\varepsilon(\omega)+1\big)}$ Then, we apply the resonance condition $2\pi r k_\varphi = 2m\pi$. Then, for deceleration we'll get

$$\sqrt{\varepsilon(\omega_m)/\big(\varepsilon(\omega_m)+1\big)} = -\alpha_m = m\omega_r/\omega_m.$$

Here, the value α_m is large, i.e. the ratio is provided 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 $\tilde{\omega}_P$:

$$\omega_m \approx \tilde{\omega}_P\Big/\sqrt{1+\frac{1}{(\varepsilon_L+1)[(m\omega_r/\tilde{\omega}_P)^2-1]}} \qquad (16)$$

or

$$\omega_m \approx \tilde{\omega}_P - \tilde{\omega}_P/[2(\varepsilon_L+1)(m\omega_r/\tilde{\omega}_P)^2].$$

One may also write

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

or

$$\omega_m \approx \tilde{\omega}_P\Big/\big[1+1/\sqrt{(\varepsilon_L+1)(m\omega_r/\tilde{\omega}_P)^2}\big]^{1/2},$$

which agrees with (16). Thus, dependence (16) is close to (14), and the spectral frequencies also condense towards frequency $\tilde{\omega}_P$.

Let us consider a cylindrical particle with height h and radius R. GF in the cylindrical system is expressed as[13]

$$G = \frac{1}{4\pi i}\sum_{m=-\infty}^{\infty}\exp\big(-im(\varphi-\varphi')\big)$$

$$\times\int_0^\infty \frac{\exp\big(-\sqrt{\kappa^2-k_0^2}\,|z-z'|\big)J_m(\kappa\rho)J_m(\kappa\rho')}{\sqrt{\kappa^2-k_0^2}}\,\kappa d\kappa. \qquad (17)$$

If the height is small, $h \ll R$, one may neglect the charge on the side surface and consider only the component$E_{zn} = J_n(\rho k_0\sqrt{\varepsilon})\exp(-in\varphi)$. It satisfies the two-dimensional Helmholtz equation with $\partial_z = 0$. Thus, $\xi_n(\mathbf{r}) = \varepsilon_0(\varepsilon-1)J_n(\rho k_0\sqrt{\varepsilon})\exp(-in\varphi)$. When (17) is differentiated with respect to z, the factor $-i\sqrt{k_0^2-\kappa^2}\,\mathrm{sgn}(z-z')$ emerges. We form a functional from (12) by multiplying it by $\xi_n(\mathbf{r})$ and integrating over the volume. Integral

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

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

$$\frac{2(1-\varepsilon)\int_0^\infty\int_0^R\int_0^R I(\kappa)J_n(\kappa\rho)J_n(\kappa\rho')\rho\rho'd\rho d\rho'\kappa d\kappa}{(1+\varepsilon)h\int_0^R J_0^2(\rho k_0\sqrt{\varepsilon})\rho d r} = 1. \qquad (18)$$

It is approximate. It's accuracy as higher as lower the height. Writing 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 (18) 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 only component

$$E_{\rho nk} = J_k\big(\rho k_0\sqrt{\varepsilon}\big)\exp(-ik\varphi)\cos(n\pi z/h)$$

Let us define

$$\tilde{I}_n(\kappa)=\int\limits_{-h/2}^{h/2}\int\limits_{-h/2}^{h/2}\cos^2(n\pi z/h)\exp\bigl(-\sqrt{\kappa^2-k_0^2}\,|z-z'|\bigr)dz\,dz'.$$

The characteristic equation then takes the form

$$\frac{2(1-\varepsilon)\int\limits_0^\infty\int\limits_0^R\int\limits_0^R\frac{I_n(\kappa)J_k'(\kappa\rho)J_k(\kappa\rho')}{\sqrt{\kappa^2-k_0^2}}\rho\rho'd\rho d\rho'\kappa^2d\kappa}{(1+\varepsilon)h\bigl(1+(-1)^n/(2n\pi)\bigr)\int\limits_0^R J_k^2\bigl(\rho k_0\sqrt{\varepsilon}\bigr)\rho dr}=1. \quad (19)$$

The first few resonant LP frequencies are determined approximately from equation

$$\sqrt{\varepsilon(\omega_m)/\bigl(\varepsilon(\omega_m)+1\bigr)}=\alpha_m=mc/(\omega_mR),$$

i.e. described by the formula (16) with substitution or $r\to R$. At large radii, α_m may assume a moderate value and even be of the order of unity. This corresponds to a large permittivity magnitude $\varepsilon(\omega_m)$, which is typical of a low resonant frequency and small indices m. In this case $\omega_m=m\bigl(1+1(2\varepsilon(\omega_m))\bigr)c/R$. Let us assume, e.g., that $m=1$ and $R=600\,\text{nm}$. Then $c/R=5\cdot10^{14}\,\text{Hz}$ and $\varepsilon=-347,\ 4-59i$. Taking $\omega_1=5\cdot10^{14}\,\text{Hz}$ as a first approximation, we'll find the clarification $\omega_1=5\cdot10^{14}(1-0.0014+0.00024i)$. This is the localized plasmon of the infrared range. 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 LP is formed as a resonance of a surface plasmon 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 frequency $\Omega_m=mc/L_s$ 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 $\omega_P/\Omega_m\gg\varepsilon_L$, the case $\omega_m\approx\Omega_m$ will be true. If $\varepsilon_L-(\omega_P/\omega_m)^2\approx-1$, 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 (capsule) of height h and radius R with two hemispheres of radius R on the ends. The lower LP frequencies of such a capsule may be characterized approximately by the 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 $m\omega_P\to\Omega_m$ is performed. However, modes (16) with substitution $r\to R$ are also possible for this particle.

4. Rigorous formulae

A rigorous classical problem for an arbitrary bulk particle may be formulated based on an IE or an IDE [15]. 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 for E-modes and H-modes the equations for surface LPs in fullerenes:

$$\xi\,\partial_x\psi_n^-(\chi_0)=i[f_n\psi_n^+(\chi_0)-\varepsilon\psi_n^-(\chi_0)], \quad (20)$$

$$\xi\,\psi_n^-(\chi_0)=i[g_n\partial_y\psi_n^+(\chi_0)-\partial_x\psi_n^-(\chi_0)]. \quad (21)$$

Here $\xi=\sigma\eta_0$, $\chi_0=k_0r_0$, r_0 — radius of the particle, Riccati–Bessel $\psi_n^-(x)=\sqrt{\pi x/2}J_{n+1/2}(x)$ and Riccati–Hankel $\psi_n^+(x)=\sqrt{\pi x/2}H^{(2)}_{n+1/2}(x)$ functions were introduced, as well as coefficients

$$f_n=\frac{\partial_r\psi_n^-(\chi_0)}{\partial_r\psi_n^+(\chi_0)}=\varepsilon^{1/4}\,\frac{\chi_0J_{n-1/2}(\chi_0)-nJ_{n+1/2}(\chi_0)}{\chi_0H^{(2)}_{n-1/2}(\chi_0)-nH^{(2)}_{n+1/2}(\chi_0)}, \quad (22)$$

$$g_n=\frac{\psi_n^-(\chi_0)}{\psi_n^+(\chi_0)}=\varepsilon^{1/4}\,\frac{J_{n+1/2}(\chi_0)}{H^{(2)}_{n+1/2}(\chi_0)}. \quad (23)$$

This approach was used in [9] to examine LPs in fullerenes and diffraction on them. Free oscillations for the modes E_{nm} and H_{nm} of spherical particles are characterized by equations [17]

$$\frac{n}{k_0r}(\varepsilon-1)+\frac{J_{n-1/2}(k_0r\sqrt{\varepsilon})}{J_{n+1/2}(k_0r\sqrt{\varepsilon})}=\sqrt{\varepsilon}\,\frac{H^{(2)}_{n-1/2}(k_0r)}{H^{(2)}_{n+1/2}(k_0r)}, \quad (24)$$

$$\frac{J_{n-1/2}(k_0r\sqrt{\varepsilon})}{J_{n+1/2}(k_0r\sqrt{\varepsilon})}=\frac{H^{(2)}_{n-1/2}(k_0r)}{\sqrt{\varepsilon}\,H^{(2)}_{n+1/2}(k_0r)}. \quad (25)$$

Here, $n=1,2,\ldots$ is the meridional index corresponding to dependence $P_n^m(\theta)$, and with respect to azimuthal index m with dependence $\exp(-im\varphi)$ degeneracy is observed. Equations (24) and (25) for $n=1$ may be written as

$$\frac{\sin(k_0r\sqrt{\varepsilon})}{\sin(k_0r\sqrt{\varepsilon})/(k_0r\sqrt{\varepsilon})-\cos(k_0r\sqrt{\varepsilon})}=\frac{\sqrt{\varepsilon}k_0r}{1+i(k_0r)}+\frac{1-\varepsilon}{k_0r}=\alpha, \quad (26)$$

$$\sqrt{\varepsilon}\,\frac{\sin(k_0r\sqrt{\varepsilon})}{\sin(k_0r\sqrt{\varepsilon})/(k_0r\sqrt{\varepsilon})-\cos(k_0r\sqrt{\varepsilon})}=\frac{k_0r}{1+i(k_0r)}=\beta, \quad (27)$$

or as

$$\tan(k_0r\sqrt{\varepsilon})\bigl(1-\alpha/(k_0r\sqrt{\varepsilon})\bigr)=-\alpha$$

or

$$\tan(k_0r\sqrt{\varepsilon})\bigl(1-\beta/(k_0r\varepsilon)\bigr)=-\beta/\sqrt{\varepsilon}$$

Then the first equation at $|k_0r\sqrt{\varepsilon}|\ll1$ takes the form

$$\tan(k_0r\sqrt{\varepsilon})\approx\alpha(k_0r)^3\varepsilon/3$$

and is strictly observed at $\varepsilon=0$. Let us rewrite the second equation in the form

$$\sqrt{\varepsilon}\tan(k_0r\sqrt{\varepsilon})=\beta\bigl[\tan(k_0r\sqrt{\varepsilon})/(k_0r\sqrt{\varepsilon})-1\bigr].$$

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, we may write $\omega = \omega_0 + i\omega_c$. Given the dissipation, a more accurate resonant frequency for (27) may be found:

$$\omega_1' = \mathrm{Re}(\omega_1) = \omega_0$$

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

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 (26). 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: $\varepsilon_L - \omega_P^2/(\omega^2 + \omega_c^2) = 0$, where

$$\omega' = \omega_0\sqrt{1 - \omega_c^2/\omega_0^2} = \omega_0 - \omega_c^2/(2\omega_0),$$

i.e., dissipation lifts degeneracy. The next $n = 2$ modes may be called quadrupole ones. Their resonant frequencies without dissipation also satisfy the condition $\varepsilon = 0$, but differ slightly from ω_0 due to dissipation. Using the expansions of cylindrical functions in (24) and (25), one may demonstrate that the LP spectra condense towards frequency ω_0.

We used Zenneck dispersion equation obtained for a flat surface to derive some of the formulae for complex particles. In case of particles in the medium, a modification of this equation [2] should be taken, allowing for the DP of the medium. Naturally, this is an approximation. However, it yields resonant frequencies for small conducting particles in SPR region that agree well with the results obtained in other methods, including the exact results for spherical particles. Resonances in the IR range, where SPs are slightly decelerated, 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. Let's the electrical field in it assumes the form:

$$E_z = E_0 J_0\big(\rho\sqrt{k_0^2\varepsilon - k_{zn}^2}\big)\cos(k_{zn} z),$$

$$E_\rho = ik_z E_0 J_1\big(\rho\sqrt{k_0^2\varepsilon - k_{zn}^2}\big)\cos(k_z z)/\sqrt{k_0^2\varepsilon - k_{zn}^2},$$

$E_\varphi = 0$, 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 resonant cavity (in case of a particle with some DP of the medium $\tilde{\varepsilon}$). There are no tangential electric field components at the boundary of the cylinder. Also for this mode $H_\rho = 0$ and $H_z = 0$. The magnetic field has a single component. It takes the following form inside the cavity:

$$H_\varphi = -i\omega\varepsilon_0\varepsilon E_0 J_1\big(\rho\sqrt{k_0^2\varepsilon - k_{zn}^2}\big)\cos(k_z z)/\sqrt{k_0^2\varepsilon - k_{zn}^2}. \tag{28}$$

Thus, our task is to find this component outside the resonant cavity and stitch it with (28). Here, $H_\varphi = \partial_z A_\rho - \partial_\rho A_z$. 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

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

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

Azimuthally symmetric GF (17) takes the following form in a cylindrical system:

$$G = \frac{1}{4\pi}\int\limits_0^\infty \frac{\exp\big(-\sqrt{\kappa^2 - k_0^2}\,|z - z'|\big)J_0(\kappa\rho)J_0(\kappa\rho')}{\sqrt{\kappa^2 - k_0^2}}\,\kappa d\kappa.$$

We have the following components of the vector-potential

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

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

where integrals are designated

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

$$\int\limits_0^\infty\int\limits_0^{2\pi}\int\limits_{-h/2}^{h/2}\int\limits_0^R \frac{\rho'\cos(\varphi - \varphi')J_0(\kappa\rho)J_0(\kappa\rho')J_1\big(\rho\sqrt{k_0^2\varepsilon - k_{zn}^2}\big)}{\chi}$$

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

$$I_z(\rho, z) = \int\limits_0^\infty\int\limits_0^{2\pi}\int\limits_{-h/2}^{h/2}\int\limits_0^R \frac{\rho' J_0(\kappa\rho)J_0(\kappa\rho')J_0\big(\rho\sqrt{k_0^2\varepsilon - k_{zn}^2}\big)}{\chi}$$

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

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, integrating by φ', we obtain $\sin(-\varphi) - \sin(2\pi - \varphi) = 0$. In the second integral, integration over angle yields 2π. Integration by z' in I_z results in factor

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

therefore, for derivative $\partial_\rho I_z(\rho, z)$ we have

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

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

$$I'_z(\rho, z) = \pi R I_0\left(R\sqrt{k_{zn}^2 - k_0^2\varepsilon}/2\right) \int_0^\infty \frac{J_1(\kappa\rho)\left(J_0(\kappa R) - 1\right)}{\chi} \times \kappa I_n(\chi, z) d\kappa. \quad (29)$$

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 replacement of κ by 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 equal

$$H_\varphi(R, z) = \frac{i\omega\varepsilon_0(\varepsilon - 1)}{4} E_0 R I_0\left(R\sqrt{k_{zn}^2 - k_0^2\varepsilon}/2\right) \times \int_0^\infty I_n(z, k_0, \chi) \frac{J_1(\kappa R)\left(1 - J_0(\kappa R/2)\right)}{\chi} I_n(\chi)\kappa d\kappa. \quad (30)$$

We equate it to component (28) at $\rho = R$. Here, we'll multiply the equality by $\cos(n\pi z/h)$ and integrate it in z along the interface. The integration result is

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

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

$$\frac{1 - \varepsilon}{\varepsilon} = \alpha_n(\omega) = \frac{2(h/R) I_1\left(R\sqrt{k_{zn}^2 - k_0^2\varepsilon}\right)}{\sqrt{k_{zn}^2 - k_0^2\varepsilon} I_0\left(R\sqrt{k_{zn}^2 - k_0^2\varepsilon}/2\right) \int_0^\infty \tilde{I}_n(k_0, \chi) \times \frac{J_1(\kappa R)\left(1 - J_0(\kappa R/2)\right)}{\sqrt{\kappa^2 - k_0^2}} \kappa d\kappa}. \quad (31)$$

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 (31). The initial approximation was $\omega = \omega_0$. Results are presented in the table. Note also that exact Eqs. (22) and (23) also allow formulating iterative algorithms for root refinement. Specifically, the following is derived from Eq. (23) 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 condition $\varepsilon' = 0$, i.e. $\omega_1 = \sqrt{\omega_P^2/\varepsilon_L - \omega_c^2}$. Having a non-zero complex dielectric 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 (31), (19), and (12

N	$h = 6$, nm		
	(31)	(19)	(12)
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

5. LP 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 [18]. In addition to longitudinal, 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 of $J_z = \sin(n\pi z/L)$, $n = 1, 2, \ldots$, i.e. assumed to be transformed to zero on its ends. This component produces volume charge density $\rho_V(\omega) = i(n\pi/L)\cos(n\pi z/L)/\omega$ within a particle.

Total component E_z within a particle is given by equation

$$E_z(\omega, z) = \frac{\sin(n\pi z/L)}{i\omega\varepsilon_0(\varepsilon(\omega)-1)} = \frac{1}{i\omega\varepsilon_0}\int_0^L \Big[k_0^2 K(\omega, z-z') \times \sin(n\pi z'/L) + \frac{(n\pi/L)\partial_z K(\omega, z-z')}{\omega}\cos(n\pi z/L)\Big] dz', \quad (32)$$

where kernel

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

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

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

Multiplying (32) by $\sin(n\pi z/L)$ and integrating in z, we find the characteristic equation

$$\frac{1-(-1)^n}{(n\pi z/L)(\varepsilon(\omega)-1)} = \int_0^L\int_0^L \sin(n\pi z/L)\Big[k_0^2\tilde{K}(\omega, z-z') \times \sin(n\pi z'/L) + \frac{(n\pi/L)\tilde{K}'(\omega, z-z')}{\omega}\cos(n\pi z/L)\Big] dz'dz.$$

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

$$\int_0^L \tilde{K}'(\omega, z-z')\cos(n\pi z/L)dz' = \tilde{K}(\omega, z-z')\big((-1)^n-1\big) + (n\pi z/L)\int_0^L \tilde{K}(\omega, z-z')\sin(n\pi z/L)dz'.$$

Integrals over the coordinate are taken analytically, and a convergent spectral integral remains. It is convenient to find complex roots using the iteration method. For this, the initial approximations for it, as above, may be derived from conditions $k_0\sqrt{\varepsilon/(\varepsilon+1)} = n\pi/L$. 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 [19] rather than the Zenneck equation. For Sommerfeld wave inside a wire, the only component of Hertz electric vector may be expressed through the Bessel function as

$$\Pi_z = AJ_0\big(\sqrt{\varepsilon k_0^2 - k_z^2}\big)\exp(-ik_z z),$$

while the outside component — it may be expressed through Macdonald function:

$$\Pi_z = BK_0\big(\rho\sqrt{k_z^2-k_0^2}\big)\exp(-ik_z z).$$

Stitching the fields, we find

$$\varepsilon = \alpha = -\frac{\sqrt{k_0^2-k_z^2}}{\sqrt{k_z^2-k_z^2}}\,\frac{J_0\big(R\sqrt{k_0^2\varepsilon-k_z^2}\big)K_1\big(R\sqrt{k_z^2-k_0^2}\big)}{K_0\big(R\sqrt{k_z^2-k_0^2}\big)J_1\big(R\sqrt{k_0^2\varepsilon-k_z^2}\big)}. \quad (33)$$

With a short wire length, assuming $k_z = n\pi/L$ we find the resonant frequencies under condition $\varepsilon \approx 0$. At the same time, the value

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

shall be small. 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 length, and the resonant frequencies are low. Equation (33) is inconvenient for use. At $R \to \infty$, it transforms into Zenneck equation, which is easier to use as an initial approximation.

Equations for a LP in 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 forms the surface charge density $\rho_S(\omega) = i(n\pi/L)\cos(n\pi z/L)/\omega$. Volume integrals are then replaced by the surface ones, since all quantities contain delta function $\delta(\rho-R)$. Equation (32) takes the form

$$E_z(\omega, z) = \frac{\sin(n\pi z/L)}{\sigma_{zz}(\omega)} = \frac{1}{i\omega\varepsilon_0}\int_0^L \Big[k_0^2\overline{K}(\omega, z-z') \times \sin(n\pi z'/L) + \frac{(n\pi/L)\partial_z\overline{K}(\omega, z-z')}{\omega}\cos(n\pi z/L)\Big] dz'$$

with kernel

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

Dynamic conductivity of CNT $\sigma_{zz}(\omega)$ was determined in [20]. An approximate solution for E-plasmon is derived from condition $k_z = n\pi/L = k_0\sqrt{1-4/\big(\eta_0\sigma_{zz}(\omega)\big)^2}$. It

also corresponds to the large-radius approximation. In order to obtain DE in an infinite CNT, let's write the current density as $J_z = \exp(-ik_z z)\delta(\rho - R)$ and find the field component for it:

$$E_z(R, z) = \frac{\exp(-ik_z z)}{2\pi i\omega\varepsilon_0} \int_0^\infty (k_0^2 - k_z^2) \frac{J_0(\kappa R)J_0(\kappa R)}{\kappa^2 + k_z^2 - k_0^2} \kappa d\kappa$$

$$= \frac{\exp(-ik_z z)}{\sigma_{zz}}. \quad (34)$$

Integral (34) exists, since quantity k_0 is complex. Reducing by the exponential factor, we obtain equation

$$k_z^2 = k_0^2 - \frac{2\pi i k_0}{\eta_0 \sigma_{zz}(\omega) \int_0^\infty \frac{J_0(\kappa R)J_0(\kappa R)}{\kappa^2 + k_z^2 - k_0^2} \kappa d\kappa}. \quad (35)$$

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

$$W \frac{2\pi\omega\varepsilon_0[(-1)^n - 1]}{\sigma(\omega)(n\pi/L)} = \int_0^\infty d\kappa \int_0^{\pi/2} d\varphi \int_0^L \int_0^L \sin(n\pi z/L)$$

$$\times \frac{\sin^2\big(\kappa \sin(\varphi) W/2\big)}{(k_y W)^2} \frac{\exp\big(-i\sqrt{k_0^2 - \kappa^2}|z - z'|\big)}{\sqrt{k_0^2 - \kappa^2}}$$

$$\times \sin(n\pi z'/L)\kappa^3 dz' dz.$$

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 $\pi \sin^2(\kappa\pi W/8)/2$. The integrals over coordinates z and z' are calculated explicitly. Thus, the right-hand side is represented by a convergent spectral integral.

6. Torus and dumb-bell like particles

A torus with radii R and r can support low-frequency azimuthal oscillations corresponding to lengths $L = 2\pi(R + r)$, $L = 2\pi(R - r)$ and $L = 2\pi R$. In expression $\omega_r = c/(R + r)$ complex frequency is derived from the equation

$$\tilde{\omega}_n = \sqrt{\omega_n^2 - i\omega_n\omega_c} = \omega_P \sqrt{(n\omega_r/\omega_n)^2 - 1} \Big/$$

$$\sqrt{(n\omega_r/\omega_n)^2(\varepsilon_L + 1) - \varepsilon_L} \approx \omega_n - i\omega_c/2. \quad (36)$$

Here, $\omega_r/\omega_n > 1$ and it is implicit. The solution in the first approximation can be written, neglecting the roots of unity and ε_L in the form:

$$\omega_n^{(1)} = \omega_P/\sqrt{\varepsilon_L + 1} + i\omega_c/2.$$

By substituting it into (36), we'll obtain (convergence takes place in two iterations)

$$\omega_n = i\omega_c/2 + \omega_P \sqrt{(n\omega_r/\omega_n^{(1)})^2 - 1} \Big/$$

$$\sqrt{(n\omega_r/\omega_n^{(1)})^2(\varepsilon_L + 1) - \varepsilon_L}. \quad (37)$$

If we neglect dissipation, i.e. take

$$\varepsilon_L\omega_n^2 - \omega_P^2 = (n^2\omega_r^2/\omega_n^2)[(\varepsilon_L + 1)\omega_n^2 - \omega_P^2],$$

then, we get the biquadratic equation

$$\omega_n^4 - \omega_n^2\big[\omega_P^2/\varepsilon_L + n^2\omega_r^2(1 + 1/\varepsilon_L)\big] + n^2\omega_r^2\omega_P^2/\varepsilon_L = 0.$$

Its solution

$$\omega_n^2 = \frac{\omega_P^2/\varepsilon_L + n^2\omega_r^2(1 + 1/\varepsilon_L)}{2}$$

$$+ \sqrt{\frac{\omega_P^2/\varepsilon_L + n^2\omega_r^2(1 + 1/\varepsilon_L)}{4} - \frac{n^2\omega_r^2\omega_P^2}{\varepsilon_L}}$$

may be transformed at $n = 1$:

$$\omega_n^2 = \frac{\omega_P^2/\varepsilon_L + \omega_r^2 + \omega_r^2/\varepsilon_L}{2} + \frac{|\omega_P^2/\varepsilon_L - \omega_r^2|}{2}$$

$$\times \sqrt{1 + \omega_r^2 \frac{2\omega_P^2 + \omega_r^2}{[\omega_P^2 - \varepsilon_L\omega_r^2]^2}}.$$

If the torus is small and $\omega_r^2 > 2\omega_P^2$, we get

$$\omega_n^2 \approx \omega_r^2\big(1 + 3/(4\varepsilon_L)\big) - \omega_P^2/(4\varepsilon_L^3).$$

This solution should be rejected, since the frequency is significantly higher than SPR frequency. The applicability of SPR method meets the condition $\mathrm{Re}(\varepsilon < 1)$. If the torus is large and $\omega_P^2/\varepsilon_L > \omega_r^2$, then, the frequency lies near SPR:

$$\omega_n^2 \approx \frac{\omega_P^2}{\varepsilon_L} - \frac{\omega_r^2(1 - 1/\varepsilon_L)}{2} + \frac{\omega_r^2}{\omega_P^2} \frac{\omega_P^2/\varepsilon_L - \omega_r^2}{2}.$$

This approximation is more rough, compared to (37). Similarly, we can consider fluctuations with the substitution of $R + r \to R - r$ (Fig. 1). Such oscillations create magnetic-dipole fields. High-frequency oscillations in the form of a traveling wave along a circle of radius r can exist if they are synchronized, namely, the fields at points $\rho = -(R \mp R)$ and $\rho = (R \pm r)$ shall be in phase or reverse phase. For SP frequencies, running circumferentially we obtain $rk_s = m$. For frequencies along the large circumference $Rk_x = n$. Therefore, $r/R = m/n < 1/2$, where m and n are integers, and the parity of $-$the odd of the oscillations is determined by n. Although these ratios are approximate, they determine the dimensions at which such LP exist. In particular at $m = 1$ and $n = 3$ the oscillations are in reverse phase at $\rho = \pm R$, and at $n = 4$ — in-phase. As for DE (36), these are magnetic dipole fields with distributed

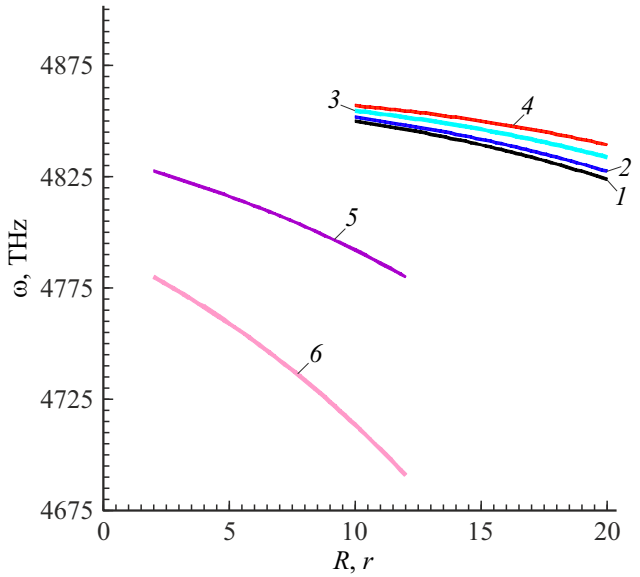

Figure 1. Resonant frequencies (THz) for contour $R+r$ (curves *1, 2*), R (*3*) and $R-r$ (*4*) depending on R (nm) at $r = 2$ nm (curves *2–4*) and 3 nm (*1*), as well as frequencies for contour$R+r$ depending on r (nm) at $R = 20$ nm (curve *5*) and $R = 30$ nm (*6*). Material — silver, $\omega_c = 3.57 \cdot 10^{16}$ Hz.

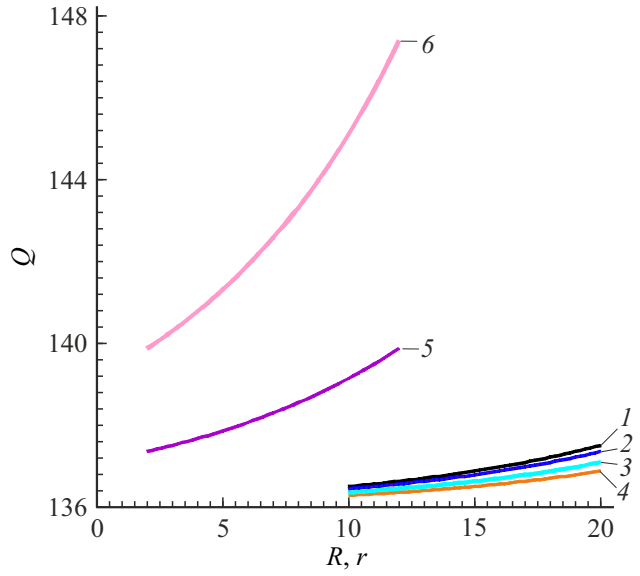

Figure 2. Q-factors of oscillations, corresponding to Fig. 1 (numbers of curves of resonances and numbers of Q-factors coincide).

magnetic dipoles, with opposite magnetic dipoles oriented either in the same direction or in opposite directions. Here, the origin of the cylindrical system coordinates is taken in the center of torus. Calculations according to formula (36) allowing for losses are given in Fig. 1 and 2. It is enough to use two iterations.

The dumbbell-shaped particles will be considered under the assumption that the radius of the balls r is much larger than the radius of the cylinder connecting them. The length of the cylinder l. Then, there are„low-frequency oscillations“ $k_s = k_0\sqrt{\varepsilon/(\varepsilon+1)} = n/(2r+l)$, $n = 1, 2, \ldots$ and „high frequency oscillations“ with Zenneck wavelength $\lambda_s = 2\pi/k_s$, lying on the circumference $2\pi r$, i.e. $k_s r = m$. But at the same time, an integer number of half-waves shall also fit the length of l, i.e. $l/r = n\pi/m$. The orientations of magnetic dipoles (polarization of oscillations) are different, as in the case of a torus. The type of dipoles of the corresponding LP is determined by the pattern of current flowing in the particle. The higher oscillations correspond to quadrupoles and multipoles. Since all SP in a non-magnetic particle correspond to E-SP, the polarization can be determined by the tangent component of the electric field to the surface. So, for a spherical particle in a spherical coordinate system, three polarizations with the same frequencies are possible: SP moves along the equator, SP moves along the prime meridian ($\varepsilon = 0$), and SP moves along the meridian $\varepsilon = 90°$. Of course, these are approximations, since the curved surface has been replaced by a flat one, and the exact fields have a rather complex appearance. But if we solve the problem strictly, rotating the planes by an angle φ and θ will also give a threefold polarization degeneracy. Be designating $\omega_r = c/(2r+l)$, we obtain the equation to define the frequencies in the absence of losses

$$\omega_n^4 - \omega_n^2\left[\omega_P^2/\varepsilon_L + \omega_r^2 n^2(1+1/\varepsilon_L)\right] - n^2\omega_r^2\omega_P^2/\varepsilon_L = 0.$$

After finding solutions to ω_n, the losses can be approximately accounted for by replacing $\omega_n \to \omega_n + i\omega_c/(2\omega_n)$.

7. Discussion of results and conclusions

It is demonstrated that SPR method is a fine approximation for calculating LP frequencies. This is attributable to the quasi-static nature of these resonances. All the resonant frequencies described above ω_n correspond to the formula

$$\sqrt{\varepsilon(\omega_n)/\left(\varepsilon(\omega_n)+1\right)} = n\omega_r/\omega_n,$$

where frequency $\omega_r = c/L$ is associated with a certain size L. If it's large and $n\omega_r/\omega_n \ll 1$, then, resonance stands for $\varepsilon(\omega_n) \approx 0$. This is resonance of the bulky plasmon $\omega_n = i\omega_c/2 + \sqrt{\omega_P^2/\varepsilon_L - \omega_c^2/4}$, i.e. $\omega_n = \omega_0 + i\omega_c/2$. With the growth of n the right-hand side increases at $n\omega_r/\omega_n \gg 1$ and condition $\varepsilon(\omega_n) \approx -1$ is met. This is SPR. For $n \to \infty$ we have

$$\omega_\infty = i\omega_c/2 + \sqrt{\omega_P^2/(\varepsilon_L+1) - \omega_c^2/4} = \omega_{spr} + i\omega_c/2.$$

For a small particle, the right-hand side is always large, i.e. $\varepsilon(\omega_n) + 1 \approx 0$, and the equality is more accurate the greater n. Correspondingly, ω_{spr} — point of condensation The higher the deceleration of SP, the higher the method accuracy. The frequencies ω_{spr} and ω_0 differ little, and if the resonant frequency is close to them, the deceleration of SP

is significant. An increase in SP deceleration is associated with a decrease in losses. It is possible to significantly reduce losses in metal particles (for example, by two orders of magnitude) using low temperatures. Macroscopic parameters for nanoparticles were used throughout analysis. This is a strong assumption. The microscopic 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. 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 impossible to solve even in approximations. The presence of boundaries and free electrons leads to a significant change in the collision frequency [2]. Problems associated with dimensional quantization and ballistic transport arise in the case of nanoclusters characterized by conductivity. Electrons involved in conduction move at the Fermi velocity; i.e., they are characterized by de Broglie wavelength $\lambda = 2\pi\hbar/(m_e v_F)$. Particles with lower energies are not involved in directional motion. In case of a large electron free path $\bar{\lambda}_e \gg L$, when moving along the longitudinal dimension, $n = 2L/\bar{\lambda}$ levels corresponding to it occur (the effect of dimensional quantization). In addition, we have $m = 2W/\bar{\lambda}$ levels corresponding to the transverse dimension W. These latter levels for a long graphene nanoribbon correspond to the number of longitudinal modes of conductivity and transverse modes which are quantized. In reality, for such a QW (graphene nanoribbons), it is necessary to solve the SE with a vector 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 $8LWt/\bar{\lambda}^3$ levels emerges. These levels correspond to conduction electrons. The known result (1) with an overestimation of energy corresponds to the model of absolutely high walls with WF $\psi = \sin(n\pi z/L)\sin(m\pi y/W)\sin(k\pi x/t)$, so it does not allow to obtain any results for transition frequencies. If the potential with account for all atoms or the approximate potential for conductivity electrons (for which the single-particle Schrödinger equation may be solved) in this QB is known, the energy levels and the transition frequencies may be determined. The polarizability of such a meta-atom (quantum dot or QB) 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. The macroscopic experimental parameters of metals near the transition of the real part of DP through zero shall be approximated fairly accurately. The accuracy of the approximation used with one term ε_L deteriorates in this range, so two or three Lorentz terms should be used. For a particle that is not too small, when it is still possible to enter the macroscopic Fermi velocity for it, and the flight time $\tau = 2r/v_F$, for which the macroscopic relaxation time $\tau_r = 1/\omega_c$ is significantly less, the collision frequency can be taken in the form $\omega_c = v_F$, where v_F — Fermi velocity, considering that the current-carrying electrons are located in the vicinity of the Fermi level. However, at an elastic (specular) distance from the walls, the momentum is to modulo conserved, and losses are associated with elastic scattering, i.e., with a specular scattering coefficient, so the real CF ω_c will be less. When exposed to rapidly alternating fields with an amplitude of E_0 and a frequency ω_n , electrons oscillate near the lattice ions with this resonant frequency of ω_n, while the peak-to-peak swing decreases with a frequency of $r_n = E_0(e/m_e)/|\omega_n^2 - i\omega_n\omega_c|$ [14]. All electrons are considered in this model. With the sizes of particle significantly higher than r_n the boundaries stop influencing ω_c. As the frequency grows, the offset decreases, and the influence of boundaries goes down, i.e., CF ω_c should decrease. In strong fields, the offset is greater, and in free oscillations, the amplitude decays with time, i.e. the directional offset of electrons becomes smaller. At that, CF ω_c should decrease. Thus, ω_c depends on the resonant frequency and amplitude of oscillations. With a small amplitude, the influence of the boundaries does not affect, and the frequencies ω_n change slightly near the frequency of SPR, which makes it possible to neglect the dependence $\omega_c(\omega_n)$. To assess the LP frequencies we may use macroscopic value of CF ω_c. Obtaining these models for collision frequencies is a separate difficult task, leading to nonlinear equations for determining the frequencies ω_n.

Let us consider as an example the meta-atom in the form of graphene 2DEG-domain with dimensions 2DEG and L. The surface conductivity of graphene derived from linear dispersion (for electrons and holes in the vicinity of Dirac points) without regard to inter-band transitions is actually given by the Drude formula [21]:

$$\sigma(\omega, \mu, \omega_c, T) = \frac{\sigma_{\text{intra}}(0)}{1 + i\omega/\omega_c}, \tag{38}$$

$$\sigma_{\text{intra}}(0) = \sigma_0 = \frac{e^2 k_B T}{\pi\hbar^2\omega_c} \ln\left(2\left[1 + \cosh\left(\frac{\mu_c}{k_B T}\right)\right]\right). \tag{39}$$

Here, μ_c — is the electrochemical potential and T — temperature. Since, according to Drude, the DC value $\sigma(0) = \sigma_0 = en_S v_F$, we determine from (38) the surface concentration of conductivity electrons and holes $n_S = \sigma_0/(ev_F)$. The free path λ_e in graphene is very long (about μm). If a cluster is significantly smaller in size, collisions may be neglected. At low frequency $\omega/\omega_c \ll 1$ the conductivity (38) is of ballistic nature $\sigma_{\text{intra}}(0)$ for cluster $L \ll \lambda_e$ and of diffusive nature at $L \gg \lambda_e$. In general case $\sigma = \sigma_{\text{intra}}(0)(1 + L/\lambda_e)$. At high frequency, the path length λ_e decreases, so the conductivity becomes reactive (inductive), small and ballistic $\sigma = -i\sigma_{\text{intra}}(0)\omega_c/\omega$. 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 run between collisions drops with the decreasing period). Then, kinetic inductance begins to play an essential role, which, when the current is directed along a large size in such a 2DEG, has the form $L_Q = m_e v_F L/(W\sigma_0 e)$. This inductance

and quantum capacitance C_Q contribute to the surface conductivity of the graphene fragment:

$$\sigma(\omega) = -i\sigma_0(1 + L/\lambda_e)\omega_c/\omega + iW\omega C_Q + W/(i\omega L_Q),$$

where $C_Q = e^2\mu_c/(\pi v_F\hbar^2)$. Writing down the resonance condition $k_0 L\sqrt{1 - 4/\sigma^2} = n\pi$, we obtain

$$\omega_n^4 + \frac{\omega_n^2}{4[WC_Q\omega_n^2 - W/L_Q - \sigma_0(1 + L/\lambda_e)\omega_c]^2} = \frac{n^2\Omega^2}{[WC_Q\omega^2 - W/L_Q - \sigma_0(1 + L/\lambda_e)\omega_c]^2}.$$

Here $\Omega = c\pi/(2L)$. Explicit solutions can be obtained if the quantum capacity is neglected. Transverse resonances are obtained by substituting $L \leftrightarrow W$. These formulae are true for small n.

As for Drude–Lorentz formula for DP of a metal, it is quite accurate in IR and lower-frequency ranges. In case of optical LPs, it is advisable to take several Lorentz terms in it to approximate real experimental DP of metals. Specifically, for silver$\varepsilon'(\omega)$ 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 rigorous formulae leads to a spectrum that condenses toward frequency $\omega_0 = \omega_P/\sqrt{\varepsilon_L}$, while the quasi-static approach and SPR method yield to the point of spectrum condensation $\tilde{\omega}_P = \omega_P/\sqrt{\varepsilon_L + 1}$. Note also that particles are often examined in a certain transparent medium with dielectric permittivity of $\tilde{\varepsilon}$. In this case all results are obtained by substitutions of $k_0 \to k_0\sqrt{\tilde{\varepsilon}}$ and $\varepsilon_L \to \varepsilon_L - \tilde{\varepsilon}$. Finally, we used Zenneck dispersion for a flat interface. At the same time, we got fairly simple results. Similarly, it is possible to obtain Zenneck dispersion equation for spherical and cylindrical particle surfaces if, similarly to derivation of formula(33), we consider SPs running along the coordinate φ for a cylinder or sphere. Such dispersion equations are much more complex and implicit, but they correctly take into account the curvature of the surface and give more accurate results.

Funding

This study was supported by the Ministry of Education and Science of the Russian Federation under the state assignment (project No. FSRR-2023-0008).

Conflict of interest

The author declares that he has no conflict of interest.

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Translated by T.Zorina