Surface response of spherical core-shell structured nanoparticle by optically induced elastic oscillations of soft shell against hard core

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Abstract

The optically induced oscillatory response of a spherical two-component, shell-core structured, nanoparticle by nodeless elastic vibrations of soft peripheral shell against hard and dynamically immobile inner core is considered. The eigenfrequencies of the even-parity, spheroidal and odd-parity torsional vibrational modes trapped in the finite-depth shell are obtained which are of practical interest for modal specification of individual resonances in spectra of resonant scattering of long wavelength ultrafine particles.

1 Introduction.

Current increasing interest in the peculiarities of electromagnetic response of ultrafine particles (nano and micro dimensions) of different materials is motivated by their practical utilization for biomedical purposes. The well-know example is the nanoparticles of noble metals, like gold and silver, whose capability of responding by surface plasmon resonances (optically induced oscillations of valence electrons against immobile ions well-recognizable in the optical spectra of resonant photoabsorption) is of practical interest in the usage of these metallic nanoparticles as biolabels (e.g [1-3]). In [3 4], the model of electromagnetic response of a metallic nanoparticles

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placed in a permanent magnetic field by surface gyromagnetic plasmons (optically induced cyclotron oscillations of valence electrons about the lines of magnetic field threading the nanoparticle) have been theoretically studied with concomitant suggestion that the considered effect can too be utilized in biomedical by applications. Continuing investigations in this direction, in present paper we consider two-component, hard core - soft shell, model of dielectric nanoparticle responding to externally induced electromagnetic load by shear elastic oscillations of the peripheral soft shell against hard dynamically inert core. The focus is laid on some technical aspect of solid-mechanical calculations of frequency of resonant oscillations. Specifically, our prime purpose is to elucidate how the frequencies of optically induced elastic shell-against-core oscillations (which in resonant photo absorption equal the frequency of impinging on particle AC electromagnetic field) depend upon material parameters and size of nanoparticle. Before embarking into details, it may be worth noting that theoretical treatment of experiments on electromagnetic response of ultrafine particles with relaxed surface from point of view of solid-mechanical model of elastic oscillations of soft finite-depth surface layer against hard core has first been considered, to the best of our knowledge, in work [5]. In this paper we consider non-studied before regime of nodeless shear elastic shell-against-core oscillations which is interesting in its own right and, first of all, because the obtained for the this case analytical expressions for frequencies of two fundamental vibrational modes, spheroidal and torsional, oscillations of shell against core clearly exhibit the set of characteristic parameters of nanoparticle.

2 General equations of elastic shell-against-core nodeless vibrations

In what follows we study Rayleigh’s regime of electromagnetic response of heterogenic shell-core structured spherical solid particle of radius $R$ to long wavelength electromagnetic field by non-compressional, pure shear, elastic oscillations of surface shell of finite depth $\Delta R = R - R_c$ against inner static core of radius $R_c$. This means that the wavelength of electromagnetic field is much large than spacing between sites of crystalline structure of particle (and may be even larger than the particle sizes) so that the particle material can be regarded in approximation of incompressible continuous medium. The fact that oscillations of peripheral shell are not accompanied by fluctuations in density means $\delta \rho = -\rho \nabla u_k u_k = 0$, where $u_i(r, t)$ is the material displacements in the peripheral shell. This is the case when crystalline structure undergo solely shear (reversal) distortions obeying the Hooke’s law of linear relation between tensors of shear stresses $\sigma_{ik}$ and shear strains $w_{ik}$. All the above means that optically induced oscillations can be modeled by the standard equation of solid-mechanics for elastically deformable continuous
medium
\[ \rho \ddot{u}_i = \nabla_k \sigma_{ik}, \quad \sigma_{ik} = 2 \mu u_{ik}, \quad u_{ik} = \frac{1}{2} [\nabla_i u_k + \nabla_k u_i]. \]  

(1)

The density \( \rho \) and the shear modulus \( \mu \) of particle material are regarded as constant input parameters of the model. The energy of oscillations is controlled by equation
\[ \frac{\partial}{\partial t} \int \frac{\rho \ddot{u}^2}{2} dV = - \int \sigma_{ik} \dot{u}_{ik} dV = -2 \int \mu u_{ik} \dot{u}_{ik} dV. \]  

(2)

As was said in introduction we focus on the regime of nodeless shear elastic oscillations in which fluctuations of material displacements \( u(r, t) \) are described by solutions of the vector Laplace equation
\[ \nabla^2 u(r, t) = 0 \quad \nabla \cdot u(r, t) = 0. \]  

(3)

In order to compute frequencies of nodeless oscillations in two fundamental modes - spheroidal and torsional, the material displacement \( u(r, t) \) can be conveniently represented in the form
\[ u(r, t) = a(r) \dot{\alpha}(t). \]  

(4)

On substituting (4) in (2) we arrive at equation for \( \alpha \) having the form of standard equation of linear oscillations
\[ \frac{dE}{dt} = 0 \quad E = \frac{M \dot{\alpha}^2}{2} + \frac{K \alpha^2}{2} \quad \rightarrow \quad \ddot{\alpha} + \omega^2 \alpha = 0 \quad \omega^2 = \frac{K}{M} \]  

(5)

\[ M = \int \rho a_i a_i dV \quad K = 2 \int \mu a_{ik} a_{ik} dV \quad a_{ik} = \frac{1}{2} [\nabla_i a_k + \nabla_k a_i] \]  

(6)

where the above introduced the field of instantaneous displacement \( a_i \) obeys too the Laplace equation
\[ \nabla^2 a_k(r) = 0 \quad \nabla_k a_k(r) = 0 \]  

(7)

which follows from substitution of (4) in (3). Two fundamental vibrational modes in an elastic spherical shell, spheroidal and torsional, are described by two fundamental solutions of (3) built on general solution to the scalar Laplace equation
\[ \nabla^2 \chi(r) = 0 \quad \chi(r) = f_\ell(r) P_\ell(\zeta) \quad f_\ell(r) = [A_\ell r^\ell + B_\ell r^{-(\ell+1)}] \]  

(8)

In the coordinate system with polar axis, the fields of displacements in the spheroidal mode \( a_s \) and torsional mode \( a_t \) of shear elastic vibrations are described by the poloidal and toroidal fields
\[ a_s = \nabla \times \nabla \times (r \chi) \quad a_t = \nabla \times (r \chi) \]  

(9)

\[ \chi(r) = f_\ell(r) P_\ell(\zeta) \quad f_\ell(r) = [A_\ell r^\ell + B_\ell r^{-(\ell+1)}] \]  

(10)
respectively. Henceforth $P_\ell(\cos \theta)$ stands for the Legendre polynomial of multipole degree $\ell$ and arbitrary constants $A_\ell$ and $B_\ell$ must be eliminated from boundary conditions of the core-shell interface and on the particle surface. Remarkably, these above fields $a_s$ and $a_t$ as function of radial coordinate $r$ have no nodes along the shell thickness $R_c < r < R$. The corresponding vibrational modes are specified, thereby, as modes of nodeless irrotational spheroidal oscillations (it can easily be verified that $\nabla \times a_s = 0$) and differentially rotational torsional oscillations. The case of nodeless global oscillations, in entire volume of spherical mass of a viscoelastic solid, pictured in Fig. 1, has been considered in details in [6].

In this work we derive spectral formulae for both spheroidal and torsional vibrational modes trapped in the peripheral shell. Following the above outlined computational scheme we compute separately the frequencies of elastic spheroidal and torsional shear oscillations of the soft shell against hard core.

3 Nodeless spheroidal oscillations of soft shell against hard core

In case spheroidal response the arbitrary constants $A_\ell$ and $B_\ell$ can be eliminated from condition of impenetrability of perturbation in the core, $u_r|_{r=R_c} = 0$, and condition of compatibility of rate of radial component of poloidal displacements with the rate of harmonic spheroidal distortions of the particle surface, $\dot{u}_r|_{r=R_c} = \dot{R}(t)$, where $R(t) = R[1 + \alpha(t) P_\ell(\cos \theta)]$. The computed along the above scheme frequency of spheroidal nodeless oscillations is given by

$$\omega_0^2 = c_t^2 = \frac{\mu}{\rho} \quad \lambda = \frac{R_c}{R} = 1 - h \quad h = \frac{\Delta R}{R}. \quad (12)$$

where $c_t = [\mu/\rho]^{1/2}$ is the speed of transverse wave of elastic shear in the bulk of the shell material. Note, that geometrical parameter $\lambda$ strongly less than unit, $\lambda < 1$. Deserved for particular comment is the dipole overtone of these oscillations which possesses properties of Goldstone’s soft mode. To see this, consider the limit of zero-size radius of the core, $\lambda = (R_c/R) \to 0$, which corresponds global nodeless spheroidal elastic shear vibrations in entire spherical volume of particle. In this limit we arrive at known result (e.g.[6-8])

$$\omega_0^2((\ell \geq 2, \lambda = 0) = \omega_0^2[2(2\ell + 1)(\ell - 1)] \quad (13)$$

which shows that lowest overtone of global, in entire volume, of nodeless spheroidal oscillations is of quadrupole degree, $\ell = 2$. However, this is not the case when we are oscillations trapped
Figure 1: Material displacements (arrows) in spherical mass of elastic matter undergoing nodeless spheroidal and torsional vibrations of quadrupole $\ell = 2$ and octupole $\ell = 3$ degree. In spheroidal mode with frequency $\omega_s(\ell) = \omega_0[2(2\ell + 1)(\ell - 1)]^{1/2}$ and in torsional mode with frequency $\omega_t(\ell) = \omega_0[(2\ell + 3)(\ell - 1)]^{1/2}$, where natural unit of frequency $\omega_0 = c_t/R$ with $c_t = [\mu/\rho]^{1/2}$ being the speed of transverse wave of elastic shear in the bulk elastically deformable material of particle and $R$ is the particle radius.
Figure 2: Irrotational displacements in dipole spheroidal soft mode of shear elastic oscillations of peripheral shell against core.

In the peripheral layer of finite depth. In this latter case from equation (??) it follows that lowest overtone is of dipole degree and the frequency of this dipole vibration is given by

\[
\omega_s^2(\ell = 1, \lambda) = \omega_0^2 \frac{9\lambda(1 - \lambda^5)}{(1 - \lambda^3)(1 + \lambda^3/2)}. \quad (14)
\]

The dipole spheroidal elastic oscillations of soft layer against inert hard are pictured in Fig. 2.

Thus, in case of global oscillations, in the whole volume, the dipole overtone of spheroidal mode disappears what is means that the frequency of dipole overtone tends to zero, as \( \lambda \to 0 \). This behavior of fractional frequency of dipole spheroidal irrotational oscillations of peripheral shell against core as a function of fractional thickness \( h = \Delta R/R \) is shown in Fig. 3.

In this sense the dipole vibration can be specified regarded as, so called, Goldstone soft mode, whose most conspicuous feature is to vanish, when some parameter of oscillating system turn to zero. In the model under consideration this parameter is \( \lambda = (R_c/R) \). Thus, the emergence of dipole overtone in the long wavelength oscillatory response of two-ply particle is the most striking feature of its vibratory behavior as compared to homogeneous particle.

4 Nodeless torsional oscillations of soft shell against hard core

In torsional mode of differentially rotational oscillations of elastically deformable soft shell against hard inert core, the constants \( A_\ell \) and \( B_\ell \) entering in expression for the field of toroidal instantaneous displacements, \( a_\ell \), are eliminated from the no-slip condition on the core-shell interface, \( u_\phi|_{r=R_c} = 0 \), and on the globe surface \( u_\phi|_{r=R} = [\Phi \times R]|_\phi \), where \( \Phi = \alpha(t)\nabla_{r=R}P_\ell(\zeta) \);
Figure 3: Fractional frequencies of dipole, $\ell = 1$, spheroidal $\omega_s/\omega_0$ and torsional $\omega_t/\omega_0$ oscillations of surface shell against hard core as functions of its fractional thickness $h = (R - R_c)/R$. When $h \to 1$, the radius of core $R_c \to 0$. The smooth decreasing of frequency shows the more mass (volume) of nanoparticles sets in dipole vibrations of shell against core the less frequency of these vibrations. The Goldstone’s feature of this soft mode is that when all the mass of elastic matter of particle involves in oscillations, the dipole oscillatory excitation does not appear.

the last condition is dictated by the form of general toroidal field whose correctness is discussed below. The resultant expression for the frequency of torsional oscillations of the soft layer against hard core is given by

$$\omega^2(\ell, \lambda) = \omega_0^2 (2\ell + 3)(2\ell - 1)(1 - \lambda^{2\ell+1}) \times$$

$$\left\{ \frac{1 - \ell - \lambda^{2\ell+1}[(\ell + 2) + (2\ell - 1)(2\ell + 3) - (2\ell + 1)^2\lambda^2 + (2\ell + 3)\lambda^{2\ell+1}]}{(2\ell - 1) - \lambda^{2\ell+1}[(2\ell - 1)(2\ell + 3) - (2\ell + 1)^2\lambda^2 + (2\ell + 3)\lambda^{2\ell+1}]} \right\}$$

$$\omega_0^2 = \frac{c^2}{R^2} = \frac{\mu}{\rho} \quad \lambda = \frac{R_c}{R} = 1 - h \quad h = \frac{\Delta R}{R}. \quad (18)$$

In the limit of zero-size radius of the core, $\lambda = (R_c/R) \to 0$, corresponding to torsional oscillations in the entire volume of homogeneous elastic particle we regain the known result [6-8]:

$$\omega^2_t(\ell \geq 2, \lambda = 0) = \omega_0^2[(2\ell + 3)(\ell - 1)]. \quad (19)$$

One sees that in this limit the lowest overtone is again of quadrupole degree $\ell = 2$. In the mean time, when the torsional vibrations are locked in the surface layer, the lowest overtone is of dipole degree and the frequency of $\ell = 1$ torsional vibration is given by

$$\omega^2_t(\ell = 1, \lambda) = \omega_0^2 \frac{15\lambda^3(1 - \lambda^3)}{(1 - \lambda)^3(1 + 3\lambda + 6\lambda^2 + 5\lambda^3)}. \quad (20)$$
In Fig. 3 we plot fractional frequencies of dipole both spheroidal $\omega_s(\ell = 1)/\omega_0$ and torsional $\omega_t(\ell = 1)/\omega_0$ oscillations as functions of $h = \Delta R/R$, the fractional thickness of the peripheral shell (see Fig. 4), which is the measure of amount of mass that sets in vibrations.

The smooth decreasing of frequency shows the more mass (volume) of nanoparticles sets in dipole vibrations of shell against core the less frequency of these vibrations. This figure clearly exhibits the Goldstone’s soft-mode nature of dipole overtones of both spheroidal and torsional oscillations of the shell against core (Figs. 2 and 4).

5 Summary

The two-component continuum model has been considered of a solid spherical nanoparticle, thought of as soft shell covering hard core, responding to optically induced perturbations by nodeless spheroidal and torsional shear elastic oscillations of peripheral finite-depth shell against hard immobile core. The practical usefulness of obtained Analytic equations for spectral formulae for the frequencies of the even-parity spheroidal (electric) spheroidal and the odd-parity (magnetic) torsional modes trapped in the peripheral shell have been obtained in analytic form whose practical usefulness is that they provide a basis for constructive spectral analysis of resonance state of photoabsorption by ultrafine elastically deformable solid nanoparticles. Highlighted are the dipole overtones of nodeless elastic vibrations in the finite-depth peripheral layer as Goldstone’s soft vibrational modes owing its existence to vibrations trapped in the peripheral shell, not in the entire volume of the particle. The obtained spectral equations clearly show how the frequencies of optically induced elastic resonances depend upon particle material – the shear modulus $\mu$, the density $\rho$ and on geometrical sizes of two-component nanoparticles – depth of dynamical peripheral shell $\Delta R$ and the particle radius $R$. Such information is indispensable to identification of experimentally observed picks of resonant photoabsorbtion
by ultrafine micro and nanoparticles with eigenmodes of optically induced elastic oscillations (e.g.\cite{9,10}). Finally, we would like to point out that presented mathematical treatment of oscillatory behavior of a spherical mass of elastically deformable matter in the core-shell picture is quite general, so that obtained spectral formulae can found application to more wide class of physical objects of current basic and applied research.

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