Mathematical Modeling of Electromagnetic Response of Non-metallic Nanoparticles for Application as Biolabels

I.V. Molodtsova[1], D.V. Podgainy[1], S.I. Bastrukov[2], H.-K. Chang[2], Pik-Yin Lai[3]

[1]Laboratory of Information Technologies, JINR, Dubna; [2]Department of Physics and Institute of Astronomy, National Tsing Hua University, Hsinchu, 30013 Taiwan; [3]Department of Physics and Center of Complex Systems, National Central University, Chung-li, 320 Taiwan

Abstract. Current interest in peculiarities of electromagnetic response of nanometer scale particles of different materials is due primarily to their practical applications in such areas of nanotechnology as optoelectronics, biosensors, defense, health care, communication, and biomedicine, etc. Motivated by this, in the below cited papers, the method has been developed to evaluate frequencies of resonance response of nanoparticles of non-metallic materials for their usage as biolabels in modern medico-biological fundamental investigations and applied research.

Optically induced electrostriction modes in a nanoparticle of a uniformly charged electret

The electromagnetic response of a nanoparticle of an ion-doped polymeric elastic insulator, commonly called as an electret, is considered in the continuum model of a uniformly charged elastic sphere [1]. The spectral formulae for the frequency of optically induced spheroidal and torsional shear oscillations driven by bulk force of elastic and dielectric stresses are obtained in analytic form. Particular attention is given to relaxation dielectric mode of the electrostriction response and its stability in the lowest quadrupole mode.

The optically-induced, by ac electromagnetic field, electro-mechanical distortions in the volume of uniformly charged electret are characterized by the tensor of dielectric stresses:

$$p_{ik} = \frac{1}{8\pi}[E_i\,\delta D_k + E_k\,\delta D_i - (E_j\,\delta D_j)\delta_{ik}] \quad (1)$$

where E_i are components of electrostatic field produced in the particle volume by extraneous charge uniformly distributed with the charge density ρ_e:

$$\nabla\cdot\mathbf{E} = 4\pi\frac{\rho_e}{\epsilon}, \quad \nabla\times\mathbf{E} = 0 \quad (2)$$

whose solution is well known:

$$\mathbf{E}(\mathbf{r}) = -\nabla\Phi(\mathbf{r}), \quad \Phi(r) = -\frac{2\pi}{3\epsilon}\rho_e(r^2 - 3\,R^2), \quad (3)$$
$$[E_r = \frac{4\pi}{3}\,\frac{\rho_e}{\epsilon}\,r, \quad E_\theta = 0, \quad E_\phi = 0].$$

The electro-mechanical effect is described by constituting equation[1]

$$\delta D_i = -4\pi\rho_e\,u_i \quad (4)$$

showing that optically induced fluctuations of dielectric induction δD_i are linearly proportional to material displacements u_i and inextricably related to the storage of extraneous charge uniformly dispersed with density ρ_e over the sample volume; note, the dielectric materials can accommodate only extraneous charge.

We confine our analysis to the Rayleigh's regime of optical perturbation resulting in non-compressional fluctuations of the electret material (the charge density remains unchanged $\delta\rho_e = -\rho_e\,\nabla_k\,u_k = 0$) which are described by nodeless field of material displacements u_i obeying the vector Laplace equation, $\nabla^2\mathbf{u} = 0$.

The eigenfrequency can be computed with help of the energy variational method whose key point is the separable representation of fluctuating material displacements and strains in the following separable form

$$\mathbf{u}(\mathbf{r},t) = \mathbf{a}(\mathbf{r})\,\alpha(t), \quad u_{ik}(\mathbf{r},t) = a_{ik}(\mathbf{r})\alpha(t), \quad (5)$$
$$a_{ik} = \frac{1}{2}[\nabla_i\,a_k + \nabla_k\,a_i]$$

Then, for the perturbation-induced dielectric induction one has

$$\delta D_i(\mathbf{r},t) = -4\pi\rho_e\,a_i(\mathbf{r})\alpha(t) \quad (6)$$

and the tensor of dielectric stress is given by

$$p_{ik}(\mathbf{r},t) = [\tau_{ik}(\mathbf{r}) - \frac{1}{2}\tau_{jj}\delta_{ik}]\alpha(t), \quad (7)$$
$$\tau_{ik}(\mathbf{r}) = -\rho_e[E_i(\mathbf{r})\,a_k(\mathbf{r}) + E_k(\mathbf{r})\,a_i(\mathbf{r})].$$

From the energy balance equation

$$\frac{\partial}{\partial t}\int\frac{\rho\dot{u}^2}{2}\,d\mathcal{V} = -\int\sigma_{ik}\dot{u}_{ik}\,d\mathcal{V}, \quad \sigma_{ik} = 2\,\mu\,u_{ik} \quad (8)$$

[1]The constitutive equation for δD_i is compatible with the Maxwell equation $\nabla\times\delta\mathbf{H} = (4\pi/c)\delta\mathbf{j} + (1/c)\delta\dot{\mathbf{D}}$. Applying to this latter equation operator of divergence and taking into account that $\delta\mathbf{j} = \rho_e\delta\mathbf{v}$ and the continuity equation of the charge conservation $\delta\dot{\rho}_e = -\nabla\,\delta\mathbf{j}$, we obtain $\delta\dot{\mathbf{D}} = -4\pi\rho_e\delta\mathbf{v}$. Bearing in mind that $\delta\mathbf{v} = \dot{\mathbf{u}}$ and eliminating in the last equation the time derivative one arrives at (4).

where ρ stands for the density the shear modulus μ, we obtain

$$\ddot{\alpha}(t) + \omega^2 \alpha(t) = 0, \quad \omega^2 = \frac{K_d}{M} \tag{9}$$

$$M = \int \rho a_i \, a_i d\mathcal{V}, \quad K_d = \int \tau_{ik}(\mathbf{r}) a_{ik}(\mathbf{r}) d\mathcal{V}.$$

The fact that such response is accompanied by internal shear deformations suggests that dielectric modes in question can be specified in a manner of vibrational modes in an elastic sphere, that is, as spheroidal and torsional ones.

Dielectric spheroidal mode. In this positive parity mode the displacements are described by the poloidal (polar) vector field

$$\mathbf{a}_s = \mathcal{N}_\ell \nabla \times \nabla \times \mathbf{r}\, r^\ell \, P_\ell(\cos\theta). \tag{10}$$

For the frequency ω_{ds} of spheroidal dielectric mode we obtain

$$\omega_{ds}^2(\ell) = -\frac{2}{3}\omega_d^2 \, (\ell - 1), \quad \omega_d^2 = \frac{4\pi}{\epsilon}\frac{\rho_e^2}{\rho} \tag{11}$$

where ω_d is the natural unit of dielectric fluctuations.

Dielectric toroidal mode. The material displacements in negative parity torsional mode are described by the axial toroidal (axial) vector field

$$\mathbf{a}_t = \mathcal{N}_\ell \nabla \times \mathbf{r}\, r^\ell \, P_\ell(\cos\theta). \tag{12}$$

Computation of the the frequency ω_{dt} of torsional dielectric mode yields

$$\omega_{dt}^2(\ell) = -\frac{1}{3}\omega_d^2 \, (\ell - 1), \quad \omega_d^2 = \frac{4\pi}{\epsilon}\frac{\rho_e^2}{\rho}. \tag{13}$$

The obtained spectral equations represent one of the main newly obtained result of the presented theory showing that optical response of nanoparticle of electret are characterized by two different in parity modes, even-parity spheroidal dielectric mode and odd-parity torsion one. The basic *dielectric* frequency ω_d depends upon the dielectric constant ϵ in such a way that in the limit $\epsilon \to \infty$, as is the case of conductors, $\omega_d \to 0$. This means that, contrary to the surface plasmons in a nanoparticle of a highly conducting noble metals, the electrostatic fluctuations in a nanoparticle of a uniformly charged electret are manifested as relaxation modes, not oscillatory.

As a representative example let us consider a case of nanoparticle with shear modulus profile given by

$$\mu(r) = \mu \left[1 - \left(\frac{r}{R}\right)\right] \tag{14}$$

In this case the frequency of spheroidal electrostriction mode can be conveniently represented in the following form

$$\omega_s^2 = \omega_e^2 \, 2(2\ell+1)(\ell-1)\ell^{-1}\left[1 - \frac{\ell}{3(2\ell+1)}\beta\right],$$

and for the torsional electrostriction mode as follows

$$\omega_t^2 = \omega_e^2 \, \frac{(2\ell+3)(\ell-1)}{2(\ell+1)}\left[1 - \frac{2(\ell+1)}{3(2\ell+3)}\beta\right],$$

with $\beta = \omega_d^2/\omega_e^2$. One sees that the lowest overtone of both spheroidal and torsional modes is of quadrupole degree $\ell = 2$. The absence of monopole $\ell = 0$, breathing overtone, is the consequence of adapted approximation of incompressible matter. The dipole fields of both poloidal and toroidal displacements describe center-of-mass translation and rigid-body rotation, respectively, that is, the non-vibrational reaction of nanoparticle.

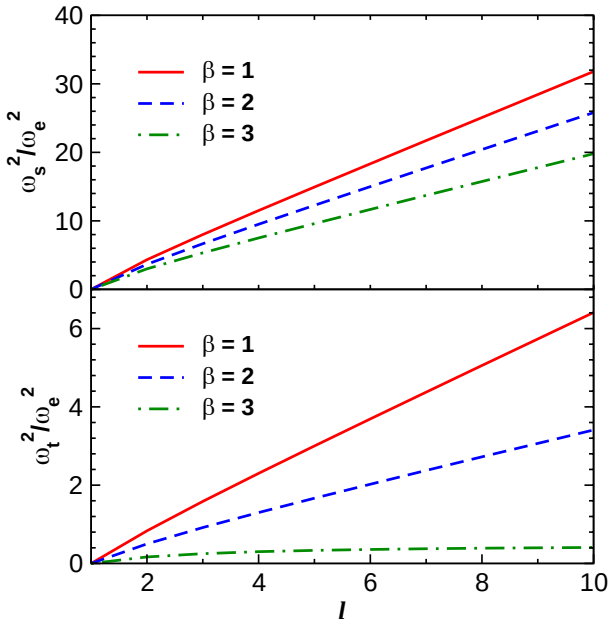

Figure 1: Ratio of the squared frequency of spheroidal (upper panel) and torsional (down panel) electrostriction modes to the squared frequency of elastic shear oscillations as a function of multipole degree at indicated values of parameter of stability β

In Fig.1 we plot the ratio ω_s^2/ω_e^2 and ω_t^2/ω_e^2 as functions of the multipole degree of spheroidal and torsional vibrations ℓ, respectively, showing that the larger the ℓ the higher is the frequency. Also, this figure exhibits strong dependence of frequencies upon the parameter

$$\beta = \frac{\omega_d^2}{\omega_e^2} = \frac{3}{4\pi}(\epsilon\mu)^{-1}\frac{Q^2}{R^4}, \quad Q = \rho_e \mathcal{V}, \quad \mathcal{V} = (4\pi/3)R^3.$$

carrying information about total charge Q accumulated by particle of radius R and shows that the

larger β (the large the ratio Q/R^2) the lower is the frequency. The most conspicuous feature of electrostriction response in question is that the lowest, quadrupole, overtones become unstable when the parameter β attains critical value $\beta = \beta_c$. Specifically, the spheroidal electrostriction vibrational mode becomes unstable, meaning $\omega_s(\ell = 2) = 0$, when

$$\left[1 - \frac{\ell}{3(2\ell+1)}\beta\right]_{\ell=2} = 0 \quad \rightarrow \quad \beta_c^s = \frac{15}{2}. \qquad (15)$$

The lowest quadrupole torsional electrostriction vibrational mode unstable, $\omega_s(\ell = 2) = 0$, when

$$\left[1 - \frac{2(\ell+1)}{3(2\ell+3)}\beta\right]_{\ell=2} = 0 \quad \rightarrow \quad \beta_c^t = \frac{7}{2}. \qquad (16)$$

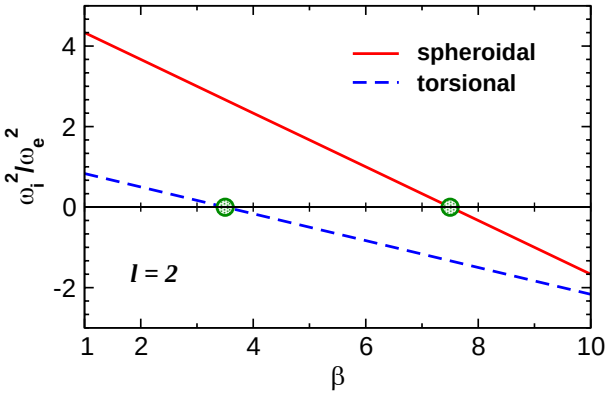

Figure 2: The frequency of quadrupole spheroidal and torsional electrostriction modes as a function of the stability parameter β. The circles on 0X-axis mark values of β at which the electrostriction mode becomes unstable undergoing transition from regime of oscillations to the relaxation regime.

In Fig.2 we plot the ratio of squared frequencies of quadrupole, $\ell = 2$, overtones of both spheroidal and torsion electrostriction modes as functions of the stability parameter β by highlighting the above critical values of stability parameter β_c by circles on the 0X-axis. In this points the electrostriction modes undergo transition from the oscillatory regime to the relaxation regime. This leads us to conclude that nanoparticle of uniformly charged electret is stable to optically induced deformation oscillations when

$$\frac{Q}{R^2} < C(\sqrt{\epsilon\mu}) \qquad (17)$$

where constant C falls in the range $5 < C < 10$; understandably that the lowest β_c should be regarded as genuine critical value of this parameter. The practical usefulness of the above established conditions of instability is that it imposes severe constrain on the size and total charge accommodated by the electret nanoparticles and this must be taken into account in the process for technological fabrication. As a representative example, for the nano and micro dimensions $10^{-8} < R < 10^{-6}$ m whose total charge is of the order of $Q \approx 10^2 e \approx 10^{-16}$ (in SI units) from polymers with dielectric constant $1 < \epsilon < 15$, and shear modulus $10^6 < \mu < 10^9$ (in SI units), from above obtaned condition it follows that $10^{-4} < Q/R^2 < 1$. So that for ultra fine particles of nano sizes this condition is always fulfilled.

The obtained criteria of electro-elastic instability of the electret nano-particle is crucialt to practical utilization of uniformly charged polymeric ultra fine particles which are currently fabricated by jammed technologies to be used as biolabels.

Elastic Shell-against-Core Nodeless Vibrations of a Spherical Nanoparticle

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 has been considered [2]. Focus was laid on Rayleigh's regime of electromagnetic resonance in which particle material can be regarded in approximation of incompressible continuous medium.

Using the energy variational method, the following spectral equations for the frequencies of the even-parity spheroidal and odd-parity torsional vibrational modes, acoustic phonons, trapped in the finite-depth shell have been obtained:

$$\omega_s^2(\ell,\lambda) = \omega_0^2 \frac{2(2\ell+1)}{(1-\lambda^{2\ell+1})} \times \qquad (18)$$
$$\left[\frac{(\ell^2-1)(1-\lambda^{2\ell-1}) + \ell(\ell+2)\lambda^{2\ell-1}(1-\lambda^{2\ell+3})}{(\ell+1)+\ell\lambda^{2\lambda+1}}\right],$$
$$\omega_0^2 = \frac{c_t^2}{R^2} = \frac{\mu}{\rho} \quad \lambda = \frac{R_c}{R} = 1-h \quad h = \frac{\Delta R}{R}.$$

where $c_t = [\mu/\rho]^{1/2}$ is the speed of transverse wave of elastic shear in the bulk of the shell material, R – radius of nanoparticle, R_c – radius of the inner static core, ℓ – multipole degree of acoustic phonon. Note, that geometrical parameter λ 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, $\lambda = (R_c/R) \rightarrow 0$, which corresponds global nodeless spheroidal elastic shear vibrations in entire spherical volume of particle. In this limit we arrive at known result:

$$\omega_s^2((\ell \geq 2, \lambda = 0) = \omega_0^2[2(2\ell+1)(\ell-1)] \qquad (19)$$

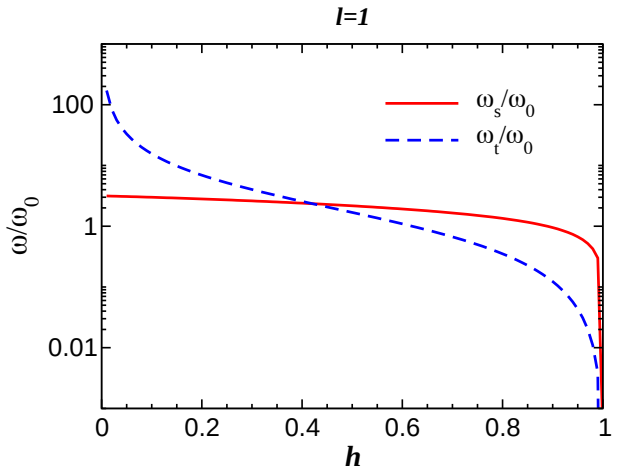

Figure 3: Fractional frequencies of dipole, $\ell = 1$, spheroidal ω_s/ω_0 and torsional ω_t/ω_0 oscillations of surface shell against hard core as functions of its fractional thickness $h = (R - R_c)/R$. When $h \to 1$, the radius of core $R_c \to 0$. The smooth decreasing of frequency shows the more mass (volume) of nanoparticles sets in dipole vibrations of shell against core the less frequency of these vibrations.

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 in the peripheral layer of finite depth. In this latter case from equation (18) it follows that lowest overtone is of dipole degree and the frequency of this dipole vibration is given by

$$\omega_s^2(\ell = 1, \lambda) = \omega_0^2 \frac{9\lambda(1 - \lambda^5)}{(1 - \lambda^3)(1 + \lambda^3/2)}. \qquad (20)$$

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 $\lambda \to 0$.

The resultant expression for the frequency of torsional oscillations of the soft layer against hard core is given by

$$\omega^2(\ell, \lambda) = \omega_0^2 \, (2\ell + 3)(2\ell - 1)(1 - \lambda^{2\ell+1}) \times \qquad (21)$$
$$\left[1 - \frac{\ell - \lambda^{2\ell+1}[(\ell + 2) + X]}{(2\ell - 1) - \lambda^{2\ell+1} X}\right],$$
$$X = (2\ell - 1)(2\ell + 3) - (2\ell + 1)^2\lambda^2 + (2\ell + 3)\lambda^{2\ell+1},$$
$$\omega_0^2 = \frac{c_t^2}{R^2} = \frac{\mu}{\rho} \quad \lambda = \frac{R_c}{R} = 1 - h \quad h = \frac{\Delta R}{R}.$$

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:

$$\omega_t^2(\ell \geq 2, \lambda = 0) = \omega_0^2[(2\ell + 3)(\ell - 1)]. \qquad (22)$$

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

$$\omega_t^2(\ell = 1, \lambda) = \omega_0^2 \frac{15\lambda^3(1 - \lambda^3)}{(1 - \lambda)^3(1 + 3\lambda + 6\lambda^2 + 5\lambda^3)}. \qquad (23)$$

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, which is the measure of amount of mass that sets in vibrations.

The obtained spectral equations clearly show how the frequencies of optically induced elastic resonances depend upon particle material – the shear modulus μ, the density ρ – and on geometrical sizes of two-component nanoparticles – depth of dynamical peripheral shell ΔR 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.

References

[1] S.I.Bastrukov, I.V. Molodtsova, P.-Y. Lai: *Optically induced electrostriction modes in a nanoparticle of a uniformly charged electret.* International Journal of Nanoscience, Vol. 7 (2008), p. 291-298.

[2] S.I. Bastrukov, P.-Y. Lai, I.V. Molodtsova, H.-K. Chang, D.V. Podgainy: *Surface response of spherical core-shell structured nanoparticle by optically induced elastic oscillations of soft shell against hard core*, Surface Review and Letters, Vol. 16 (2009), p.5-10.