Vibrational Modes of Metal Nanoshells

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Abstract

We study coherent oscillations of radial breathing modes in metal nanoparticles with a dielectric core. Vibrational modes are impulsively excited by a rapid heating of the particle lattice that occurs after laser excitation, while the energy transfer to a surrounding dielectric leads to a damping of the oscillations. In nanoshells, the presence of two metal surfaces leads to a substantially different energy spectrum of acoustic vibrations. The lowest and first excited modes correspond to in-phase (n=0) and out-of-phase (n=1) contractions of shell-core and shell-matrix interfaces respectively. We calculated the energy spectrum as well as the damping of nanoshell vibrational modes in the presence of surrounding medium, and found that the size-dependences of in-phase and anti-phase modes are different. At the same time, the oscillator strength of the symmetric mode is larger than that in solid nanoparticles leading to stronger oscillations in thin nanoshells.

Keywords: Nanoparticles, surface plasmon, vibrational modes, ultrafast spectroscopy

1 INTRODUCTION

Acoustic vibrational modes in nanoparticles are impulsively excited by a rapid heating of the lattice that takes place after laser excitation. After initial period of rapid expansion, a nanoparticle undergoes radial contractions and expansions around the new equilibrium. The periodic change in nanoparticle volume translates into a modulation in time of the surface plasmon resonance (SPR) energy that dominates nanoparticle optical absorption spectrum. The spectrum of vibrational modes manifests itself via coherent oscillations of differential transmission at SPR energy measured using ultrafast pump-probe spectroscopy [1], [2]. Since the size of laser spot is usually much larger than nanoparticle diameter, the initial expansion is homogeneous so that predominantly the fundamental ($n = 0$) breathing mode, corresponding to oscillations of nanoparticle volume as a whole, is excited. The lowest excited ($n = 1$) mode has weaker oscillator strength ($\approx 1/4$ of that for $n = 0$), and has also been recently observed [3]. When nanoparticle is embedded in a dielectric medium, the oscillations are damped due to the transfer of latice energy to acoustic waves in surrounding dielectric. In solid particles, the size dependences of eigenmodes energy and decay rate are similar – both are inversely proportional to nanoparticle radius [4].

Here we study the vibrartional modes of metal nanoshells. These recently manufactured metal particles with dielectric core [5] attracted much interest due to unique tunability of their optical properties. By varying the shell thickness during the manufacturing process, the SPR can be tuned in a wide energy interval [6]. Recent pump-probe measurements of vibrational modes dynamics in gold nanoshells submerged in water revealed characteristic oscillation pattern of differential transmission. However, the oscillations period and amplitude as well as their damping were significantly larger than those for solid nanoparticles. We perform detailed analysis of energy spectrum of lowest vibrational modes of a nanoshell in a dielectric medium. We find that the modes eigenenergies exhibit a strong dependence on nanoshell aspect ratio, $\kappa = R_1/R_2$, where R_1 and R_2 are inner and outer radii, respectively. Specifically, for thin nanoshells, the fundamental mode energy is consirerably lower than for solid particles while the damping is significantly larger. At the same time, in the thin shell limit, the fundamental mode carries the *entire* oscillator strength which results in an enhanced oscillations amplitude as compared to solid particles. The analysis also reveals two regimes, where the spectrum is dominated by nanoslell geometry or by surrounding medium, with a sharp crossover governed by the interplay between aspect ratio and impendance.

2 SPECTRUM OF VIBRATIONAL MODES FOR A NANOSHELL

We consider radial normal modes of a spherical nanoshell with dielectric core extending up to inner radius R_1 in a dielectric medium over outer radius R_2. The core, shell, and medium are characterized by densities $\rho^{(i)}$ longitudinal and tranverse sound velicities $c^{(i)}_{L,T}$ with $i = c, s, m$, respectively. The radial displacement $u(r)$ is determined from the Helmholtz equation (at zero angular momen-

tum) [7]

$$u'' + \frac{2u'}{r} + k^2 u = 0, \tag{1}$$

where $k = \omega/c_L$ is the wave-vector with the boundary conditions that the displacement u and the radial component of stress tensor,

$$\sigma = \rho\Big[c_L^2 u' + (c_L^2 - 2c_T^2)\,\frac{2u}{r}\Big], \tag{2}$$

are continuous at core/shell and shell/medium interfaces. In the three regions divided by shell boundaries, the solution has the form

$$u^{(c)} \sim \frac{\partial}{\partial r}\frac{\sin k^{(c)} r}{r}, \quad u^{(s)} \sim \frac{\partial}{\partial r}\frac{\sin(k^{(s)} r + \phi)}{r},$$
$$u^{(m)} \sim \frac{\partial}{\partial r}\frac{e^{ik^{(m)} r}}{r}, \tag{3}$$

where ϕ is the phase mismatch. The corresponding eigenenergies are, in general, complex due to energy transfer to outgoing wave in the surrounding medium. Matching $u(r)$ and $\sigma(r)$ at $r = R_1, R_2$, we obtain the following equations for eigenvalues $\xi = kR_2$

$$\frac{\xi^2}{\xi\cot(\xi+\varphi) - 1} + \frac{\eta_m \xi^2}{1 + i\xi/\alpha_m} + \chi_m = 0,$$
$$\frac{\xi^2\kappa^2}{\xi\kappa\cot(\xi\kappa+\varphi) - 1} - \frac{\eta_c \xi^2\kappa^2}{(\xi\kappa/\alpha_c)\cot(\xi\kappa/\alpha_c) - 1} + \chi_c = 0, \tag{4}$$

where $\kappa = R_1/R_2$ is nanoshell aspect ratio and the parameters

$$\alpha_i = c_L^i/c_L^{(s)}, \quad \eta_i = \rho^{(i)}/\rho^{(s)}, \quad \chi_i = 4(\beta_s^2 - \eta_i\delta_i^2)$$
$$\beta_i = c_T^{(i)}/c_L^{(i)}, \quad \delta_i = c_T^{(i)}/c_L^{(s)}. \tag{5}$$

characterize the metal/dielectric interfaces. For the ideal case of free boundary conditions, we have $\alpha_c = \eta_m = \eta_c = 0$ and $\chi_c = \chi_m = 4\beta_s^2$. For a thin nanoshell, $1 - \kappa \ll 1$, we then easily recover the known expression for the fundamental mode

$$\xi_0 = 2\beta_s\sqrt{3 - 4\beta_s^2}. \tag{6}$$

The eigenvalue is purely real since no energy leaks through the interface.

In the realistic case of a nanoshell in a medium, the following simplification occurs. The initial laser pulse causes rapid expansion of both dielectric core and metal shell. However, due to a larger value of the metal thermal expansion coefficient, the shell expands to a greater extend than the core, so at the new equilibrium the core and the shell are, in fact, no longer in contact. In this case, the boundary conditions at he core/shell interface should be taken as stress free. For a thin nanoshell, $1 - \kappa \ll 1$, Eqs. (4) are then reduced to

$$\lambda_c\left[\lambda_m - \lambda_c + \frac{\alpha_m\eta_m\xi^2}{\alpha_m - i\xi}\right] = (1-\kappa) \times \left[\left(\lambda_m + \frac{\alpha_m\eta_m\xi^2}{\alpha_m - i\xi}\right)\xi_0^2 - \lambda_c\xi^2\right]. \tag{7}$$

Typically, the metal density of the shell is much large that that of the sorrounding dielectric, i.e., the parameter η_m is small. For $\eta_m \ll 1$, using $\chi_m - \chi_c = -4\eta_m\alpha_m^2\beta_m^2$ and $\chi_m/\chi_c = 1 - \eta_m\beta_m^2$, we obtain

$$x^2 - 1 + \eta_m\beta_m = \frac{\alpha_m\eta_m}{\xi_0(1-\kappa)}\left[\frac{4\alpha_m\beta_m^2}{\xi_0} - \frac{x^2}{\alpha_m/\xi_0 - ix}\right], \tag{8}$$

where $x = \xi/\xi_0$. It can be easily seen that there are two regimes governed by the parameter

$$\lambda = \frac{\alpha_m\eta_m}{\xi_0(1-\kappa)}. \tag{9}$$

For a very thin nanoshell, $\lambda \gg 1$, the lowest eigenvalue is given by

$$\xi \simeq \alpha_m\beta_m - i\frac{\eta_m\alpha_m\beta_m^2}{\xi_0}. \tag{10}$$

In this regime, the energy and damping are comptetely determined by the surrounding medium and do not depend on nanoshell geometry. Note that if the transverse sound speed of the medium is zero (e. g., for water), then both energy and the decay rate vanish. In the opposite case, $\lambda \ll 1$, the solution can be obtained as

$$\omega \approx \frac{c_L\xi_0}{R_2}\left(1 + \frac{\alpha_m^2\eta_m}{2\xi_0^2(1-\kappa)}\left[4\beta_m^2 - \frac{1}{(\alpha_m/\xi_0)^2 + 1}\right]\right),$$
$$\gamma \approx \frac{c_L\alpha_m^2\eta_m}{2\xi_0(1-\kappa)(\alpha_m^2/\xi_0^2 + 1)R_2}. \tag{11}$$

In this case, the spectrum is mostly dominated by nanoshell geometry. Note that in typical experimental situations, the parameter λ is small, and with a good approximation, $\xi \simeq \xi_0$, which is considerably lower that the fundamental mode energy for solid particles, and it depends only weakly on aspect ratio.. At the same time, the damping rate γ is very sensitive to aspect ratio κ and is considerably higher than that for solid particles.

3 DISCUSSION

Here we present the results of our numerical calculations of vibrational mode spectrum for Au nanoshells in water. In Figs. 1 and 2 we show the energies and damping rates for fundamental ($n = 0$) and first excited ($n = 1$) modes. For fundamental mode, the energy decreases with increasing aspect ratio and, for thin nanoshells, is considerably lower that for nanoparticles,

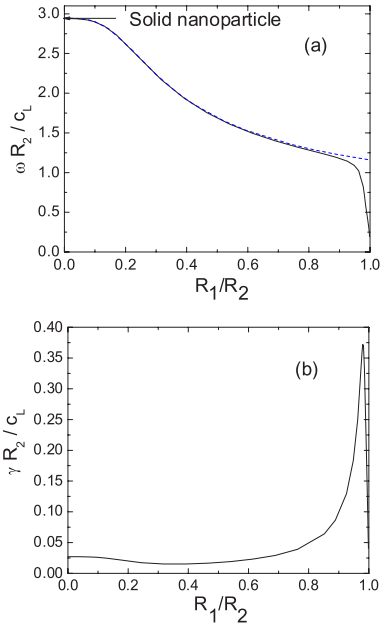

Figure 1: Spectrum for fundamental breathing radial mode in gold nanoshell versus its aspect ratio R_1/R_2. (a) Solid line: eigenfrequency versus R_1/R_2 in the model with free inner boundary and ideal contact between outer shell and matrix. Dashed line: eigenfrequency in the model with free boundaries. (b) Solid line: normalized damping rate versus aspect ratio. Longitudinal sound speed in gold $c_L = 3240$ m/s, transverse sound speed $c_T = 1200$ m/s, the density of gold $\rho = 19700$ kg/m^3. Surrounding matrix is water with c_L= 1490 m/s and $c_T = 0$, $\rho = 1000$ kg/m^3.

while the damping rate experiences a rapid increase as nanoshell becomes thiner. The sharp crossover for very thin nanoshells corresponds to the transition between geometry and medium dominated regimes, as discussed above. Note that for water ($c_T = 0$) both energy and damping rate vanish in the thin shell limit. In contrast, for $n = 1$ mode, no such transition takes place, and both energy and damping rate increase with aspect ratio.

Let as now turn to the relative contributions of fundamental and excited modes to the pump-probe signal. Since the intial rapid expansion of nanoshell is homogeneous, the oscillator strength of fundamental (symmetric) mode is expected to be larger than that of $n = 1$ (antisymmetric) mode. The expression for oscillator strength of nth mode has the form

$$C_n = \frac{R_2^{-1}\int r\,U_n(r)dV}{V^{1/2}\Big[\int U_n^2(r)dV\Big]^{1/2}}. \qquad (12)$$

In Fig. 3 we show calculated oscillator strengths for $n = 0$ and $n = 1$ modes versus aspect ratio. In contrast

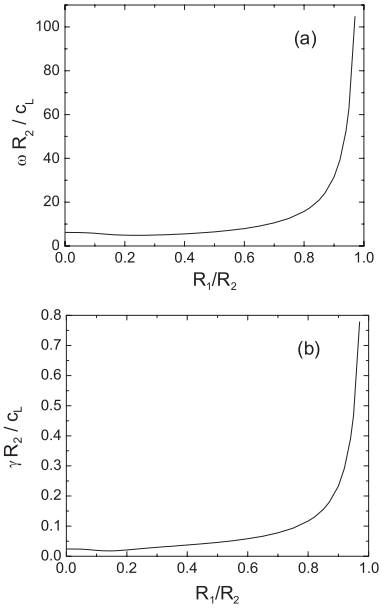

Figure 2: Spectrum for $n = 1$ radial mode in gold nanoshell versus its aspect ratio R_1/R_2. (a) Eigenfrequency calculated with free inner boundary and ideal contact between outer shell and matrix. (b) Normalized damping rate versus aspect ratio.

to solid particles, where the relative strengths of two modes is constant, $C_1/C_0 = 1/4$, here C_1 vanishes in the $\kappa = 1$ limit, while C_0 reaches it maximal value, $C_0 = 1$. Thus, in thin nanoshells, the fundamental mode carries almost entire oscillator strength. As a result, in nanoshells, excitation of the fundamental mode should result in a greater amplitude of oscillations as compared to solid particles while the $n = 1$ should be practically undetectable.

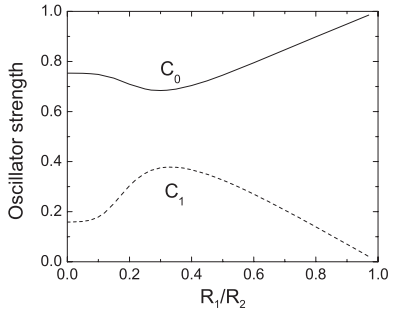

Figure 3: Oscillator strengths for symmetric (solid line) and antisymmetric (dashed line) breathing modes of nanoshell versus nanoshell aspect ratio R_1/R_2. At $R_1 = 0$ oscillator strength coincide with one for nanoparticle.

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