Localized surface plasmons in coupled metallic nanospheres

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ABSTRACT

An approximate analytical solution of the problem of the spectrum of plasma oscillations in a system of two metallic nanospheres is presented. The essence of the approximation is that the field of each sphere is replaced by the field of a dipole with a finite arm, the center of the dipole being shifted from the sphere center. The magnitudes of the shift and the arm are determined from the boundary conditions for the electric field in quasistatic approximation. The results are in good agreement with previous results of other studies. The proposed method has several advantages compared with numerical methods and other approximate analytical methods.
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INTRODUCTION

It is well-known that for a system of two interacting metal nanosphere strong dependence of surface plasmon (SP) frequency ω_{sp} on interparticle center to center distance a is revealed by both experimental data and numerical calculations[1-10]. This fact gives new opportunities for the applications of interacting metal nanoparticles in a molecular medicine as a nano dimensional ruler[10, 11].

The peculiarities of optical properties of coupled particles can also be used for chemical or biological imaging, catheterization, and surface-enhanced Raman scattering (SERS). The dependence of SP frequency of nanopair on interparticle distance is more intense when a <1.1D (D-diameter of the sphere). However, for such small distances a variety of numerical methods requiring a huge amount of calculations are used[7, 12], which becomes a major obstacle for obtaining reliable results.

It is important to note that all known methods of numerical calculations of ω_{sp} such as widely used

DDA, or T-matrix bring to a cumulative error of few percents, which increases with the size of particle or as a result of surface or volume discretization. This arguments force us to develop a new approaches which allows to analytically make approximate calculations of the SP resonance frequencies for any value of interparticle distance. A physically simple approach called eliminated quadrupole moment approximation (EQMA) has been developed recently[13], which allows to easily obtain the longitudinal and transverse frequency of SP resonance for small nanoparticles pair $D < \lambda / 2\pi$. The essence of the method is that the electric field of each sphere is substituted by the field of a point dipole, located at the point shifted from the sphere centre by certain distance. Further, corresponding boundary problem is solved, which allows determining the dipole position and the resonance frequency in a self-consistent manner. It has been shown that for up to 1.1D interparticle centre-to-centre distances the deviation from results for SP frequencies obtained by numerical methods is smaller than 2%. It has been also

shown that $\omega_{sp}(\alpha)$ dependence is well approximated by an exponential function, although analytically described in very different functions. However, for smaller distances (less than 1.1D) the difference between results obtained through numerical calculation and approximate analytical method increases. This fact shows the limited application of this approach for almost touching (very close) nanospheres case. It should be mentioned that for exactly touching spheres reliable analytical solutions are known[14], however we are interested in the change of frequency depending on the distance in case of very small distances.

Other approach[15] is based on the theory of infinite fractions[16], which results in a strictly convergent iteration procedure and due to that significantly reduces both calculation errors and calculation time (the results are obtained in few seconds). The method does not require powerful computer tools and allows quick and efficient processing of experimental data, it can be regarded as the theoretical basis for theory of "plasmon nanoruler" in extremely small range of interparticle separations. The advantage of this method is shown for the interparticle gaps much smaller than 0.1 D (almost touching nano particles). Despite the advantages of this method, it does not allow determination of the field distribution, and on the other hand the physical meaning of the mathematical procedure remains unclear.

In order to avoid these difficulties in this communication we apply the generalization of the EQMA, formulated in[13]. In this approach the improvement of the accuracy of the EQMA calculation for smaller interparticle distances is achieved by introducing the nonzero arm of the dipoles. We substitute the ûeld of each sphere by the ûeld of a nonpoint dipole, that is, by the ûeld of two equal point charges of opposite sign separated by a ûnite distance and solve the boundary problem.

IMPROVED ANALYTICAL APPROACH

As it is mentioned we substitute the field of each sphere by the field of a nonpoint dipole, that is, by the field of two equal point charges of opposite sign, q_1 in the first sphere and q_2 in the second one, sepa-

rated by a finite distance 2η. The geometrical center of this dipole is located on the straight line connecting the centers of the spheres at the point O'. It is obvious that the charge distribution has only odd multipolar moments with respect to the dipole center. We suppose the system to be smaller than the wavelength of the radiation arising during the plasma oscillations.

In the general case of dissimilar spheres, we derive six equations with given values of R_1, R_2, and a for the following quantities: the surface plasmon frequency of the coupled spheres ω_{sp} which enters the equations through the real part of metal dielectric function $\varepsilon(\omega)$; the arms of the dipoles in the first and second spheres $2\eta_1$ and $2\eta_2$, respectively (the corresponding dipole moments being $2q_1\vec{\eta}_1$ and $2q_2\vec{\eta}_2$); the charge ratio q_1/q_2; and the displacements δ_{1z} and δ_{2z} of the geometrical centers of the charges. Note that the dipole moments in the case of longitudinal oscillations are directed along the Z axis, whereas for transverse oscillations, they are directed perpendicular to the Z axis.

The boundary conditions for the electric field potential Φ and the normal component of the electric field strength $E_n = \dfrac{\partial \Phi}{\partial R}$ on the surface of the right hand sphere (see Figure 1) (sphere II) are of the form

$$\Phi_{ext} = \Phi_{int}, \quad \varepsilon_0 E_{ext,n} = \varepsilon(\omega) E_{int,n},$$

where the resultant external potential $\Phi_{ext} = \varphi_1(R) + \varphi_2(R)$, and $\varphi_2(R)$ is the field potential of the sphere II in the outer region and ε_0 is the dielectric constant of the surrounding media. For
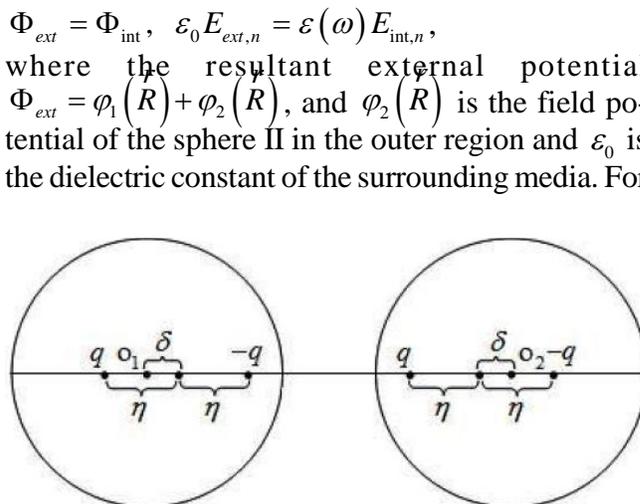
Figure 1

simplicity, we consider the longitudinal oscillations and derive the basic equations in the following way. The total potential, ϕ_1, of two charges that mimic the field of the first sphere

$$\phi_1 = q_1 \left(\frac{1}{\left| \vec{r} - \vec{\delta}_1 - \vec{\eta}_1 \right|} - \frac{1}{\left| \vec{r} - \vec{\delta}_1 + \vec{\eta}_1 \right|} \right) \tag{1}$$

can be expanded with respect to the center of the second sphere

$$\phi_1 = q_1 \sum (-1)^l \left(\frac{1}{a_{1+}^{l+1}} - \frac{1}{a_{1-}^{l+1}} \right) R_2^l P_l (\cos\theta) \tag{2}$$

where $\vec{a}_{1+} = \vec{a} - \vec{\delta}_1 - \vec{\eta}_1$ and $\vec{a}_{1-} = \vec{a} - \vec{\delta}_1 + \vec{\eta}_1$. The boundary problem we solve using the result for the problem of dielectric sphere in field of a point charge[17], which leads to following expression for the electric field potential created by the polarization of the second sphere in the outer space

$$\phi_1 = q_1 \sum (-1)^l \left(\frac{1}{a_{1+}^{l+1}} - \frac{1}{a_{1-}^{l+1}} \right)$$

$$\frac{\varepsilon_0 - \varepsilon(\omega)}{l\varepsilon_2(\omega) + \varepsilon_0(l+1)} P_l (\cos\theta) \tag{3}$$

Further, for the lowest-order multipoles (l = 1, 2, 3), we approximate the potential in eq 3 as the potential created by two charges located in the second sphere at the points $\vec{\delta}_2 \pm \vec{\eta}_2$ with respect to its center, which leads to the relation

$$(-1)^l \, l R_2^{2l+1} \frac{q_1}{q_2} \left(\frac{1}{\left| \vec{r} - \vec{\delta}_1 - \vec{\eta}_1 \right|^{l+1}} - \frac{1}{\left| \vec{r} - \vec{\delta}_1 + \vec{\eta}_1 \right|^{l+1}} \right) \frac{1}{l}$$

$$\left| \frac{\varepsilon_0 - \varepsilon(\omega)}{l\varepsilon_2(\omega) + \varepsilon_0(l+1)} \right| = \left| \vec{\delta}_2 + \vec{\eta}_2 \right|^l - \left| \vec{\delta}_2 - \vec{\eta}_2 \right|^l \tag{4}$$

As the first sphere is polarized in the field created by two charges located at the points in the second sphere, the expression analogous to Eq. 4 takes the form

$$l R_1^{2l+1} \frac{q_1}{q_2} \left(\frac{1}{\left| \vec{r} - \vec{\delta}_2 - \vec{\eta}_2 \right|^{l+1}} - \frac{1}{\left| \vec{r} - \vec{\delta}_2 + \vec{\eta}_2 \right|^{l+1}} \right)$$

$$\frac{\varepsilon_0 - \varepsilon(\omega)}{(\omega) + \varepsilon_0(l+1)} = \left| \vec{\delta}_1 + \vec{\eta}_1 \right|^l - \left| \vec{\delta}_1 + \vec{\eta}_1 \right|^l \tag{5}$$

Equations 4 and 5 for l = 1, 2, 3 form the required set for determining the SP spectrum. Eliminating the five auxiliary quantities $\vec{\eta}_1, \vec{\eta}_2, \vec{\delta}_{1z}, \vec{\delta}_{2z}$ and q_1/q_2, we find the frequency ω_{sp} as a function of the parameters. These equations in the case of identical spheres $\vec{\delta}_{2z} = -\vec{\delta}_{1z}$, $\vec{\eta}_{1z} = \vec{\eta}_{2z}$ can be simplified to take the form

$$2R^3 \frac{\varepsilon(\omega) - \varepsilon_0}{\varepsilon(\omega) + 2\varepsilon_0} \frac{a - \delta_z}{\left[(a - \delta_z)^2 - \eta^2 \right]^2} = 1 \tag{6}$$

$$R^5 \frac{\varepsilon(\omega) - \varepsilon_0}{2\varepsilon(\omega) + 3\varepsilon_0} \frac{3(a - \delta_z)^2 + \eta^2}{\left[(a - \delta_z)^2 - \eta^2 \right]^3} = \delta_z \tag{7}$$

$$12R^7 \frac{\varepsilon(\omega) - \varepsilon_0}{3\varepsilon(\omega) + 4\varepsilon_0} (a - \delta_z) \frac{(a - \delta_z)^2 + \eta^2}{\left[(a - \delta_z)^2 - \eta^2 \right]^4} = 3\delta_z^2 + \eta^2 \tag{8}$$

where the upper sign relates to the in-phase oscillations of charges in the spheres, which can be excited optically. It is easy to see that, if the arms of the dipoles tend to zero, the Eqs (6) and (7), as expected, are reduced to the equations of EQMA.

RESULTS AND DISCUSSION

The numerical solution of Eqs (6) - (8) is as simple as in the case of the EQMA with zero-arm dipoles. First we introduce new dimensionless unknown quantities instead of η and δ

$$\Delta = \frac{\delta}{R}, \qquad H = \frac{\eta}{R}, \tag{9}$$

and change the notations

$$\frac{a - \delta}{R} = x, \qquad \frac{\varepsilon(\omega)}{\varepsilon_0} = y, \qquad \frac{a}{R} = 2s, \qquad 2s - \Delta = x, \tag{10}$$

where s is the interparticle center-to-center distance divided by the particle diameter. Now the equations (6)-(8) take the form

$$2\frac{y-1}{y+2}\frac{x}{\left(x^2-H^2\right)^2}=1 \qquad (11)$$

$$\frac{y-1}{2y+3}\frac{3x^2+H^2}{\left(x^2-H^2\right)^3}=\Delta \qquad (12)$$

$$12\frac{y-1}{3y+4}x\frac{x^2+H^2}{\left(x^2-H^2\right)^4}=3\Delta^2+H^2. \qquad (13)$$

Eq. 11 allows to determine the dependemce of H on x and y as follows

$$H^2\left(x,y\right)=x^2-\sqrt{2\frac{y-1}{y+2}x}\,, \qquad (14)$$

and then eliminate H from Eqs. 12 and 13. Next, we divide the Eq. 13 by the Eq. 11 to obtain the final equation to be solved

$$\frac{y+2}{3y+4}-\frac{1}{6}\left[3\Delta^2\left(x,y\right)+H^2\left(x,y\right)\right]\frac{\left[x^2-H^2\left(x,y\right)\right]^2}{x^2+H^2\left(x,y\right)}=0, \quad (15)$$

where the function $\Delta\left(x,y\right)$ is determined by substituting H from Eq. 11 into 12

$$\Delta\left(x,y\right)=\frac{y-1}{2y+3}\cdot\frac{3x^2+H^2\left(x,y\right)}{\left[x^2-H^2\left(x,y\right)\right]^3}. \qquad (16)$$

Note that when s varies from unity to infinity Δ varies from 0 to 1, so that we can assign to the auxiliary parameter x values starting with 1 to infinity. We determine graphically the roots of the equation (15) for given value of x and then the values of x and y substitute into the Eq. 16 and the last of the Eqs. 10 in order to obtain corresponding values of s. Thus we can plot the dependence of the resonance value of dielectric function y on the dimensionless interparticle center-to-center distance $s=a/2R$ that is shown on the Figure 2 (red circles). For comparison we also present the same dependence calculated with use of the infinite fraction method[15] (blue solid line), which is the simplest method, which leads to results close to the published in the papers cited here for arbitrary interparticle distances.

It is clear, that our method fails in case of very small interparticle gaps, e.g. for s=1.03 the discrep-
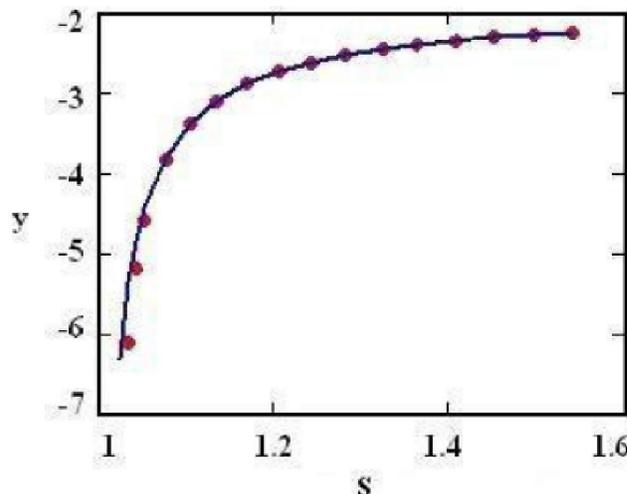
Figure 2

ancy reaches 7%, while decreases rapidly for smaller interparticle separations, and for s=1.04 we obtain an error of 3%. At the same time the EQMA based method for s=1.04 gives a deviation from the exact result as large as 22%. It is must be emphasized that the calculation error for frequency is smaller than that for the dielectric function. Indeed, consider the model for $\varepsilon(\omega)$ used in Ref.[8], namely with $h\omega_p\approx 9\,eV$. Then for a typical value $h\omega=2\,eV$ we obtain

$$\frac{\Delta\varepsilon(\omega)}{\varepsilon(\omega)}:\quad 4\frac{\Delta\omega}{\omega}.$$

Note that the resonance frequencies can be determined from the experimental data for the function $\varepsilon(\omega)$ [18].

It is important to mention that the approach developed in this communication is not applicable for gap distances comparable to atomic size. For example, in the case of identical spheres with $2R=20$ nm, the interparticle distance $a/2R=1.02$ presented above corresponds to only 4 Å of the gap distance between the particles, and obviously, the microscopic considerations must be invoked.

Further for each value of x and y we find the dependence of the dipole semi-arm from the Eq. 14 and the magnitude of the shift of the dipole center from the sphere center Δ using the Eq. 16. These dependences are presented on the Figure 3, where red squares relate to the dipole semi-arm and the

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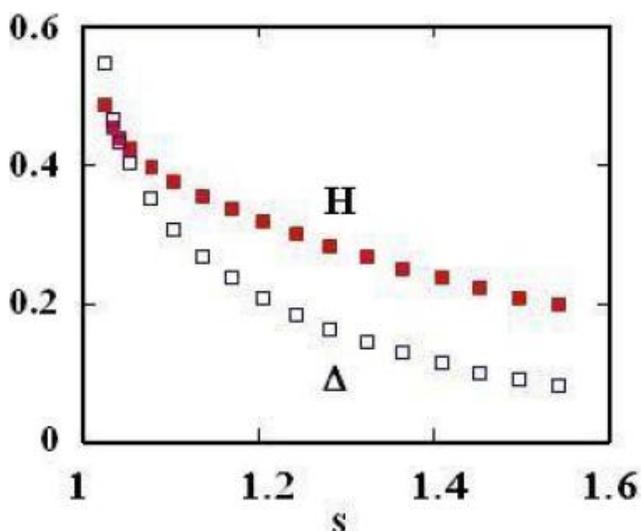
Figure 3

open squares to the shift of the center of the dipole.

It can be seen that the shift of the center of the dipole δ tends to zero much faster than the semi-arm η. This means that the finiteness of the semi-arm is more important than the shift of the dipole center. This is why the presented approach gives more reliable results than the EQMA based calculations where the electric field of the sphere is substituted by the field of a point dipole.

In conclusion, we note the advantages of the proposed approach compared with the method of continued fractions. Firstly our approach allows to calculate the field distribution using expressions (3) - (5) with known values of ε(ω), δ and η. Second, calculated field can be used as a zero-order approximation for the calculation of higher approximations by iteration. As is known from potential theory[19] using the approximate expression for the field, one can calculate the charge distribution induced by this field, then calculate new field configuration, which is closer to the exact value than the zero-order approximation. Third, our approach can be generalized to calculate SP spectra and field of more complicated systems of nanoparticles.

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