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Research Article

Polarizability of a metallic nanosphere: Local random-phase approximation (LRPA)

Prabath Hewageegana[*]

Department of Physics, University of Kelaniya, Kelaniya 11600, Sri Lanka

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Abstract

We develop a method for calculating the polarizability of a spherical nano particle by taking in to account the temporal and spatial dispersion where dispersion due to the Landau damping. To describe these phenomena, we developed analytical theory based on local random-phase approximation. Our theory is very general in the sense that it can be applied to any material which can be characterized by a bulk dielectric function of the form $\varepsilon(k,\omega)$. The theory is applied to calculate the polarizabilities of dielectric and metallic nanospheres.

Keywords: metallic nanosphere; polarizability; random-phase approximation

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1. INTRODUCTION

Recently, there has been explosive growth of nanoscience and nanotechnology. Nanosystems possess unique properties different from those of macroscopic materials when characteristic lengths govern their properties. Therefore, the spatial dispersion becomes much more important where the characteristic size of the particle or distances between them becomes comparable to the characteristic scale of the system[1-5]. One example of such a scale is the lattice constant in metals which is on the order of the electron wavelength at the Fermi surface $\lambda_F \sim 1$Å. Another important scale in nanooptics: which is a modern branch of optical science that explores how optical frequency radiation can be confined on the nanoscale, i.e.,1-100 nm (much smaller than the optical wavelength) is the Debye screening radius $r_D = \sqrt{\varepsilon_h E_F /(6\pi n e^2)}$ (or Thomas-Fermi screening radius) where ε_h is the background dielectric constant of the

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[*] *Corresponding Author E mail*: psh@kln.ac.lk

metal that is due to the core (valence) electrons and ion motion (phonons), *n* is the concentration of electrons in c.g.s units and E_F is the electron Fermi energy $E_F = \hbar^2 k_F^2 / 2m^*$, where $k_F = (3\pi^2 n)^{1/3}$ is the electron wave vector at the Fermi surface and m^* is electron effective mass in the metal.

Using the Bohr radius, $a_B = \varepsilon_h \hbar^2 / m^* e^2$ and k_F, one can rewrite r_D for most metals, including noble metals, as $r_D \cong 2.9 \times 10^5 (n^{-1/6}) < 1$ Å. One of the other length is the correlation length, l_c: that an electron at the Fermi surface travels during a period of the optical radiation, is another important scale for optical interactions in a metal system, which is on the order of $\sim v_F / \omega$, where v_F is the electron speed at the Fermi surface; for metals $v_F \sim 10^8$ cm s^{-1} and $\omega \sim 10^{15}$ s^{-1} is the optical frequency. This yields an estimate $l_c \sim 1$ nm which is the largest spatial scale compared with the other two scales. Therefore, when a characteristic size *a* of the nanosystem becomes small, it may become comparable to l_c which will make important for the nonlocality in the optical responses of the electron system. Therefore, macroscopic description of nanostructured system may not be applicable even on the order of magnitude.

It is very clear now that the optical properties of nanospheres, whose size ~ 10 nm or less, are very different from those of the corresponding bulk materials[3,6]. This is due to the surface effect: large surface to volume ratio. One of the consequences of such a small size of the system is that the electric field ***E*** magnetic induction ***B***, magnetic field ***H*** and the displacement vector ***D*** are related by a nonlocal relationship instead of the usual local relation. Assuming that fields are weak enough that displacement vector ***D*** and magnetic induction ***B*** can be obtained by perturbation theory therefore, one can obtain integral linear-response relation in terms of the corresponding fields (i.e., relations between ***D*** and electric field ***E***, and ***B*** magnetic filed ***H***)

$$\mathbf{D}(\mathbf{r},t) = \int_{-\infty}^{\infty} dt' \int_{V} \varepsilon(\mathbf{r}-\mathbf{r}', t-t')\, \mathbf{E}(\mathbf{r}', t') d\mathbf{r}' \tag{1}$$

$$\mathbf{B}(\mathbf{r},t) = \int_{-\infty}^{\infty} dt' \int_{V} \mu(\mathbf{r}-\mathbf{r}', t-t')\, \mathbf{H}(\mathbf{r}', t') d\mathbf{r}' \tag{2}$$

here $\varepsilon(\mathbf{r}-\mathbf{r}', t-t')$ (dielectric function) and $\mu(\mathbf{r}-\mathbf{r}', t-t')$ (magnetic permeability) denote the response functions in space and time. The displacement ***D*** at time *t* depends on the electric field at time t' previous to *t* (temporal dispersion or frequency dispersion). In addition to that the displacement at point *r* also depends on the values of the electric field at neighboring points *r'* (spatial dispersion). A spatially dispersive medium is therefore also called a *non-local* medium. This effect can be observed at interface between different media or in metallic objects with sizes comparable with the mean-free path of electrons. In most cases of interest the effect of the spatial dispersion is very week, therefore we can assume that the materials of the system are isotropic. Otherwise, both ε and μ would have been tensors, which would make no principal difficulty but make formulas somewhat more complicate. However, on the other hand temporal dispersion, is a widely encountered phenomenon and it is important to take it accurately into account.

As we discussed above relations (1) and (2) are non-local both in space and time.

However, one can use mathematically equivalent description in Fourier domain which is local,

$$\mathbf{D}(\mathbf{k},\omega)=\varepsilon(\mathbf{k},\omega)\mathbf{E}(\mathbf{k},\omega), \qquad \mathbf{B}(\mathbf{k},\omega)=\mu(\mathbf{k},\omega)\mathbf{H}(\mathbf{k},\omega) \tag{3}$$

Here we have introduced the corresponding arguments in Fourier domain which is wave vector k and frequency ω. Therefore, the Fourier transform of the electric field is defined as,

$$\mathbf{E}(\mathbf{k},\omega)=\int \mathbf{E}(\mathbf{r},\omega)e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}d\mathbf{r}dt \tag{4}$$

and one can get similar expressions for other quantities.

2. MODEL AND EQUATIONS

We will employ local random-phase approximation (LRPA): suppose that locally the electron Fermi liquid everywhere has the same properties as in the bulk metal, a microscopic approach based on random-phase approximation (RPA)[7] where the dielectric function $\varepsilon(k,\omega)$ possesses both the temporal and spatial dispersion, and dissipation is due to the Landau damping[8]. Earlier, approach based on RPA[9] was developed for somewhat large radii, $a >> r_D$. In contrast, our theory is valid for the intermediate scale, $l_c \geq a \geq r_D$, which is of high importance for nanooptics. Such a nanolocalized fields are due to the interaction processes (oscillation of polarization charges) between electromagnetic radiation and conduction electrons at metallic interfaces or in small metallic nanostructures, leading to an enhanced optical near field of sub-wavelength dimension. Such oscillations on the nanoscale are called surface plasmons.

In LRPA, we consider electrons of the metal as a degenerate electron plasma that possesses dissipation due to Landau damping and whose dielectric function depends on both ω (temporal) and k (spatial dispersion). Well known Lindhard formula[10] is one of the closed solutions in the theory of the Fermi systems that explicitly gives the nonlocal dielectric response function (longitudinal) $\varepsilon(k,\omega)$.

$$\varepsilon(k,\omega)=\varepsilon_h+\frac{3\varepsilon_h\omega_p^2}{k^2v_F^2}\left[1-\frac{\omega}{2kv_F}\ln\left(\frac{\omega+kv_F}{\omega-kv_F}\right)\right] \tag{5}$$

where ω_p is plasma frequency which is define as $\omega_p=\sqrt{\dfrac{4\pi ne^2}{\varepsilon_h m^*}}$. The complex function in Eq.(5), $\ln\left(\dfrac{\omega+kv_F}{\omega-kv_F}\right)$ is defined as $\ln\left(\dfrac{\omega+kv_F}{\omega-kv_F}\right)=\ln\left|\dfrac{\omega+kv_F}{\omega-kv_F}\right|-i\pi$ for $\left(\dfrac{\omega+kv_F}{\omega-kv_F}\right)<0$. Note that $\varepsilon(k,\omega)$ has a non-zero imaginary part, which describes optical losses, only when $\omega<kv_F$. These optical losses can be connected to the excitation by a field of incoherent electron-hole pairs. This phenomenon is called Landau damping, which is described by Eq (5). The Landau damping actually is

dephasing, where coherent field oscillations are transformed into incoherent electron hole pairs, but the total energy of the system is not changed. Landau damping is fulfilled when the size of the system is comparable to or less than the correlation length, l_c then condition, $\omega < kv_F$, is satisfied. In this limit, the expression, Eq. (5) for the longitudinal dielectric function can be written as,

$$\varepsilon(k,\omega) \cong \varepsilon_h + \frac{3\varepsilon_h \omega_p^2}{k^2 v_F^2}\left[1 - \frac{\omega^2}{k^2 v_F^2} + i\frac{\pi\omega}{2kv_F}\right]. \tag{6}$$

Considering LRPA, an external field penetrates a metal mainly to a depth on order of $r_D \sim v_F / \omega_p$. In a real metal r_D is very small (~ 1 nm) hence the contributing wave vectors $k \sim r_D^{-1}$ are large. For such a k the Eq. (5) has an imaginary part,

$$\mathrm{Im}[\varepsilon(k,\omega)] = \frac{3\pi\varepsilon_h \omega_p^2 \omega}{2(kv_F)^3} \sim \omega_p^2 \omega\, r_D^3 / v_F^3 \tag{7}$$

This has the same order of magnitude as $\mathrm{Re}[\varepsilon(k,\omega)]$. This effect (Landau damping) is not a small effect even at its onset. As explicitly demonstrated in Eq. (7) it is obvious that the relaxation and losses in the electron system comes only with a strong spatial dispersion (dependence on k). The Landau damping and the spatial dispersion are highly important for the nanoplasmonics, because they are the most pronounced for the low-frequency. In particular, small-size range of parameters where the nanoplasmonic effects are strongest and most interesting. Even though these phenomena are very important for nanooptics, it is very difficult to take into account because the expression for the dielectric response is relatively complex in the k space [see Eq. (5)]. Note that the boundary conditions at the surfaces of the nanostructure are to be imposed in the real r space.

In the limit $k > \omega / v_F$ and taking $\varepsilon_h = 1$, from Eq. (6) we get the inverse dielectric function, $\varepsilon(k,\omega)^{-1}$ as,

$$\varepsilon(k,\omega)^{-1} \cong \frac{1}{1 + i\xi\omega / k^5} \tag{8}$$

where $\xi = 9\pi\omega_p^4 / v_F^5$. Eq. (8) is identical to the corresponding result of the random phase approximation (RPA), which is expected to work well in our case when $\omega << \omega_p$ and $k << k_F$. This formula satisfies general properties of the spatial dispersive dielectric response, in particular, it describes Landau damping for $k > \omega / v_F$.

Let us assume that an external electric field $\mathbf{E} = E_0(\omega)\hat{z}$ is applied to a nanosphere whose radius is a and material is describe by longitudinal dielectric function $\varepsilon(k,\omega)$. Here retardation is neglected: size of the nanosphere is much smaller than the wavelength of the excitation field. The potential ϕ and the radial component of the displacement vector $\mathbf{D_r}$ for $r > a$ is given by

$$\phi(r) = -E_0 r\cos\theta + \frac{p}{r^2}\cos\theta \tag{9}$$

$$\mathbf{D_r}(\mathbf{r}) = \mathbf{E_r}(\mathbf{r}) = E_0 r\cos\theta + \frac{2p}{r^3}\cos\theta \tag{10}$$

The resulting equation for optical polarizability at $r = a$ can be written as $\alpha(\omega) \equiv p/E_0$, where $p = E_0 a^3[(\varepsilon(\omega)-1)/(\varepsilon(\omega)-1)]$ is the induced dipole moment of the sphere and θ is the angle between the vectors $\mathbf{r}$ and $\mathbf{E}$. Then the final results for the $\alpha(\omega)$ including nonlocal effects is given by[3].

$$\alpha(\omega) = a^2\left[\frac{1-3a\Re(a)}{1+6a\Re(a)}\right] \tag{11}$$

where $\Re(a) = \Re(r)\big|_{r=a}$ and

$$\Re(r) = \frac{2}{\pi}\int_0^\infty \frac{J_1(kr)J_1(ka)}{\varepsilon(k,\omega)}dk = \frac{2}{\pi}\int_0^\infty \frac{k^5 J_1(kr)J_1(ka)}{k^5 + i\xi\omega}dk. \tag{12}$$

In the local limit, i.e., $\varepsilon(k,\omega) \equiv \varepsilon(\omega)$, $\Re(a) = \dfrac{1}{3a\varepsilon(\omega)}$. (13)

Then $\alpha(\omega)$ reduces to well known expression[11],

$$\alpha(\omega) = a^3\,\frac{\varepsilon(\omega)-1}{\varepsilon(\omega)+1}. \tag{14}$$

3. NUMERICAL RESULTS AND DISCUSSION

The inverse dielectric function, $\varepsilon(k,\omega)^{-1}$ is shown in Figure 1 for $\hbar\omega = 1, 2$ and 3 eV. Here we can clearly see the significance of the $\mathrm{Im}[\varepsilon(k,\omega)]$, which is same order of magnitude as $\mathrm{Re}[\varepsilon(k,\omega)]$ (not shown in the graph).

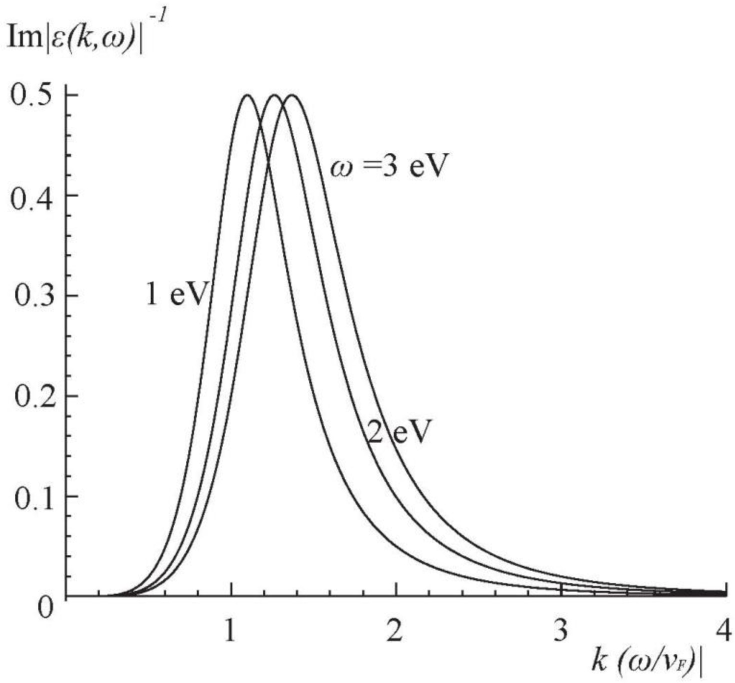

Figure 1: Absolute value of the imaginary part of the inverse dielectric function $\varepsilon(k,\omega)^{-1}$ plotted against wave vector k for $\hbar\omega = 1, 2$ and 3 eV, $\hbar\omega_p = 9.24$ eV and $v_F = 10^6$ m s-1.

The results of numerical computation from Eq. (12) of the imaginary part of the normalized polarizability for silver nanospheres of radii 2.5 nm, 5 nm, 10 nm, 50 nm and 100 nm are shown in Figure 2. Our numerical calculation qualitatively agrees with Ref. [3], it indicates that the essential physics of the system is contained in our simple treatment even for particle radii as small as 2.5 nm. The slight variation in the peak position is presumably due to the different formalism of the used dielectric function[3]. Toward the smaller particle size the peak position has been changed significantly. This is due to the Landau damping which is fulfilled when the size of the system is comparable to or less than the correlation length, l_c, then condition, $k > \omega / v_F$ is satisfied.

Since we used more general dielectric function for the model, two major advantages of the results can be seen: (a) they can be applied to various different materials and (b) the model is capable of giving quantitatively correct results as shown in Figure 2. Farther, one can easily conceder the higher order terms of the $\varepsilon(k,\omega)^{-1}$ in our formalism to show that this agreement would continue for even smaller particles as well. Another advantage of our theory is that one can use this model to study the spatial variations of quantities like electric field, polarization, induced charge density, etc., within the sphere in a simple analytical way.

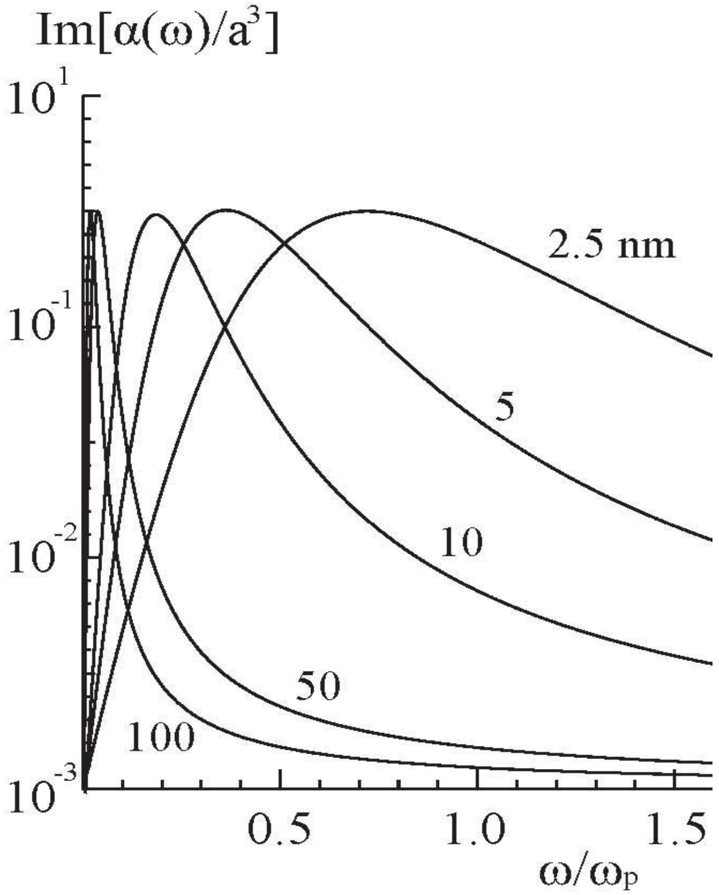

Figure 2: Variation of the imaginary part of $\alpha(\omega)/a^3$ for silver spheres of radii 2.5 nm, 5 nm, 10 nm, 50 nm and 100 nm. Here $\hbar\omega_p = 9.24$ eV and $v_F = 10^6$ m s^{-1}.

To briefly summarize the main results, we have developed LRPA theory to describe the polarizability of nanosize meatal sphere including nonlocal effects. We hope that our work will be useful in studying the optical properties of nanoparticles of other materials (such as semiconductors, ionic crystals, etc.) which we did not consider here. In particular, there are two areas of considerable current interest where a theory like LRPA can play a significant role: It is known that absorption by phonons might be responsible for the anomalously large absorption of infrared radiation by very small metallic particles, one could try to see whether LRPA theory would explain this large absorption by adding a *phonon term* to the dielectric function, Some of the theories of the surface-enhanced Raman scattering are based on an enhancement of the effective polarizability due to image effects. As a better approximation, one can assume the molecules to be dielectric spheres and our expressions for $\alpha(\omega)$ can provide a simple but accurate way for taking into account both the size as well as the frequency dependence of the polarizability.

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