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Surface Plasmons in Small Metal Particles

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Abstract. The dielectric response of a small metal particle to a perturbing potential $v_L = r^L Y_{LM} e^{i\omega t}$ is considered within the random phase approximation (RPA). The static dielectric polarizability is found and the size dependence of the surface plasmon frequencies are then determined from sum rule calculations. When the particle radius a is large compared to the Thomas-Fermi screening length r_0 the RPA equation is transformed into a form appropriate for an analytical solution. The dynamic electric polarizability, the position and the width of the surface plasma resonance are found in the limit $a/r_0 \gg 1$.

1. Introduction

Electromagnetic properties of small metal particles have been the subject of rather intence investigations in recent years [1–8]. These investigations have attempted to obtain a more fundamental understanding of the behavior of colloidal particles in external electromagnetic fields and considerable progress has been made. Two very different approaches have been used in the theoretical studies of the properties of small metal particles: the hydrodynamics of the charged electron gas [6, 7] and the quantum mechanical theory based on the random phase approximation [9, 14, 15]. The hydrodynamic approach leads to rather simple equations affording a determination of the charge distribution, the effective field inside the particle etc. However, there exist some doubts concerning the justification of the applicability of the hydrodynamic equations to the electron plasma in metal particles. The fact is that the free path of electrons l becomes large compared to the particle radius a at sufficiently low temperature, while the condition $l \ll a$ is required to hold for the applicability of the hydrodynamics. Therefore the RPA approach seems to be more preferable for the description of the electromagnetic properties of small metal particles. In this paper the RPA is used to calculate the frequencies and the damping of surface plasmons in small metal particles. Below we stick to the following programme. In Sect. 2 the main assumptions are outlined and the RPA equation is formulated for the renormalized electromagnetic field arising inside the particle due to the screening of an external potential by conduction electrons. The static solution of the RPA equation is found in Sect. 3. This solution allows us to obtain the static polarizability of the particle in a multipole external field. This result being combined with the Thomas-Reiche-Kuhn type sum rule defines the mean square frequency of the surface plasmon. In Sect. 4 the fact that plasmon frequencies become independent of the size of the particle is used in order to simplify the RPA equation. This simplified equation is then solved and the effective field inside the particle, the position and the width of the surface plasma resonance are determined.

2. Description of the Model Employed

Plasma oscillations of conduction electrons in metals is a typical example of collective excitations in a many-fermion system which can be successfully described within the RPA. As in the case of the bulk metal we adopt here the jellium model, i.e. conduction electron scattering by the ions is neglected. The metal particle is then replaced by a model in which the ions are spread out into a uniform distribution of positive charge and the conduction electrons move inside the potential well $u(\mathbf{r})$ forming by this positive background. The Hamiltonian of the conduction electrons then has the form ($\hbar = m = 1$, where m is the electron mass)

$$H = H_0 + H_I, \tag{2.1}$$

$$H_0 = \int d^3 r\, \psi^+(\mathbf{r}) \left[-\frac{1}{2} \frac{\partial^2}{\partial \mathbf{r}^2} + u(\mathbf{r}) \right] \psi(\mathbf{r}), \tag{2.2}$$

$$H_I = \frac{e^2}{2} \int \frac{d^3 r_1\, d^3 r_2}{|\mathbf{r}_1 - \mathbf{r}_2|}\, \psi^+(\mathbf{r}_2)\, \psi^+(\mathbf{r}_1)\, \psi(\mathbf{r}_1)\, \psi(\mathbf{r}_2). \tag{2.3}$$

Here ψ^+, ψ are the creation and annihilation electron operators.

Now consider the metal particle placed in an external electric field acting on conduction electrons $\mathscr{V}(t)$ and calculate the linear response of the electron gas to the perturbing potential $e\mathscr{V}$ in the Hamiltonian (2.1). We define the dynamic electric polarizability as follows

$$\alpha(t) = i\, e^2 \langle 0 |\, T \mathscr{V}(t)\, \mathscr{V}(0)\, | 0 \rangle \tag{2.4}$$

where

$$\mathscr{V}(t) = \int \mathscr{V}(\mathbf{r})\, \psi^+(\mathbf{r}, t)\, \psi(\mathbf{r}, t)\, d^3 r;$$
$$\psi^+(\mathbf{r}, t) = e^{iHt}\, \psi^+(\mathbf{r}, 0)\, e^{-iHt}.$$

T is the time ordering operator and $|0\rangle$ is the ground state of the electron gas. The Lehmann type expansion is known to be valid for the Fourier transform of $\alpha(t)$

$$\alpha(\omega) = \int_{-\infty}^{\infty} \alpha(t)\, e^{i\omega t}\, dt$$
$$= e^2 \sum_S |\langle 0 |\, \mathscr{V}\, | S \rangle|^2 \left(\frac{1}{\omega_S - \omega - i\delta} + \frac{1}{\omega_S + \omega - i\delta} \right) \tag{2.5}$$

where $\omega_S = E_S - E_0$ are the exitation energies of the electron gas and $\delta \to +0$. Among enormous number of exitations contributing into the sum on the right-hand side of Eq. (2.5) there are collective states (plasmons) arising due to coherent exitations of electron-hole pairs. These collective states reveal themselves as poles in $\alpha(\omega)$ with residues enhanced strongly as compared with noncollective states. The absence of the momentum conservation leads to the appearance of the plasma resonance width related to the decay of the collective state into noncollective electron-hole ones. Thus, if $\alpha(\omega)$ is known then the position and the width of the plasma resonance may be determined. In this paper we calculate $\alpha(\omega)$ within the RPA.

Let $v(\mathbf{r}, t)$ be an external electric field. Then the effective field V inside the particle is the sum of four terms

$$V = v + \delta V_e + \delta V_d + \delta V_m \tag{2.6}$$

where δV_e, δV_d, δV_m are the polarization parts of V arising due to appearance of the induced charge densities: $\delta\rho_e$ in the electron gas, $\delta\rho_d$ in the dielectric medium surrounding the particle and $\delta\rho_m$ inside the metal particle. The last term in Eq. (2.6) accounts for the polarization of the ion lattice which is assumed to be a dielectric medium with the dielectric constant ε_m.

Each polarization term on the right-hand side of Eq. (2.6) may be expressed in terms of V

$$\delta V_e = e \int \frac{1}{|\mathbf{r} - \mathbf{r}_1|}\, \delta\rho_e(\mathbf{r}_1)\, d^3 r_1$$
$$= e^2 \int \frac{1}{|\mathbf{r} - \mathbf{r}_1|}\, \Pi(\mathbf{r}_1, \mathbf{r}_2)\, V(\mathbf{r}_2)\, d^3 r_1\, d^3 r_2$$
$$\equiv e^2 (Q \Pi V). \tag{2.7}$$

(The symbolical notations ( ) will be used below in parallel with integrals.) Here $Q = |\mathbf{r} - \mathbf{r}_1|^{-1}$ and Π is the polarization operator of the electron gas which has the form within the RPA [10]

$$\Pi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{\lambda\lambda'} \varphi_\lambda(\mathbf{r}_1)\, \varphi^*_{\lambda'}(\mathbf{r}_1) \frac{n_\lambda - n_{\lambda'}}{\varepsilon_\lambda - \varepsilon_{\lambda'} + \omega}\, \varphi^*_\lambda(\mathbf{r}_2)\, \varphi_{\lambda'}(\mathbf{r}_2) \tag{2.8}$$

where ε_λ, φ_λ are the one-electron energies and functions and n_λ – the occupation numbers. The term δV_d is found in the following way [11]. The induced charge density is $\delta\rho_d = -\operatorname{div} \mathbf{P}$ where the polarization vector

$$\mathbf{P} = -n_d(\mathbf{r}) \frac{\varepsilon_d - 1}{4\pi} \nabla V.$$

Here ε_d is the dielectric constant and $n_d(\mathbf{r})$ is the dimensionless density of the surrounding dielectric medium ($n_d = 1$ in the uniform dielectric). Hence

$$\delta V_d = \int \frac{\delta\rho_d(\mathbf{r}_1)}{|\mathbf{r} - \mathbf{r}_1|}\, d^3 r_1$$
$$= \frac{\varepsilon_d - 1}{4\pi} \int \frac{1}{|\mathbf{r} - \mathbf{r}_1|} \frac{\partial}{\partial \mathbf{r}_1} \left(n_d \frac{\partial V}{\partial \mathbf{r}_1} \right) d^3 r_1. \tag{2.9}$$

Integrating twice by parts and remembering that $\Delta Q = -4\pi\, \delta(\mathbf{r}_1 - \mathbf{r}_2)$ we have

$$\delta V_d = -(\varepsilon_d - 1)\, n_d\, V$$
$$+ \frac{\varepsilon_d - 1}{4\pi} \int \left(\frac{\partial}{\partial \mathbf{r}_1} \cdot \frac{1}{|\mathbf{r} - \mathbf{r}_1|} \right) \frac{\partial n_d}{\partial \mathbf{r}_1}\, V(\mathbf{r}_1)\, d^3 \mathbf{r}_1$$
$$= -(\varepsilon_d - 1)\, n_d\, V + \frac{\varepsilon_d - 1}{4\pi} (\nabla Q \cdot \nabla n_d\, V). \tag{2.10}$$

The term δV_m is obtained from Eq. (2.10) by replacing of the indices d to m. Finally we get the equation for determination of the effective field V:

$$V = v + e^2(Q\Pi V) - (\varepsilon_d - 1)\, n_d\, V - (\varepsilon_m - 1)\, n_m\, V + \frac{\varepsilon_d - 1}{4\pi}(\nabla Q \cdot \nabla n_d\, V) + \frac{\varepsilon_m - 1}{4\pi}(\nabla Q \cdot \nabla n_m\, V). \tag{2.11}$$

The polarizability $\alpha(\omega)$ may be expressed in terms of V [12]

$$\alpha(\omega) = -e^2(\mathscr{V}\Pi V) \tag{2.12}$$

where $\mathscr{V}$ is the field acting on the electron gas. It differs from the external field due to presence of two dielectric media (the surrounding dielectric and the ion lattice) and is determined by the following equation:

$$\mathscr{V} = v - (\varepsilon_d - 1)\, n_d\, \mathscr{V} - (\varepsilon_m - 1)\, n_m\, \mathscr{V} + \frac{\varepsilon_d - 1}{4\pi}(\nabla Q \cdot \nabla n_d\, \mathscr{V}) + \frac{\varepsilon_m - 1}{4\pi}(\nabla Q \cdot \nabla n_m\, \mathscr{V}). \tag{2.13}$$

Below we confine ourselves to the consideration of the multipole external fields

$$v_L(\mathbf{r}) = r^L\, Y_{LM}(\boldsymbol{\Omega}) \tag{2.14}$$

where Y_{LM} are the normalized spherical harmonics

$$\int Y_{LM}(\boldsymbol{\Omega})\, Y^*_{L'M'}(\boldsymbol{\Omega})\, d\boldsymbol{\Omega} = \delta_{LL'}\, \delta_{MM'}. \tag{2.15}$$

3. Sum Rule Calculations

The solution of Eq. (2.11) is impossible without simplifications. However, if one wishes to know the plasmon frequency only, then the solution of Eq. (2.11) with $\omega \neq 0$ may be avoided and instead the sum rule technique may be employed [13]. Once two sum rules

$$w_1 = e^2 \sum_S \omega_S\, |\langle 0|\, \mathscr{V}\, |S\rangle|^2 \tag{3.1}$$

and

$$w_{-1} = e^2 \sum_S \omega_S^{-1}\, |\langle 0|\, \mathscr{V}\, |S\rangle|^2 \tag{3.2}$$

are known the mean square plasmon frequency can be extracted from the ratio

$$\omega_L^2 = w_1 / w_{-1}. \tag{3.3}$$

The sum rule w_{-1}, as is seen from Eq. (2.5), is expressed in terms of the static polarizability

$$w_{-1} = \tfrac{1}{2}\, \alpha(0) \tag{3.4}$$

while w_1, as shown below, depends only on the ground state density distribution of the electron gas. Since the plasma resonance is very narrow (see Sect. 4) the frequency ω_L as defined by Eq. (3.3) coincides with the position of the plasma resonance.

We begin by calculating $\alpha_L(0)$. The main simplification in Eq. (2.11) arising in the static limit is related to the possibility of the replacement of $\Pi(\mathbf{r}_1, \mathbf{r}_2)$ by a delta function (see e.g. Ref. 10)

$$\Pi(\mathbf{r}_1, \mathbf{r}_2) = -\frac{p_F}{\pi^2}\, \delta(\mathbf{r}_1 - \mathbf{r}_2) \tag{3.5}$$

where p_F is the Fermi momentum. Next, the dimensionless densities $n_d(r)$ and $n_m(r)$ are assumed to be step functions:

$$n_d(r) = \theta(r - a), \qquad n_m(r) = \theta(a - r) \tag{3.6}$$

where a is the particle radius and $\theta(x) = 1$ at $x > 0$ and 0 otherwise. With these simplifications Eq. (2.11) takes the form at $r < a$

$$\varepsilon_m\, V = v_L - \frac{e^2 p_F}{\pi^2} \int \frac{d^3 r_1}{|\mathbf{r} - \mathbf{r}_1|}\, V(\mathbf{r}_1) + \frac{\varepsilon_d - \varepsilon_m}{4\pi} \int \left(\frac{\partial}{\partial r_1} \frac{1}{|\mathbf{r} - \mathbf{r}_1|}\right) \delta(r_1 - a)\, V(\mathbf{r}_1)\, d^3 r_1. \tag{3.7}$$

Let us define the function $f_L(r/r_0)$ by the equality

$$\varepsilon_m\, V(\mathbf{r}) = f_L(r/r_0)\, v_L(\mathbf{r}) \tag{3.8}$$

where $r_0 = (\pi \varepsilon_m / 4 e^2 p_F)^{1/2}$ is the Thomas-Fermi screening length. Using the well-known expansion for $|\mathbf{r} - \mathbf{r}_1|^{-1}$

$$\frac{1}{|\mathbf{r} - \mathbf{r}_1|} = \sum_{L=0}^{\infty} \frac{4\pi}{2L+1}\, B_L(r, r_1) \sum_{L=-M}^{M} Y_{LM}(\boldsymbol{\Omega})\, Y^*_{LM}(\boldsymbol{\Omega}_1) \tag{3.9}$$

where

$$B_L(r, r_1) = r^L\, r_1^{-L-1}\, \theta(r_1 - r) + r_1^L\, r^{-L-1}\, \theta(r - r_1)$$

we come to the following equation for $f_L(x)$

$$f_L(x) = 1 - \frac{1}{(2L+1)} \left[x^{-(2L+1)} \int_0^x y^{2L+2} f_L(y)\, dy + \int_x^{a/r_0} y\, f_L(y)\, dy \right] - \frac{(\varepsilon_d - \varepsilon_m)(L+1)}{\varepsilon_m (2L+1)}\, f_L\!\left(\frac{a}{r_0}\right). \tag{3.10}$$

Instead of $f_L(x)$ it is convenient to introduce a new unknown function $g_L(x)$ connected with $f_L(x)$ by the equality

$$f_L(x) = g_L(x) \left[1 + \frac{1}{2L+1} \int_0^{a/r_0} y\, g_L(y)\, dy + \frac{(\varepsilon_d - \varepsilon_m)(L+1)}{\varepsilon_m (2L+1)}\, g_L\!\left(\frac{a}{r_0}\right) \right]^{-1}. \tag{3.11}$$

This expression substituted into Eq. (3.10) gives

$$g_L(x)=1-\frac{1}{2L+1}\left[\frac{1}{x^{2L+1}}\int_0^x y^{2L+2}\,g_L(y)\,dy-\int_0^x y\,g_L(y)\,dy\right]. \quad (3.12)$$

Eq. (3.12) can be transformed into the linear second order differential equation

$$g_L''+\frac{(2L+2)}{x}g_L'-g_L=0 \quad (3.13)$$

with the initial conditions $g_L(0)=1$, $g_L'(0)=0$. The solution of this equation is

$$g_L(x)=2^{L+\frac{1}{2}}\,\Gamma(L+\tfrac{3}{2})\,x^{-(L+\frac{1}{2})}\,I_{L+\frac{1}{2}}(x) \quad (3.14)$$

where $I_{L+\frac{1}{2}}(x)$ is the modified Bessel function.
In order to calculate $\alpha(\omega)$ we must also solve Eq. (2.13) for $\mathscr{V}(\mathbf{r})$ at $r<a$. It is not very difficult to conclude from Eqs. (2.13), (3.6) and (3.9) that

$$\mathscr{V}(\mathbf{r})=v_L(\mathbf{r})\left[\varepsilon_m+(\varepsilon_d-\varepsilon_m)\frac{L+1}{2L+1}\right]^{-1}. \quad (3.15)$$

Hence

$$\alpha_L(0)=\frac{e^2\,p_F\,r_0^{2L+3}}{\pi^2\,\varepsilon_m}\int_0^{a/r_0} y^{2L+2}\,g_L(y)\,dy \cdot\left[\varepsilon_m+(\varepsilon_d-\varepsilon_m)\frac{L+1}{2L+1}\right]^{-1}\left[1+\frac{1}{2L+1}\int_0^{a/r_0} y\,g_L(y)\,dy +\frac{(\varepsilon_d-\varepsilon_m)(L+1)}{\varepsilon_m(2L+1)}\,g_L\left(\frac{a}{r_0}\right)\right]^{-1} \quad (3.16)$$

(Eqs. (2.12), (3.8), (3.11) and (3.15) are taken into account in deriving of Eq. (3.16)). The integrals on the right-hand side of Eq. (3.16) are

$$\int_0^{a/r_0} y^{2L+2}\,g_L(y)\,dy=2^{L+\frac{1}{2}}\,\Gamma(L+\tfrac{3}{2})\int_0^{a/r_0} y^{L+\frac{3}{2}}\,I_{L+\frac{1}{2}}(y)\,dy =2^{L+\frac{1}{2}}\,\Gamma(L+\tfrac{3}{2})\left(\frac{a}{r_0}\right)^{L+\frac{3}{2}} I_{L+\frac{3}{2}}\left(\frac{a}{r_0}\right)$$

$$\int_0^{a/r_0} y\,g_L(y)\,dy=2^{L+\frac{1}{2}}\,\Gamma(L+\tfrac{3}{2})\int_0^{a/r_0} y^{-(L-\frac{1}{2})}\,I_{L+\frac{1}{2}}(y)\,dy =2^{L+\frac{1}{2}}\,\Gamma(L+\tfrac{3}{2})\left(\frac{a}{r_0}\right)^{-(L-\frac{1}{2})} I_{L-\frac{1}{2}}\left(\frac{a}{r_0}\right)-(2L+1).$$

Using the relation

$$I_{L+\frac{3}{2}}(z)=I_{L-\frac{1}{2}}(z)-(2L+1)\,z^{-1}\,I_{L+\frac{1}{2}}(z)$$

we finally get

$$\alpha_L(0)=\frac{2L+1}{4\pi}\,\frac{a^{2L+1}}{\left[\varepsilon_m+(\varepsilon_d-\varepsilon_m)\frac{L+1}{2L+1}\right]}\,M_L\left(\frac{a}{r_0}\right) \quad (3.17)$$

where the size dependent factor $M_L(x)$ is

$$M_L(x)=\frac{1-(2L+1)\,x^{-1}\,I_{L+\frac{1}{2}}(x)/I_{L-\frac{1}{2}}(x)}{1+\frac{\varepsilon_d-\varepsilon_m}{\varepsilon_m}(L+1)\,x^{-1}\,I_{L+\frac{1}{2}}(x)/I_{L-\frac{1}{2}}(x)}. \quad (3.18)$$

At $x\to\infty\, M_L(x)\to 1$. This expression is an extension of our previous result obtained for the case $L=1$ and $\varepsilon_d=\varepsilon_m=1$ [14].
Now let us calculate w_1. The sum on the right-hand side of Eq. (3.1) may be transformed in the following way

$$\sum_S \omega_S\,|\langle 0|\mathscr{V}|S\rangle|^2=\tfrac{1}{2}\langle 0|[\mathscr{V},[H,\mathscr{V}]]|0\rangle \quad (3.19)$$

where $[a,b]=a\,b-b\,a$. The double commutator $[\mathscr{V},[H,\mathscr{V}]]$ is easily found with the aid of Eqs. (2.1) to (2.3)

$$[\mathscr{V},[H,\mathscr{V}]]=\int\left(\frac{\partial\mathscr{V}}{\partial\mathbf{r}}\right)^2\psi^+(\mathbf{r})\,\psi(\mathbf{r})\,d^3r.$$

Hence

$$w_1=\frac{e^2}{2}\int\langle 0|\psi^+(\mathbf{r})\,\psi(\mathbf{r})|0\rangle\left(\frac{\partial\mathscr{V}}{\partial\mathbf{r}}\right)^2 d^3r =\frac{e^2}{2}\int n(\mathbf{r})\left(\frac{\partial\mathscr{V}}{\partial\mathbf{r}}\right)^2 d^3r \quad (3.20)$$

where $n(\mathbf{r})$ is the conduction electron density. Integrating Eq. (3.20) by parts we have

$$\int n(\mathbf{r})\left(\frac{\partial\mathscr{V}}{\partial\mathbf{r}}\right)^2 d^3r=\int n\mathscr{V}\,\frac{\partial\mathscr{V}}{\partial\mathbf{r}}\,d\mathbf{s} -\int n\mathscr{V}\,\frac{\partial^2\mathscr{V}}{\partial\mathbf{r}^2}\,d^3r-\int\mathscr{V}\,\frac{\partial\mathscr{V}}{\partial\mathbf{r}}\,\frac{\partial n}{\partial\mathbf{r}}\,d^3r.$$

Taking into account the facts that $\Delta\mathscr{V}\sim\Delta v_L=0$ and $n(\mathbf{r})=0$ at $r\to\infty$ one sees that the last integral only contributes to w_1. Assuming $n(r)=n\,\theta(a-r)$ and using Eq. (3.15) we obtain

$$w_1=\frac{e^2}{2}\,\frac{L\,n\,a^{2L+1}}{\left[\varepsilon_m+(\varepsilon_d-\varepsilon_m)\frac{L+1}{2L+1}\right]^2}. \quad (3.21)$$

Now the plasmon frequency is easy determined from Eqs. (3.3), (3.4), (3.17), (3.18) and (3.21)

$$\omega_L^2=\omega_0^2\,\frac{L}{2L+1}\left[\varepsilon_m+(\varepsilon_d-\varepsilon_m)\frac{L+1}{2L+1}\right]^{-1} M_L^{-1}\left(\frac{a}{r_0}\right) \quad (3.22)$$

where $\omega_0^2=4\pi\,n\,e^2$ is the plasma frequency of the bulk metal.

4. The Limit of Large a/r_0. Position and Width of the Surface Plasma Resonance

This section is concerned with the solution of Eq. (2.11) for the effective field V at $\omega \neq 0$ in the limit of large a/r_0. Notice, that the matrix elements $V_{\lambda\lambda'}$ differs appreciably from zero at energy differences $\varepsilon_\lambda - \varepsilon_{\lambda'} \sim L v_F/a \sim \varepsilon_F N^{-\frac{1}{3}}$ where N is the total number of conduction electrons in the particle and ε_F is the Fermi energy. These energy differences are seen to decrease with increase of the particle size whereas the surface plasma frequencies remain finite at large a/r_0 (see Eq. (3.22)). This circumstance allows us to simplify considerably Eq. (2.11) by expanding the denominator $(\varepsilon_\lambda - \varepsilon_{\lambda'} + \omega)^{-1}$ in the polarization operator (2.8) in powers of $(\varepsilon_\lambda - \varepsilon_{\lambda'})/\omega$. Instead of this we represent $\Pi(\mathbf{r}_1, \mathbf{r}_2)$ as the sum of two terms

$$\Pi(\mathbf{r}_1, \mathbf{r}_2) = \Pi_1(\mathbf{r}_1, \mathbf{r}_2) + \Pi_2(\mathbf{r}_1, \mathbf{r}_2) \tag{4.1}$$

where

$$\Pi_1(\mathbf{r}_1, \mathbf{r}_2) = -\omega^{-2} \sum_{\lambda\lambda'} \varphi_\lambda(\mathbf{r}_1)\, \varphi^*_{\lambda'}(\mathbf{r}_1)\, (n_\lambda - n_{\lambda'})\, (\varepsilon_\lambda - \varepsilon_{\lambda'}) \cdot \varphi^*_\lambda(\mathbf{r}_2)\, \varphi_{\lambda'}(\mathbf{r}_2) \tag{4.2}$$

and $\Pi_2 = \Pi - \Pi_1$. The contribution of Π_2 is small $(\sim v_F/a\omega_L \sim r_0/a \sim N^{-\frac{1}{3}})$ as compared with Π_1. Noticing that

$$(\varepsilon_\lambda - \varepsilon_{\lambda'})\, V_{\lambda\lambda'} = ([H_0, V])_{\lambda\lambda'} = \left(-\frac{1}{2}\frac{\partial^2 V}{\partial \mathbf{r}^2} - \frac{\partial V}{\partial \mathbf{r}}\frac{\partial}{\partial \mathbf{r}}\right)_{\lambda\lambda'} \tag{4.3}$$

and taking into account the relations

$$\sum_\lambda \varphi_\lambda(\mathbf{r})\, \varphi^*_\lambda(\mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}'); \quad \sum_\lambda n_\lambda |\varphi_\lambda(\mathbf{r})|^2 = n(\mathbf{r}) \tag{4.4}$$

we transform the right-hand side of Eq. (2.7) in the following way:

$$\delta V_e = e^2 (Q\Pi V) \approx e^2 (Q\Pi_1 V).$$

But

$$\int \Pi(\mathbf{r}, \mathbf{r}_1)\, V(\mathbf{r}_1)\, d^3 r_1 = \omega^{-2} \sum_{\lambda\lambda'} \varphi_\lambda(\mathbf{r})\, \varphi^*_{\lambda'}(\mathbf{r})\, (n_\lambda - n_{\lambda'}) \int d^3 r_1 \cdot \varphi^*_\lambda(\mathbf{r}_1) \frac{\partial V}{\partial \mathbf{r}_1} \frac{\partial \varphi_{\lambda'}(\mathbf{r}_1)}{\partial \mathbf{r}_1} = -\omega^{-2} \frac{\partial}{\partial \mathbf{r}} \left(n(\mathbf{r}) \frac{\partial V}{\partial \mathbf{r}}\right). \tag{4.5}$$

(The term $\partial^2 V/\partial \mathbf{r}^2$ in Eq. (4.3) does not contribute into this sum.) Hence

$$\delta V_e = -\omega^{-2} e^2 \int \frac{1}{|\mathbf{r} - \mathbf{r}_1|} \frac{\partial}{\partial \mathbf{r}_1} \left(n(\mathbf{r}_1) \frac{\partial V}{\partial \mathbf{r}_1}\right) d^3 r_1. \tag{4.6}$$

Eq. (4.6) is similar to Eq. (2.10) and may be transformed in the same way

$$\delta V_e = \frac{4\pi n(\mathbf{r}) e^2}{\omega^2} V - \frac{e^2}{\omega^2} \int \frac{\partial}{\partial \mathbf{r}_1} \frac{1}{|\mathbf{r} - \mathbf{r}_1|} \cdot \frac{\partial n}{\partial \mathbf{r}_1} V(\mathbf{r}_1)\, d^3 r_1. \tag{4.7}$$

The substitution of this expression into Eq. (2.11) yields:

$$V(\mathbf{r}) = v(\mathbf{r}) + \frac{4\pi n(\mathbf{r}) e^2}{\omega^2} V(\mathbf{r}) - \frac{e^2}{\omega^2} (\nabla Q \cdot \nabla n V) + \frac{(\varepsilon_d - 1)}{4\pi} (\nabla Q \cdot \nabla n_d V) + \frac{(\varepsilon_m - 1)}{4\pi} (\nabla Q \cdot \nabla n_m V) - (\varepsilon_d - 1)\, n_d(\mathbf{r})\, V(\mathbf{r}) - (\varepsilon_m - 1)\, n_m(\mathbf{r})\, V(\mathbf{r}). \tag{4.8}$$

It should be emphasized that the particle shape has not been specified when deriving Eq. (4.8). Therefore this equation is applicable for consideration of particles with arbitrary shape of boundary surface.

Now we solve (4.8) for the spherical particle assuming the conduction electron density to have the sharp edge $n(r) = n\theta(a - r)$ and $v = v_L = r^L Y_{LM}$. Let us seek the solution of Eq. (4.8) in the form $V(\mathbf{r}) = A_L v_L(\mathbf{r})$ at $r < a$. Then we obtain:

$$A_L = \left[\varepsilon_m - \frac{\omega_0^2}{\omega^2} \cdot \frac{L}{2L+1} + (\varepsilon_d - \varepsilon_m) \frac{L+1}{2L+1}\right]^{-1} \tag{4.9}$$

and

$$V(\mathbf{r}) = \frac{\omega^2}{\left[\varepsilon_m + (\varepsilon_d - \varepsilon_m) \dfrac{L+1}{2L+1}\right] (\omega^2 - \bar{\omega}_L^2)}\, v_L(\mathbf{r}) \tag{4.10}$$

where

$$\bar{\omega}_L^2 = 4\pi n e^2 \frac{L}{2L+1} \cdot \frac{1}{\left[\varepsilon_m + (\varepsilon_d - \varepsilon_m) \dfrac{L+1}{2L+1}\right]}. \tag{4.11}$$

We see from Eq. (4.10) that $V(\mathbf{r})$ has a pole at $\omega = \bar{\omega}_L$, which means the existence of nondamping plasma oscillations with the frequency $\omega = \bar{\omega}_L$. In order to obtain the damping arising due to the plasmon decay into noncollective electron-hole states, transitions with energy difference $\varepsilon_\lambda - \varepsilon_{\lambda'} \sim \bar{\omega}_L$ have to be taken into account. We make it including Π_2 into our consideration in a perturbation manner. According to the ideology of the first order perturbative theory the coordinate dependence $r^L Y_{LM}$ of the solution of Eq. (2.11) is assumed to be not affected by the presence of Π_2 on the right-hand side of Eq. (2.11), but the eigenfrequency $\bar{\omega}_L$ is slightly modified by shifting into the lower half-plane of the complex variable ω. This means the solution of Eq. (2.11) to have the form at $r < a$:

$$V_L(\mathbf{r}) = C_L(\omega)\, v_L(\mathbf{r}) \tag{4.12}$$

where the function $C_L(\omega)$ is to be determined. To this end we substitute Eq. (4.12) into Eq. (2.11), multiply both sides of Eq. (2.11) by $v_L(\mathbf{r}')\, \Pi(\mathbf{r}', \mathbf{r})$ and integrate over $\mathbf{r}$ and $\mathbf{r}'$. The result is

$$C_L(\omega) = \frac{(v_L \Pi v_L)}{\left[\varepsilon_m + (\varepsilon_d - \varepsilon_m)\dfrac{L+1}{2L+1}\right](v_L \Pi v_L) - e^2 (v_L \Pi Q \Pi v_L)}. \tag{4.13}$$

The term $e^2(v_L \Pi Q \Pi v_L)$ is transformed by using the relation $e^2(Q\Pi_1 v_L) = L\omega_0^2 v_L/\omega^2(2L+1)$ as follows

$$e^2(v_L \Pi Q \Pi v_L) = e^2(v_L \Pi Q \Pi_1 v_L) + e^2(v_L \Pi Q \Pi_2 v_L)$$

$$\approx [(v_L \Pi v_L) + (v_L \Pi_2 v_L)] \frac{\omega_0^2}{\omega^2} \frac{L}{2L+1}$$

and the term $e^2(v_L \Pi_2 Q \Pi_2 v_L)$ is neglected. Hence

$$C_L(\omega) = \frac{\omega^2}{\left[\varepsilon_m + (\varepsilon_d - \varepsilon_m)\dfrac{L+1}{2L+1}\right][\omega^2 - \bar{\omega}_L^2(1-2ig)]} \tag{4.14}$$

where, to within the accuracy of the terms of the first order in Π_2

$$2g = \frac{\operatorname{Im}(v_L \Pi_2 v_L)}{(v_L \Pi_1 v_L)} = \frac{\omega^2}{nLa^{2L+1}} \operatorname{Im}(v_L \Pi_2 v_L). \tag{4.15}$$

It is not very difficult to recognize that $\operatorname{Im}(v_L \Pi_2 v_L) = \operatorname{Im}(v_L \Pi v_L)$ i.e.

$$\operatorname{Im}(v_L \Pi_2 v_L) = \pi\omega \sum_{\lambda\lambda'} |(v_L)_{\lambda\lambda'}|^2 \,\delta(\varepsilon_\lambda - \varepsilon_F)\,\delta(\varepsilon_\lambda - \varepsilon_{\lambda'} + \omega) \tag{4.16}$$

where the expansion $n_\lambda - n_{\lambda'} = \dfrac{dn_\lambda}{d\varepsilon_\lambda}(\varepsilon_\lambda - \varepsilon_{\lambda'})$ is used.

The calculation of g is performed in the Appendix. The final result is very simple:

$$g = \frac{6}{\pi} \frac{L}{2L+1} \frac{p_F}{a\omega}. \tag{4.17}$$

The dependence $g \sim \omega^{-1}$ can be understood from semi-classical arguments. The matrix element $(v_L)_{\lambda\lambda'}$ is proportional to the Fourier component of $v_L(\mathbf{r}(t))$ where $\mathbf{r}(t)$ is defined by the classical equation of motion. If the potential $u(\mathbf{r})$ in Eq. (2.2) is a rectangular well, then $\ddot{\mathbf{r}}(t)$ has a δ-function singularity at the moment of collision between electron and the particle boundary. Therefore the Fourier transform of $v_L(\mathbf{r}(t))$ behaves like ω^{-2} at $\omega \gg v_F/a$ where a/v_F is the electron free path time. Since $\omega \sim \bar{\omega}_L \gg v_F/a$ then

$$\operatorname{Im}(v_L \Pi v_L) \sim \omega^{-3},$$

and accounting for the factor ω^2 in Eq. (4.15) we conclude that $g \sim \omega^{-1}$.

Now we calculate the dynamic electric polarizability

$$\alpha_L(\omega) = -e^2(\mathcal{V} \Pi V)$$

$$= \frac{-e^2 nLa^{2L+1}}{\left[\varepsilon_m + (\varepsilon_d - \varepsilon_m)\dfrac{L+1}{2L+1}\right]^2 (\omega^2 - \bar{\omega}_L^2(1-2ig))}.$$

5. Discussion

In Sect. 2 we have calculated the dependence of the plasmon frequencies and the static polarizabilities on the particle size. This dependence is determined by the factor $M_L(a/r_0)$ which is shown in Fig. 1 for the case of silver particles in the glass: $\varepsilon_d = 2.25$, $\varepsilon_m = 4.9$. The influence of the particle size on the dipole static electric polarizability has been discussed in Refs. [14,15] in connection with the experimental observation [16] of the absence of the Gor'kov-Eliashberg effect [17] in small metal particles. There has been shown that the appreciable deviation from the classic value a^3 of the static dipole polarizability might appear in very small particles. The results of the present paper show that the size effect can be enhanced considerably if the particle is embedded into a dielectric medium with the large dielectric constant. In Fig. 1 the function $M_L(a/r_0)$ is shown for $\varepsilon_d = 40$.

The plasma resonance wave length $\lambda_L = 2\pi c/\omega_L$ $(L=1)$ is shown in Fig. 2 as the function of a/r_0 for the silver particle in glass. It is interesting to note, that this dependence is in a sharp contradiction with recent observations by Smithard [8] who has discovered the increase of λ_1 with decrease of the particle size. Reasons for this disagreement is not clear to us. Further experiments are required.

Our result concerning the plasma resonance width is very close to that of Kawabata and Kubo [9] ob-

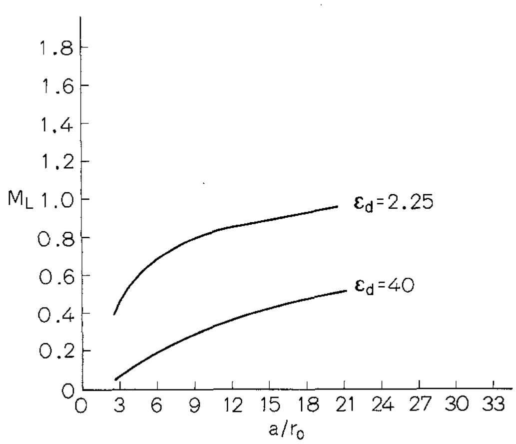

Fig. 1. Size dependence of the dimensionless static polarizability M_L $(L=1)$ for silver particles in glass $(\varepsilon_m = 4.9,\ \varepsilon_d = 2.25)$ and in a dielectric medium with $\varepsilon_d = 40$

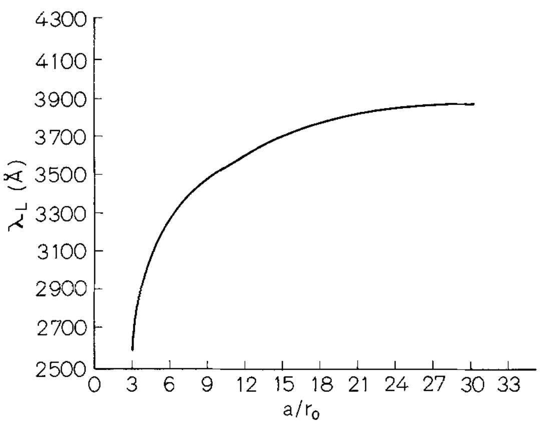

Fig. 2. Size dependence of the dipole plasma resonance wave length for silver particles in glass ($\varepsilon_m = 4.9$, $\varepsilon_d = 2.25$)

tained for the case $L=1$. However, our expression for the width (Eq. (4.17)) is somewhat simpler since we have used the formal requirement $\omega_0/\varepsilon_F \ll 1$ of the validity of the RPA. In real metals this condition does not hold, therefore other mechanismes such as decay of the plasma resonance into two electron – two hole states may contribute to the plasma resonance width. Thus the comparison of the theoretical and experimental widths contains the information about the relative contribution to the width of different mechanismes. Our width is half the experimental one [4] for silver particles with $a = 60$ Å.

Appendix

Here we calculate

$$\operatorname{Im}(v_L \Pi v_L) = \pi \omega^3 \sum_{\lambda\lambda'} (\varepsilon_\lambda - \varepsilon_{\lambda'})^4 |(v_L)_{\lambda\lambda'}|^2 \delta(\varepsilon_\lambda - \varepsilon_{\lambda'} + \omega) \cdot \delta(\varepsilon_\lambda - \varepsilon_F). \tag{A 1}$$

Let us begin with the calculation of the matrix element. We choose the one-electron potential in the form

$$u(r) = u_0 \theta(a - r). \tag{A 2}$$

Then

$$(\varepsilon_\lambda - \varepsilon_{\lambda'})^2 v_{\lambda\lambda'} = ([H, [H, v]]) = (\nabla v \cdot \nabla u)_{\lambda\lambda'} + \text{volume terms}. \tag{A 3}$$

The volume terms decrease with increase $(\varepsilon_\lambda - \varepsilon_{\lambda'})$ whereas the surface term $(\nabla v \cdot \nabla u)_{\lambda\lambda'}$ is independent of $(\varepsilon_\lambda - \varepsilon_{\lambda'})$. Indeed

$$\int d^3 r \frac{\partial V_L}{\partial r} u_0 \delta(r - a) \varphi_\lambda \varphi_{\lambda'}^* = L a^{L+1} u_0 R_{n_1 L_1}(a) R_{n_2 L_2}(a) \int d\Omega\, Y_{LM} Y_{L_1 M_1}^* Y_{L_2 M_2} \tag{A 4}$$

where R_{nL} is the radial part of φ_λ. It is not very difficult to obtain (see Ref. 9)

$$\lim_{u_0 \to \infty} u_0 R_{n_1 L_1}(a) R_{n_2 L_2}(a) = k_{n_1 L_1} k_{n_2 L_2} a^{-3} \tag{A 5}$$

where

$$k_{nL} = 2\pi a^{-1}(L + 2n) \quad \text{and} \quad \varepsilon = k^2/2. \tag{A 6}$$

Hence

$$([H, [H, v_L]])_{\lambda\lambda'} = L a^{2L-2} k_1 k_2 \int d\Omega\, Y_{LM} Y_{L_1 M_1}^* Y_{L_2 M_2} \tag{A 7}$$

and

$$\operatorname{Im}(v_L \Pi v_L) = \pi \omega^{-3} L^2 a^{2L-4} \sum_{n_1 n_2 L_1 L_2} k_1^2 k_2^2 \delta(\varepsilon_F - \varepsilon_1) \cdot \delta(\varepsilon_1 - \varepsilon_2 + \omega) \sum_{M_1 M_2} |(Y_{LM} Y_{L_1 M_1}^* Y_{L_2 M_2})|^2. \tag{A 8}$$

The angular part of the sum is evaluated as follows

$$\sum_{M_1 M_2} |(Y_{LM} Y_{L_1 M_1}^* Y_{L_2 M_2})|^2 = \frac{1}{2L+1} \sum_{M M_1 M_2} |(Y_{LM} Y_{L_1 M_1}^* Y_{L_2 M_2})|^2 = \frac{(2L_1+1)(2L_2+1)}{2(2L+1)} \int_{-1}^{1} dx\, P_L(x) P_{L_1}(x) P_{L_2}(x) \tag{A 9}$$

where $P_L(x)$ is the Legendre polinomials. Since $L_1, L_2 \sim a p_F \gg L$ we replace the integral on the right-hand side of Eq. (A 9) by $\delta_{L_1 L_2}$ i.e.

$$\int_{-1}^{1} dx\, P_L(x) P_{L_1}(x) P_{L_2}(x) = \frac{2}{2L_2+1} \delta_{L_1 L_2}. \tag{A 10}$$

Combining Eqs. (A 9) and (A 10) we get:

$$\sum_{M_1 M_2} |(Y_{LM} Y_{L_1 M_1}^* Y_{L_2 M_2})|^2 \approx \frac{L_1}{L+1/2} \delta_{L_1 L_2}. \tag{A 11}$$

Substituting Eq. (A 11) into Eq. (A 8) gives:

$$\operatorname{Im}(v_L \Pi v_L) = \frac{\pi}{\omega^3} \frac{L^2 a^{2L-4}}{L+1/2} \sum_{n_1 n_2 L_1} L_1 k_1^2 k_2^2 \delta(\varepsilon_F - \varepsilon_1) \cdot \delta(\varepsilon_1 - \varepsilon_2 + \omega). \tag{A 12}$$

Let us replace the sums on the right-hand side of Eq. (A 12) by integrals

$$\sum_n = \int dn = \int d\varepsilon \cdot \frac{dn}{d\varepsilon} = \frac{a}{\pi} \int \frac{d\varepsilon}{\sqrt{2\varepsilon}}. \tag{A 13}$$

Then we obtain instead of Eq. (A 12):

$$\operatorname{Im}(v_L \Pi v_L) = \frac{L^2 a^{2L-2} p_F^2}{\pi \omega^3 (L+1/2)} \int_0^{L_M} L_1\, dL_1 \tag{A 14}$$

where we put $\sqrt{2(\varepsilon_F-\omega)} \approx \sqrt{2\varepsilon_F} = p_F$ and $L_M = 2a p_F/\pi$. Finally we get

$$2g = \frac{\operatorname{Im}(v_L \Pi v_L)}{(v_L \Pi_1 v_L)} = \frac{12L}{\pi(2L+1)} \frac{p_F}{a\omega}. \tag{A 15}$$

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