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Surface plasmon dispersion relation for spherical metal particles

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Abstract. Using the hydrodynamical model, we have obtained the surface plasmon dispersion relation for spherical metallic particles in the following two cases: (1) a sharp surface cut off in electron density and (2) a diffused electron density at the surface. The diffused density is modelled with a step function. The diffuse nature of the electron density at surface of the metal particle is necessary to understand the experimental result for particles with small radii. Shift in the absorption frequency is estimated and found to be small.

Keywords. Hydrodynamical model; diffused surface; surface plasmons.

1. Introduction

Recently considerable interest has grown in the surface plasmon modes of small spherical metallic particles, with the experimental investigations of Smithard (1973) and Gariere *et al* (1975). According to these experiments, the Mie optical absorption peak shifts to longer wavelengths with the decrease of the radius of sphere. Gariere *et al* (1975), using a homogeneous sphere model and dielectric response theory have shown that the experimental results are exactly opposite to the theoretical expectations. They have come to a similar conclusion using classical theory also. Ruppin(1976) has taken a step in the right direction by considering the diffused nature of the electron density at the metal surface of the particles. Assuming a linear density profile, he has shown that the absorption frequencies are lowered with the decrease in sphere radius, in qualitative agreement with the experimental results. His theory, however, does not include the pressure effects and hence is purely static. The quantum hydrodynamical model of Bloch (1933, 1934) as developed by Ritchie and Wilems (1969) can incorporate the pressure effects in the calculations of collective modes in a natural way. Ritchie and Wilems (1969) have obtained electron-plasmon, photon-plasmon vertices for the metallic slab system using this model. In view of the simplicity of the model, and the possibility of finding the above vertices, we have embarked on a programme to study the spherical metal surface in the quantum hydrodynamical model and have obtained the surface plasmon dispersion relations (non retarded) for the following two cases of interest (a) sharp electron density cut off at the surface (b) diffused surface for which we have used the double step model of Boardman *et al* (1976). The double step model has an advantage that the solutions of the concerned differential equation can be obtained analytically and at the same time the results are qualitatively similar to those obtainable for more realistic density distributions such as Gaussian or exponential profiles (Boardman *et al* 1975). This conclusion also finds the support in recent work of Cunningham *et al* (1974) on the effect of depletion layers on the surface plasmon polariton of semiconductors.

2. Calculations of dispersion relation

2.1. *Sharp cut off*

We have a uniform positive neutralising background for our electron gas in a spherical boundary. We use (1) Euler equation for momentum transfer in which imbalance of electrostatic force and gradient of pressure give the acceleration. We use Fermi pressure to take into account the Pauli principle; (2) Equation of continuity; and (3) Poisson equation. Thus the equations of motion for the hydrodynamic velocity $\mathbf{v}$ and the potential ϕ in electrostatic approximation are,

$$m\frac{D\mathbf{v}}{Dt} = e\bar{\nabla}\phi - \nabla \int_0^{n(\mathbf{r},t)} \frac{d\zeta(n')}{n'} \tag{1}$$

$$\nabla^2\phi = 4\pi e\,[n(\mathbf{r},t) - Z\,l(\mathbf{r})]. \tag{2}$$

We use the pressure $\zeta(n)$, the Fermi pressure, as

$$\zeta(n) = \frac{\hbar^2(3\pi^2)^{2/3}}{5m}\, n^{5/3}$$

$l(\mathbf{r})$ is the +ve ion density. D/Dt represents a co-moving time derivative. The hydrodynamic equations can be simplified by introducing the velocity potential $\psi(\mathbf{r}, t)$ according to the definition,

$$\mathbf{v} = -\nabla\psi. \tag{3}$$

This transforms eq. (1) to the following form

$$\frac{\partial\psi}{\partial t} = \frac{1}{2}(\nabla\psi)^2 + \frac{1}{m}\int_0^n \frac{d\zeta(n')}{n'} - \frac{e}{m}\phi. \tag{4}$$

The equation of continuity can be written down as

$$\frac{\partial n}{\partial t} = \nabla\cdot[n\nabla\psi]. \tag{5}$$

We shall now follow the standard procedure of linearisation of these equations and expand the hydrodynamical variables as,

$$n(\mathbf{r},t) = n_0(\mathbf{r}) + n_1(\mathbf{r},t) + n_2(\mathbf{r},t) + \ldots \tag{6}$$

$$\phi(\mathbf{r}, t) = \phi_0(\mathbf{r}) + \phi_1(\mathbf{r}, t) + \phi_2(\mathbf{r}, t) + \ldots \tag{7}$$

$$\psi(\mathbf{r}, t) = \psi_1(\mathbf{r}, t) + \psi_2(\mathbf{r}, t) + \ldots \tag{8}$$

Here it has been assumed that $n_0 \gg n_1 \gg n_2$. Using these expansions in eqs (2), (4) and (5) and collecting quantities of the same order we get in zeroth order,

$$\frac{5}{2}\xi\, n_0^{2/3} = e\phi_0 \tag{9}$$

$$\nabla^2\phi_0 = 4\pi e\,(n_0 - Zl_0). \tag{10}$$

And in first order,

$$\frac{\partial\psi_1}{\partial t} = -\frac{e}{m}\phi_1 + \frac{5\xi}{3m\, n_0^{1/3}}\, n_1 \tag{11}$$

$$\nabla^2\phi_1 = 4\,\pi e n_1 \tag{12}$$

$$\frac{\partial n_1}{\partial t} = \nabla\cdot[n_0(\mathbf{r})\nabla(\psi_1)]. \tag{13}$$

Here

$$\xi = \frac{\hbar^2\,(3\pi^2)^{2/3}}{5m}.$$

In our particular problem,

$$n_0(\mathbf{r}) = n_0 \quad r<R$$

$$= 0 \quad r>R. \tag{14}$$

Hence eqs (11), (12) and (13) take still simpler forms viz.,

$$\frac{\partial\psi_1}{\partial t} = -\frac{e}{m}\phi_1 + \frac{V_F^2}{3\,n_0}\, n_1 \tag{15}$$

$$\nabla^2\phi_1 = 4\pi e n_1 \tag{16}$$

and

$$\frac{\partial n_1}{\partial t} = n_0\nabla^2\psi_1 \tag{17}$$

Here $V_F = \hbar\,(3\pi^2 n_0)^{1/3}/m$, the speed of the most energetic electrons in the Fermi sea at $T=0$.

Eliminating ψ_1 between (15) and (17) and then using (16) we get,

$$\left(\frac{\partial^2}{\partial t^2} + \omega_p^2 - \beta^2 \nabla^2\right) n_1 = 0. \tag{18}$$

Here

$$\omega_p^2 = \frac{4\pi n_0 e^2}{m} \text{ and } \beta^2 = \frac{V_F^2}{3}.$$

It is obvious from (18) that space and time can be separated as $n_1(\mathbf{r}) \exp(-i\omega_l t)$ and since the problem has spherical symmetry, expanding $n_1(\mathbf{r})$ in spherical harmonics we get for the interior,

$$n_1(\mathbf{r}) = \sum_{l,m} R_l(r)\, Y_{lm}(\theta,\phi). \tag{19}$$

Substituting (19) into (18) with $K^2 = (\omega_l^2 - \omega_p^2)/\beta^2$ we get the equation for $R_l(r)$ as,

$$\frac{d^2 R_l}{dr^2} + \frac{2}{r}\frac{dR_l}{dr} + \left[K^2 - \frac{l(l+1)}{r^2}\right] R_l = 0. \tag{20}$$

The solution of eq. (20) with the boundary condition of finiteness of R_l at origin is $R_l = A u_l(Kr)$. Here

$$u_l(Kr) = \sqrt{\frac{\pi}{2Kr}}\, I_{l+1/2}(Kr),$$

the modified Bessel's function. From (16) we note that $\phi_1(\mathbf{r}, t)$ can also be separated as,

$$\phi_1(\mathbf{r}, t) = \phi_1(\mathbf{r}) \exp(-i\,\omega_l\, t) \tag{21}$$

expanding $\phi_1(\mathbf{r})$ as,

$$\phi_1(\mathbf{r}) = \sum_{l,m} \phi_l(r)\, Y_{lm}(\theta, \phi). \tag{22}$$

Using (16), and (22) we get the equation for $\phi_l(r)$ to be,

$$\frac{d^2\phi_l}{dr^2} + \frac{2}{r}\frac{d\phi_l}{dr} - \frac{l(l+1)}{r^2}\phi_l = C u_l(Kr) \tag{23}$$

where

$$C = 4\pi e A.$$

Addition of $K^2\phi_l$ on both sides of (23) gives,

$$\frac{d^2\phi_l}{dr^2} + \frac{2}{r}\frac{d\phi_l}{dr} + \left[K^2 - \frac{l(l+1)}{r^2}\right]\phi_l = C u_l(Kr) + K^2\phi_l. \tag{24}$$

The interior solution of eq. (24) clearly is,

$$\phi_l(r) = -\frac{C}{K^2} u_l(Kr) + Br^l . \tag{25}$$

For exterior there are no real charges and therefore $n_1=0$ and the equation for $\phi_l(r)$ simply becomes $\nabla^2\phi_1=0$ which clearly has the exterior solution as,

$$\phi_l(r) = \frac{F}{r^{l+1}} \tag{26}$$

Putting continuity condition on $\phi_l(r)$ and $\partial\phi_l/\partial r$, we get by solving,

$$B = \frac{C}{K^2R^l}\left(\frac{l+1}{2l+1}\right)\left[\frac{KR}{(l+1)} u'_l(KR) + u_l(KR)\right]. \tag{27}$$

Thus we have got the complete solution for the interior.

$$n_1^I(\mathbf{r}) = \sum_{l,m} Au_l(Kr)\, Y_{lm}(\theta,\phi) \tag{28}$$

And,

$$\phi_1^I(\mathbf{r}) = \sum_{l,m} \frac{4\pi eA}{K^2}\left\{-u_l(Kr) + \left(\frac{l+1}{2l+1}\right)\left[u_l(KR) + \frac{KR}{(l+1)} u'_l(KR)\right]\left(\frac{r}{R}\right)^l\right\} \times XY_{lm}(\theta,\phi). \tag{29}$$

Putting the usual hydrodynamical condition that the electronic velocity normal to the surface must vanish we get the surface-plasmon dispersion relation.
Since,

$$\dot{\mathbf{V}}_1 = \frac{e}{m}\nabla\phi_1 - \frac{\beta^2}{n_0}\nabla n_1. \tag{30}$$

In our case the condition simply becomes,

$$\frac{e}{m}\frac{\partial\phi_1^I}{\partial r} - \frac{\beta^2}{n_0}\frac{\partial n_1^I}{\partial r} = 0 \qquad \text{at } r = R. \tag{31}$$

This gives,

$$\frac{u_l(KR)}{KR} = u'_l(KR)\left\{\frac{1}{l} + \frac{\beta^2K^2}{\omega_p^2}\frac{(2l+1)}{l(l+1)}\right\} \tag{32}$$

which is the dispersion relation.
The dispersion relation given in eq. (32) is valid when the medium in which the embedded sphere is vacuum.

If on the other hand, ϵ_m is a dielectric constant of a medium in which the metal sphere is embedded, eq. (32) can easily be modified to,

$$\frac{u_l(KR)}{KR} = \frac{1}{l}\left[1+\frac{\beta^2K^2}{\omega_p{}^2}\left(\frac{\epsilon_m l+l+1}{\epsilon_m l+1}\right)\right]u'_l(KR). \tag{33}$$

Equation (33) reduces to a well known cold plasma result,

$$\omega_l{}^2 = \frac{l\omega_p{}^2}{\epsilon_m l+l+1} \qquad \text{as } KR\to\infty \tag{34}$$

Further, as $l\to\infty$ eq. (34) reduces to,

$$\omega^2 = \omega_p{}^2/(\epsilon_m+1)$$

which is the well known result of Stern and Ferrell (1960) for plane interface.

Actually, the model of a metal sphere with sharp density cut off in the electron density is rather artificial. If one analyses the expression (32) for ω_l versus R, one can see that ω_l depends very weakly on R, increasing as R decreases. This clearly is a wrong behaviour. If one looks closely at the surface, the electron distribution oozes out, going to zero within the distance of the order of one or two Fermi wavelength. For exact profile calculation, one will have to solve the equation of Kohn and Sham (1965) and Hohenberg and Kohn (1964). This is a rather complicated density profile to handle. Benett (1970) and Feibelman (1971) investigated the plane surface with a linear density profile and have obtained a qualitatively correct behaviour of ω_l versus R. The same problem can be tackled with different density profiles and the qualitative behaviour of the dispersion relation does not change with the nature of the profile. We assume that this is true for the sphere as well. For this case, the double step model of Boardman *et al* (1975) is rather easy to handle.

2.2. *Double step model*

We take the density of electron as

$$\begin{aligned} n(\mathbf{r}) &= n_0 & r<R \\ &= an_0 & R<r<R+\Delta \\ &= 0 & r>R+\Delta \end{aligned}$$

In this case one has to solve the basic eq. (18) in three different regions. The radial solution in the three regions for density fluctuation will be,

$$\begin{aligned} R_l(r) &= A_1u_l(Kr); & r<R \\ &= B_1u_l(K_1r)+C_1v_l(K_1r), & R<r<R+\Delta \\ &= 0; & r>R+\Delta \end{aligned}$$

For

$$K_1^2 = (\omega_l^2 - \omega_{p_1}^2)/\beta_1^2 < 0 \quad \text{and} \quad K^2 < 0,$$

u_l and v_l are modified Bessel's functions

$$\left(\frac{\pi}{2Kr}\right)^{1/2} I_{l+(1/2)}\,(Kr) \text{ and } \left(\frac{\pi}{2Kr}\right)^{1/2} I_{-l-(1/2)}\,(Kr)$$

respectively. With this choice of a density fluctuation, one can solve Poisson's equation (analogus to eq. 23) and can obtain

$$\phi_l\,(r) = -\frac{A_1}{K^2}\,u_l(Kr) + Dr^l; \quad r < R$$

$$= -\frac{B_1}{K_1{}^2}u_l(K_1r) - \frac{C_1}{K_1{}^2}v_l\,(K_1r) + Er^l + \frac{F}{r^{l+1}};\ R < r < R + \triangle$$

$$= G/r^{l+1}; \qquad r > R + \triangle.$$

Here ω_{p_1} and β_1 are parameters corresponding to density αn_0. The boundary conditions that fix the constants are as follows. The density fluctuation is continuous at $r{=}R$ and the normal component of velocity must be continuous at R. Then we have the continuity of ϕ_l and $d\phi_l/dr$ at $r{=}R$ and at $r{=}R{+}\triangle$. These six conditions are sufficient to express all the constants of the previous equations in terms of one. To get the dispersion relation, as usual, we impose the condition similar to eq. (31) at $r{=}R{+}\triangle$ and we obtain,

$$q_1\left\{u'_l\,(K_1\,[R+\triangle])\left[+\,K_1\frac{\omega_{p_1}^2}{\beta_1^2}\cdot\frac{1}{K_1}\left(\frac{l+1}{2l+1}\right)\right]-\right.$$

$$\frac{l\,(l+1)}{(2l+1)}\frac{1}{(R+\triangle)}\frac{u_l\,(K_1\,[R+\triangle])}{K_1{}^2}\frac{\omega_{p_1}^2}{\beta_1^2}-$$

$$\left.\left(\frac{R}{R+\triangle}\right)^{l+2}\frac{1}{(2l+1)}\left[\frac{u'_l\,(K_1\,R)}{K_1}-\frac{l}{R}\frac{u_l(K_1\,R)}{K_1{}^2}\frac{\omega_{p_1}^2}{\beta_1^2}\right]\right\}+$$

$$q_2\left\{v'_l\,(K_1\,[R+\triangle])\left[K_1+\frac{\omega_{p_1}^2}{\beta_1^2}\cdot\frac{1}{K_1}\left(\frac{l+1}{2l+1}\right)\right]-\right.$$

$$\frac{l(l+1)}{(2l+1)}\cdot\frac{1}{(R+\triangle)}\frac{v_l(K_1[R+\triangle])}{K_1{}^2}\cdot\frac{\omega_{p_1}^2}{\beta_1^2}-$$

$$\left(\frac{R}{(R+\triangle)}\right)^{l+2}\cdot\frac{1}{(2l+1)}\left[\frac{v_{l}'(K_1R)}{K_1}-\frac{l}{R}\frac{v_l(K_1R)}{K_1^2}\cdot\frac{\omega_{p_1}^2}{\beta_1^2}\right]\Bigg\}$$

$$=\left\{\frac{l}{R}\frac{u_l(KR)}{K^2}-\frac{u_l'(KR)}{K}\right\}\left(\frac{R}{R+\triangle}\right)^{l+2}\cdot\frac{1}{(2l+1)}\frac{\omega_{p_1}^2}{\beta_1^2} \qquad (35)$$

where,

$$q_2 = (K_1R)^2\,[pu_l'(KR)\,u_l(K_1R) - u_l\,(KR)\,u_l'\,(K_1R)]$$

$$p = \left(\frac{\beta^2K}{n_0}\bigg/\frac{\beta_1^2K_1}{n_{0_1}}\right) \qquad \text{with } n_{0_1} = an_0$$

and

$$q_1 = \frac{u_l(KR) - q_2\,v_l\,(K_1R)}{u_l\,(K_1R)}.$$

This expression, certainly not very transparent, reduces to eq. (32) when $\triangle \to 0$, $a \to 1$.

In this case $K_1 \to K$, $\beta_1 \to \beta$, $n_{0_1} \to n_0$.

Hence $q_2 \to 0$ and $q_1 \to 1$.

The extension of the result in eq. (35) to the case when the sphere is embedded in a dielectric is straightforward.

3. Discussion

The plasmon dispersion relations for both the cases discussed earlier are quite complicated and require a large computer programming and due to its inadequacy, we could not carry out intensive calculations. We have obtained a set of computer results which is sufficient to indicate the purpose behind this paper and the success achieved therein.

For our theoretical calculations we have taken the Smithard's (Smithard 1973) case of silver particles embedded in glass. For this case

$$\beta = 3{\cdot}6\times 10^{-3}c \quad \text{and} \quad \epsilon_m = 2{\cdot}3.$$

In figure 1 we have shown the variation of ω_l/ω_p with R, for l=1 and l=2 modes. It can be clearly seen that ω_l increases as R decreases in contradiction with the experiments.

In figure 2 we have shown the variation of ω_l/ω_p with R for $a = 0{\cdot}12$ and $\triangle = 2$Å, 3Å and 5Å. Our calculations indicate that the trend of decrease in ω_l with decrease in R sets in at $\triangle \sim 2{\cdot}5$Å; however, a sufficiently diffused electron surface profile with $\triangle = 5$Å is necessary to obtain an agreement with experimental results. Though the total inhomogenity at the surface of silver particles exists over a radial

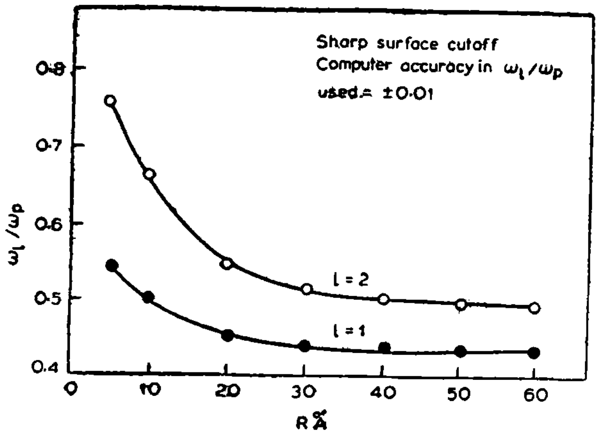

Figure 1. Dependence of ω_l/ω_p on the radius of a silver sphere embedded in glass (ϵ_m=2·3) for l=1 and l=2 modes. Here ω_l is the surface plasmon frequency for the sharp electron density cut off at the surface.

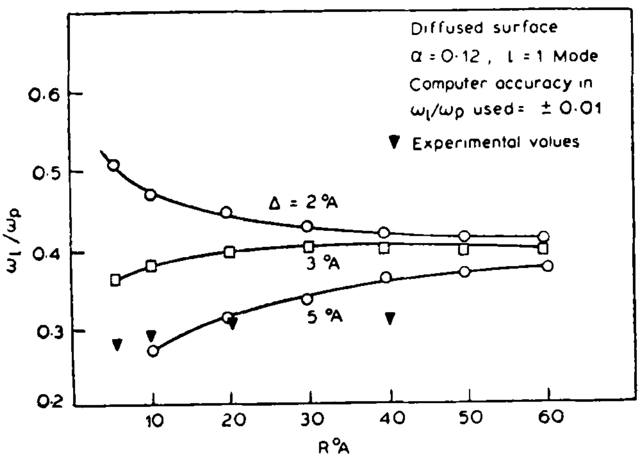

Figure 2. Dependence of ω_l/ω_p on the radius of a silver sphere with diffused surface, embedded in glass (ϵ_m=2·3) for l=1 mode with $\triangle$=2 Å, 3Å and 5Å [α=0·12].

dimension of 4–5Å; for α = 0·12 the model value of 5Å is not very realistic. One would rather expect a value $\triangle \sim$ 2·5 to 3Å. We feel that more refined experimental investigations are necessary for arriving at definite conclusions. The present model value of $\triangle$ = 5Å may therefore be considered as partially empirical.

The question arises here that the shift in the frequency may occur because of photon plasmon coupling. This interaction part of the Hamiltonian will naturally be

$$H' = \frac{e}{c}\, \alpha\, n_0 \int \mathbf{A} \cdot \nabla \psi_1 \, d\tau$$

where **A** is a vector potential for photon field. By applying a second order perturbation theory and expressing ψ_1 and **A** in second quantised form one can obtain the shift. Wilems (1968) has obtained the shift for the case of slab. His results of shift are

$$\triangle \omega = - \frac{\pi^4 a^2 c}{2K\lambda^4_p}$$

where a is the width of the slab and λ_p is wavelength corresponding to plasmon frequency ω_p. With the dimensional argument, we expect the shift in our case to be

$$\triangle\omega_l \sim - a_1 . \frac{ca^2R^3}{l\,\lambda^4_p}$$

where a_1 is a constant. With $a \sim 0{\cdot}1$, $R \sim 50$ Å, $l = 1$ and $\lambda_p \sim 3000$ Å, we find $\triangle\omega_l \sim a_1 \times 10^8$. The constant a_1 can be found by exact calculations. However, we do not expect it to be large enough so that $\triangle\omega_l \sim \omega_l$ which is of the order of 10^{15}. From the theoretical calculations and the results given in this paper, the following conclusions can be drawn.

(1) The double step model gives a simple representation of a diffused surface, which is easy to use and which has sufficient parametric freedom. (2) The surface profile must be taken into account to obtain the correct plasmon dispersion for the spatially dispersive electrostatic modes of small metal spheres.

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