Optical Properties of Small Metal Spheres: Surface Effects

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It has been assumed that the optical properties of small spheres can be understood by means of a Drude dielectric function that incorporates a boundary scattering rate $1/\tau_s \simeq v_F/R$, where v_F is the Fermi velocity and R is the sphere radius. An effective scattering rate $1/\tau_s = f v_F/R$ is calculated and f is evaluated as a function of photon frequency. The largest contribution to f is due to the electron density profile of the sphere rather than the boundary scattering that is reduced an order of magnitude by electron screening.

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When the overall size of a sample becomes smaller than the ordinary mean free path due to phonons, impurities, etc., surface scattering can be important. This observation dates back eighty years for the case of thin films[1,2] and twenty five years for the case of small spheres.[3-5] Simple classical considerations led to a surface scattering rate $1/\tau_s = v_F/L_{\text{eff}}$ where v_F is the Fermi velocity and L_{eff} is the effective size of the particle, equal to the radius R in the case of a sphere with diffuse surface scattering.[3] This surface rate combined with the ordinary Drude bulk scattering has been rather successful in describing the optical properties of small metal particles.[6] These classical observations[1-5] were followed by a number of quantum mechanical calculations[7-13] beginning with Kawabata and Kubo[7] who considered the case of noninteracting electrons for a frequency regime where the level spacing due to the finite particle size is smaller than the excitation energy of the light. These calculations indicated a reduction in the classical scattering rate, v_F/R, of about a factor of 2 and are thus in quantitative disagreement with experiment but do not present a gross discrepancy. Recently Penn and Rendell[14] have carried out calculations for a sphere in which screening by the metal electrons was included. The calculations were based on a model in which the electron density was terminated abruptly at the sphere boundary. The optical absorption was calculated and its magnitude could be roughly described by an effective scattering rate $\simeq 10^{-1} v_F/R$. Thus the electron-electron interaction, i.e., the screening of the external field, reduces the effective scattering rate an order of magnitude below that indicated by the classical arguments.[3-6]

This situation is somewhat similar to the case of the static polarizability of a small metal particle where an early estimate by Gorkov and Eliashberg[15] indicated an enormous enhancement compared to the classical value which was later rejected on experimental as well as theoretical grounds[16] because electron screening was neglected. Calculations[17] for thin films that include electron screening and require the electron density to vanish at the film surface, the infinite barrier model, also predict an effective scattering rate an order of magnitude smaller than v_F/L where L is the film thickness.

The purpose of this Letter is to point out the incorrectness of the classical picture regarding the boundary scattering and to present a calculation which actually restores agreement with the experimental results.[6] We will show that allowing for a smooth transition in the electronic properties of the surface, i.e., taking into account the real electron density profile, greatly increases the optical absorption and consequently the effective scattering rate. The importance of the surface electron density has been established for the case of a plane surface in a very elaborate calculation carried out by Feibelman[18] and we are here concerned with the sphere.

On dimensional grounds we can write the effective surface scattering rate as

$$1/\tau_s = f(\omega/\omega_p, Rk_F, r_s) v_F/R \tag{1}$$

for a free electron metal sphere where f is a function of the order unity and depends only on the dimensionless quantities that describe the sphere. Here k_F is the Fermi momentum and r_s is the average distance between electrons in units of Bohr radii. The mere presence of a surface is sufficient to obtain Eq. (1); however, f is determined by such physical effects as electron screening and the smoothness of the surface. To obtain an expression for f consider an irradiated sphere of radius R which is much smaller than the wavelength of the incident field, λ, so that the field is essentially constant over the sphere. The total potential outside the sphere in the region with no charge has the form

$$\varphi^> = E_0[r - (\alpha R^3/r^2)]\cos\theta, \tag{2}$$

where E_0 is the incident field strength and $\alpha = \alpha(\omega, R)$ is the polarizability of the sphere. Because $\lambda \gg R$ we are considering only the dipolar fields corresponding to $l = 1$. In the classical case of a sharp interface and a sphere dielectric function $\epsilon(\omega)$ which neglects nonlocal effects (i.e., its dependence on position) one obtains the result $\alpha = \alpha_{\mathrm{cl}}$ where

$$\alpha_{\mathrm{cl}} = (\epsilon - 1)/(\epsilon + 2) \tag{3}$$

and a singular induced charge located at the sphere surface. For the real situation the dielectric properties of the interface change in a continuous way and the nonlocality of the dielectric function must also be taken into account. We now carry out a calculation of the absorption of a sphere which includes the diffuse charge density at the surface as well as the dynamic nonlocal response.

In the classical case one finds the radial component of the displacement field D_r and the θ component of the electric field E_θ are continuous while E_r and D_θ are discontinuous. The induced charge density is the factor most important in determining the optical absorption and this is essentially determined by E_r. We thus focus on E_r and assume that D_r, E_θ, and D_θ have the same form as in the classical case, i.e., they can be derived from a potential

$$\varphi_{\mathrm{cl}}^< = E' r\cos\theta; \quad r < R, \tag{4a}$$

where

$$E_\theta = (-1/r)\partial\varphi_{\mathrm{cl}}^</\partial\theta, \tag{4b}$$

$$D_\theta = \epsilon E_\theta, \tag{4c}$$

$$D_r = -\epsilon\partial\varphi_{\mathrm{cl}}^</\partial r, \tag{4d}$$

where $\epsilon = \epsilon(\omega)$ is the Drude dielectric function and E' in (4a) is determined from the condition D_r continuous using Eqs. (2) and (4a). In short we have assumed that D_r, E_θ, and D_θ have the same form as in the classical calculation. They do not have the classical values because we do *not* use Eq. (4a) to determine E_r.

The absorption is given by the time-averaged power absorbed in the sphere normalized to the incident flux, $I_0 = (c/8\pi)|E_0|^2\pi R^2$,

$$\begin{aligned} a(\omega) &= (1/2I_0)\,\mathrm{Re}\int d^3r\,\vec{J}^*\cdot\vec{E} \\ &= (-\omega/8\pi I_0)\,\mathrm{Im}\int d^3r\,\vec{D}^*\cdot\vec{E}. \end{aligned} \tag{5}$$

Define $a(\omega) = a_1(\omega) + a_2(\omega)$ where

$$a_1(\omega) = (-\omega/8\pi I_0)\,\mathrm{Im}\int d^3r\,\{D_\theta^* E_\theta + D_r^* E_r^{\mathrm{cl}}\}, \tag{6a}$$

$$a_2(\omega) = (-\omega/8\pi I_0)\,\mathrm{Im}\int d^3r\,D_r^*(E_r - E_r^{\mathrm{cl}}). \tag{6b}$$

Use of Eqs. (2) and (4a), the condition D_r continuous and the approximations that D_θ, E_θ, and D_r have their classical form given by Eqs. (4b), (4c), and (4d) yields

$$a_1(\omega) = \tfrac{4}{3}qR|1 + 2\alpha|^2\,\mathrm{Im}\{1/\epsilon\}, \tag{7a}$$

where $q = \omega/c$ and

$$a_2(\omega) = \tfrac{4}{3}qR|1 + 2\alpha|^2(1 - 1/\epsilon)\,\mathrm{Im}(-d_r/R), \tag{7b}$$

where

$$d_r/R = \int_0^\infty dr\,r(R - r)\delta\bar{\rho}\Big/\int_0^\infty dr\,r^2\delta\bar{\rho}. \tag{7c}$$

Here $\delta\rho = \delta\bar{\rho}\cos\theta$ is the charge induced by the external field and d_r is its center of gravity. Equation (7b) is derived by integrating Eq. (6b) by parts with respect to the r integration and by using the relation $\vec{\nabla}\cdot\vec{E} = -4\pi\delta\rho$. The quantity d_r can be obtained in a straightforward manner only if the nonlocal dielectric function of the sphere (including surface effects) is known. However, d_r can be estimated by other means. The polarizability can be used to define an effective dielectric function

$$\alpha \equiv (\epsilon_{\mathrm{eff}} - 1)/(\epsilon_{\mathrm{eff}} + 2). \tag{8}$$

The total absorption $a = a_1 + a_2$ is given by

$$a = 4qR\,\mathrm{Im}\{\alpha\}. \tag{9}$$

Use of Eqs. (7a), (7b), and (8) in Eq. (9) yields an expression for ϵ_{eff}

$$\epsilon_{\mathrm{eff}} = \epsilon/[1 + (\epsilon - 1)d_r/R]. \tag{10}$$

An effective lifetime, τ_s, is obtained by equating $\mathrm{Im}\epsilon_{\mathrm{eff}}$ to its Drude form $\omega_p^2/\omega^3\tau_s$. Consequently Eq. (10) gives

$$1/\tau_s \simeq (\omega_p^2/\omega)(1 - \omega^2/\omega_p^2)\,\mathrm{Im}(-d_r/R), \tag{11}$$

where it has been assumed that $|d_r/R| \ll 1$. The apparent lifetime for the sphere is $\tau^{-1} = \tau_0^{-1} + \tau_s^{-1}$

where τ_0 is due to phonons, impurities, etc. It is expected that τ_s will be relatively temperature independent in contrast to τ_0.

Use of Eq. (11) in Eq. (1) yields

$$f=\gamma^2(3r_s)^{1/2}(\Omega^{-1}-\Omega)\,\mathrm{Im}(-\bar{d}_r), \qquad (12)$$

where $\Omega=\omega/\omega_p$, $\bar{d}_r=d_r k_F$, and $\gamma=(4/9\pi)^{1/3}$. We can now obtain f to lowest order in $1/R$ by replacing d_r by its value for the plane surface, $d_\perp$, where $d_\perp$ represents the average position of the induced charge as can be seen from Eq. (7c) in the limit $R\to\infty$. Feibelman introduced $d_\perp(\omega)$ and calculated it for $\omega>\omega_p/2$. In order to compare our theory with the experimental results of Kreibig we require $d_\perp(\omega)$ for $\omega<\omega_p/2$. Recently Persson and Apell[19] have determined $d_\perp(\omega)$ for all $\omega<\omega_p$ by means of the *Ansatz*

$$\mathrm{Im}(-k_F d_\perp)=A(1+a\Omega^2+b\Omega^4)\Omega\theta(1-\Omega), \qquad (13)$$

where A, a, and b are determined by sum rules that relate $d_\perp(\omega)$ to ground-state properties of the metal which are then determined as a function of r_s via density functional calculations.[19] Reasonable agreement to the results of Feibelman[18] for $\omega>\omega_p/2$ are obtained. Use of the Persson-Apell values of $\bar{d}_\perp(\Omega)$ in Eq. (12) yields the values for f shown in Fig. 1 for $r_s=2$, 3, and 4. The strong dependence of f on r_s at zero frequency is similar to that found in other density functional calculations. For example, the height of the electrostatic dipole barrier, which is the surface contribution to the total work function, is also a very strong function of r_s.[20] It is characteristic of nonlocal calculations (see Ref. 18 and references cited therein) that the absorption goes to zero at $\omega=\omega_p$ and thus $f(\Omega=1)=0$ as shown in Fig. 1 for the nonclassical calculation of f. The classical value for f is also shown in Fig. 1 where $f_{\mathrm{cl}}=1$ for all Ω. The value for f found by Kawabata and Kubo[7] and subsequent workers,[8-12] with the assumption of noninteracting electrons, is $f(0)\simeq 0.6$ where f is a very weakly decreasing function of Ω.

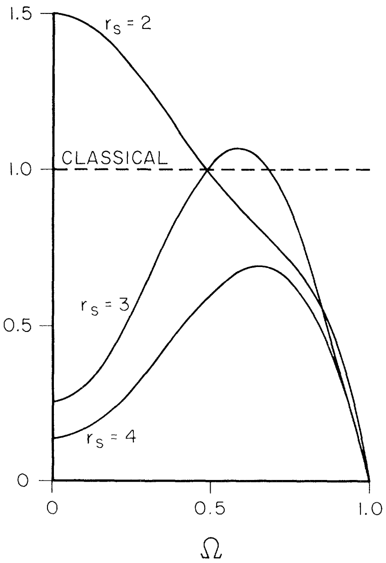

FIG. 1. Graph of $f(\Omega, r_s)$ as a function of $\Omega=\omega/\omega_p$ for various values of r_s. The solid curves are the results of the present calculation and the classical result, $f=1$, is also indicated. The effective scattering rate is given by $1/\tau_s=fv_F/R$.

Kreibig[6] analyzed his data on small Ag particles according to free and bound contributions;

$$\epsilon(\omega,R)=1-\omega_p^2/\omega(\omega+i/\tau)+\chi_d, \qquad (14a)$$

where χ_d represents the bound d-electron contribution to the dielectric function and

$$1/\tau=1/\tau_0+\beta v_F/R, \qquad (14b)$$

where $1/\tau_0$ is the bulk scattering time, β is a constant, and ω_p is the plasmon frequency appropriate to the s-p electrons in Ag, $h\omega_p=9.2$ eV. For the frequency corresponding to the Ag surface plasmon in this experiment, $h\omega_s\simeq 3.1$ eV, Kreibig measured $\epsilon(\omega_s,R)$ as a function of R and determined $\beta\simeq 1$ in Eq. (14b). From Fig. 1 and $r_s=3$ for Ag we find $f(\omega_s/\omega_p=0.35)\simeq 0.75$ in relatively good agreement with the results of Kreibig. Our result neglects the effect of the d electrons on f; however, the d electrons cannot be excited at energies less than about 4 eV so that their influence is presumably small. It should be pointed out that there have not been any calculations of the surface absorption for nonfree electron materials, even for the case of a planar surface.

In summary we have pointed out that electron screening substantially reduces the scattering rate v_F/R expected on classical grounds. However, a careful treatment of the surface yields an effective scattering rate that is comparable to the classical result. This result is obtained only if the electron density profile is not terminated at the surface (as in previous calculations) but is treated in a realistic manner, e.g., via density functional theory. The greatly enhanced optical absorption that occurs in the case of a realistic surface profile is due to the increased ability of the electrons to respond to the external field. This increased absorption results in a much greater effective scattering rate for the realistic sphere and for the case of Ag it mimics the classical result.

The principal difference between this work and previous theories lies in both the physical interpretation of the absorption and its predicted frequency dependence. We expect a strong frequency dependence while all previous workers have found a weak one and this should ultimately provide a critical test of the theory.

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